

The Interaction of Multi-Component Rare Earth Element-bearing Aqueous Solution with Ca-Mg-Fe-Carbonates and Fe- Phosphates under Hydrothermal Conditions

PhD Thesis

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A handwritten signature in black ink, reading "M. Madlin". The signature is written in a cursive style, with the first letter "M" being large and stylized, followed by a period and the name "Madlin".

Dedicated to the brilliant and brave Mileva Marić, for all of her incredible contributions to mathematics and physics, in particular, for the astounding work that she was never credited for.

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Commonly used acronyms

BSE – back-scattered electron

PHREEQC – PH Redox Equilibrium (in C language) and is a widely used public-domain geochemical modelling software available for the United State Geological Survey

REE(s) – Rare Earth Element(s)

SEM-EDS – scanning electron microscopy – energy dispersive x-ray

TOPAS – an optimization program integrating computer algebra and crystallographic objects written in C⁺⁺

XRD – X – ray diffraction

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The Interaction of Multi-Component Rare Earth Element-bearing Aqueous Solution with Ca-Mg-Fe-Carbonates and Fe-Phosphates under Hydrothermal Conditions

SUMMARY

This study aims to investigate the uptake and fractionation of rare earth elements (REEs) by divalent carbonates and Fe-phosphate minerals and to better understand the reaction pathways and crystallisation sequences that lead to the formation of REE-bearing minerals. Three main studies were conducted in which host grains (Mg-Ca carbonates, Fe-carbonate, and Fe-phosphate) were reacted with multi-component (La, Ce, Pr, Nd and Dy)- bearing aqueous solutions with varying REE ratios. Each experiment was a progression, with an increase in chemistry complexity, the introduction of redox reactions, crystallisation of nanophases and simultaneous, coupled reactions. This allowed for the study of more progressively dynamic reactions, such as solution mediated-dissolution and oxidation sequences as well as the formation of multiple REE, Fe, and P-bearing phases. Better insight into the intricacies of REE-mineral formation in the presence of foreign ions such as Fe and P in various environmental conditions could positively impact improved resource separation and recovery. The significance of this is described in **Chapter 1**, which offers a review of the current REE supply situation and provides the reader with the context of the thesis.

The findings of our studies are presented in three core chapters (Chapters 2-4)

In **Chapter 2**, we investigated the interaction of REE-bearing aqueous solutions with carbonate grains of dolomite ($\text{CaMg}(\text{CO}_3)_2$), aragonite (CaCO_3), and calcite (CaCO_3) at ambient and hydrothermal conditions (21-210 °C). Our replacement reactions showed a preferential uptake of REE in kozoite and bastnäsite and the formation of symplectic textures. Solubility differences and the effect of molar volume are discussed as well as the role of temperature and ionic radii.

Current commercially significant REE deposits are associated with alkaline igneous rocks and carbonatites. There are also several examples of REE-rich carbonatite complexes exhibiting high REE concentrations connected to hematite-bearing rocks and iron ores. Therefore, in **Chapter 3**, we examined the interaction of REE-bearing aqueous solutions with siderite (FeCO_3), which is commonly associated with carbonatite ore deposits, under hydrothermal conditions (50-205 °C). The aim of this study was to better understand the formation of rare earth carbonates during the oxidation and replacement of siderite as well as the extent to which the REE are incorporated into the iron oxides that may form. In this chapter we discuss two oxidation processes (Fe^{2+} to Fe^{3+} and Ce^{3+} to Ce^{4+}) and their temperature dependency.

In **Chapter 4**, we once again studied the interaction between our multi-component REE-bearing solutions, this time with vivianite ($\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) grains under hydrothermal conditions (50-165 °C). Phosphate rocks are gaining increased interest as a potential REE source. In particular, the recent discovery by Swedish mining company, LKAB (Luossavaara-Kiirunavaara AB), has the potential to become a substantial REE source for Europe. Therefore, the aim of this study was to gain a better understanding of the

stability of iron phosphates, their transformation products, and their capacity to incorporate REEs. In this chapter, we discuss three simultaneous processes: (i) the solution-mediated oxidation of vivianite during its dissolution, coupled with the formation of secondary iron phosphates, (ii) the replacement of the iron phosphates by REE phosphates, and (iii) REE phosphate mineral transformation reactions.

Chapter 5 consists of a summary of the findings, their applications, and potential future work.

Chapter 1: Thesis Context

Rare earth elements (REEs), a group comprised of the 15 lanthanides as well as scandium (Sc) and yttrium (Y), are vital for various modern industries such as novel green technologies, electronics, medical devices, and national defence applications (1). They are also considered critical due to their scarceness, lack of mineable concentrations and supply chain constraints (2). Advances in technology products such as computers, high strength permanent magnets and automobiles are increasing the usage rate of REEs. Technological advances that are improving energy efficiency and relinquishing dependency on fossil fuels are also boosting demand for REEs by approximately 8% per year (3). The current processing methods being employed today, such as gravity, magnetic and electrostatic separation as well as froth flotation have been deemed inefficient and environmentally aggressive (4). The production and processing of rare earths around the world is also highly unbalanced. As of 2022, China still dominates in rare-earth oxide production at 70%, with the US and Australia lagging at 14 and 4% respectively (5). Such an uneven distribution in resource and production is contributing and maintaining a global supply instability.

Contrary to their name, the rare earths are not actually that rare, with the most common (Ce) being as abundant in the earth's crust as copper at 66.5 ppm. However, the problem lies in the production cost of rare earths and extracting them from their host ores (6). The 15 naturally occurring REEs are never found as pure metals and instead form in mineral deposits such as oxides, carbonates, and phosphate (4), forming complex solid-solutions due to similarities in ionic radii, charge, and coordination numbers. Also, their similar

chemical properties make separation and refining costly and challenging (7). Exacerbating this challenge is the fact that the elements are never found in equal and economic distributions (4).

The coherent geochemical behaviour of the rare earths is caused by the filling of the inner 4f orbitals (8). All of the lanthanides exhibit the same configuration in their outermost valence electron shell, however, the 4f orbitals are progressively filled with increasing atomic number (9). The 4f electrons imperfectly shield each other from the increasing positive charge of the nucleus. This screening of the 4f orbitals causes the ‘lanthanide contraction’ which is the progressive less than expected decrease in atomic radius from La (1.06 Å) to Lu (0.85 Å) (9). With the lanthanide contraction keeping the REEs relatively the same size as well as them gradually presenting in the 3⁺ oxidation state, the REEs exhibit similar chemical properties. The similarities in their chemical properties also create challenges in terms of their separation, both financially and environmentally. Despite their similar chemical properties, individual REEs exhibit unique magnetic, optical, and catalytic properties, making the substitution of one for another for industry applications complex and complicated (10).

REEs are generally found in the Earth’s crust, with the exception of promethium (Pm) which is very scarce because it is a byproduct in the decay of U and Th isotopes, but it is not stable and decays to stable neodymium isotopes (11). The REEs for industrial use are commonly obtained from the minerals bastnasite (REECO₃OH), monazite (REEPO₄), and xenotime (REEPO₄) (12). Hydrothermal alteration refers to the chemical and mineralogical changes that rocks undergo due to the interaction with hot aqueous fluids and plays a crucial role in enriching primary deposits through the chemical alteration of minerals and the generation of new REE-rich phases (13). It also leads to the production of secondary REE deposits by weathering processes that form ion-adsorption clays (14).

The fluids responsible for these processes can derive from magmatic, metamorphic, and surface water sources, enabling significant mobility and concentration of REEs in the Earth's crust. Hydrothermal fluids often originate from magmatic sources, which are derived from the crystallization and differentiation of magma. As magma cools, volatiles (including water and gases) are released, forming hydrothermal fluids that migrate through fissures and fractures in the rock. The heat from the magmatic body instigates convection, driving fluids into surrounding rock, which facilitates the dissolution and mobilization of REEs (15). In some cases, hydrothermal fluids can also originate from metamorphic processes, where water is released from minerals during metamorphism. These fluids are produced during regional metamorphism and can interact with existing mineral matrices, furthering the release and mobility of REEs (15). This can lead to the alteration of surrounding rocks and the transport of REEs. Additionally, meteoric water (surface water from rainfall) can contribute to hydrothermal systems, particularly in laterite deposits. As this surface water infiltrates through the soil, it can interact with minerals and facilitate the leaching of REEs from primary sources. This process is particularly relevant in regions with a high groundwater influx, leading to enhanced chemical weathering and subsequent REE leaching (16). Hydrothermal fluids elevate temperatures and pressures, facilitating the alteration of primary minerals in REE deposits, particularly in granite and carbonatite formations. REE-ore deposits can be categorized into primary deposits, such as carbonatites, alkali granite, and iron oxide deposits, and secondary deposits, such as laterites and ion adsorption clays, with, each exhibiting distinct mechanisms and mineralogical characteristics. The primary minerals involved in the hydrothermal alteration of REE deposits include monazite, bastnaesite, apatite, fluorite, zircon, mica, and clay minerals. These minerals play a critical role in the mobilization and concentration of REEs during the alteration process, contributing to the

formation of economically viable REE resources. For example, the phosphate mineral monazite is particularly rich in cerium (Ce), lanthanum (La), and thorium (Th). During hydrothermal alteration, monazite can be broken down to release REE into solution, which can then transform into secondary minerals or be re-deposited in altered zones. Hydrothermal processes can also enhance the solubility of minerals, such as the fluorocarbonate bastnaesite, leading to the mobilization of REEs into hydrothermal fluids and the potential precipitation elsewhere,

Carbonatite-associated REE deposits are among the most significant sources of light rare earth elements (LREEs). These deposits are formed from carbonatite magmas, which can strongly partition REEs during their crystallization processes. The formation of these deposits is closely linked to mantle-derived processes, where REEs are concentrated through magmatic differentiation and hydrothermal alteration (17,18). The mineralization of REEs in carbonatites is influenced by the recycling of marine sediments and tectonic activities, which contribute to the enrichment of these elements in the crust (19). Mountain Pass (USA), and Bayan Obo (China) are two of the world's largest carbonatite-hosted LREE deposits, with bastnaesite as their host rare earth mineral (2). (20)The Bayan Obo deposit is estimated to host roughly 100 million metric tonnes of REE reserves, with an average grade of about 5.6% for total rare earth oxides (21,22). This grade constitutes a significant portion of the global REE supply and is estimated to account for approximately 59.3% of the world's REE reserves (23). This mine is particularly rich in LREE, which dominate the overall distribution, with Ce being the most abundant (Fig. 1). The hosted minerals within the Bayan Obo deposit include monazite and bastnaesite, along with other REE-bearing minerals. The Bayan Obo deposit is primarily situated within dolomitic marble and associated dolostones. Studies indicate that the mineralization process evolved over approximately 1 billion years,

marked by various geological events, including magmatic intrusions and hydrothermal alterations (24,25).

The Kvanefjeld deposit, located in southern Greenland is known for its rich concentrations of REE, as well as uranium and zinc. The mineralization occurs within an alkaline granite

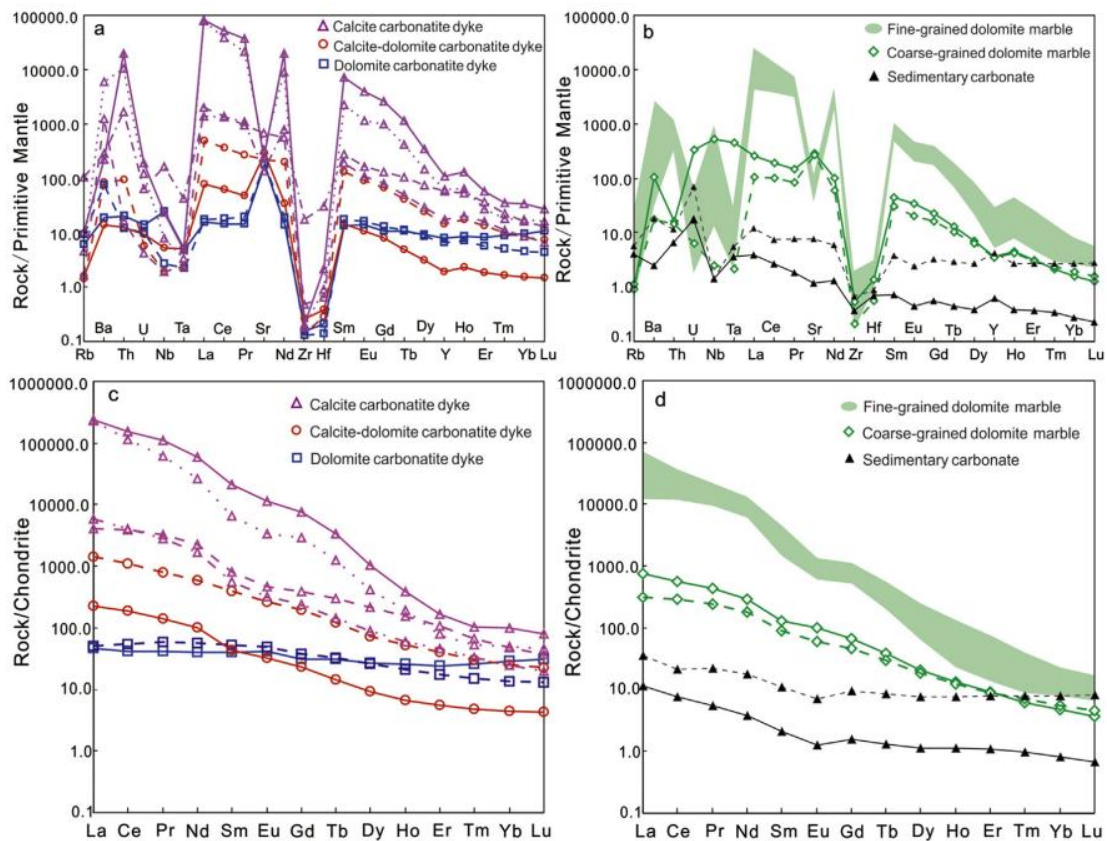


Figure 1 (a,b) Primitive mantle-normalized trace element abundance pattern, and (c,d) chondrite-normalized REE abundance diagram for carbonatite dykes, ore-hosting dolomite marble and sedimentary carbonate rocks at Bayan Obo, figure from (26)(27)

complex, making it a prime target for mining due to its diverse research potential. The deposit is noteworthy for containing approximately 620 million tonnes of ore, with an average of 1.06% rare earth oxides (Guyonnet et al., 2015). The Kvanefjeld area predominantly features lujavrites, which are fine-grained, melanocratic apgaitic

nepheline syenites. The rocks are classified into northern and southern groups, separated by an intermediate zone, suggesting complex emplacement and crystallization sequences (29). Concomitantly, the Tanbreez deposit, located in the Illimaussaq alkaline complex also in southern Greenland, is noteworthy for its substantial reserves of REEs, particularly heavy REEs, as well as zirconium, niobium, and tantalum. It is characterized by an average grade of approximately 1.28% total rare earth oxides, with total resources estimated at around 40 million tonnes. Geologically, the Tanbreez deposit is classified within the Kakortokite, which is rich in eudialyte, a mineral identified as the primary carrier of REEs in the deposit. This mineral association is significant, as it influences both the concentration and extraction potential of REEs available in the deposit (30).

The Lofdal Rare Earth Project, located in Namibia, has also garnered substantial attention due to its significant REE deposit, particularly the presence of heavy REE such as dysprosium and terbium. It consists primarily of calcite carbonatite rocks and displays a significant grade of REEs, particularly in the form of xenotime – a REE-bearing phosphate mineral known for its high HREE content. The geological setting of the Lofdal deposit is characterized by its association with carbonatite and alkaline igneous intrusion (Fig. 2), processes that facilitate the concentration of REEs. The mineralization at Lofdal primarily consists of bastnasite and monazite, both of which are crucial REE sources (31).

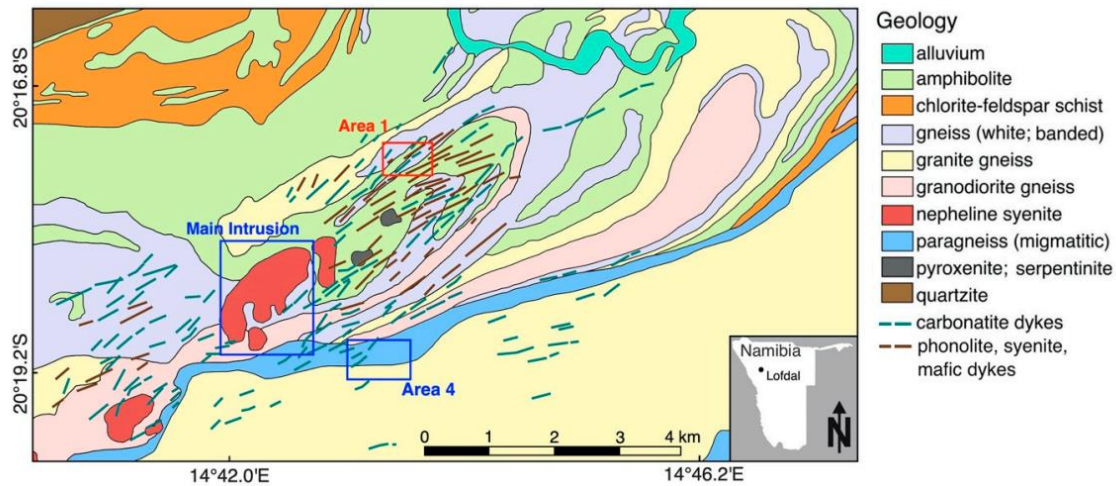


Figure 2 Geological map of the Lofdal Alkaline Carbonatite Complex, including the location from the dyke swarms. Area 1 is located from the Main intrusion (adapted from the Geological Survey of Namibia) From (32)

Secondary sources, such as weathered crust-elution deposited rare earth ores, are primarily found in regions with significant weathering processes, such as southern China. These ores are characterized by the adsorption of REEs onto clay minerals, where they exist predominantly as hydrated ions or hydroxyl ions. The leaching processes that lead to the formation of these deposits involve the mobilization of REEs from primary mineral deposits through weathering and the subsequent accumulation in secondary clay-rich environments (33–35). The unique geochemical behaviour of these REEs makes conventional physical separation methods less effective, necessitating specialized chemical leaching techniques for their recovery (36,37).

Another significant source of REE are laterite deposits. These are a type of mineral-rich soil and rock formation that typically form in tropical and subtropical climates through the intense weathering of parent rocks, particularly silicate rocks. The intense rainfall and high temperatures in tropical regions promote chemical weathering, leading to the leaching of soluble minerals and the accumulation of less soluble minerals like iron and

aluminium oxides. Laterite deposits can also be enriched in REEs, particularly in certain weathering profiles that undergo further transformations. They often exhibit a layered structure, with different horizons developed based on the degree of weathering and mineral accumulation, with the upper layers containing a mix of iron and aluminium minerals, and deeper layers more enriched in bauxite and kaolinite. The Nolans Bore Project, developed by Arafura Resources in the Northern Territory of Australia, has emerged as a prominent REE and phosphate deposit (Fig. 3). It is primarily hosted is a lateritic weathering profile developed over granite and, more specifically, contains a REE resource in the form of monazite and bastnaesite. Geologically, the Nolans Bore deposit is categorized as a Mesoproterozoic P-REE-Th-U ore body. The notable mineralogy includes centimetre to meter-wide veins and dikes, predominantly comprised of fluorapatite, which serves as a host for various REEs, particularly those associated with phosphate-rich hydrothermal fluids (38).

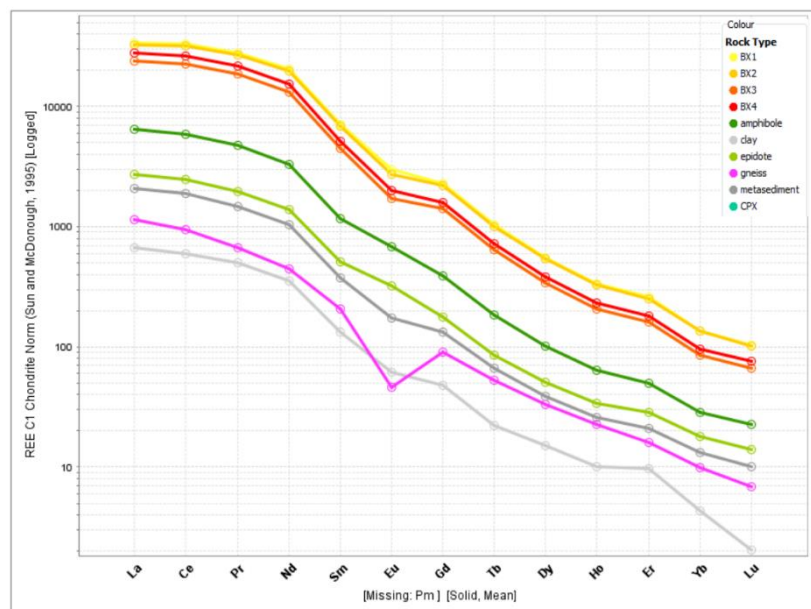


Figure 3 REE diagram for rock types from bulk rock chemistry of the central zone of the Nolans Bore REE deposit, Northern Territory, Namibia. This data constitutes the bulk rock geochemistry data that was collected by rock type from holes NBDH1068, NBDH1071, NBDH1099 and NBRD104 From (39)

Laterite deposits can also consist of ion-adsorption clays that are particularly rich in REEs. These clay deposits are often found in areas with extensive lateritic weathering, especially in regions like southern China and Southeast Asia. Ion-adsorption clays are particularly rich in heavy REEs, such as dysprosium, terbium, and yttrium, and are distinct because they primarily contain REEs in an ionic form on the surface of clay minerals, such as kaolinite and halloysite. The absorption mechanisms for REEs in these clays have been explored extensively. (Ding and Azimi, 2025), highlight that in South American ion-adsorption clays, REE adsorption tends to form a homogenous monolayer in alignment with the Langmuir isotherm. Geochemical studies, such as those by (41), on ion-adsorption clays in Gua Musang, Kelantan, Malaysia, have provided insights into the weak adsorption characteristics of REEs within kaolinite and halloysite. Their research indicated that during chemical weathering of REE-bearing minerals, REE are initially dissolved and subsequently interact with the surfaces of these clay minerals, The interaction leads to the formation of ion-adsorption clays under specific geochemical conditions prevalent in high-temperature environments. The extraction of REEs from ion-adsorption clays can be more cost-effective compared to traditional mining methods for hard rock sources. The clays can often be upgraded with relatively simple and low-impact processing techniques, which require less energy and water than other methods. (42) investigated the interactions between clay particles and the leaching processes involved in ion-adsorption-type rare earth ores. They emphasize that in situ leaching is a common method employed for the efficient recovery of REEs, making it essential to understand physiochemical properties of the clays involved. Effective leaching strategies can facilitate recovery of significant quantities of REEs while potentially minimizing environmental impacts.

(14,43)(14)Most of the studies on rare earth deposits thus far have focussed primarily on the geological characteristics, with investigations providing key insights into the geological settings, REE distribution patterns and mineralogical assemblage characterization (44,45). However, when we study natural samples, we only see the “end products” and quite often miss some of the mineralogical and geochemical evolution that occurs as the deposit is forming. There is an abundance of diverse crystallisation processes that can occur in relatively short time scales involving the formation and breakdown of metastable phases. These complex processes ultimately affect and control the final nature of the rock, its chemical textures, as well as the abundance and distribution of REEs. Therefore, there still remains a knowledge gap in the reaction pathways and crystallization sequences in the formation of rare earth ore deposits when multiple rare earths are involved. Therefore, we have mimicked natural systems by conducting hydrothermal replacement experiments using multi-component REE-bearing solutions with carbonates, Fe-carbonate, and Fe-phosphates, which are commonly found in carbonatite and REE-mineral deposits. A better understanding of the mechanisms controlling the REE concentration in minerals would have applications in more efficient practices as well as separation techniques and recycling.

Therefore, this study aimed to:

1. Investigate the reaction pathways and crystallisation processes that control the formation of rare earth carbonates during mineral replacement reactions and their chemical textures.
2. Elucidate the kinetics and nanoscale mechanisms involved in the development of secondary rare earth minerals during solution-mediated replacement reactions of divalent alkaline-earth carbonates, with a focus on the chemical texture of the newly formed phases.

3. Investigate rare earth carbonate formation during the oxidation and replacement of Fe-carbonates, including the analysis of REE uptake by Fe oxides and the resulting chemical textures.
4. Examine the interactions of multiple rare earth elements with Fe phosphate minerals in aqueous solutions, emphasizing the nanoscale mechanisms and chemical textures that guide transformation into REE-phosphates.

Overall, the findings reported in this PhD thesis have advanced our understanding of rare earth mineral formation by:

1. Mimicking natural carbonate, phosphate, and oxide systems.
2. Demonstrating the sequential replacement of carbonate hosts by REE-bearing phases.
3. Exploring the transient phases and textural evolution that occur under varied hydrothermal conditions.

We have provided key insights into the mechanisms of chemical texture formation, of potential zoning of REEs in rare earth minerals, the formation of REE minerals in tandem with Fe and Ce oxidation, and the transformation of Fe phosphate into stable REE phosphates. A better understanding of the mechanisms controlling the REE concentration in minerals would contribute to the development of more efficient practices in separation techniques and recycling via the following:

1. A broader knowledge of zoning could also have potential applications in better rare earth separation techniques, as well and beneficiation.
2. As there is often an association hematite-bearing ores with carbonatites, the formation of Fe oxides in parallel with REE minerals has potential applications in Fe separation from REE ore deposits.

3. Transforming Fe phosphates into more stable REE-phosphates would have important implications for resource recovery by significantly enhancing the recovery of economically valuable REEs from industrial waste, contaminated soils, and mine waste-waters.

Co-Author Statement and Layout of Thesis

The core chapters (2-4) of this thesis are comprised of two published papers and one paper in review. I am the lead author of the three manuscripts, the work which was undertaken and produced during the duration of my PhD at Trinity College Dublin. As the lead author of these manuscripts, I was responsible, where applicable, for sample preparation and analysis, data collection, interpretation and reduction, and all stages of the manuscript preparation through to publication. A list of other published works during my PhD study is also provided. The contributions from each co-author for the core chapters are outlined below:

Chapter 2: Chemical textures on rare earth carbonates: an experimental approach to mimic the formation of bastnäsite

- ❖ Melanie Maddin: lead author, experimental set up, sample handing, sample analysis and interpretation
- ❖ Adrienn Szucs: experimental setup, occasional sample handling.
- ❖ Remi Rateau: SEM imaging
- ❖ Luca Teribili: XRD analysis
- ❖ Brendan Hoare: SEM analysis techniques

- ❖ Paul Guyett: SEM training
- ❖ Juan Diego Rodriguez-Blanco: conceptualisation, training in XRD and SEM, experimental design, supervision, manuscript review and editing.

Chapter 3: Transient crystallisation of rare earth carbonates during the hydrothermal oxidation of siderite

- ❖ Melanie Maddin: lead author, experimental set up, sample handling, sample analysis and interpretation.
- ❖ Remi Rateau: occasional sample handling, SEM imaging
- ❖ Adrienn Szucs: SEM-EDS elemental mapping
- ❖ Luca Terribili: XRD analysis
- ❖ Juan Diego Rodriguez-Blanco: conceptualisation, experimental design, supervision, manuscript review and editing.

Chapter 4: Nanophase REE phosphate crystallisation induced by vivianite oxidation: mechanistic insights and mineralogical implications

- ❖ Melanie Maddin: lead author, experimental set up, sample handling, sample analysis and interpretation
- ❖ Luca Terribili: XRD analysis
- ❖ Remi Rateau: occasional sample handling, SEM imaging
- ❖ Adrienn Szucs: PHREEQS calculations
- ❖ Juan Diego Rodriguez-Blanco: conceptualisation, experimental design, supervision, manuscript review and editing.

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Chapter 2: Chemical textures on rare earth carbonates: an experimental approach to mimic the formation of bastnäsite

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Abstract

The interaction between multi-component rare earth element (REE) aqueous solutions and carbonate grains (dolomite, aragonite, and calcite) were studied under hydrothermal conditions (21-210 °C). The effect of ionic radii of five REEs (La, Ce, Pr, Nd, Dy) on solid formation were analysed using two solution types: equal REE concentrations and concentrations normalized to Post Archean Australian Shale Standard (PAAS). The interaction replaces the host Ca-Mg carbonate grains with a series of REE minerals (lanthanite → kozoite → bastnäsite → cerianite). At 165 °C, equal concentration solutions promote kozoite crystallization, maintaining similar REE ratios in solids and solution. PAAS solutions result in zoned REE-bearing crystals with heterogeneous

elemental distributions and discrete REE phases (e.g., cerianite). Chemical signatures indicate metastable REE-bearing phases transforming into more stable polymorphs, along with symplectite textures formed by adjacent phase reactions. Overall, experiments highlight the dependence of polymorph selection, crystallization pathway, mineral formation kinetics, and chemical texture on REE concentrations, ionic radii, temperature, time, and host grain solubility.

1. Introduction

As rare earth elements are essential in many green technologies, they play a critical role in a more sustainable future. However, there is a substantial risk to their supply as the availability of REE deposits with minable concentrations are limited. A better understanding of the mechanisms controlling REE concentration in minerals would have applications in more efficient mining practices as well as REE separation techniques and recycling.

REES are critical materials with their applications spanning a wide range including hybrid vehicles, rechargeable batteries, and wind turbines, as well as medical and military technologies (1,2). With increased demand from the green energy market as well as REE applications migrating into common domestic items such as computer parts and television screens, the pressure is building on the current global REE supply chain. Presently, REE processing is dominated by China ($\approx 85\%$) (3). However, in recent years, a significant reduction in export quotas from China is leading to supply chain instability (4).

REE deposits can be categorized as either primary or secondary deposits. Magmatic, hydrothermal and/or metamorphic processes are responsible for the formation of primary deposits which are generally associated with alkaline igneous rocks and carbonatites.

Some examples of these types of deposits include Mountain Pass, California, and China's Bayan Obo, which is the world's largest REE deposit. In secondary deposits, formation occurs as a consequence of weathering and erosion, such as placers, laterites, and bauxites (5). For example, the weathering of tin granite in south China has resulted in REE-laterite. Also, the humid, subtropical climatic conditions in northeast India have also promoted the formation of a thick laterite profile offering a promising alternative for this type of REE deposit (6). Presently, the world reserves of REE amount to approximately 130 million tonnes and are under the control of China, Brazil, Vietnam, Russia, and India (7). However, China holds one-third of the world's REE reserves and dominates in REE exploration and production. Bastnäsite, monazite and xenotime are currently the principal economic resources of REE minerals and can be sourced from these geological deposits (8).

In our study, we focussed on bastnäsite as it is one of the major sources of REE found in commercial deposits such as Bayan Obo, China (9). Three natural carbonate-fluoride minerals comprise the bastnäsite family each with varying amounts of REE. These include (Ce)-bastnäsite; $(\text{Ce},\text{La})[\text{CO}_3]\text{F}$, which is the most abundant, (La)-bastnäsite; $(\text{La},\text{Ce})[\text{CO}_3]\text{F}$, and (Y)-bastnäsite; $(\text{Y},\text{Ce})[\text{CO}_3]\text{F}$ (10). Synthetic bastnäsites are gaining increased attention as they can be used as precursors for rare earth oxycarbonate ($\text{RE}_2\text{O}_2\text{CO}_3$) and oxyfluorides (REOF) synthesis, both of which can be utilized as host lattices for phosphors. (Ce)-bastnäsite together with the phosphate mineral (Ce)-monazite $(\text{Ce},\text{La},\text{Nd},\text{Th})[\text{PO}_4]$, make up our major source of Ce as well as additional REE such as La, Nd, and Y (10).

When studying natural ore deposits, researchers will generally only characterize the final mineralogical assemblage. However, the aim of this study is to better understand the reaction pathways and crystallization sequence that leads to some rare earth carbonates.

A better understanding of the mechanisms controlling the REE concentration in minerals would have applications in more efficient practices as well as separation techniques and recycling. Therefore, we have mimicked natural systems by carrying out replacement experiments using multi-component REE aqueous solutions and carbonate host grains of dolomite, aragonite, and calcite, which are commonly found in carbonatite ore deposits. All of the products obtained in our experiments were characterized with high resolution electron microscopy and powder X-ray diffraction, allowing us to show that temperature as well as aqueous chemistry are key in controlling the mineralogy and distribution of REE in carbonate rocks.

2. Methods

The interaction of calcite, dolomite, and aragonite with multi-component REE (La, Ce, Pr, Nd, and Dy) aqueous solutions was investigated at ambient and hydrothermal conditions (21-210 °C). Calcite (Iceland spar), aragonite (Sputnik variety) and light-pink dolomite (Morocco) crystals were crushed in a ceramic mortar and sieved to extract 0.5-1.0 mm clasts. Five single REE bearing solutions were prepared, (La, Ce, Pr, Nd, and Dy), with a REE concentration of 50 mM. These solutions were produced via the dissolution of single rare earth element nitrate salts, $\text{REE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.9% purity), in de-ionized water (18.18 M Ω ·cm). These five specific REE were chosen as they are representative of both the light (La, Ce, Pr, and Nd) and heavy REE (Dy). This suite of REE from La to Dy also represents 72% of the ionic radii of the lanthanides as well as being some of the most abundant REE in the earth's crust (11) In order to understand the effect of ionic radii of the five REEs and to what extent these ions are taken up by the carbonate host, two different sets of experiments were conducted, one

with equal concentrations of the five REEs and one with the concentrations of the five REEs normalized to the commonly used Post Archean Australian Shale standard (PAAS) (12) to mimic the rare earth element concentrations found in continental crust and natural geo fluids. For the equal concentration experiments 4 mL of each of the five REEs were used to give a total solution volume of 20mL for each experiment. For the PAAS experiments, a 1 L bulk solution, comprised of 11.8 mM $\text{La}(\text{NO}_3)_3$, 24.3 mM $\text{Ce}(\text{NO}_3)_3$, 2.70 mM $\text{Pr}(\text{NO}_3)_3$, 10.0 mM $\text{Nd}(\text{NO}_3)_3$, and 1.20 mM $\text{Dy}(\text{NO}_3)_3$, was made and 20 mL of this was used for each experiment.

For each experiment, 0.1 g of either calcite, dolomite, or aragonite grains were added to 20 ml of each of the 50 mM REE-bearing solutions and placed in 25 mL Teflon-lined and capped stainless-steel autoclaves (for the 80, 165 and 210 °C experiments). For the lower temperatures (21 and 50 °C), narrow-mouth Nalgene polypropylene PPCO bottles (Thermo Fisher Scientific) were used. The reactors were then placed in a pre-heated oven at 50, 80, 165 and 210 °C. The room temperature experiments were kept undisturbed in a laboratory cupboard. Solid samples were then extracted using a sterilized metal spatula at increasing time intervals from 24 hours to 8 weeks. The samples were placed in plastic Eppendorf tubes and dried in a 30 °C oven, with the exception of the 21 °C samples, which were dried at room temperature. A summary of the experimental protocol is presented in figure SI-1.

In order to identify and quantify the formation of crystalline solids present in our samples, several grains were selected from each experiment ensuring that each time and temperature variable was represented. The selected grains were ground to a consistently fine powder using an agate pestle and mortar. The powders were analysed, and minerals characterized with powder X-ray diffraction (XRD). Conventional powder XRD patterns were collected using a Siemens/Bruker D5000 powder X-ray diffractometer ($\text{Cu K}\alpha$

radiation, 0.01° step⁻¹ from 5 to 60° 2θ at $0.2^\circ \text{ min}^{-1}$, 4.5 hours scans per samples, with a detection limit of $\sim 1\%$). Identification of crystalline phases was carried out with the Diffract Suite EVA software from Bruker in combination with the Powder Data File (PDF-4, the International Centre for Diffraction Data) (13) Pattern-matching refinement and quantification of crystalline phases were carried out with the Rietveld refinement software TOPAS (14). Finally, scanning electron microscopy (SEM) was used to obtain high resolution images to characterize changes in the morphology of the carbonate host grains and identify newly formed phases. Analyses were conducted in the iCRAG laboratory at Trinity College Dublin using a TIGER S8000 FEG-SEM operating under high vacuum conditions and equipped with two Oxford X-Max 170 mm² EDS detectors and an X4 pulse processor running the Oxford Aztec analysis software version 5.1 and subsequently version 6.1

Two methods of sample preparation were employed, (i) standard SEM sample stubs with intact grains mounted to examine surface morphology, and (ii) polished epoxy resin pucks that provided a cross section of the grains, allowing for the identification of potential differences in spatial distribution and internal chemical textures. The epoxy mounts (2.5cm wide) were made using Epoxy resin (Struers Epofix) mixed with the accompanying hardener and then polished using a three-step process (Struers Diapro, 6 and 1 μm) to expose the internal cross section of the grains. The pucks were then cleaned in an ultrasonic bath of deionized water to remove any residual polishing fluid and then dried. Both the stubs and the pucks were then coated with either carbon (for elemental mapping and analysis) or gold (for high resolution imaging). Analysis at a working distance of 15 mm was performed using an accelerated voltage of 20kV, a 4.5 nm wide beam with a beam current of 300pA, and a process time of five, following the SEM-EDX protocol defined in Ubide et al., 2017 (15). Beam current drift was controlled by analysis

of cobalt after each sample change (16) while imaging carried out at a working distance of 5mm was performed using an accelerating voltage of 10kV. X-ray peak energies for each peak were calibrated to concentrations using a range of mineral and glass standards. The following phases on the Astimex MINM25-53 standard mount for standardization were used: apatite, chromite, diopside, kaersutite, magnetite, olivine, orthoclase, pentlandite, rhodonite, rutile and tugtupite. Standard phases were analyzed for 2M counts. The images and maps were processed using the AZtec v6.1 X-ray microanalysis software suit (Oxford Instruments).

3. Results

The analysis of all solid samples obtained from the replacement experiments resulted in the formation of a series of surface precipitates that partially or totally replaced the host carbonate grain. The combination of powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) allowed us to identify and quantify the newly formed phases and interpret the mechanisms responsible for some of the chemical textures exposed in the polished resin pucks.

3.1. Powder X-ray diffraction

The interaction of calcite, dolomite, and aragonite with multi-component rare earth element (La, Ce, Pr, Nd, and Dy) -bearing aqueous solutions resulted in the formation of secondary REE-bearing minerals. The characterization with powder X-ray diffraction (XRD) revealed the formation of a series of rare-earth bearing carbonate minerals: lanthanite ($\text{REE}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$), kozoite ($\text{REE}(\text{CO}_3)(\text{OH})$), hydroxylbastnäsite ($(\text{REE}(\text{CO}_3)(\text{OH},\text{F}))$ (Figure 1) and a REE oxide, cerianite (CeO_2). These newly formed

phases presented as surface precipitates that partially replaced the host mineral. In some experiments, the host carbonate minerals were fully replaced. The extent of the replacement reaction was found to be temperature and time dependent (Figure 2). At certain temperatures, the formation of specific crystalline polymorphs was hindered during reaction. Lanthanite was found to be present and stable at low temperature only (21 °C), with minor amounts found in the aragonite experiments at 50 °C. Kozoite precipitated and remained stable at 50 and 80 °C. At 165 and 205 °C, kozoite also formed but it quickly transformed to hydroxylbastnäsite and cerianite. At 205 °C, hydroxylbastnäsite and cerianite precipitated after short reaction times (i.e., within 24 hours). In some cases, the host mineral (e.g., calcite) was fully consumed by cerianite and/or hydroxyl-bastnäsite. Cerianite was the end product of the higher temperature experiments, replacing the host and the REE carbonates. The formation of the REE carbonates in the reaction sequence was also found to relate to the nature of the host mineral (e.g., at 165 °C, hydroxylbastnäsite and cerianite precipitated faster in the aragonite experiments compared to the dolomite and calcite experiments). The REE concentration in the initial solution also played a key role, an example being the 21 °C experiments with lanthanite precipitating in the PAAS solution experiments for all three host grains, however, in the non-PAAS experiments, lanthanite only formed on the surface of aragonite, with no additional phases being detected by XRD on the surface of calcite or dolomite. There was a small amount of lanthanite precipitated in the aragonite experiments at 50 °C in the PAAS solution, compared to only kozoite in the dolomite and calcite experiments. At 80 °C, kozoite was the sole main stable phase in both the non-PAAS and PAAS experiments. At 165 and 210 °C, kozoite quickly transformed to hydroxy-bastnäsite and cerianite, with only slightly prolonged stability in the non-PAAS solutions with dolomite and calcite grains. Also, at 165 and 210 °C, the amount of

cerianite that formed in the non-PAAS solution ranged from <1-5%, while in the PAAS solutions, Ce was the most highly concentrated element and resulted in cerianite replacing the host by 17-46%.

Table 1: Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of dolomite with multi-component (La, Ce, Pr, Nd, and Dy), REE-bearing aqueous solutions (non-PAAS, and PAAS). *kozoite (koz), hydroxylbastnäsite (HB), cerianite (Cer)

DOLOMITE							
T (°C)	NON-PAAS				PAAS		
	Time (days)	% Phase consumed	Phase formed	Morphology	% Phase consumed	Phase formed	Morphology
21	14	0			6		
	28	0			1	Lanthanite	Thin platy crystals
	42	0			3		
	56	0			1		
	84	0			4		
50	1	0			0		
	3	<1			3		
	7	6			5	Kozoite	small prisms, elongated prisms
	21	7	Kozoite	small prisms, elongated prisms	19		
	28	14			11		
	42	25			20		
	56	19			44		
80	1	0			3		
	3	7			9		
	7	14	Kozoite	small prisms, elongated prisms	24	Kozoite	small prisms, elongated prisms
	21	17			24		
	28	19			15		
	42	48			20		
	56	18			36		
165	1	23	Kozoite	Koz: small prisms, elongated prisms Cer: small octahedron	22	12% Koz, 8% HB, 2% Cer	Koz: small prisms, elongated prisms Cer: small octahedron HB: triangular prisms
	2	16	Kozoite		17	6% Koz, 7% HB, 2% Cer	
	3	18	17% Koz, <1% Cer	HB: triangular prisms	40	5% Koz, 29% HB, 6% Cer	
	4	28	27% Koz, <1% Cer		31	2% Koz, 25% HB, 4% Cer	
	7	22	21% Koz, <1% Cer		100	73% HB, 27% Cer	
	14	23	19% Koz, 3% HB, <1% Cer		100	43% HB, 57% Cer	
210	1	24	14% Koz, 5% HB, 5% Cer	Koz: small prisms, elongated prisms	42	25% HB, 17% Cer	Koz: small prisms, elongated prisms Cer: small octahedron HB: triangular prisms
	2	27	16% Koz, 10% HB, <1% Cer	Cer: small octahedron	38	21% HB, 17% Cer	
	3	37	13% Koz, 22% HB, 2% Cer	HB: triangular prisms	42	24% HB, 18% Cer	
	7	34	33% HB, 1% Cer		41	25% HB, 16% Cer	

Table 2: Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of aragonite with multi-component (La, Ce, Pr, Nd, and Dy), REE-bearing aqueous solutions (non-PAAS, and PAAS). * lanthanite (lan), kozoite (Koz), hydroxylbastnäsite (HB), cerianite (Cer)

		ARAGONITE					
T (°C)	NON-PAAS				PAAS		
	Time (days)	% Phase consumed	Phase formed	Morphology	% Phase consumed	Phase formed	Morphology
21	14	0			13		
	28	7	Lanthanite	Thin platy crystals	11	Lanthanite	Thin platy crystals
	42	11			22		
	56	8			15		
	84	18			13		
50	3	12	Kozoite	small prisms, elongated prisms	4	3%Koz,1% lan	Lan: Thin platy crystals Koz: Small prisms, Elongated prisms
	7	8			12	Koz	
	21	68			11	Koz	
	28				14	Koz	
	42	100			27	25% Koz, 2% Lan	
	56	16			50	48% Koz, 2% Lan	
80	1	11	Kozoite	small prisms, elongated prisms	16	Koz	Koz: small prisms, elongated prisms HB: Triangular prisms
	3	6			9		
	7	9			21		
	21	25			28	23% Koz, 5% HB	
	28	57			23	Koz	
	42	37			42		
	56	50	54				
165	1	13	Koz	Koz: small prisms, elongated prisms Cer: small octahedron HB: triangular prisms	17	14% Koz, 2% HB, 1 % Cer	Koz: small prisms, elongated prisms Cer: small octahedron HB: triangular prisms
	2	15	13% Koz, <1% Cer, <1%HB		19	13% Koz, 4% HB, 2% Cer	
	3	18	17% Koz, <1% Cer		29	11% Koz, 15%HB, 3% Cer	
	4	25	24% Koz, 1% Cer		34	12% Koz, 19% HB, 3% Cer	
	7	39	37% Koz, 2 % Cer		60	2% Koz, 45% HB, 13% Cer	
	14	25	23% Koz, <1% Cer, <1% HB				
210	1	9	7% Koz, 1% Cer		43	3% Koz, 23% HB, 17% Cer	
	2	11	6% Koz, 4% HB, 1% Cer		45	29% Hb, 16% Cer	
	3	31	12% Koz, 16% HB, 3% Cer		48	30% HB, 18% Cer	
	7	38	8% Koz, 28% HB, 2% Cer		64	49% HB, 15% Cer	

Table 3: Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of calcite with multi-component (La, Ce, Pr, ND, and Dy), REE-bearing aqueous solutions (non-PAAS, and PAAS). *lanthanite (Lan), kozoite (Koz), hydroxylbastnäsite (HB), cerianite (Cer).

CALCITE							
T (°C)	NON-PAAS				PAAS		
	Time (days)	% Phase consumed	Phase formed	Morphology	% Phase consumed	Phase formed	Morphology
21	14	0			6	Lan	
	28	0			0		Thin platy crystals
	42	0			0		
	56	0			0		
	84	0			10		
50	1	0			0		
	3	0			0		
	7	3			1		
	21	7	Kozoite	small prisms, elongated prisms	7	Kozoite	small prisms, elongated prisms
	28	7			11		
	42	12			37		
	56	14			29		
80	1	0			<1	Koz	
	3	7	Kozoite	small prisms, elongated prisms	11	6% Koz, 5% Lan	small prisms, elongated prisms
	7	10					
	21	36			40	Koz	
	28	67					
	42	76			17	Koz	
	56	53			41	Koz	
165	1	41	Koz	Koz: small prisms, elongated prisms Cer: small octahedra HB: triangular prisms	28	25% Koz, 2% HB, <1% Cer	Koz: small prisms, elongated prisms Cer: small octahedra HB: triangular prisms
	2	25	Koz		32	30% Koz, <1% HB, <1% Cer	
	3	49	Koz		35	31% Koz, 3% HB, 1% Cer	
	4	54	52% Koz, <1% Cer, <1% HB		29	25% Koz, 3% HB, 1% Cer	
	7	38	35% Koz, 1% Cer, 2% HB		37	19% Koz, 13% HB, 5% Cer	
	14	38	35% Koz, <1% Cer, 2% HB				
210	1	20	16% Koz, 4% Cer	Koz: small prisms, elongated prisms Cer: small octahedra HB: triangular prisms	72	37% HB, 35% Cer	Koz: small, elongated prisms Cer: small octahedra HB: triangular prisms
	2	13	11% Koz, 1 % HB, <1% Cer		100	54% HB, 46% Cer	
	3	17	14% Koz, 3% HB		95	58% HB, 37% Cer	
	7	100	Cerianite		80	47% HB, 33% Cer	

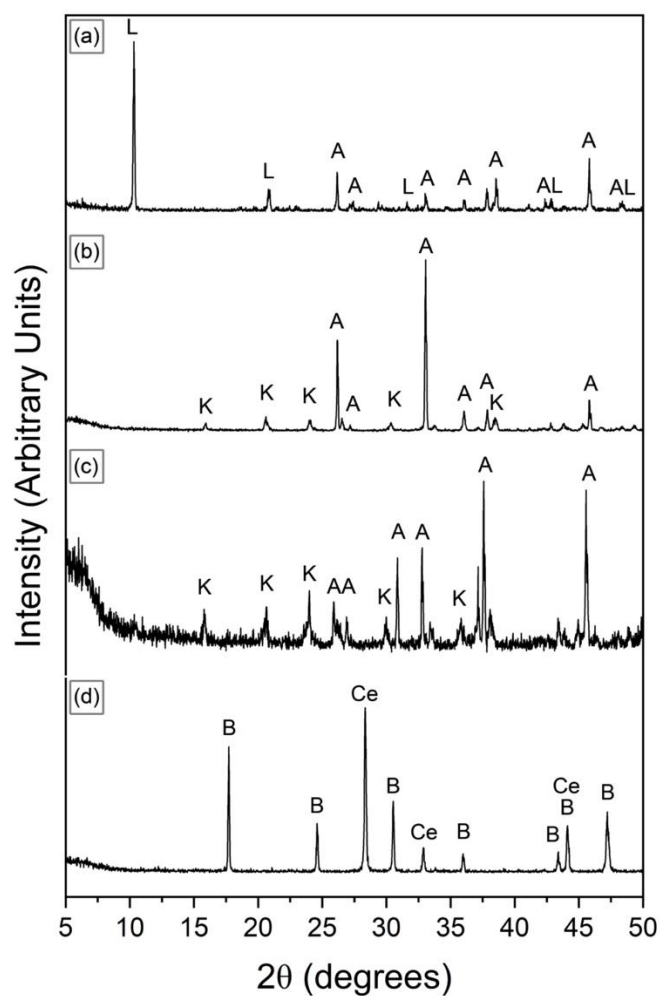


Figure 1: Powder XRD patterns of lanthanite (L), kozoite (K), hydroxylbastnäsite (B) and cerianite (Ce) obtained from experiments reacting (a) aragonite at 21 °C (non-PAAS), (b) 80 °C (non-PAAS), (c) 80 °C (PAAS) and (d) dolomite at 165 °C (PAAS).

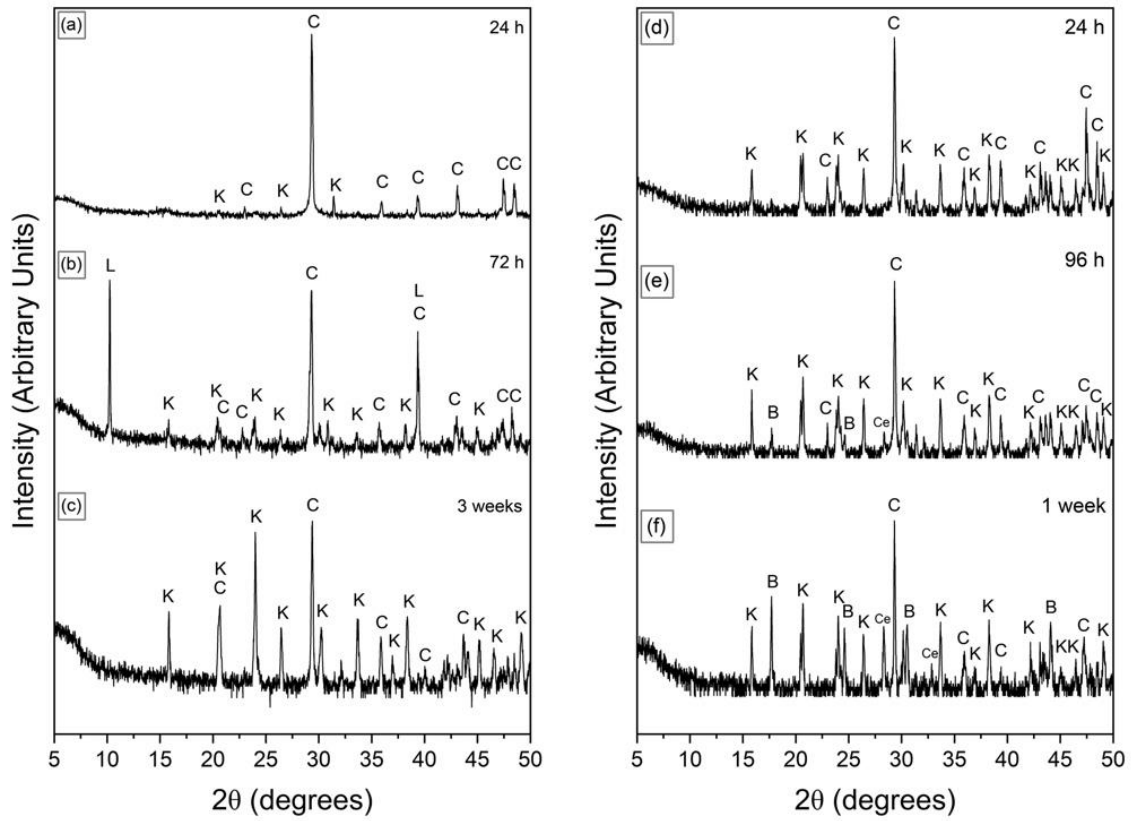


Figure 2. Powder XRD patterns of calcite in PAAS solution at 80 °C (a) 24 h, (b) 72 h, (c) 3 weeks, and 165 °C, (d) 24 h, (e) 96 h, (f) 1 week, *calcite (C), kozoite (K), bastnäsite (B)] The extent of the replacement reaction was found to be time and temperature dependent, with 40% of calcite consumed after 3 weeks at 80 °C (c), and 37% of calcite consumed after just one week (f) at 165 °C.

3.2. Scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS)

SEM imaging revealed the formation of precipitates on the surface of the calcite, dolomite, and aragonite grains. The extent to which these newly formed precipitates covered and replaced the host carbonate grain was found to be time and temperature dependent. The type of carbonate host as well as the REE concentration in solution also played a key role in the rate of replacement. For example, at ambient temperature, and in the equal concentration solutions, only the aragonite grains were seen to be fully covered by large (50-100 μm) platy lanthanite crystals, while the dolomite and calcite grains experienced only minor replacement (<1%) and few visible small (<10 μm) elongate lanthanite crystals (Tables 1-3). Comparatively, in the PAAS solution, both aragonite and calcite were both fully encased in a crust of lanthanite, while the dolomite still showed some surface area without any replacement, albeit with dissolution textures. At 50 and 80 $^{\circ}\text{C}$, all three hosts were completely encapsulated by the REE carbonate kozoite (Figure 3). Morphologies of the newly formed crystals consisted of small, elongate prisms of around 10 μm were found on all three hosts along with spherulitic aggregates in the aragonite experiments in both the equal concentration solution (after 8 weeks) and the PAAS solution (after 24 hours). In the higher temperature experiments (165-210 $^{\circ}\text{C}$) crystal morphologies consisted of triangular prisms of hydroxy-bastnäsité along with small octahedron of cerianite (Figure 4).

The polished epoxy resin pucks were subjected to energy dispersive spectroscopy (EDS). By mapping the cross section of the grains, differences in the spatial distribution of the REEs as they replaced the carbonate host grains were recorded. The replacement trends were found to be dependent on the initial concentration of REE in solution, with a more homogenous distribution in the equal concentration solution (Figure 5), and a more

heterogeneous distribution in the PAAS solution (Figure 6). The SEM-EDS analyses of the REE within the overgrowth revealed intriguing differences between the PAAS and non-PAAS samples, showing variations in the composition of both the complete overgrowth and localised differences in individual crystals. Although this trend is consistent across all experiments, both SEM-EDS and SEM-BSE analyses showed more pronounced chemical variations in the PAAS samples compared to the non-PAAS samples. In all instances, these compositional variations indicate two main trends: the first involves potential zoning, with lighter elements (La, Pr and Nd) concentrated in the centre and the heavier element (Dy) in the rims of the crystal (Figures 7, 8, and Figure SI-2), similar to the observations of Miyawaki et al. (17). Similarly, the second trend comprises a general compositional gradation in the replacement corona surrounding the Ca-Mg carbonate host, also featuring lighter REE elements (La and Nd) in the inner rim and the heavier element (Dy) in the outer rim (Figure 9 and Fig SI-3). Despite the occurrences of these chemical variations, there are limitations in our quantitative determinations which arise from the small size of individual kozoite/bastnäsite crystals (<20 μm) within the replacement corona, impeding detailed scrutiny, coupled with the subtle nature of compositional REE variations. These factors constrain the ability to carry out a precise quantification of these compositional variations.

Another feature observed in the cross-section EDS maps was symplectic textures, particularly in the PAAS samples subjected to the highest temperature of 210 °C. In the aragonite grains, we can see La, Pr-rich areas surrounded by vermicular intergrowths of Nd and Ce, radiating outwards (Figure 10), further supporting the idea that the heterogeneous distribution of REEs is dependent on the REE initial concentration in solution. In addition to the symplectic textures, we also observed areas with a significant

accumulation of cerianite, seemingly having fully replaced the rare earth carbonate minerals, with Dy being associated with Ce. (Figure 10 and 11).

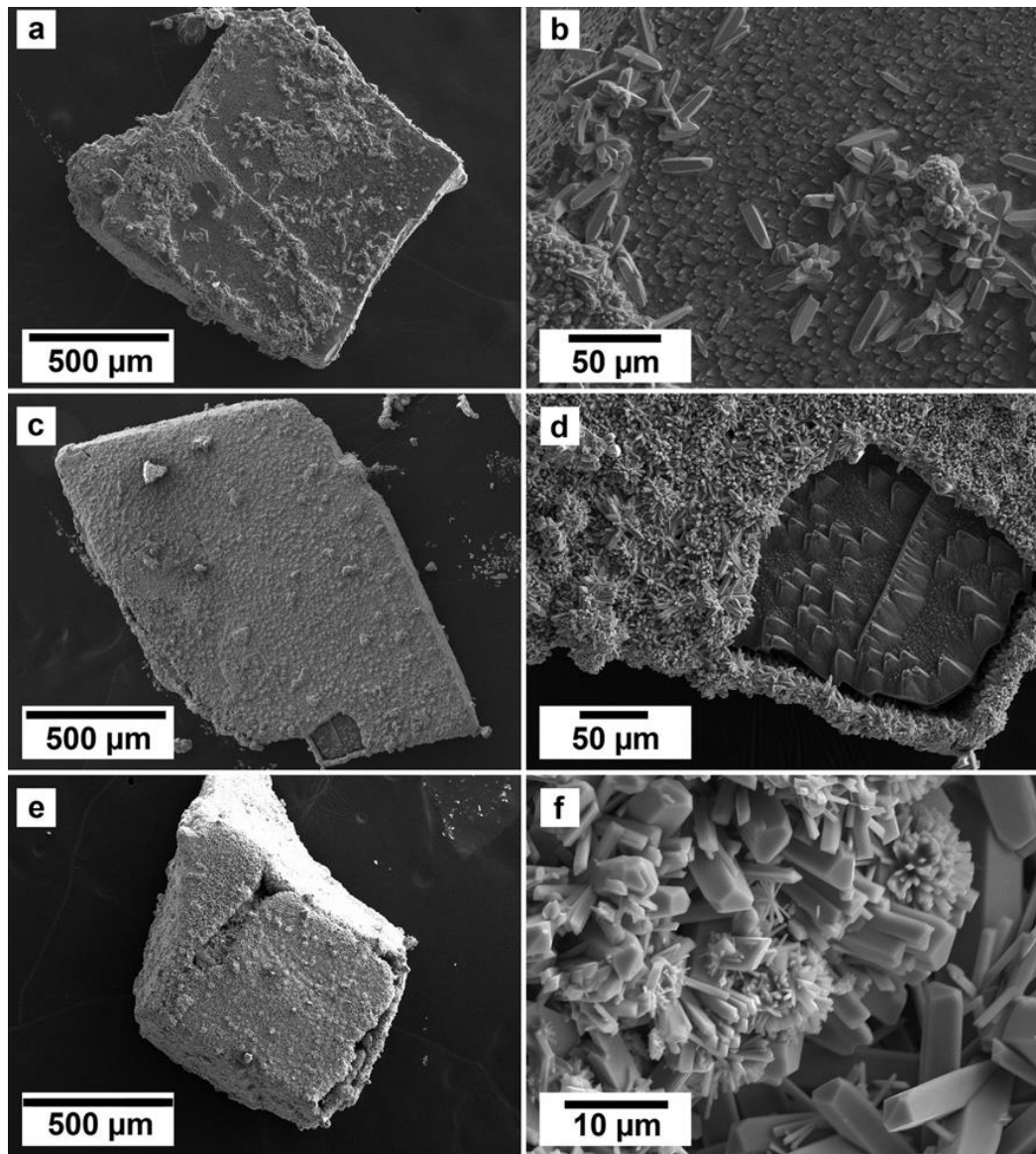


Figure 3. Secondary electron SEM images of the surface of calcite grains reacted with the PAAS solution at 80 °C showing the progressive replacement by REE carbonates (left: grain view, right: detailed view), after (a, b) 24, (c, d) 72 h, and (e, f) 4 weeks.

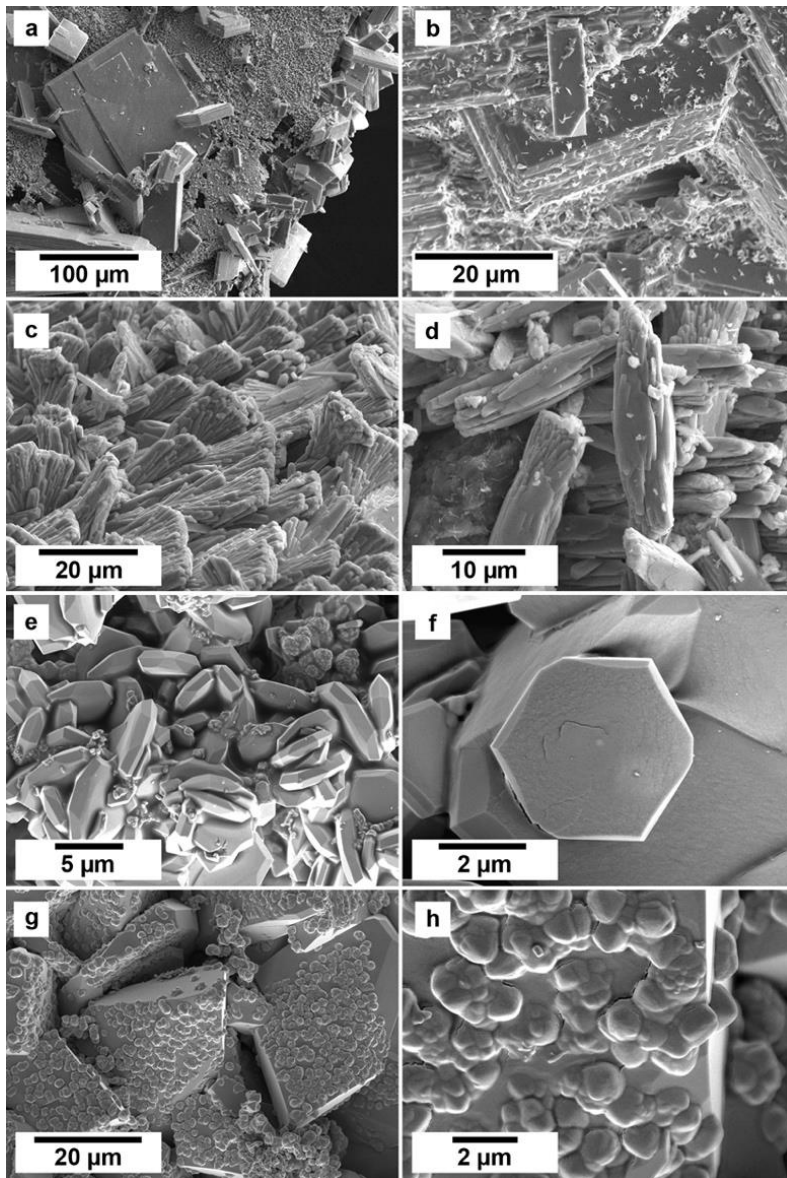


Figure 4. Secondary electron SEM images showing the series of replacement REE-bearing minerals observed on the surface of the host carbonate grains. (a) Thin, platy lanthanite crystals on calcite at 21 °C after 12 weeks in PAAS solution. (b) Detail of lanthanite with small (<1 μm) secondary kozoite crystals on aragonite at 21 °C after 8 weeks in PAAS solution. (c) Spherulitic kozoite on aragonite at 80 °C after 1 week in PAAS solution. (d) Detail of kozoite on aragonite at 80 °C after 1 week in non-PAAS solution. (e) Hydroxylbastnäsité on aragonite at 210 °C after 24 h in non-PAAS solution. (f) Detail of hydroxylbastnäsité on dolomite at 210 °C after 48 h in non-PAAS solution. (g) Secondary replacement of hydroxylbastnäsité by cerianite on calcite at 210 °C after 24 h in non-PAAS solution. (h) Detail of the early stages of nanocerianite formation on calcite at 210 °C after 24 h in non-PAAS solution.

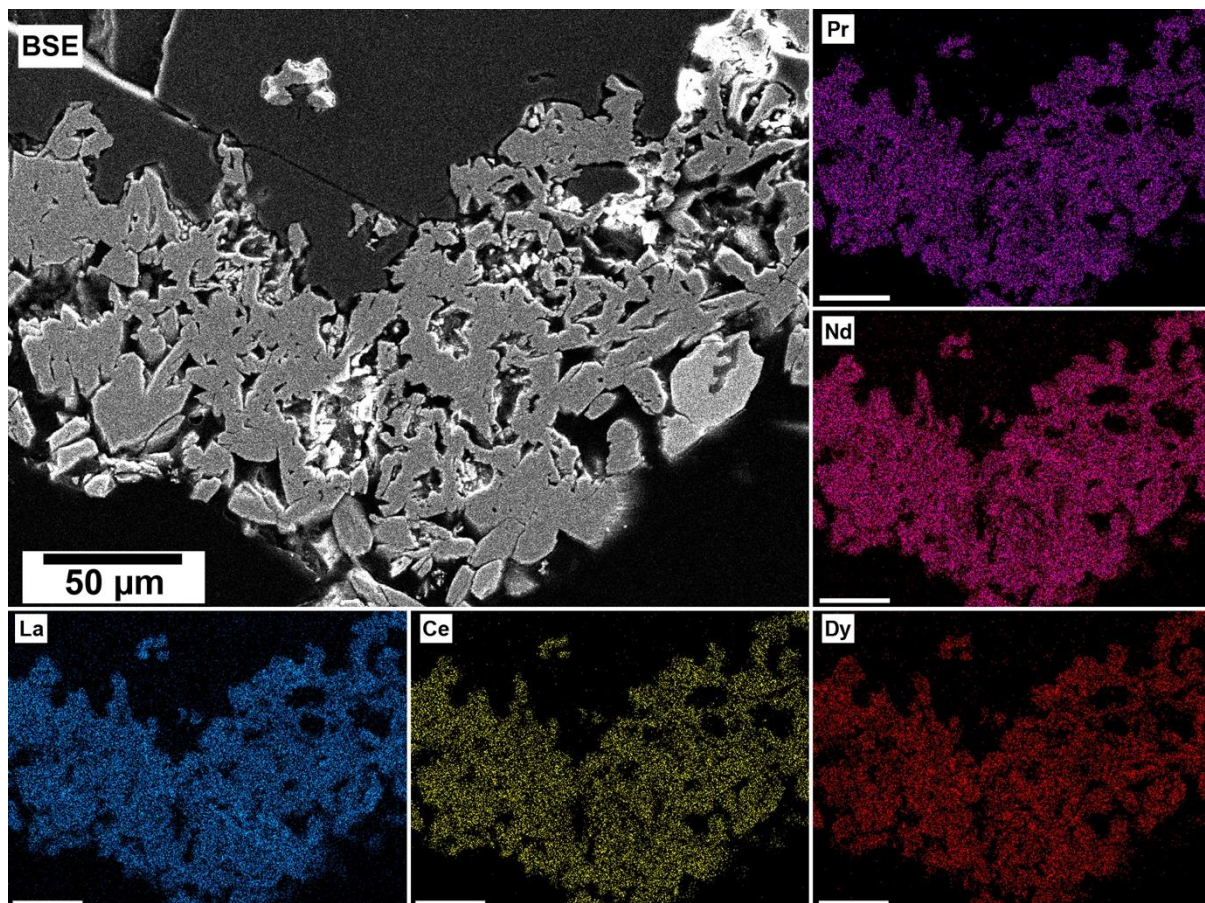


Figure 5. SEM-BSE image of calcite grain at 165 °C after 48 h in non-PAAS solution and EDS maps of La (blue), Ce (yellow), Pr (purple), Nd (pink), and Dy (red) showing the homogenous distribution of the REE. Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

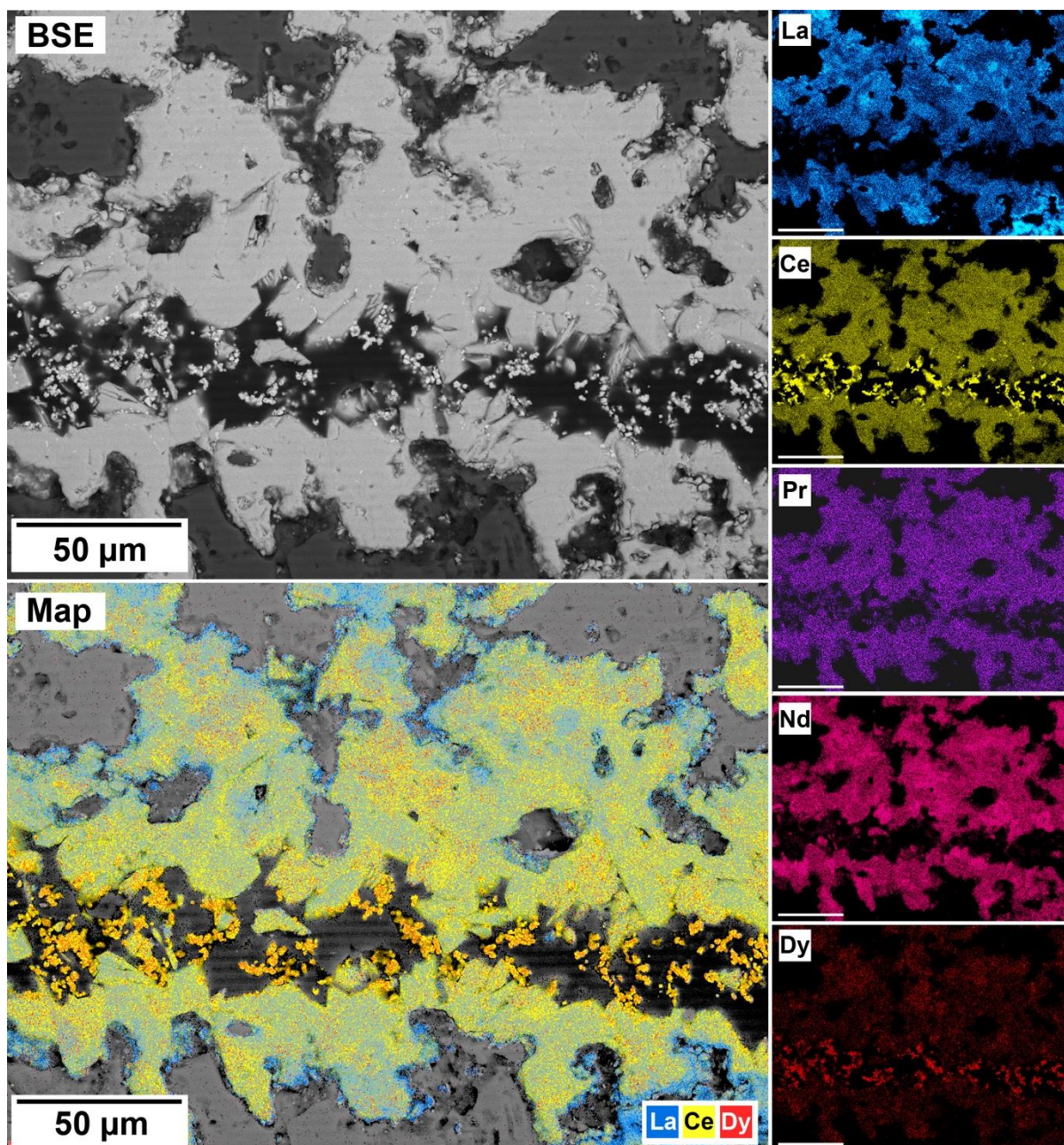


Figure 6. SEM-BSE image and EDS elemental maps of an aragonite grain at 165 °C after 24 h in PAAS solution showing the heterogenous distribution of the REE and the association of cerianite (yellow) and Dy (red). Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

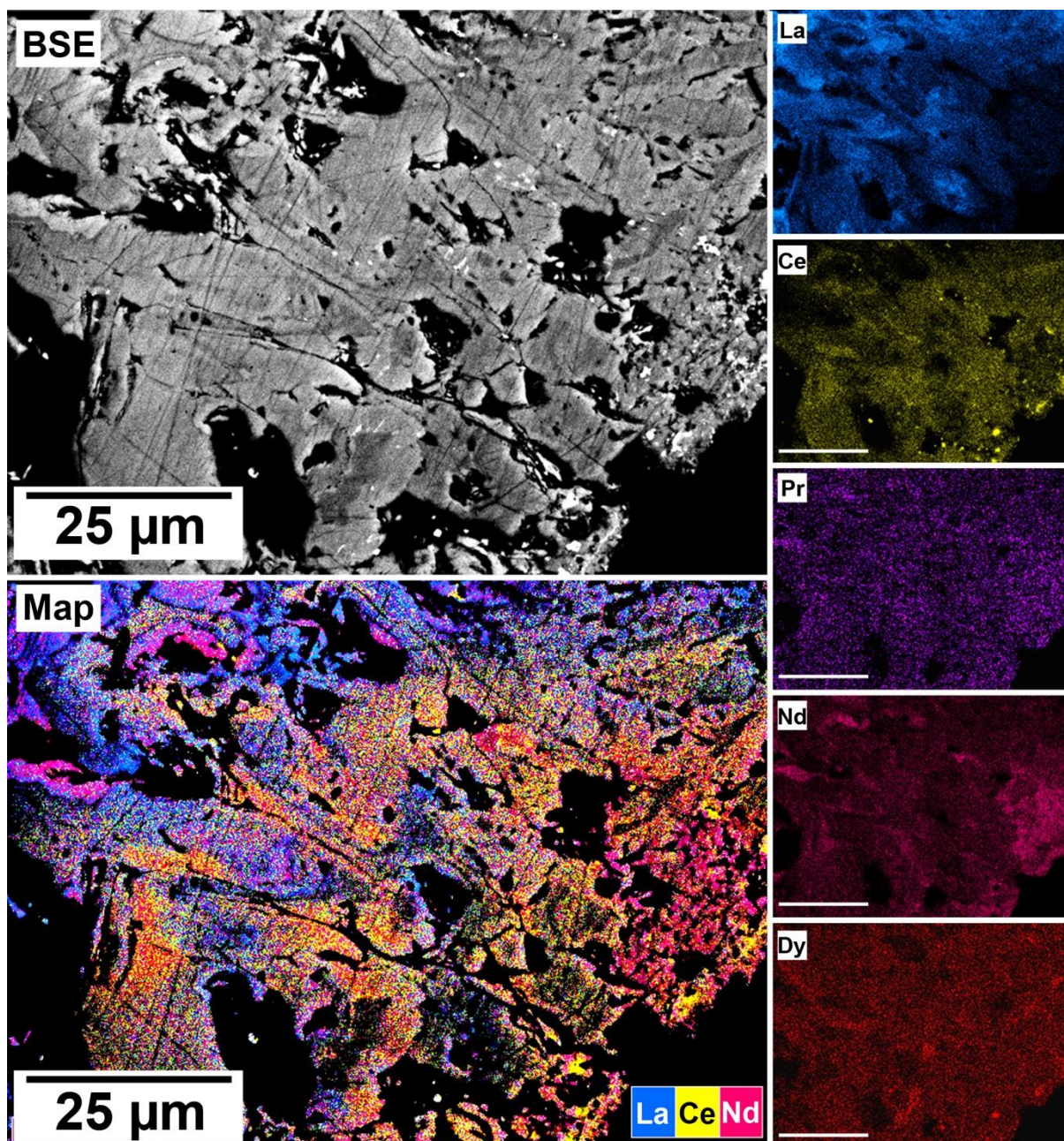


Figure 7. SEM-BSE image and EDS elemental maps of a calcite grain at 165 °C after 96 h in PAAS solution showing potential zoning in kozoite crystal, with lighter REE concentrated in the centre and heavier REE in the outer edges of the crystals. Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

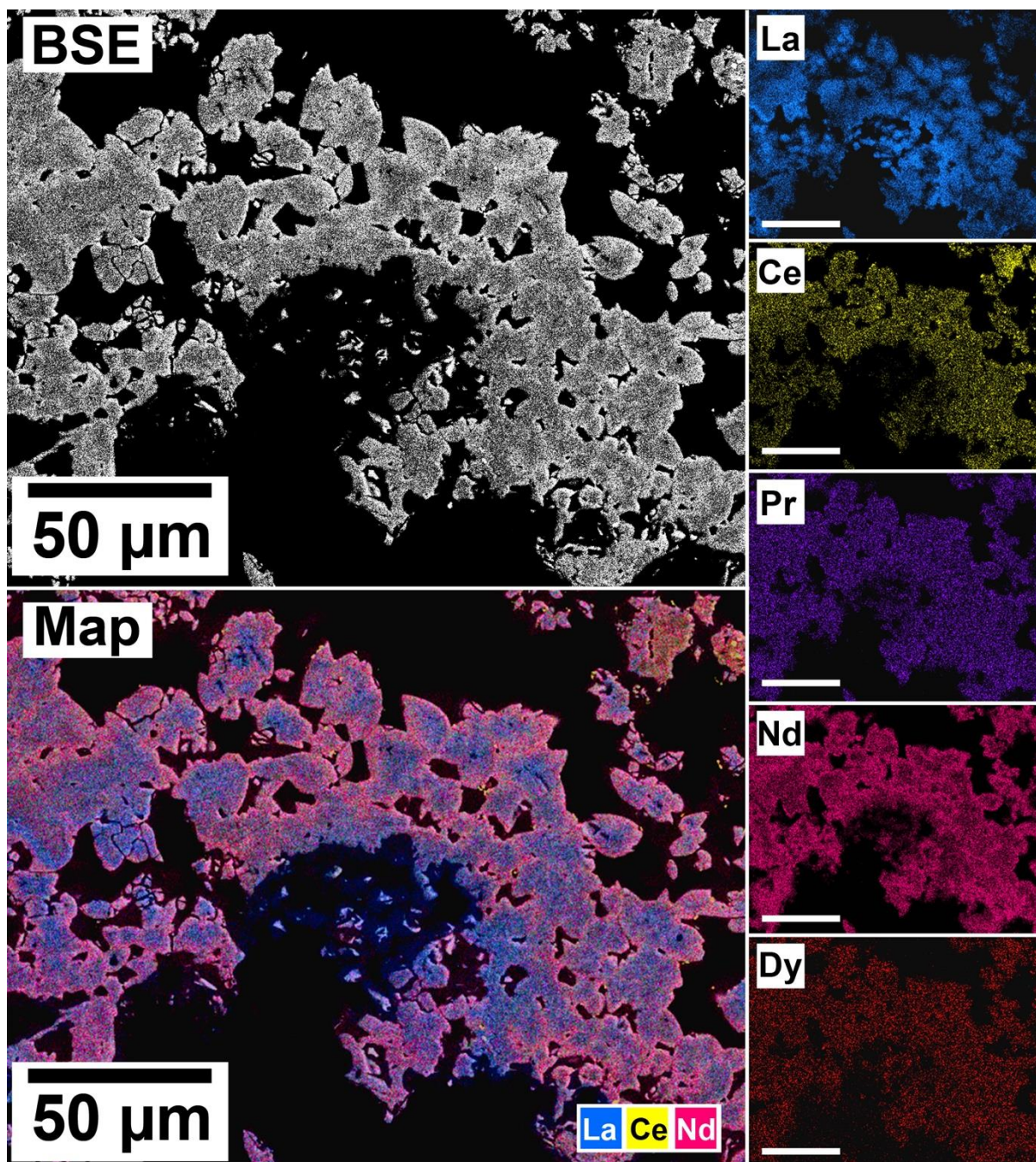


Figure 8. SEM-BSE image and EDS elemental maps of an aragonite grain at 165 °C after 72 h in PAAS solution showing potential zoning in kozoite crystal, with lighter REE concentrated in the centre and heavier REE in the outer edges of the crystals. Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

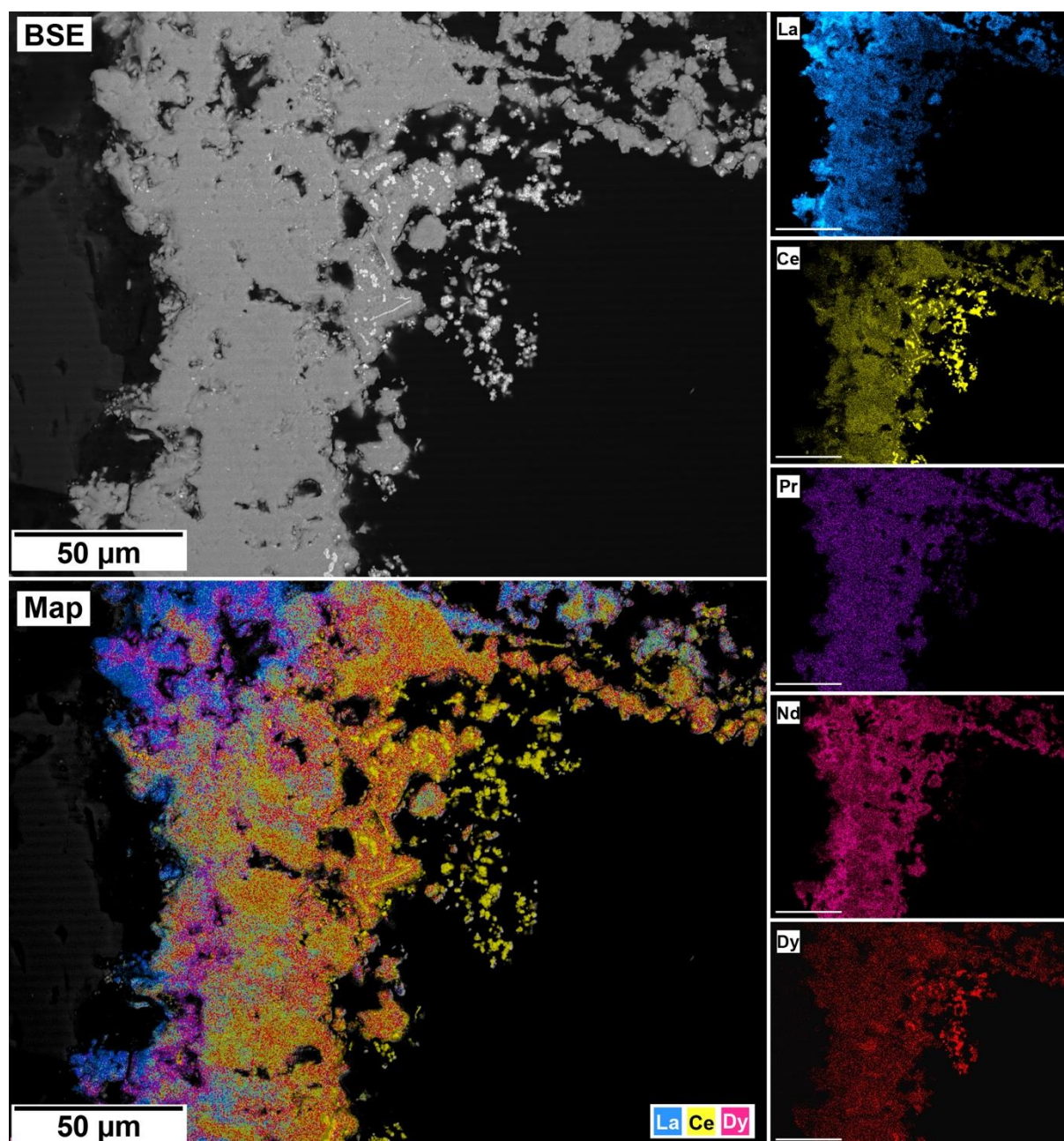


Figure 9. SEM-BSE image and EDS elemental maps showing the compositional gradation of REE in the replacement corona surrounding the aragonite host at 165 °C after 96 h in PAAS solution, with lighter REE accumulated towards the inner rims and heavier REE in the outer rim. Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

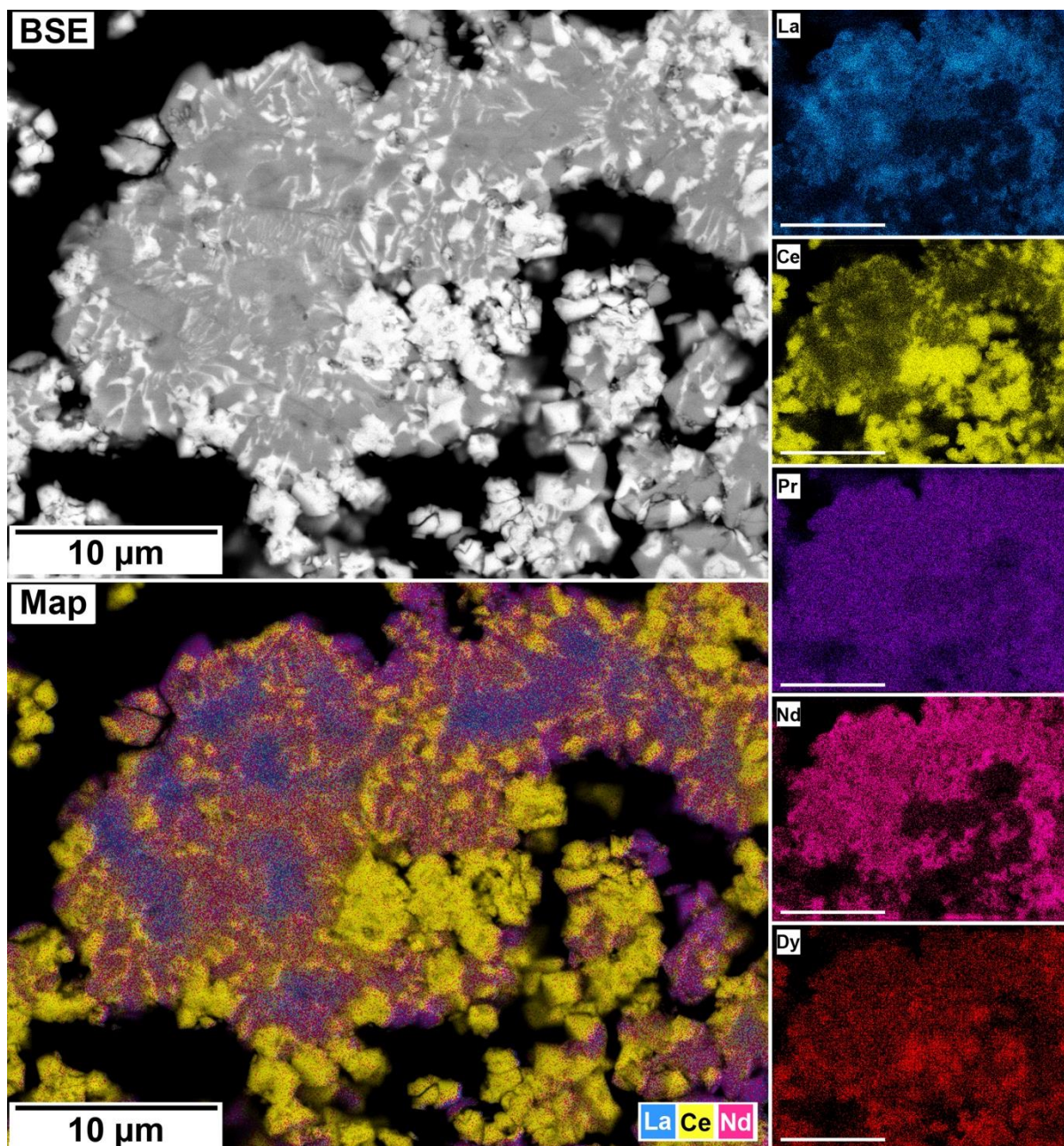


Figure 10. SEM-BSE image and EDS elemental maps of an aragonite grain at 210 °C after 24 h in PAAS solution. Areas of La-rich areas surrounded by vermicular intergrowths of Nd and Ce radiating outwards form the symplectic textures. Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

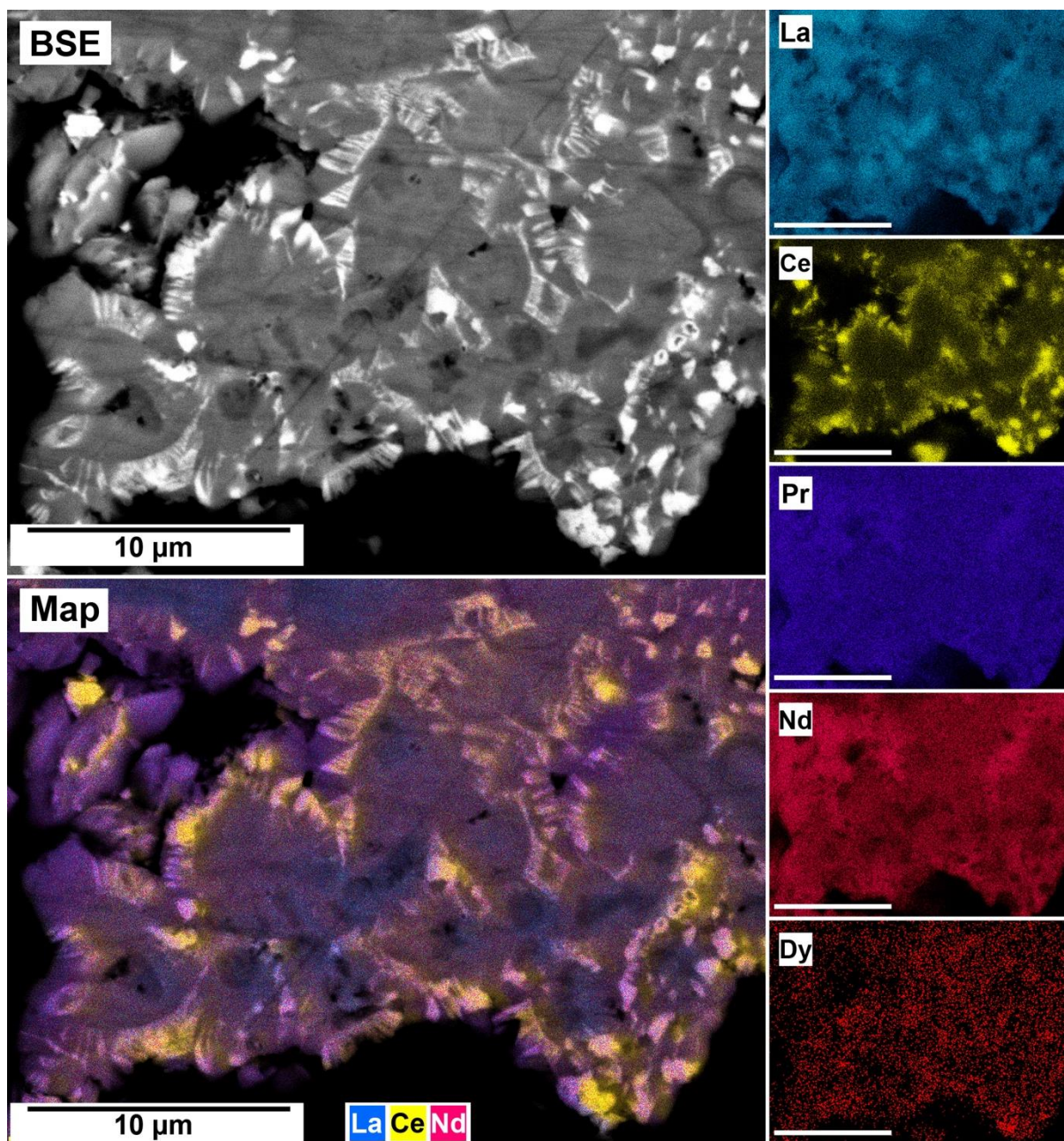


Figure 11. SEM-BSE image and EDS elemental maps of an aragonite grain at 210 °C after 24 h in PAAS solution showing how the location of cerianite defines the boundaries between pre-existing spindle-shaped kozoite crystals. Resolution (width) 2048 pixels, resolution (height) 1536 pixels, accelerating voltage: 20.0 kV, magnification: 1196 x, working distance: 15.0 mm.

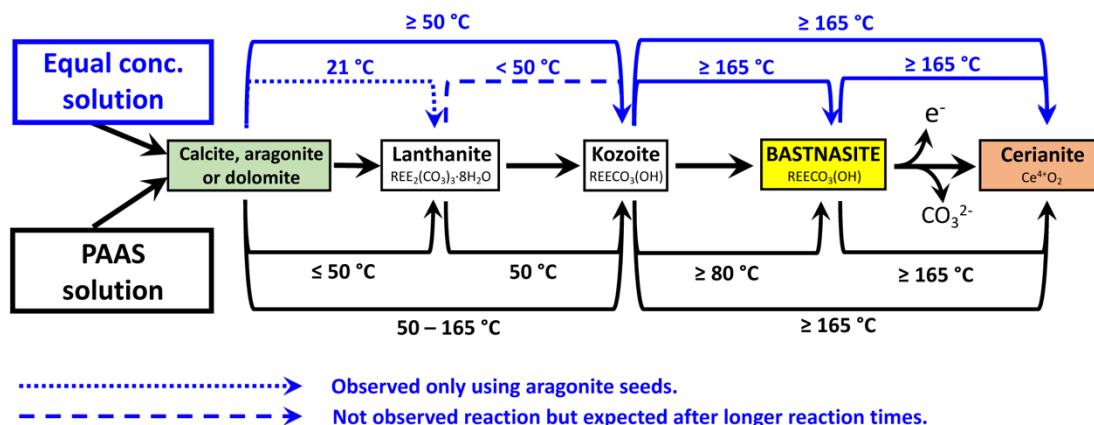


Figure 12. Reaction pathways during the replacement of Ca(-Mg) carbonates by rare earth carbonates and cerianite. Continuous lines correspond to observed reactions, dotted lines to observed reactions only using aragonite seeds, while dashed lines correspond to expected reactions that were not observed in our experiments. Each line shows the temperature at which the reaction takes place.

4. Discussion

The interaction of the Ca-Mg carbonates with the REE-bearing solutions resulted in the initial dissolution of the host grain, releasing Ca^{2+} and CO_3^{2-} (and Mg^{2+} from dolomite) into the aqueous solution. This dissolution of the host Ca(-Mg) carbonates rapidly increased the supersaturation of the solution, especially at the carbonate surface/solution interface, triggering the surface precipitation of REE-bearing carbonates, with some grains being fully replaced from the periphery inwards. Also, at the highest temperatures (210 °C), a secondary replacement occurred, with the REE-carbonate minerals being partially or totally replaced by cerianite. The reaction sequence (lanthanite → kozoite → hydroxylbastnäsite → cerianite) was time- and temperature-dependant, with some of the intermediate, metastable phases not forming at higher temperatures (≥ 165 °C) (Figure 12). The rate of crystallisation and composition of the main REE-bearing phases as well

the observed textures (Figures 5 to 11) were controlled by the solubilities and dissolution rates of the host grains and the REE ratio in solution, combined with the evolving fluid composition during the gradual replacement process. The influence of temperature is also a key factor, as it affects the dehydration of specific REE^{3+} before being incorporated into the growing crystals as well as the oxidation of Ce^{3+} to Ce^{4+} in solution.

4.1. Solubility, dissolution rate and chemical textures

In all of our experiments we observed a centripetal replacement of the host mineral, as they were replaced from the periphery inwards by the newly formed REE carbonates. This is a consequence of the lower solubilities of REE carbonates compared to the host minerals at the specific pressure-temperature conditions studied (18–20). For example, the solubility products for pure Nd-hydroxylbastnäsite, La-hydroxylbastnäsite, and Nd-Kozoite have been calculated to be $\log(K_{\text{sp}}) = -23.8 \pm 0.1$, $\log(K_{\text{sp}}) = -24.1 \pm 0.3$, and $\log(K_{\text{sp}}) = -22.3 \pm 0.2$, respectively (19), while the solubility products of calcite, $\log(K_{\text{sp}}) = -8.480 \pm 0.020$, aragonite, $\log(K_{\text{sp}}) = -8.336 \pm 0.020$ (21) and dolomite, $\log(K_{\text{sp}}) = -18.14$ (22) are much higher. Determining the solubility of solid phases with intermediate compositions is not feasible due to the absence of relevant data. Existing literature suggests that lighter REE carbonates are more soluble than their heavier counterparts (18). However, conflicting trends and discrepancies have been reported by other researchers (19,20), highlighting the complexity of this system, with some reported variations potentially arising from the occurrence of different crystalline (nano)phases during synthesis, each possessing different solubility products and different kinetics of crystallization (23,24). Also, measuring the solubility products at elevated temperatures is challenging because of insufficient availability of reliable data pertaining to the

stability of diverse aqueous complexes formed by REEs with carbonate and hydroxyl ions (19).

While these large differences in solubility influence the polymorph selection and its chemistry, it is the dissolution rate of the host mineral that determines the rate at which the new phase can precipitate. For example, the dissolution rates of calcite, aragonite, and dolomite at 25 °C have been calculated to be $\log R_{\text{cal}} = -8.8 \text{ mol}^{-2}\text{s}^{-1}$, $\log R_{\text{arg}} = -9.2 \text{ mol}^{-2}\text{s}^{-1}$ and $\log R_{\text{dol}} = -10.1 \text{ mol}^{-2}\text{s}^{-1}$ (25) meaning that e.g. aragonite will dissolve almost an order of magnitude faster than dolomite at the initial pH of 5.1. This is particularly evident in our ambient and 50 °C experiments, with replacement of aragonite commencing after 3 days compared to the replacement of calcite and dolomite initiating after 7 and 21 days respectively. The higher dissolution rates of aragonite and calcite mean that carbonate ions are released faster into the aqueous solution compared to the dolomite experiments, resulting in higher supersaturation levels needed to initiate the nucleation of the REE carbonates. Using calcite as an example, PHREEQC calculations (Supplementary Information, Fig S2-3) show that even when the saturation index for calcite is -5 , the concentration of Ca^{2+} and CO_3^{2-} released into the aqueous solution is high enough to allow the supersaturation with respect to REE carbonate minerals. Therefore, at ambient temperature, even small amounts of the host mineral dissolution would promote the precipitation and growth of REE carbonates (e.g., lanthanite in our ambient temperature experiments). Another factor to consider is that we did not stir our experiments, meaning that our grains remained static inside the reactors. As a consequence, the concentrations of Ca^{2+} , Mg^{2+} and CO_3^{2-} at the interface between the host mineral and the aqueous solution should have been even higher, resulting in higher supersaturation levels with respect to REE carbonates. This means that dissolving just a few monolayers of the host grain would sufficiently promote the nucleation and surface crystallization of the REE

carbonates. This process, in turn, would lower the concentration of CO_3^{2-} in the solution, further enhancing the dissolution of the host grain.

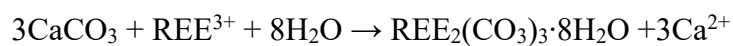
Additionally, it is important to emphasise the role of ionic potentials of the REE^{3+} cations in this process (26). Lighter trivalent ions require lower energy for dehydration from solution compared to heavier ones (23,24), kinetically favouring the formation of La-rich crystals in the initial stages of the replacement reaction. As the lighter elements are gradually consumed, the solution becomes enriched in heavier ions, resulting in the development of crystals characterised by heavier-REE rims.

Although our SEM-BSE-EDS analyses of REE carbonates (Figures 5 to 9, SI-2, and SI-3) would suggest lighter REE carbonates exhibiting lower solubility compared to their heavier counterparts, it is crucial to emphasize that these replacement reactions present a multi-variable challenge. The chemical textures observed in kozoite may be subject to local reorganisation during its transformation to secondary bastnäsite. This gradual process observed in our experiments (Tables 1-3, Figure 2), is known to occur via dissolution-recrystallization (23,24,27–29) and introduces an additional layer of complexity, potentially influencing the complex chemical variations occurring in the replacement rim at the micro- and nanoscale. Overall, the intricate interplay of crystal structures, variable solid-solution compositions and solubilities, ionic potentials, temperature, evolving solution composition, available reactive surface, as well as temperature-dependant dissolution-recrystallization processes, collectively contribute to the observed chemical variability within the single crystals and in the replacement ring. Quantifying the preferential incorporation of REEs in our samples is also highly complicated due to the small size and random orientation of the individual kozoite or bastnäsite crystals within the replacement corona. Therefore, a more comprehensive

examination would require the production of larger or isolated single crystals, a task that exceeds the scope of the current study.

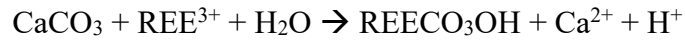
4.2. The effect of molar volume

With the exception of two of our experiments (e.g., dolomite, PAAS solution at 165 °C, and calcite, non-PAAS solution at 210 °C), none of the experiments resulted in the complete replacement of the host grain. This can be explained by difference in molar volume between the minerals in the host grain and the overgrowth. If the newly forming REE carbonate overgrowth has a larger molar volume compared to the host mineral, it will begin to encapsulate the host. As the host is being covered, its dissolution rate will decrease, triggering a decrease in REE carbonate precipitation as there are less CO_3^{2-} ions entering the aqueous solution. When this overgrowth is large and dense enough and completely isolates the host grain from the aqueous solution, the dissolution of the host stops and a 'partial equilibrium' with respect to the REE carbonates is reached (30). We can use the reaction of calcite (molar volume of 36.93 cm^3/mol) being replaced by lanthanite (molar volume 216.70 cm^3/mol) as an example:



The difference between the molar volumes of the reagents and the products is so great that the lanthanite replacement can fully encapsulate the host. In our ambient temperature experiments, the maximum consumption of the host phase was only 18%, even after a

duration of 84 days (Table 1-3). Comparatively, we can look at the replacement of calcite by kozoite or bastnäsite (molar volumes 45.48 and 44.91 cm³/mol respectively):



Here, the difference in molar volumes also results in the encapsulation of the host, however, the difference is not substantial compared to the difference between lanthanite and calcite. This very small difference in molar volume, combined with the morphology of kozoite and bastnäsite consisting of many small micrometric crystals, allows for the development of microporosity during the replacement process. This causes some fluid to remain in contact with the host grain, enabling its dissolution and the potential full replacement of the host grain, as seen in our high temperature (>165 °C) experiments.

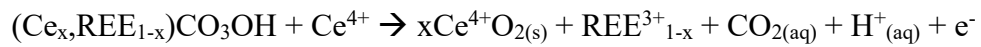
4.3. Secondary replacement of the REE carbonates with cerianite and formation of symplectic textures

In all of our experiments above 165 °C we observed a secondary replacement of kozoite and hydroxylbastnäsite by cerianite (Figure 10). The onset of cerianite formation is a consequence of the oxidation of Ce³⁺ to Ce⁴⁺, with several factors promoting this transition. First, Ce⁴⁺ has the electron structure of a noble gas, making it more stable than Ce³⁺, and the higher temperatures provide the energy needed to facilitate the loss of an electron. Also, as our systems progressed towards equilibrium, the pH would increase from ~ 5 to 8.1-8.2. The higher concentration of OH⁻ ions allows the formation of Ce-hydroxo-complexes which facilitate the Ce³⁺ to Ce⁴⁺ oxidation process (27,31), especially

at the surface-solution interface of the REE or Ca-Mg-carbonate minerals (27,31). As Ce^{4+} is incompatible within the carbonate structure, it combines with oxygen, forming the oxide cerianite (CeO_2), which is the most insoluble and the most thermodynamically stable phase in our system. Our experimental setup (sealed hydrothermal reactors containing a limited atmosphere, under conditions of autogenous pressure) inherently creates an oxidising environment favouring the oxidation of Ce^{3+} to Ce^{4+} reaction. Had we conducted the experiments using anoxic water and a pure N_2 atmosphere, the presence of carbonates like calcite and dolomite would have also buffered the pH of the aqueous solution, increasing the stability of the HCO_3^- ions relative to CO_2 , but these changes would have a negligible influence on the redox state. This means that the formation of cerianite would likely not have occurred, and Ce would have been incorporated to the newly formed carbonates as Ce^{3+} along with the other REEs in the system.

The SEM-EDS images and maps (Figures 10 and 11) show a very specific intergrowth of the REE carbonates and cerianite at high temperatures ($>165^\circ\text{C}$), a textural feature known as a symplectite. These textural features are common in metamorphic rocks that have undergone high pressure-temperature conditions (32) and have also been found in REE-bearing deposits (33). The exact mechanisms behind the formation of symplectites can vary depending on the specific mineral assemblages and geological conditions. However, we propose that in our experiments this texture results from a fluid-mediated mineral replacement, driven by dissolution-precipitation mechanisms and intra-mineral diffusion processes (34). In all of our experiments, all of the REE carbonates formed prior to cerianite, and the latter always crystallized exclusively in association with the surface of the pre-existing REE carbonates, indicating that this process takes place at the solution-surface interface, in agreement with Szucs et al., (27). As cerianite is more insoluble ($\log(K_{\text{sp}}) = -59.3 \pm 0.3$; (35)) compared to kozoite ($\log(K_{\text{sp}}) = -22.3 \pm 0.2$) or bastnäsite

($\log(K_{sp}) = -23.8 \pm 0.1$) or the host Ca-Mg carbonates, it can replace any carbonate crystals in our system until the Ce^{4+} is depleted from the aqueous solution. This replacement is also enhanced by the smaller molar volume of cerianite ($23.86 \text{ cm}^3 \text{ mol}^{-1}$) compared to kozoite ($45.59 \text{ cm}^3 \text{ mol}^{-1}$) or bastnäsite ($44.91 \text{ cm}^3 \text{ mol}^{-1}$) which increases the porosity of the parent phase (36). The kozoite / bastnäsite replacement by cerianite can be expressed by the following reaction:



As the molar volume of cerianite is the smallest of all phases present in our system, when this oxide replaces any REE carbonate, or the host, it creates porosity. This allows fluid access to the pre-existing REE carbonates, and the continuation of the replacement reaction, releasing previously immobilized REEs from the carbonate minerals back into the solution. As some of the REE have similar ionic radii to Ce^{4+} (1.220 Å), in particular Dy^{3+} (1.075 Å), and to a slightly lesser extent, Nd^{3+} (1.175 Å), they can be incorporated into cerianite as impurities. If there is enough Ce in the system, cerianite has the potential to fully replace all of the other mineral phases, with the remaining incompatible REE^{3+} ending up in the aqueous solution.

Concomitantly, any Ce^{3+} located in the non-replaced kozoite or bastnäsite structures will also tend to oxidise to Ce^{4+} . Assuming an REE-O coordination of 9 in kozoite and bastnäsite, the Ce^{3+} to Ce^{4+} oxidation is also translated into a decrease in the ionic radius from 1.33 to 1.16 Å (26), making Ce^{4+} incompatible with these REE carbonates. Therefore, the oxidation process would trigger a solid-state phase transformation from REE-carbonates to cerianite at the local scale. This process would involve the migration of Ce^{4+} ions through the existing REE carbonate structure, leading to their accumulation

at the nanoscale, triggering the nucleation of nm-sized cerianite. Our EDS maps (Figures 10 and 11) reveal a depletion of Ce in the REE carbonate phases and the accumulation of this element as a discrete phase (cerianite), while the rest of the REEs tend to concentrate in the carbonate crystals.

Both our SEM-BSE images and EDS maps (Figures 10 and 11) show that the location of cerianite defines the boundaries between pre-existing spindle-shaped kozoite crystals. This indicates that the formation of these symplectic textures has been favoured by the boundaries of the original polycrystalline material, as it is easier for ions to migrate through crystal imperfections. Therefore, the local boundaries between the parent kozoite single crystals provide the ideal starting point to initiate the formation of the symplectic texture, in turn creating the visible ‘ghosts’ textures of the pre-existing kozoite.

5. Conclusion

The reaction between each of the carbonate host grains, dolomite, aragonite, and calcite, with multi-component REE-bearing (La, Ce, Pr, Nd, and Dy) aqueous solutions resulted in the replacement of the carbonate host and the formation of secondary REE-bearing minerals. The reaction followed the multi-step crystallization sequence: lanthanite → kozoite → hydroxylbastnäsite → cerianite. The REEs were preferentially incorporated into the growing REE-minerals, likely because of the combination of several factors including the solubility and dissolution rate of the carbonate host compared to the REE minerals, time, temperature, ionic radius and ionic potential of the REE as well as its concentration in solution. At higher temperatures (>165 °C) a secondary replacement of kozoite and bastnäsite by the rare earth oxide, cerianite, was observed. Differences in molar volumes between cerianite and kozoite/bastnäsite generated porosity in the newly

formed mineral and allowed for solution-mediated mineral replacements, producing symplectic textures. Our study sheds light on the uptake of multiple REEs by various carbonate minerals and provides insight into the potential zoning of REEs in rare earth minerals. A broader knowledge of REE zoning will have potential applications in rare earth separation techniques, beneficiation, and recycling.

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Supplementary Information

Chemical Textures on rare earth carbonates: an experimental approach to mimic the formation of bastnäsite

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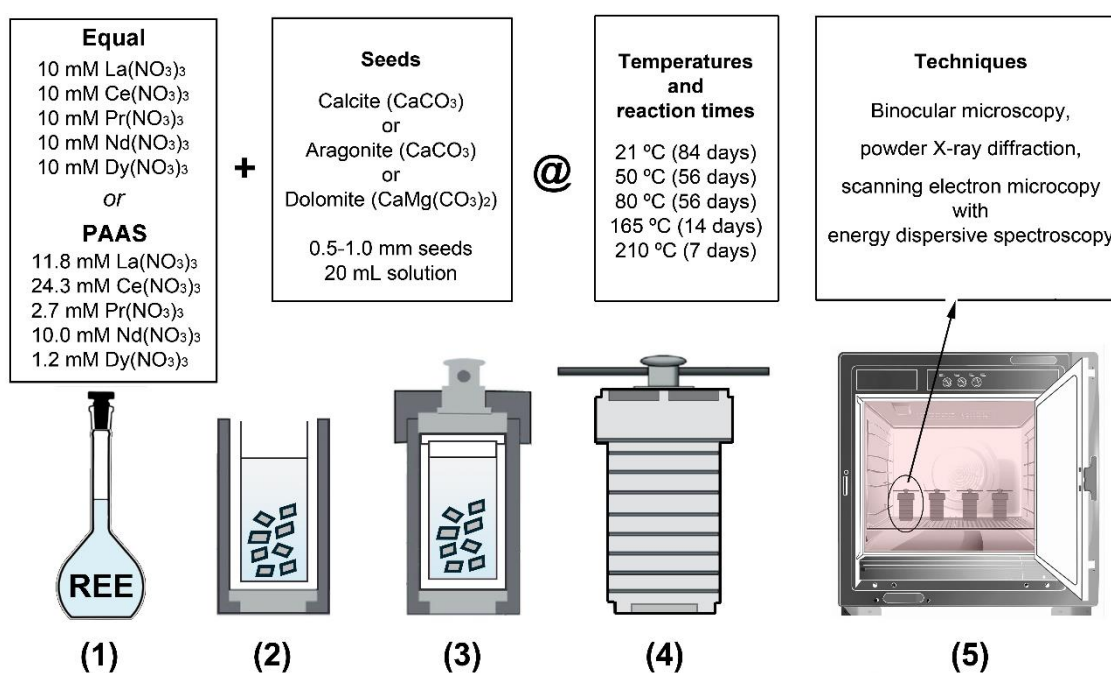


Fig. SI-1. Graphical summary showing the experimental protocol used in this study.

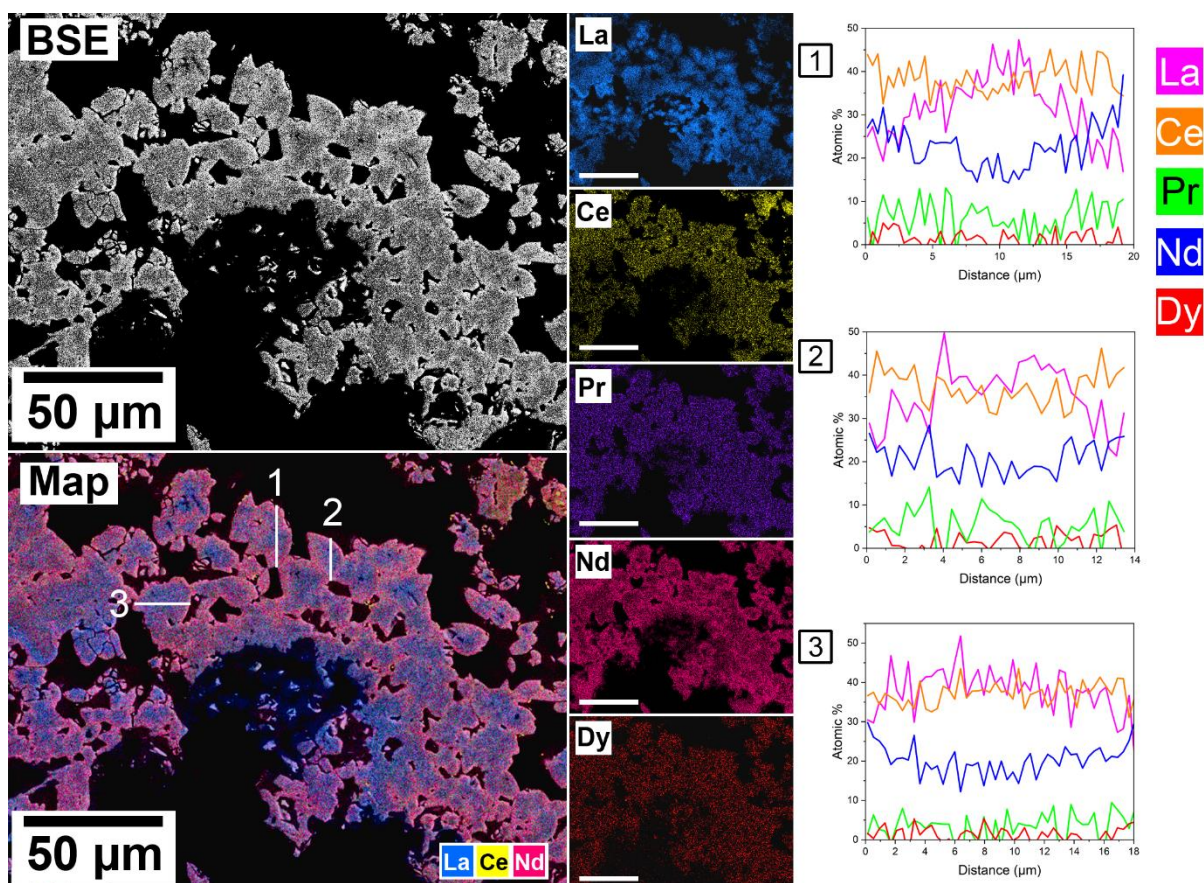


Figure S2-1. SEM-BSE image and EDS elemental maps of an aragonite grain at 165 °C after 72 hrs in PAAS solution showing potential zoning in kozoite crystals, with lighter REE concentrated in the centre and heavier REE in the outer edges of the crystals. Quantitative line analysis (Lines 1, 2 and 3) further supports this trend showing higher concentrations of La in the centre and Nd at the rim of the individual kozoite crystals.

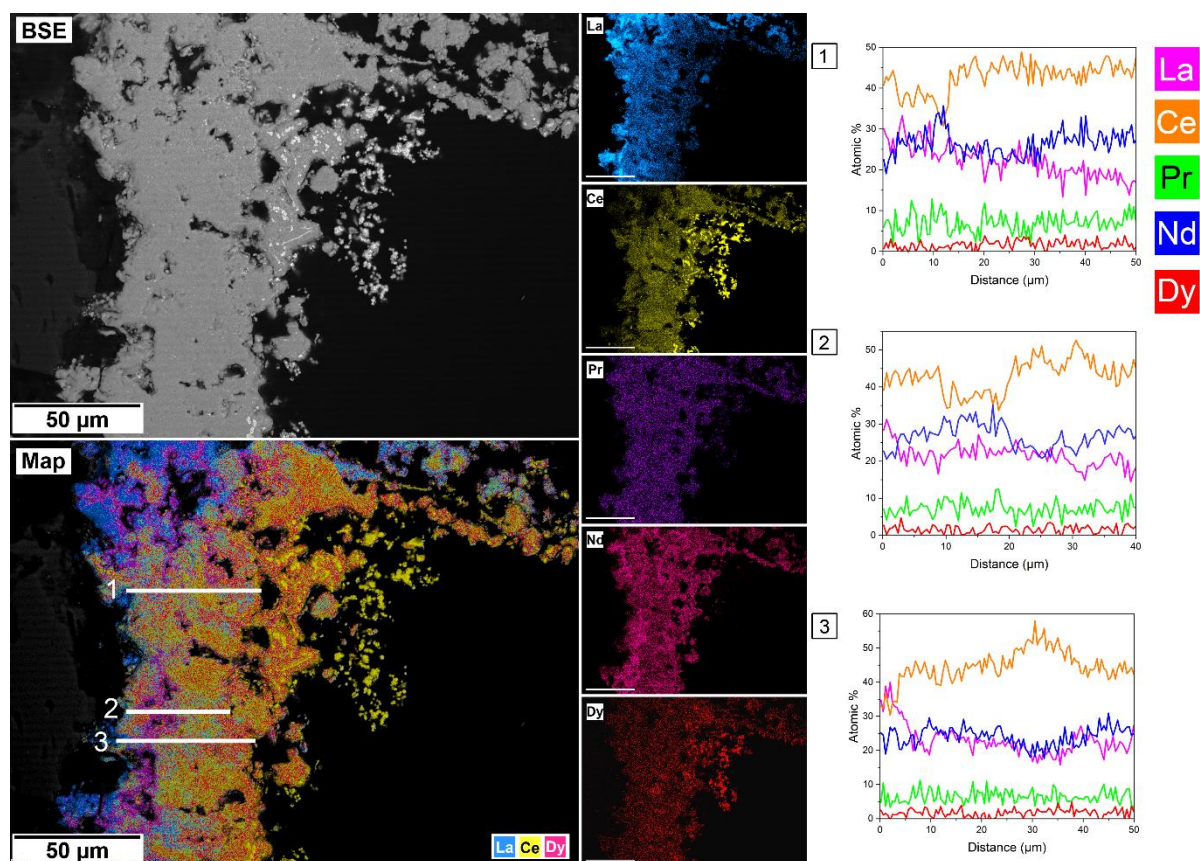


Figure S2-2. SEM-BSE image and EDS elemental maps showing the compositional gradation of REE in the replacement corona surrounding the aragonite host at 165 °C after 96hrs in PAAS solution, with lighter REE accumulated towards the outer rims and heavier REE in the inner rim. This trend is further supported by quantitative line analysis in lines 1, 2 and 3.

```

PHREEQC PROGRAM

SOLUTION 1
Temp.          25      adjusted per experiment
pH             11
pe             4
redox          pe
units          mmol/l
density        1
(-) water      1 # kg

REACTION 1          # this is for equal concentration, for PAAS, the "1" was changed to appropriate ratio as follows
La(NO3)3          1          11.8
Ce(NO3)3          1          24.3
Pr(NO3)3          1          2.7
Nd(NO3)3          1          10
Dy(NO3)3          1          1.2

EQUILIBRIUM_PHASES
calcite        0 10      # or aragonite, dolomite, siderite, vivianite

END

```

Figure S2-3. PHREEQC calculations general program.

Chapter 3: Transient crystallisation of rare earth carbonates during the hydrothermal oxidation of siderite

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Keywords: Siderite; Bastnäsite; Cerianite; Kozoite; Rare earth carbonates; Goethite; Hematite.

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Abstract

Our study investigates the interaction between multi-component rare earth element (REE; La, Ce, Pr, Nd, Dy)-bearing aqueous solutions and siderite (FeCO_3) grains under hydrothermal conditions (50-205 °C). The results revealed a solution-mediated mineral replacement reaction that occurs via a multi-step crystallisation pathway involving the formation of iron oxides (goethite, $\alpha\text{-FeO}(\text{OH})$, and hematite, Fe_2O_3), metastable REE-bearing minerals (kozoite, $\text{REE}(\text{CO}_3)(\text{OH})$, and bastnasite, $\text{REE}(\text{CO}_3)(\text{OH},\text{F})$), and cerianite (CeO_2). Siderite stability, dissolution, and subsequent mineral formation are temperature and pH-dependent. At low temperatures, REE carbonate formation is inhibited by a goethite coating, creating a partial equilibrium situation. Higher temperatures increase dissolution rates and enable kozoite and bastnasite formation. The redox behaviour of Fe and Ce

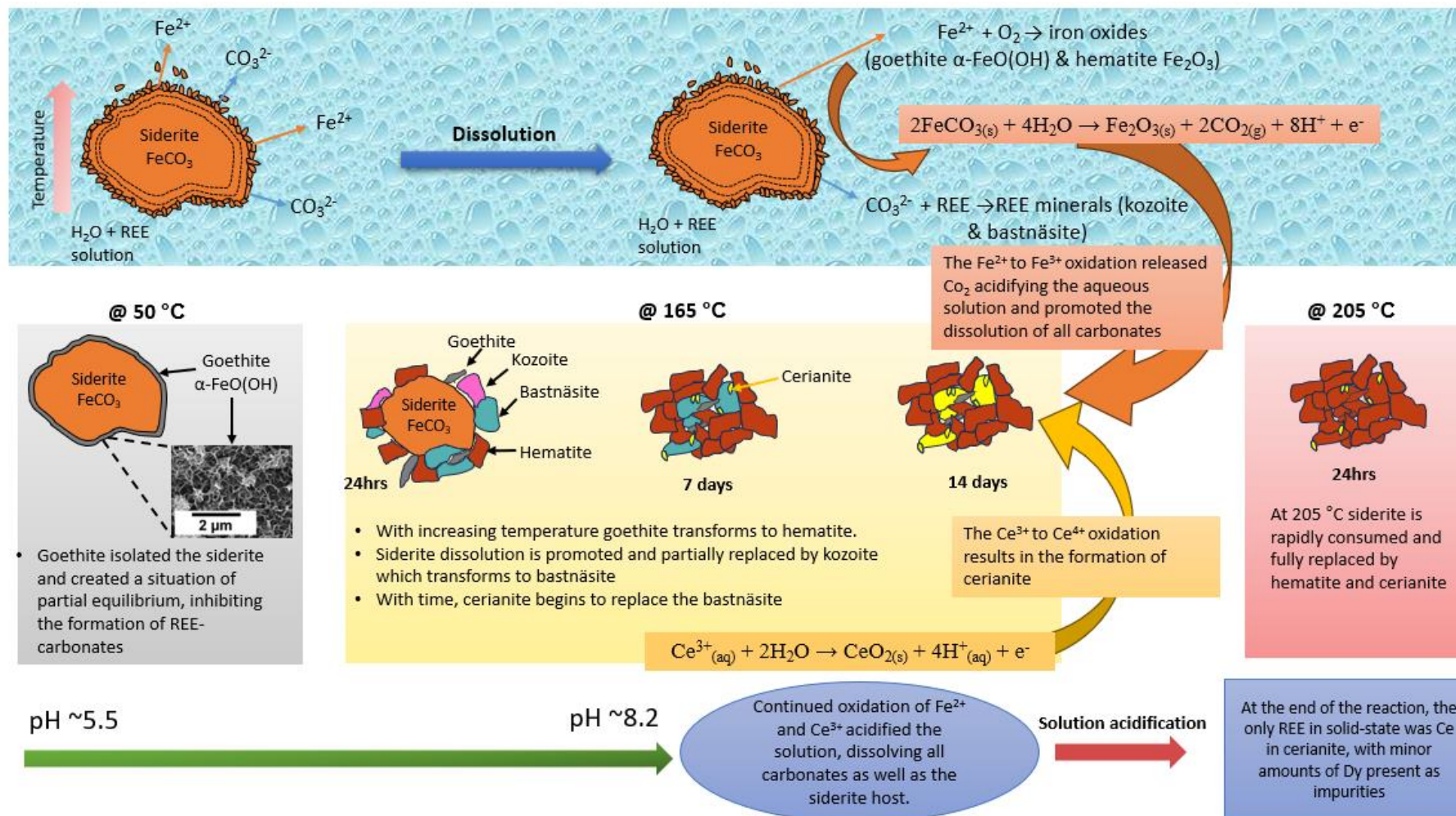


Figure 4 Graphical Abstract depicting the interaction of siderite with the multi-rare earth solution

combined with the temperature, and the availability of CO_3^{2-} govern this crystallisation sequence. Continued oxidation promotes decarbonation processes by acidifying the aqueous solution, dissolving all carbonates, and resulting in hematite and cerianite crystallisation as thermodynamically stable phases. Understanding iron carbonate, oxide and REE interactions can inform new resource targets and improve recovery and separation techniques.

1. Introduction

Due to their application in a range of green technologies and renewable energy, the demand for rare earth elements (REE) is ever increasing (1,2). While the development of recycling REE from end-products has progressed, we are still heavily reliant on natural, mineable sources (3). Currently, China is host to one-third of all known REE deposits and processes 97% of the world's REE + Y(3)(4).

Presently, commercially significant REE deposits are associated with magmatic processes related to alkaline igneous rocks and carbonatites (5). As of 2016, there were approximately 50 advanced REE exploration projects active outside of China, 20 of which are targeting carbonate igneous rocks (carbonatites) (6). Carbonatites and alkaline-carbonatite complexes have been identified as significant sources of REE and Nb, as well as hosting substantial deposits of apatite, vermiculite, copper, fluorite, thorium, uranium, and iron (7). The genesis of carbonatite-associated REE deposits, a vital global REE sources, is therefore a subject of strong interest and investigation (8).

In general, carbonatites are igneous rocks derived from the mantle and have a carbonate mineral volume of $> 50\%$ and $\text{SiO}_2 < 20\text{ wt}\%$ (9). Their formation occurs through the

immiscibility of carbonate-silicate magma and through the fractional crystallisation of carbonate minerals from carbonatite magma. The main source of these ore-forming elements comes from primitive mantle with an additional contribution from REE carrying crustal materials. (5). The REE form complexes and migrate through the magmatic-hydrothermal system. Changes in temperature, pressure, pH, and fluid composition allow their precipitation and mineralization. The formation of the world's largest REE deposit, Bayan Obo REE-Nb-Fe in China, has been linked to prolonged fluxing of carbonatite by subduction-derived fluids, and highlights the intricate interplay of geological processes involved in REE enrichment (10). It is characterized by a light rare earth (LREE) enrichment and is also hosted in hematite-bearing iron ores with high REE concentrations (11).

Investigations into the magmatic-hydrothermal processes in carbonatite-related REE deposits have offered insights into the enrichment mechanisms of REE, such as the Saint-Honoré carbonatite complex in Canada (12) and the Weishan carbonatite-related REE deposit in China (13). For example, in Weishan, two enrichment processes were responsible for the formation of the deposit: (i) the production of mineralized carbonatite and (ii) the subsequent enrichment by magmatic-hydrothermal processes. Fractures in the deposit promoted the circulation of ore-forming fluids and provided the space necessary for REE precipitation. Concomitantly, high F^- and SO_4^{2-} concentrations in the ore-forming fluids are thought to have facilitated REE transport and deposition via the formation of stable complexes (13)

The behaviour of fluids under high-pressure conditions can influence the phase transitions of carbonatitic melts and the subsequent formation of hydrothermal brines. It

has been demonstrated that under high-pressure and high-temperature conditions, the transition from carbonatitic melts to hydrothermal brines occurs, which can lead to the concentration of REE in these brines (14). The pressure conditions can also affect the stability of mineral phases, influencing which REE-bearing minerals are formed during the cooling and crystallization processes.

The pH of the fluid environment is another crucial factor influencing REE mineralization. Acidic conditions can enhance the solubility of REE and promote their mobility, while neutral to alkaline conditions may stabilize certain REE-bearing minerals. Anenburg and Mavrogenes highlighted that the transport of REE influenced by the pH of the fluids, with different REE complexes forming under varying pH conditions (15). Furthermore, the presence of ligands such as F^- , Cl^- , and CO_3^{2-} can significantly affect the solubility and transport of REE, with acidic conditions often favouring the dissolution of REE minerals and their subsequent transport in solution.

If REE carbonates are heated at temperatures up to their melting points, several processes would occur, dependent on the specific REE and temperature. Initially, dehydration would happen if the carbonates contained structural water or -OH groups, with heavier REE requiring temperatures above 700°C for water release. As temperatures rise, REE carbonates would undergo phase transitions, transforming into anhydrous oxycarbonates and eventually into oxides (16,17). This decarbonation process, releasing CO_2 , occurs at around 450-550°C for oxycarbonates, with heavier REE requiring higher temperatures due to their smaller ionic radii and ability to retain some minor amounts of structural water (16). Formation of solid solutions is expected, but differences in ionic sizes would lead to distinct hexagonal, monoclinic, or cubic structures (16,18). At more elevated

temperatures, the REE oxides would melt, and the behaviour of REE in the melt would depend on their partitioning, melt composition, and interactions with other elements from the rock.

The composition of the fluids involved in carbonatite formation is critical for the concentration of REE. Fluids rich in specific ligands (e.g., F^- , Cl^- , SO_4^{2-}) can enhance the mobility of REE and facilitate their precipitation as economically viable minerals. Pokrovsky et al., 2002 (19) noted that the fluids involved in REE transport and deposition are characterized by high activities of ligands and brines, which play a significant role in the mineralization processes. Additionally, the presence of carbonate-rich fluids can lead to the formation of REE-bearing minerals through complexation and precipitation reactions (5). The interaction of these fluids with the host rocks can also lead to metasomatic processes that enrich the REE content in carbonatites (20).

There are also several examples of REE-rich carbonatite complexes containing high REE concentrations connected to hematite-bearing rocks and iron ores (11), one being the Mountain Pass complex in California. Another example is the Fen complex, Telemark, southeast Norway where REE concentrations of up to 15,000 ppm have been recorded and originate from hematite-carbonatite and iron ores (21–23). The Fen complex was formed by the alteration of ankeritic ferrocarbonatite which included the oxidation of ferrous minerals in the primary ferrocarbonatite assemblages (21,24–26). One of the largest concentrations of Fe-oxides on Earth is the Olympic Dam Cu-U-Au-Ag iron oxide copper-gold (IOCG-type) deposit, in South Australia (27), with hematite being the most abundant mineral in the deposit (26). REE-rich hematite carbonatites are found in several carbonatite complexes worldwide and are commonly associated with ankerite $[Ca(Fe, Mg, Mn)(CO_3)_2]$ - and siderite ($FeCO_3$)-bearing carbonatites (11).

In this experimental study we aim to better understand the formation of rare earth carbonates during the oxidation and replacement of siderite. Of particular interest is the crystallization of REE carbonates in the presence of multiple foreign ions during the oxidation process as well as the extent to which REE are incorporated into the iron oxides that may form. Therefore, we have mimicked natural systems by carrying out replacement experiments using multi-component REE aqueous solutions and iron carbonate host grains of siderite, which are commonly associated with carbonatite ore deposits.

2. Methods

The interaction of siderite (FeCO_3) grains with multi-component REE (La, Ce, Pr, Nd and Dy) aqueous solutions was investigated at hydrothermal conditions (50-205 °C). Siderite crystals were crushed in a ceramic mortar and sieved to extract 0.5-1.0 mm clasts. Five single REE bearing solutions were prepared, La, Ce, Pr, Nd and Dy, with a total REE concentration of 50 mM. These solutions were produced via the dissolution of single REE nitrate salts, $\text{REE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.9% purity), in de-ionized water (18.18 $\text{M}\Omega \cdot \text{cm}$). These five specific REE were chosen as they are representative of both light (La, Ce, Pr, and Nd) and heavy (Dy) REE. This suit of REE from La to Dy also represents 72% of the ionic radii of the lanthanides as well as being some of the most abundant REE in the earth's crust (28). In order to understand the effect of ionic radii of the five REEs and to what extent these ions are taken up by the siderite host, two different sets of experiments were conducted, one with equal concentrations of the five REE and one with the concentrations of the five REE normalized to the commonly used Post Archean Australian Shale standard (PAAS) (29) to mimic the REE concentrations found in continental crust and natural geologic fluids. For the equal concentration experiments,

4 mL of each of the five REE were used to give a total solution volume of 20 mL for each experiment. For the PAAS experiments, a 1 L bulk solution, comprised of 11.8 mM $\text{La}(\text{NO}_3)_3$, 24.3 mM $\text{Ce}(\text{NO}_3)_3$, 2.70 mM $\text{Pr}(\text{NO}_3)_3$, 10.0 mM $\text{Nd}(\text{NO}_3)_3$, and 1.20 mM $\text{Dy}(\text{NO}_3)_3$, was made and 20 mL of this was used for each experiment.

For each experiment, 0.1 g of siderite grains were added to 20 mL of each of the 50 mM REE-bearing solutions and placed in 25 mL Teflon-lined and capped stainless-steel autoclaves (for the 165 and 205 °C experiments). For the 50 °C experiments, narrow mouth Nalgene polypropylene PPCO bottles (Thermo Fisher Scientific) were used. The reactors were then placed in a pre-heated oven at 50, 165, and 205 °C. Solid samples were then extracted using a sterilized metal spatula at increasing time intervals from 24 hours to 12 weeks. The samples were placed in plastic Eppendorf tubes and dried in a 30 °C oven for a minimum of 1 hour. The samples were then inspected several days later before preparing them for XRD and SEM analysis.

In order to identify and quantify the formation of crystalline solids present in our samples, several grains were selected from each experiment ensuring that each time and temperature variable was represented. The selected grains were ground to a consistently fine powder using an agate pestle and mortar. The minerals were identified and quantified with powder X-ray diffraction (XRD). Conventional powder XRD patterns were collected using a Siemens/Bruker D5000 powder X-ray diffractometer ($\text{Cu K}\alpha$ radiation, $0.01^\circ \text{ step}^{-1}$ from 5 to $60^\circ 2\theta$ at $0.2^\circ \text{ min}^{-1}$; 4.5 hours scans per sample, with a detection limit of $\sim 1\%$). Identification of crystalline phases was carried out with the Diffract Suite EVA software from Bruker in combination with the Powder Data File (PDF-4, the International Centre for Diffraction Data) (30). Pattern-matching refinement and quantification of crystalline phases were carried out with the Rietveld refinement software TOPAS (31). Finally, scanning electron microscopy (SEM) was used to obtain

high resolution images to characterize changes in the morphology of the siderite host grains and identify newly formed phases. Analyses were conducted in the iCrag Lab at Trinity College Dublin using a TIGER S8000 FEG-SEM operating under high vacuum conditions and equipped with two Oxford X-Max 170 mm² EDS detectors and an X4 pulse processor running the Oxford Aztec analysis software version 5.1 and subsequently version 6.1.

Two methods of sample preparation were employed: (i) standard SEM sample stubs with intact grains mounted to examine surface morphology, and (ii) polished epoxy resin pucks that provided a cross section of the grains, allowing for the identification of potential differences in spatial distribution of elements and any internal chemical textures. The epoxy mounts (2.5 cm wide) were made using Epoxy resin (Struers Epofix) mixed with the accompanying hardener and then polished using a three-step process (Struers Diapro, 6 and 1 µm) to expose the internal cross section of the grains. The pucks were then cleaned in an ultrasonic bath of deionized water to remove any residual polishing fluid and then dried. Both the stubs and the pucks were then coated with either carbon (for elemental mapping and analysis) or gold (for high-resolution imaging). Analysis at a working distance of 15 mm was performed using an accelerated voltage of 20 kV, a 4.5 nm wide beam with a beam current of 300pA, and a process time of five, following the SEM-EDX protocol defined in Ubide et al., 2017 (32). Beam current drift was controlled by analysis of cobalt after each sample change (33), while imaging carried out at a working distance of 5 mm was performed using an accelerating voltage of 10 kV. X-ray peak energies for each peak were calibrated to concentrations using a range of mineral and glass standards. The following phases on the Astimex MINM25-53 standard mount for standardization were used: apatite, chromite, diopside, kaersutite, magnetite, olivine, orthoclase, pentlandite, rhodonite,

rutile and tugtupite. Standard phases were analyzed for 2M counts. The images and maps were processed using the Aztec v6.1 X-ray microanalysis software suit (Oxford Instruments).

Finally, the saturation indexes of solid phases during the equilibration of the REE-bearing aqueous solutions with respect to siderite were calculated with the hydro-geochemical code PHREEQC (34) using the LLNL database and the solubility products of REE-bearing carbonates determined by (35) and (36).

3. Results

The analysis of all solid samples obtained from the replacement experiments resulted in the formation of surface precipitates that partially or totally replaced the siderite host grain. The combination of powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) allowed us to identify and quantify the newly formed phases and interpret the mechanisms responsible for the alteration and decomposition of the siderite grains and the precipitation of the newly formed phases.

3.1. Powder X-ray diffraction (XRD)

The interaction between siderite and multi-component rare earth element (La, Ce, Pr, Nd and Dy) – bearing aqueous solutions resulted in the formation of iron oxides, goethite (α -FeO(OH); PDF 00-003-0249) and hematite (Fe_2O_3 ; PDF 00-024-0072), REE-bearing minerals kozoite ($\text{REE}(\text{CO}_3)(\text{OH})$; PDF 04-017-1451) and hydroxylbastnasite ($\text{REE}(\text{CO}_3)(\text{OH},\text{F})$; PDF 00-027-1295) and the rare earth oxide cerianite (CeO_2 ; PDF 00-

004-0593). The full quantitative XRD data are presented in Table 1. These newly formed phases were observed as surface precipitates that partially or fully covered the siderite host mineral. In some experiments, siderite was fully replaced from the periphery inwards.

The extent of the replacement reaction was found to be time- and temperature-dependent. At the lowest temperature (50 °C), REE-bearing mineral formation was not detected in XRD and only the precipitation of minor ($< 1\%$) amounts of goethite, below the quantification level of XRD, was recorded after 56 days (Figure 1). At higher temperatures, the extent and rate of siderite host replacement depended on the REE ratio in the aqueous solution, with faster replacement occurring in experiments using PAAS solutions: At 165 °C in the equal concentration solution, 40% of the siderite was consumed after 24 hours, compared to 70% in the PAAS solution (Table 1). In the 205 °C experiments, full replacement was observed after 1 week in the equal concentration experiments, compared to less than 24 hours in the PAAS solution experiments.

The observed mineralogy was also temperature- and REE ratio-dependent: At 165 °C, a rapid transformation (< 24 hours) of goethite to hematite was observed, accompanied by the formation of the rare earth carbonates kozoite and hydroxylbastnasite (Figure 2). After 14 days in equal concentration solutions and 7 days in PAAS solutions, a secondary replacement of the rare earth carbonates by cerianite was observed. In both the 165 and 205 °C experiments, siderite was fully replaced by hematite and cerianite after 7 days (Figure 3). While in the equal concentration experiments, not all of the goethite transformed to hematite, in the PAAS solution, hematite and cerianite were the final phases formed. In both 165 and 205 °C experiments, the final amount of cerianite in the

system was also higher in the PAAS solution experiments (18% compared to 2%, at 165 °C).

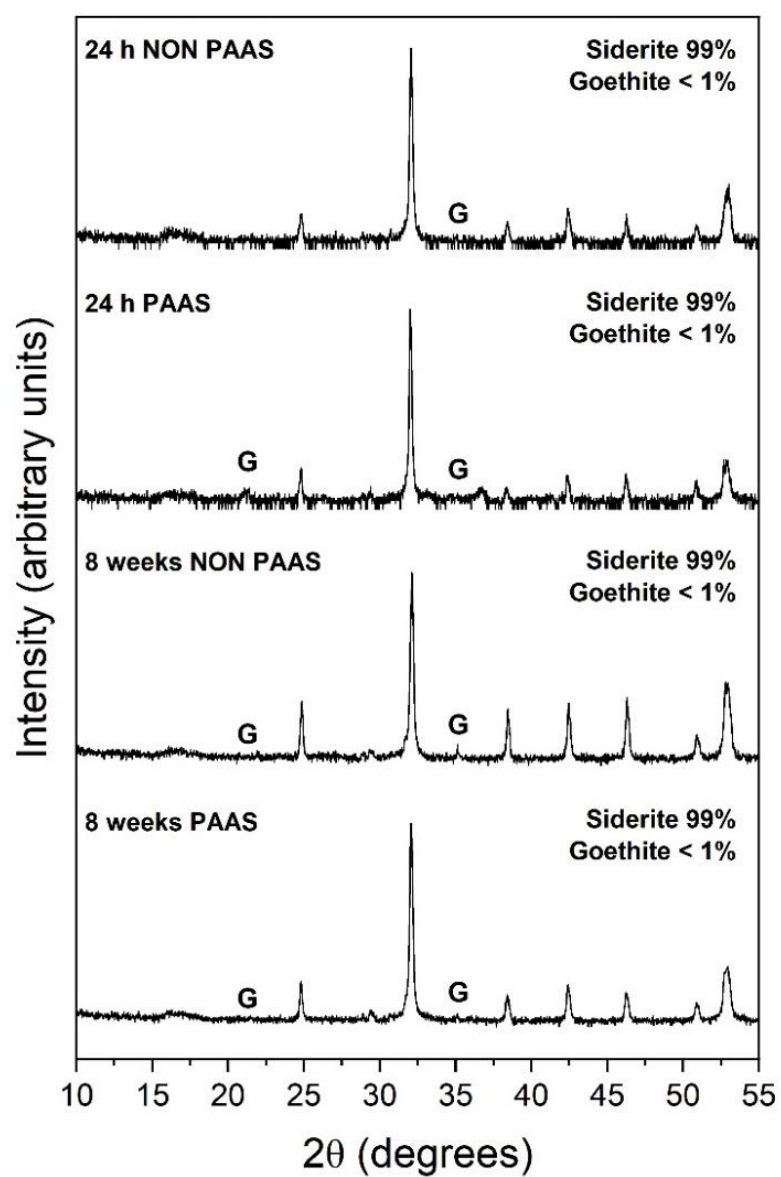


Figure 1. Powder XRD patterns of goethite (G) in the equal concentration (non-PAAS) and PAAS experiments at 50 °C after 24 hours and 8 weeks (*Bragg peaks that have not been assigned to any phase correspond to siderite).

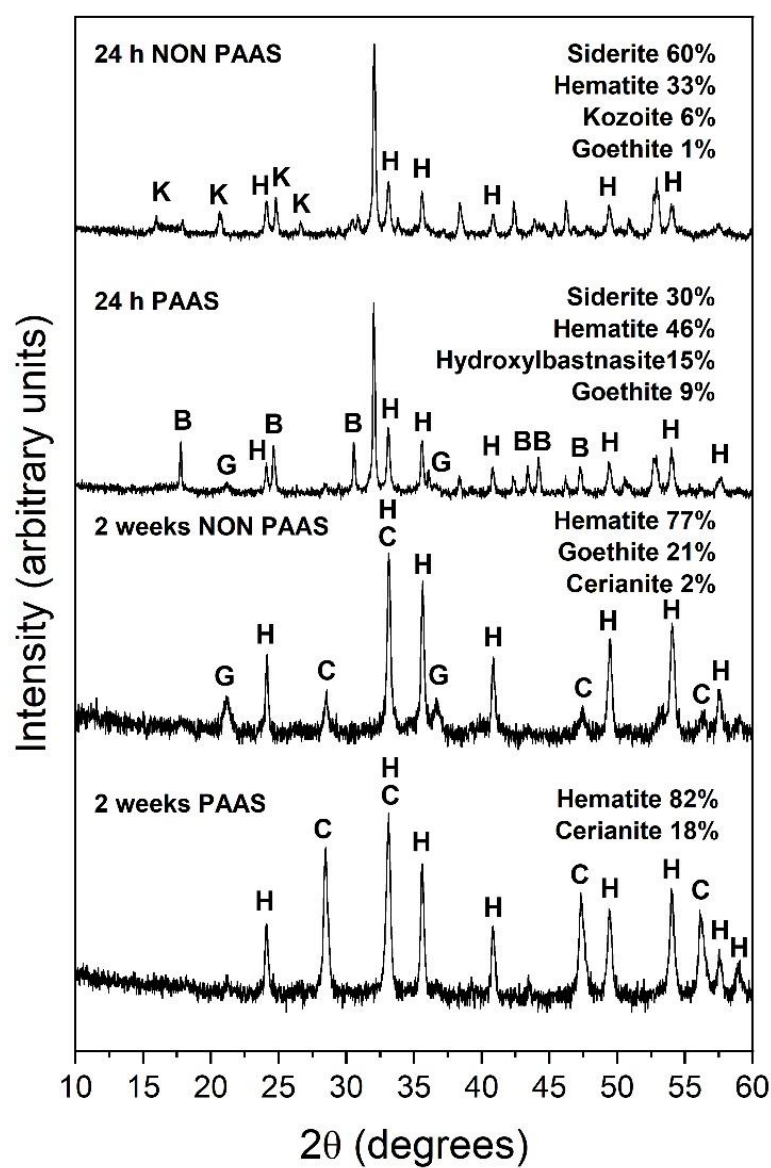


Figure 2. Powder XRD patterns of goethite (G), hematite (H), kozoite (K), hydroxylbastnäsité, (B) and cerianite (C) in the equal concentration (non-PAAS) and PAAS experiments at 165 °C

after 24 hours and 2 weeks (*Bragg peaks that have not been assigned to any phase correspond to siderite).

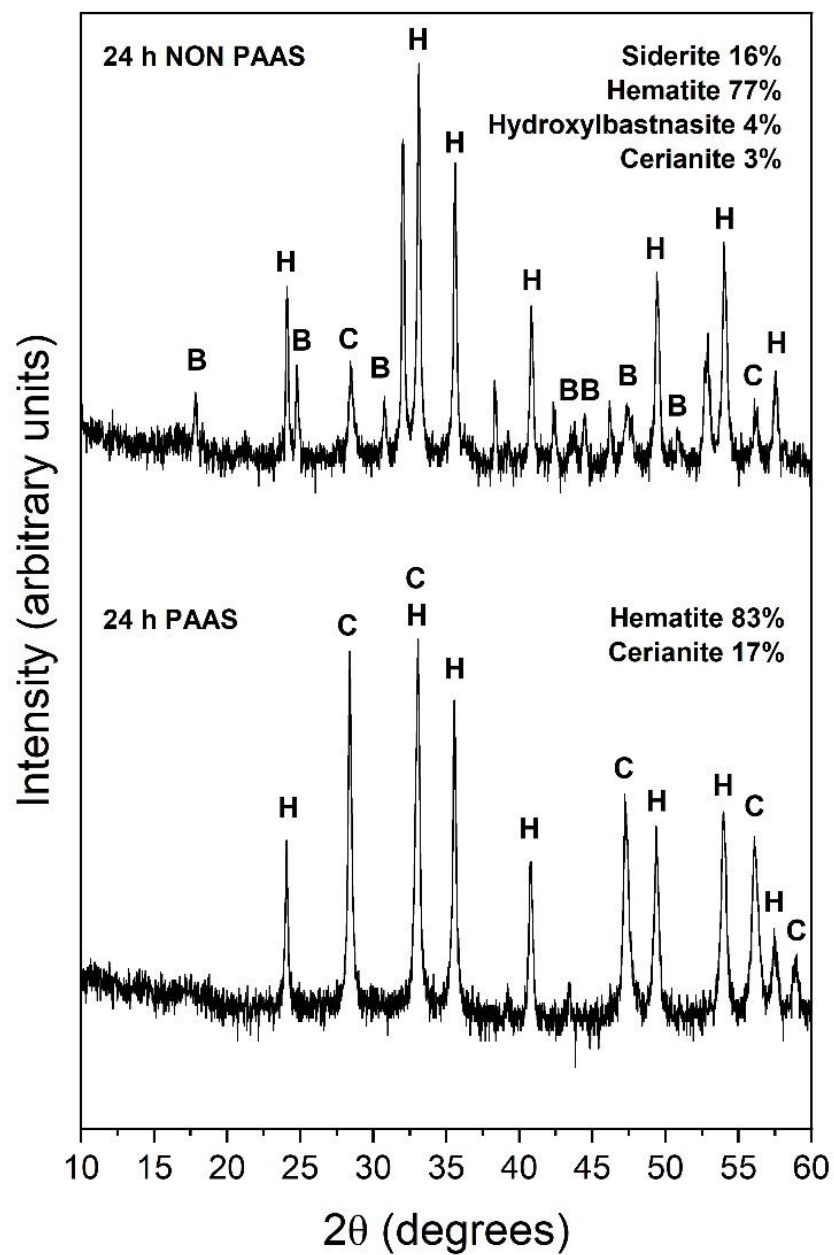


Figure 3. Powder XRD patterns of, hematite (H), hydroxylbastnäsité, (B) and cerianite (C) in the equal concentration (non-PAAS) and PAAS experiments at 205 °C after 24 hours (*Bragg peaks that have not been assigned to any phase correspond to siderite).

Table 1. Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of siderite with multi-component (La, Ce, Pr, Nd, and Dy) REE-bearing aqueous solutions (equal concentration and PAAS experiments) at 50, 165, and 205 °C (*goethite (goeth), hematite (Hem), kozoite (koz), hydroxylbastnäsite (HB), cerianite (Cer)).

Equal concentration experiments					PAAS experiments			
T(°C)	Time (days)	% Phase consumed	Phase formed	Morphology	Time (days)	% Phase consumed	Phase formed	Morphology
50	1	<1	Goethite	Flakes	1	<1	Goethite	Flakes
	2	<1			2	<1		
	3	<1			3	<1		
	4	<1			4	<1		
	12	<1			12	<1		
	56	<1			56	<1		
	84	<1			84	<1		
165	1	40	33% Hem., 6% Koz., <1% goeth.	Koz (spindle-shaped prisms), Hem (pseudo-hexagonal prisms), Cer (cubes, bipyramidal prisms), HB (triangular prisms)	1	70	46% Hem., 15% HB., 9% goeth.	Hem (pseudo-hexagonal prisms), Cer (cubes, bipyramidal prisms), HB (triangular prisms)
	7	100	87% Hem., 3% HB., 9% cer., <1% goeth.		7	100	73% hem., 20% cer., 7% goeth.	
	14	100	77% Hem., 2% cer., 21% goeth.		14	100	82% hem., 18% cer.	
205	1	84	77% Hem., 4% HB., 3% cer	Hem (pseudo-hexagonal prisms), Cer (cubes, bipyramidal prisms),	1	100	83% Hem., 17% cer.,	Hem (pseudo-hexagonal prisms), Cer (cubes, bipyramidal prisms),
	7	100	95% Hem., 5% cer.		7	100	94% Hem., 6% cer.,	

3.2 . Scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS)

SEM imaging revealed the formation of precipitates on the surface of the siderite grains. The extent to which the newly formed precipitates covered and replaced the host grain was found to be time- and temperature-dependent. For example, at 50 °C, the surface of the siderite grains became fully covered by a thin layer ($< 2\ \mu\text{m}$) of goethite nanocrystals with flaky morphologies (Figure 4). Minor amounts of kozoite with similar morphologies reported by Szucs et al., (2021) (37), Szucs et al., (2022) (38) and Maddin et al., (2024) (39) were also observed in images taken after 12 weeks in the equal concentration experiments (Figure 4d), however, the amount was too small to be detected by XRD. At 165 °C, the newly formed phases consisted of triangular prisms of hydroxylbastnäsite pseudo-hexagonal prisms of hematite, and cubes and bipyramidal prisms of cerianite (Figure 5).

SEM imaging also revealed that the early stages of hematite crystallization on the siderite surfaces were characterized by the formation of prismatic nanocrystals with diameters of $\sim 150\text{-}200\ \text{nm}$ (Figure 6a, and Figure 7). Many of these nanocrystals exhibited a transient, non-random orientation on the (104) face of siderite, indicative of epitaxial overgrowth (Figure 8). Specifically, this hematite-siderite epitaxial relationship was defined by the parallel alignment of the crystallographic axes of the hematite to those of the underlying siderite substrate (Figure 6b,). However, once the hematite crystals grew and coalesced, this orientation was lost (Figure 6c).

The EDS analyses of the cross section of the grains in the polished epoxy resin pucks revealed differences in spatial distribution of the REEs in the newly formed solids. The chemistry of the REE-bearing minerals was found to be dependent on the REE ratio in

the initial aqueous solution, with a more homogenous distribution in the equal concentration solution (Figure 9 and 10) and a more heterogenous distribution in the PAAS solution (Figure 11). A preferential uptake of Nd and La with Ce in the PAAS solution was observed at 165 °C after 24 hours (SI-1 Line Analysis, Supplementary Info), as well as Dy incorporation into the cerianite in the PAAS solution at 205 °C after 1 week (SI-2 Supplementary info), and in the equal concentration at 205 °C after 24 hours (Figure 12). In general, the composition and ratio of the REE in the bastnäsite and kozoite appeared to record the composition of the original fluid phase (equal concentration and PAAS experiments; Figure 13, 14), with almost equal uptake of REEs in bastnasite (Figure 10) and preferential uptake of La, Ce and Nd in kozoite (Figure 11). In contrast, REE incorporation in the iron oxides was below the SEM-EDS detection limit, at <0.1%. (SI-3 Supplementary Info, point analysis).

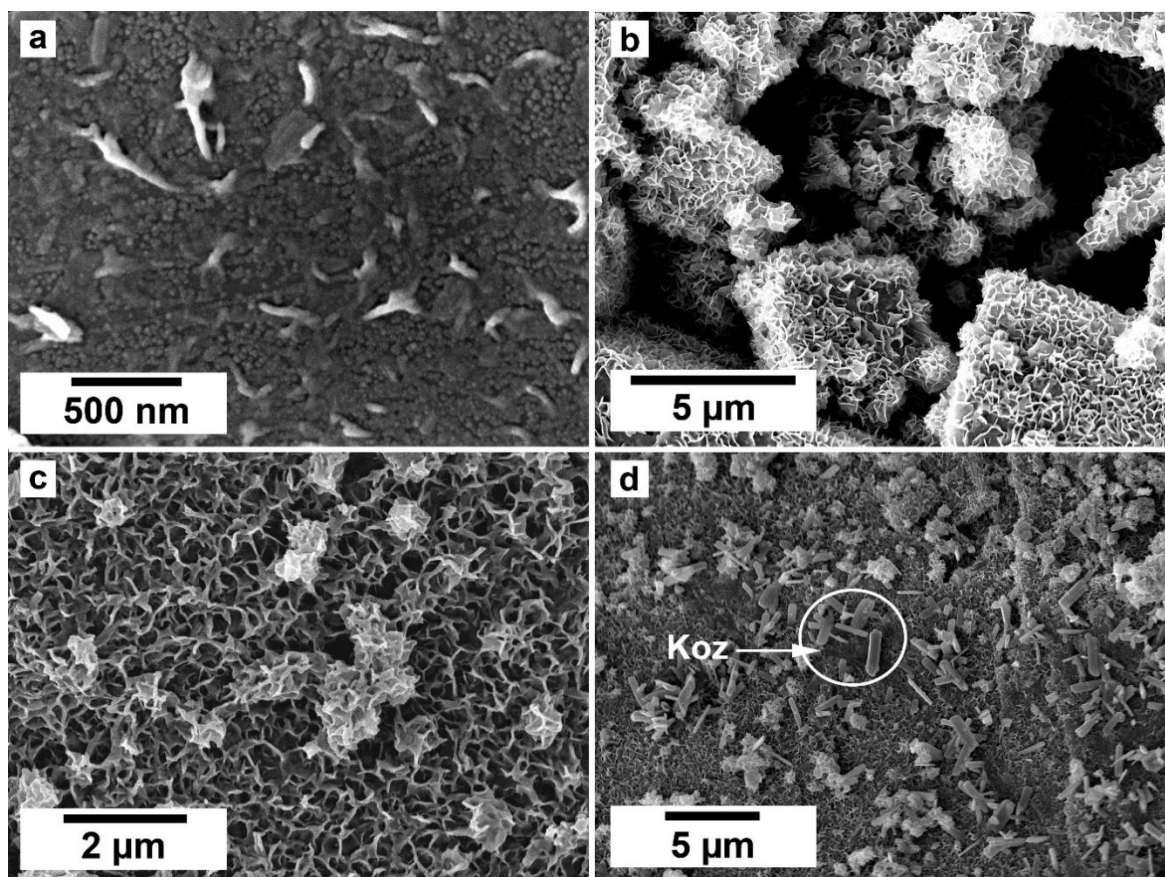


Figure 4. SEM micrographs showing the gradual and complete covering of siderite by a thin (<2 μm) layer of goethite at 50 °C after (a) 48 hours, equal concentration experiments , (b) 8 weeks, PAAS experiments, (c) 12 weeks, PAAS experiments, and (d) goethite and kozoite (koz) crystals after 12 weeks in equal concentration experiments.

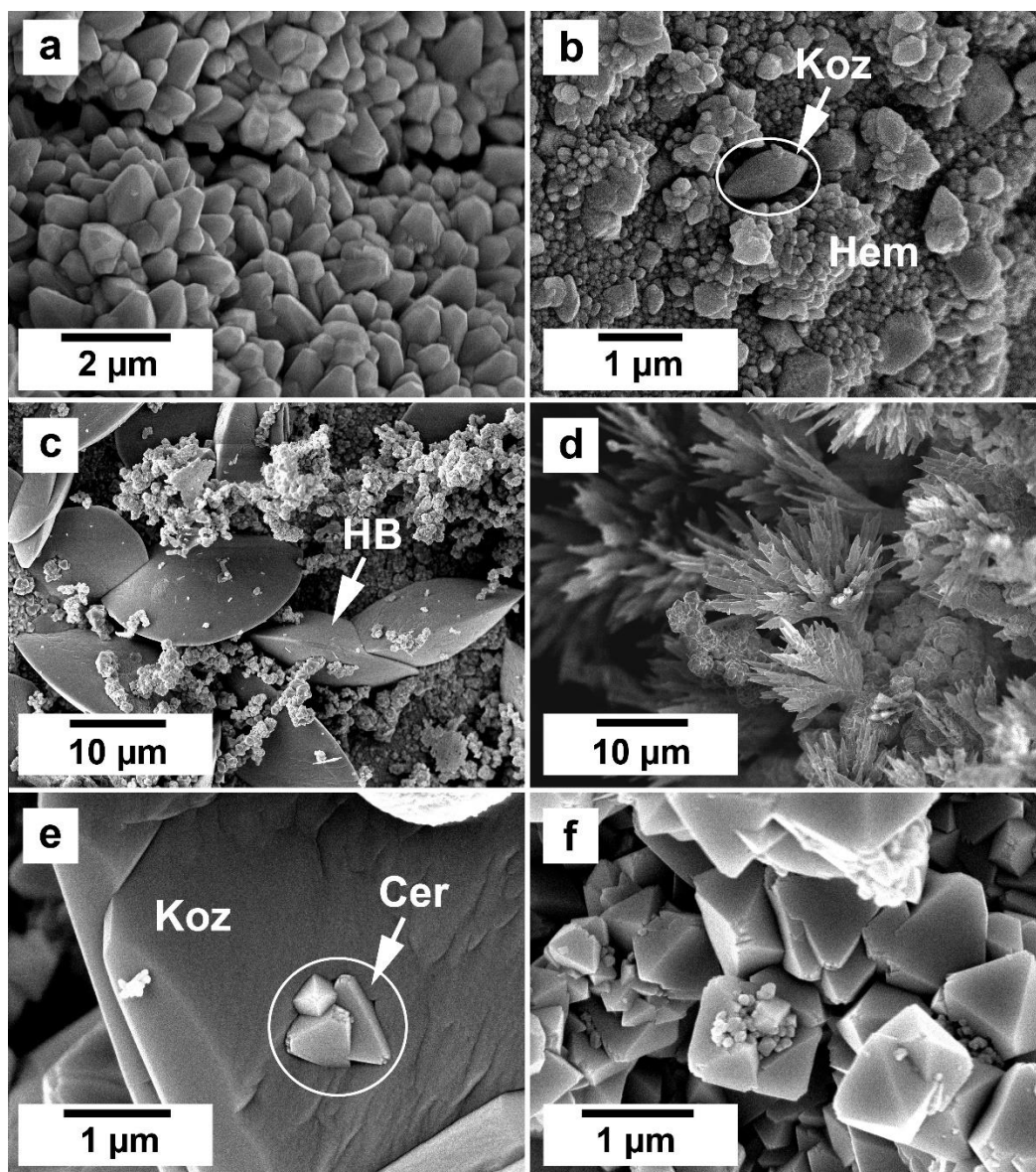


Figure 5. SEM micrographs showing the (a) Hematite prisms covering the surface of siderite in equal concentration at 165 °C after 1 week (b) Kozoite prism on hematite in equal concentration solution at 165 °C after 24 hours; (c) Hydroxylbastnäsite in a matrix of cerianite and hematite in equal concentration solution at 165 °C after 24 hours; (d) Hydroxylbastnäsite dendrites in PAAS solution 165 °C after 24 hours ; (e) cerianite growing on kozoite surface in equal concentration solution at 205 °C after 24 hours; (f) cerianite prisms in equal concentration solution at 205 °C after 1 week.

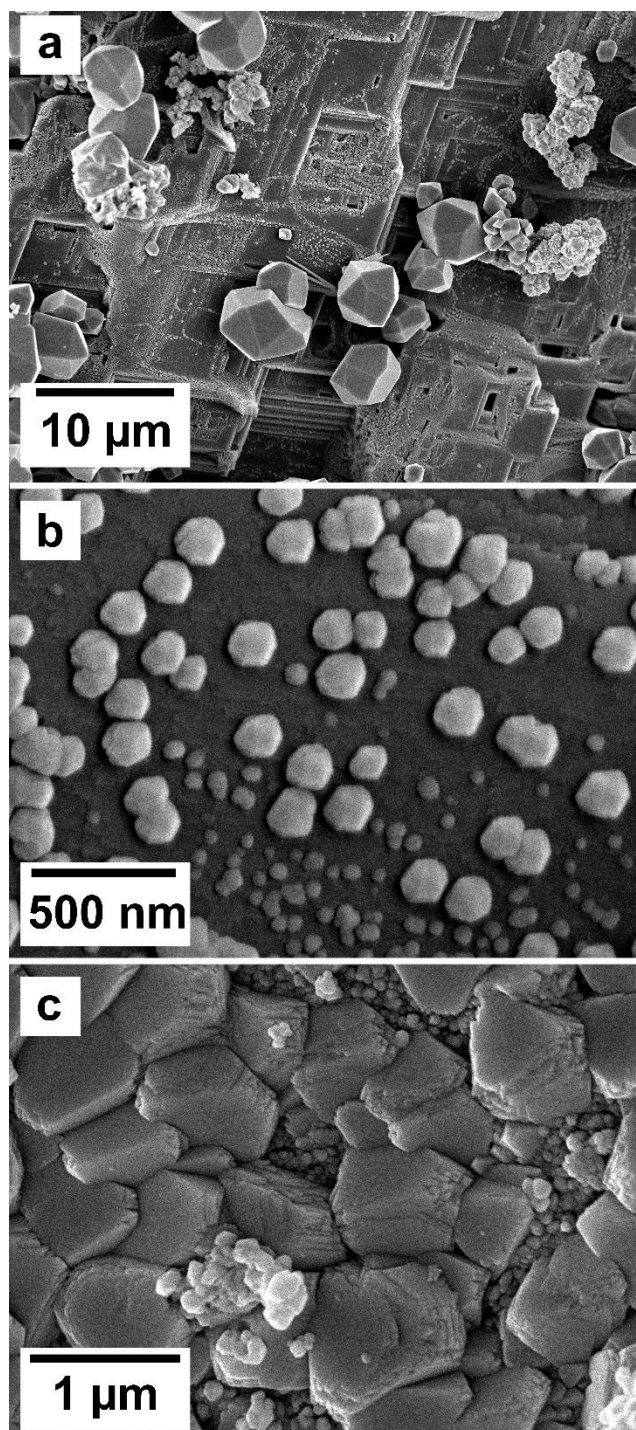


Figure 6. SEM micrographs showing the growth of hematite on siderite and epitaxial growth. (a) Hematite growing on the surface of siderite, forming μm-sized and nanocrystals on the surface of the host in equal concentration solution at 205 °C after 24 hours. (b) Hematite growing oriented on the surface of siderite in equal concentration solution at 205 °C after 24 hours. (c) μm-sized hematite coating the surface of siderite, showing a loss of their initial non-random orientation in equal concentration solution at 165 °C after 1 week.

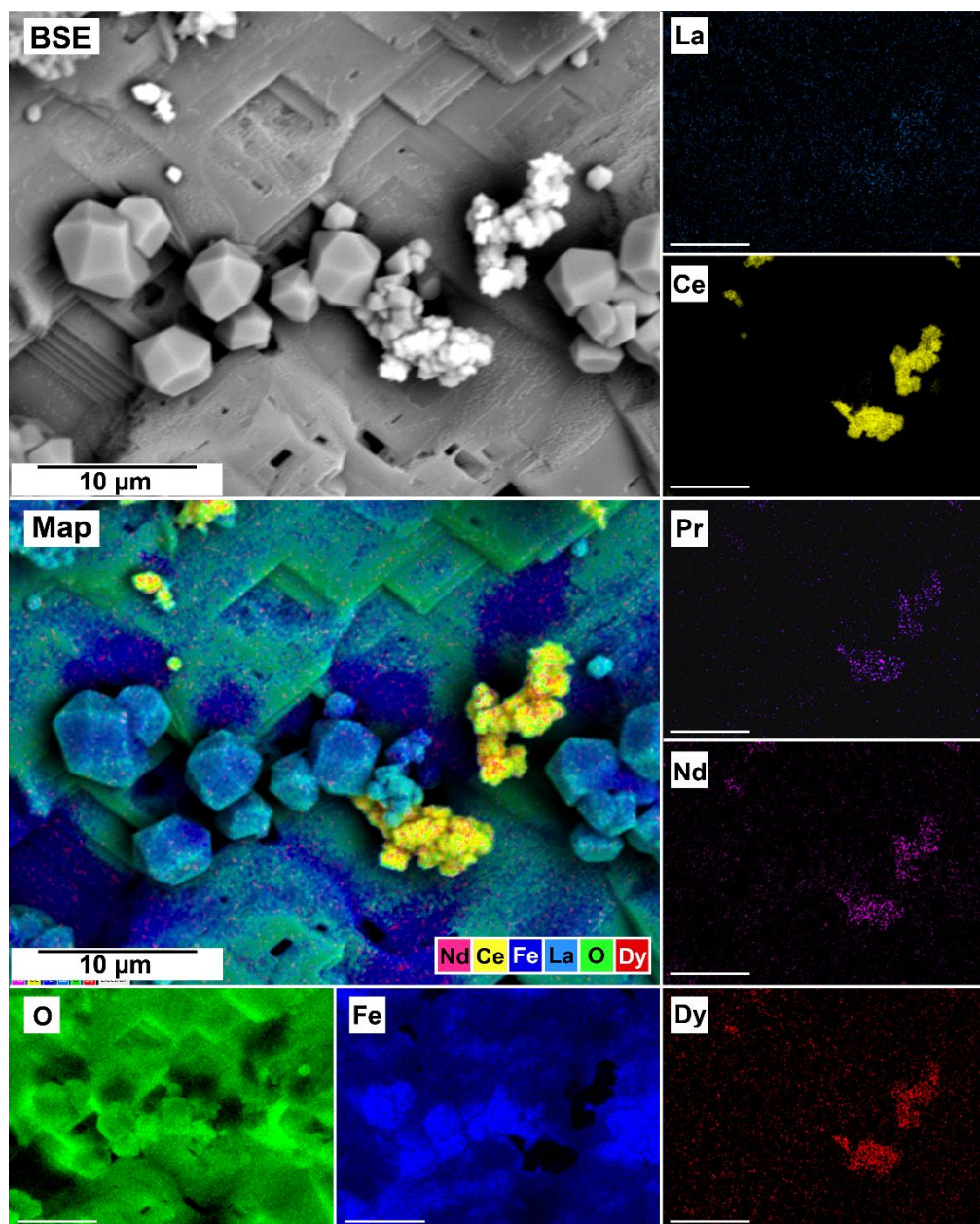


Figure 7. SEM-EDS images of the breakdown of siderite and subsequent detachment of the newly formed hematite crystals in equal concentration experiments at 205 °C after 24 hours. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.1592 µm, image width: 163 µm, image height: 122 µm, accelerating voltage: 20.0 kV, magnification: 1693 x, working distance: 15.0 mm.

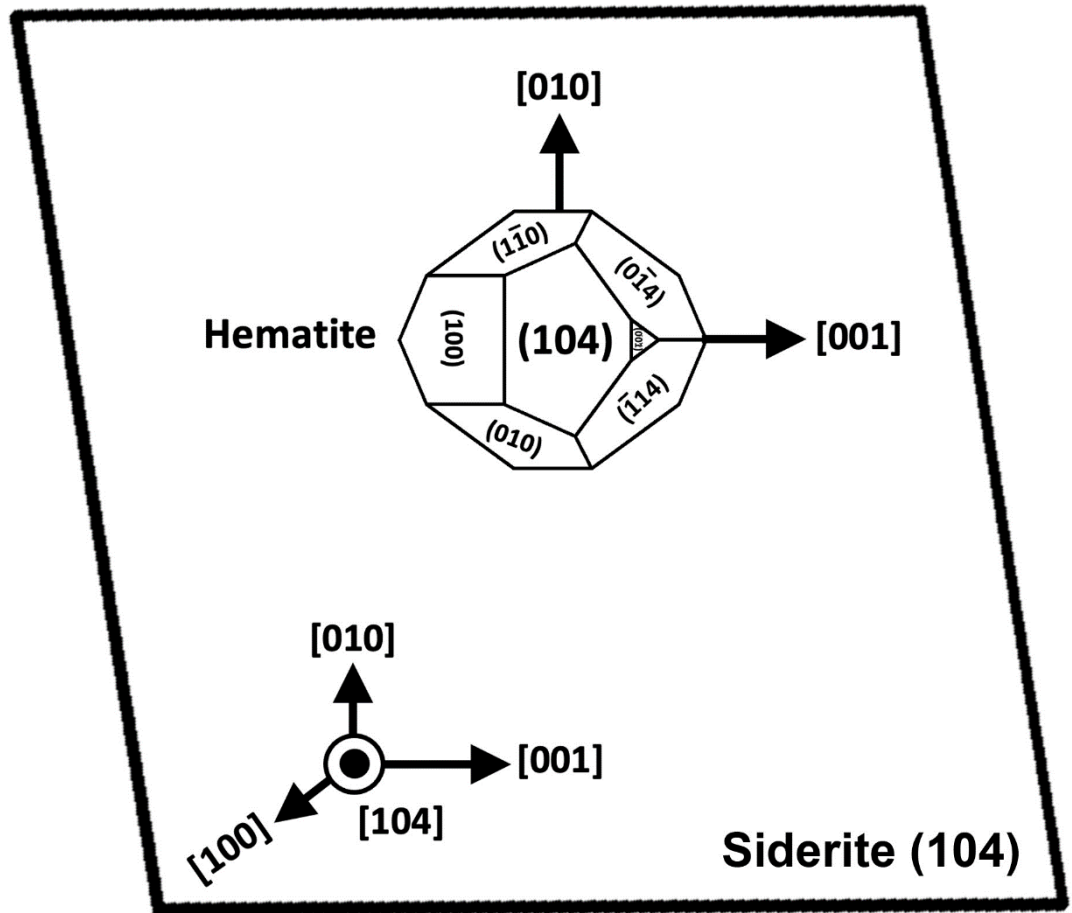


Figure 8. Schematic diagram showing the epitaxial relationship between hematite and siderite crystals.

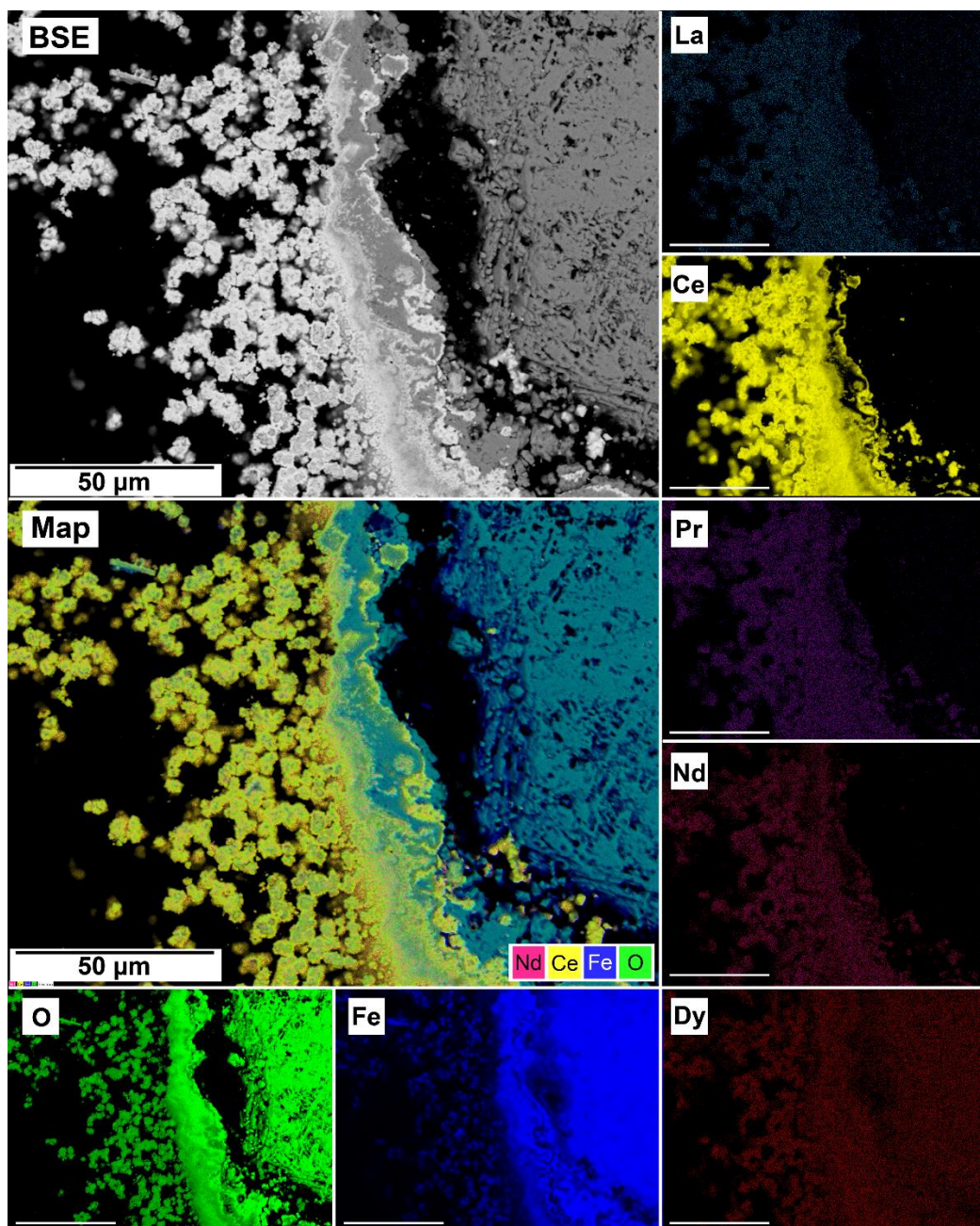


Figure 9. SEM-BSE image of siderite fully replaced by hematite and cerianite at 205 °C after 1 week in equal concentration experiments and EDS maps of La, Ce, Pr, Nd, Dy, O, and Fe showing the homogenous distribution. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.1592 µm, image width: 163 µm, image height: 122 µm, accelerating voltage: 20.0 kV, magnification: 1693 x, working distance: 15.0 mm.

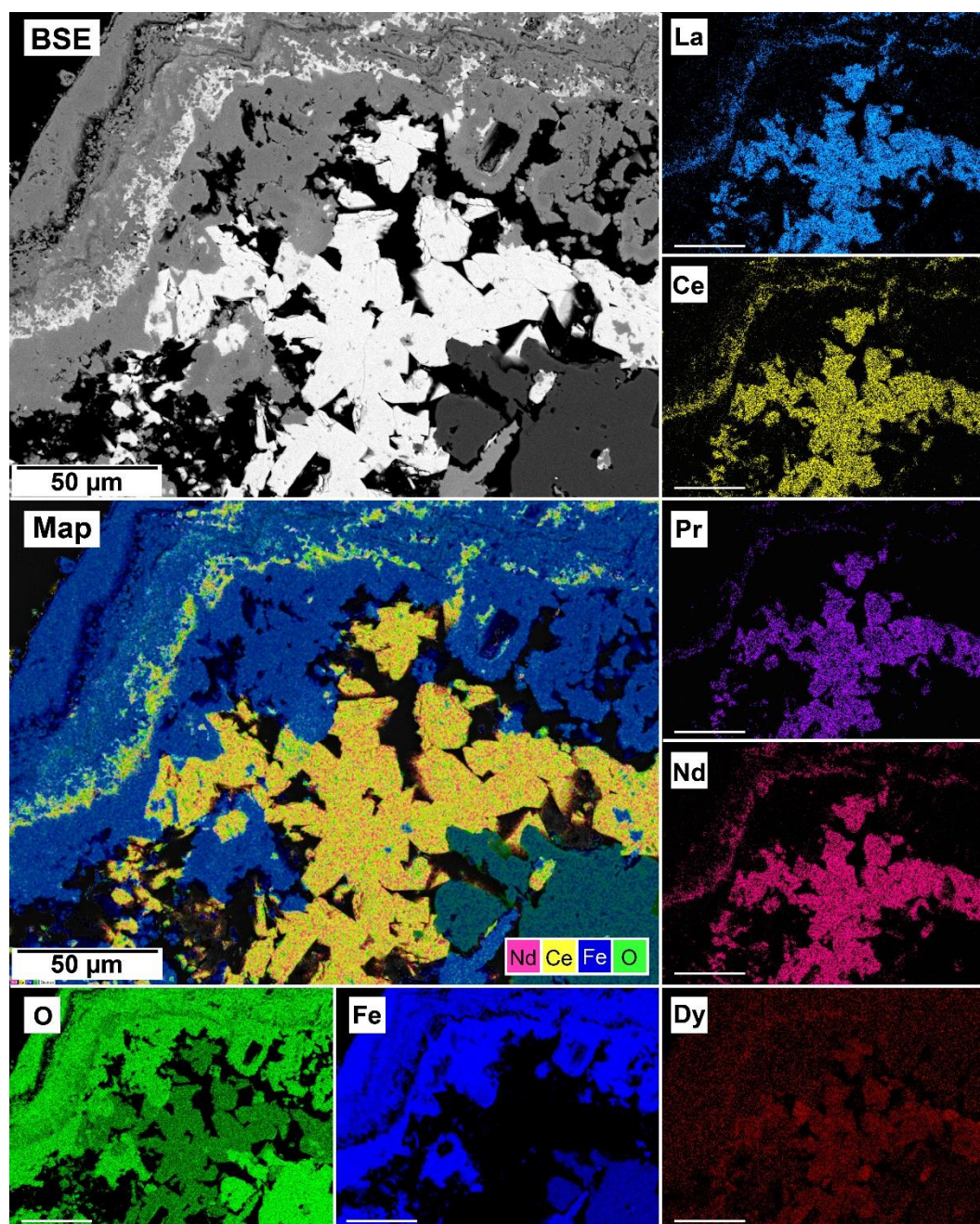


Figure 10. SEM-BSE image and elemental mapping showing the partial replacement of the siderite host with kozoite in equal concentration experiments at 165 °C after 24 hours. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.15942 µm, image width: 163 µm, image height: 122 µm, accelerating voltage: 20.0 kV, magnification: 1693 x, working distance: 15.0 mm.

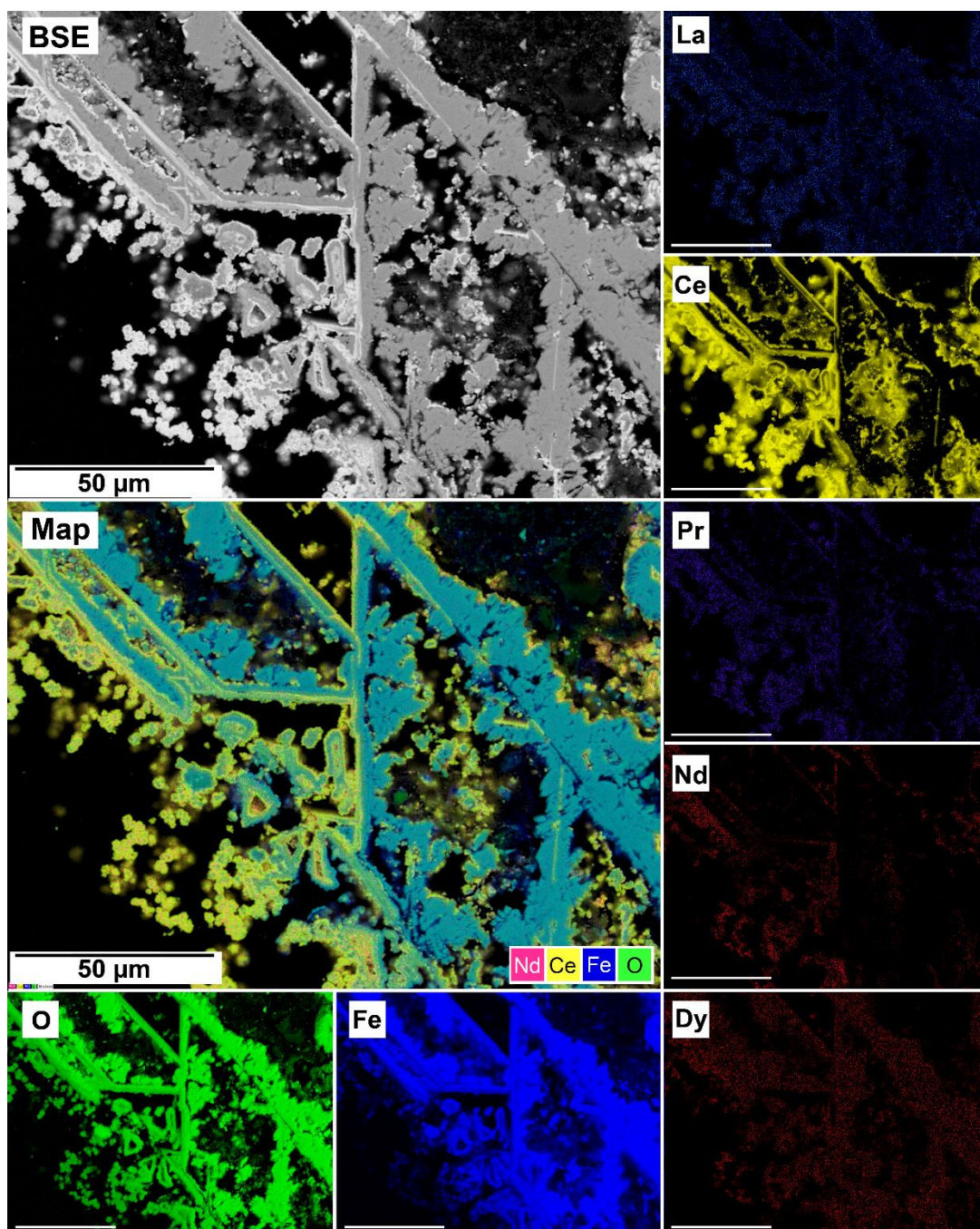


Figure 11. SEM-BSE image of siderite grain fully replaced by hematite and cerianite at 205 °C after 24 hours in the PAAS experiments and EDS maps of La, Ce, Pr, Nd, Dy, O, and Fe showing the heterogeneous distribution. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.15942 μm, image width: 163 μm, image height: 122 μm, accelerating voltage: 20.0 kV, magnification: 1693 x, working distance: 15.0 mm.

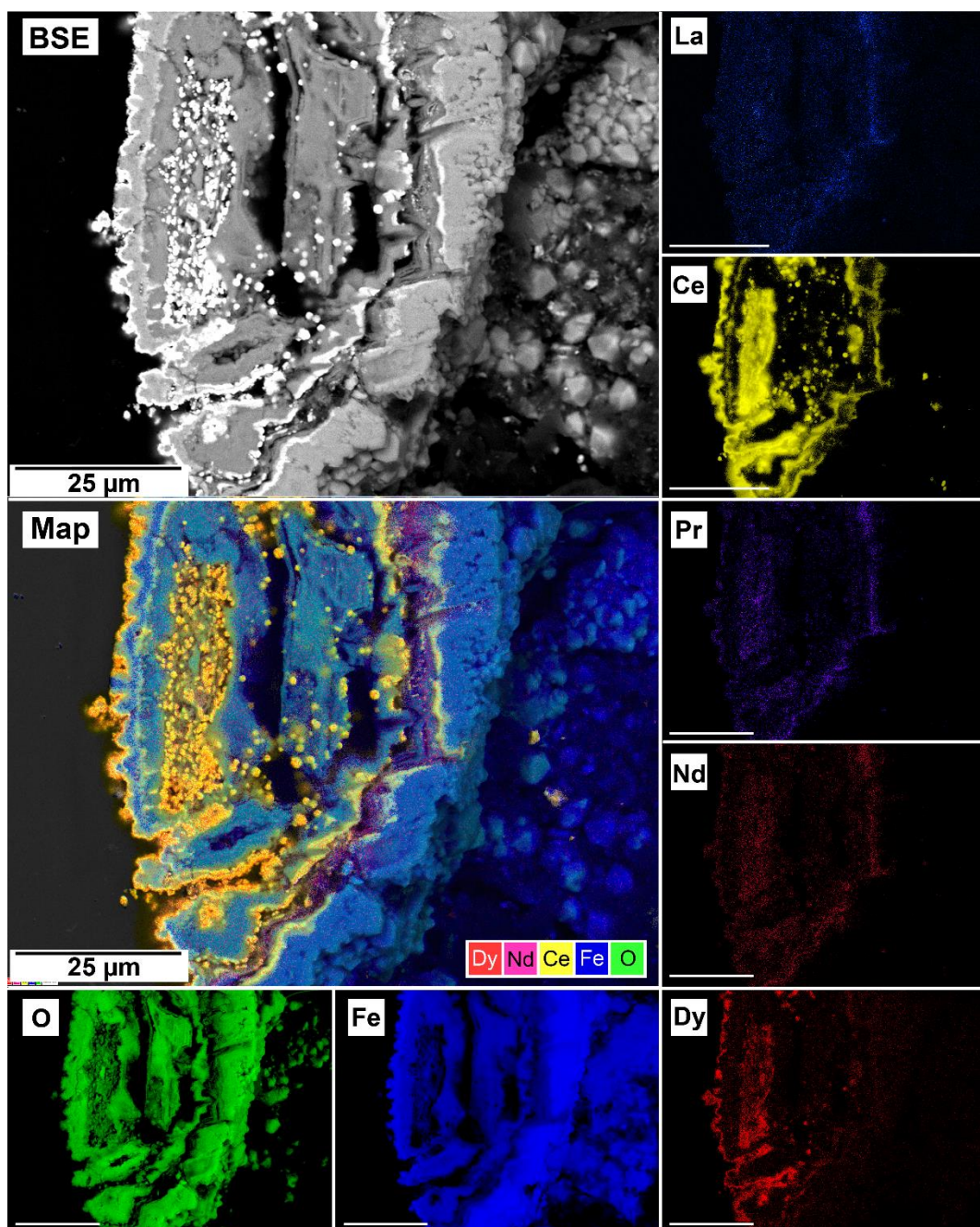


Figure 12. SEM-BSE micrograph and elemental mapping of a selected grain of siderite from an equal concentration experiment at 205 °C after 24 hours incorporation of Dy in cerianite as impurities. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.09574 µm, image width: 98 µm, image height: 73.5 µm, accelerating voltage 20.0 kV, magnification: 2819 x, working distance 15.0 mm.

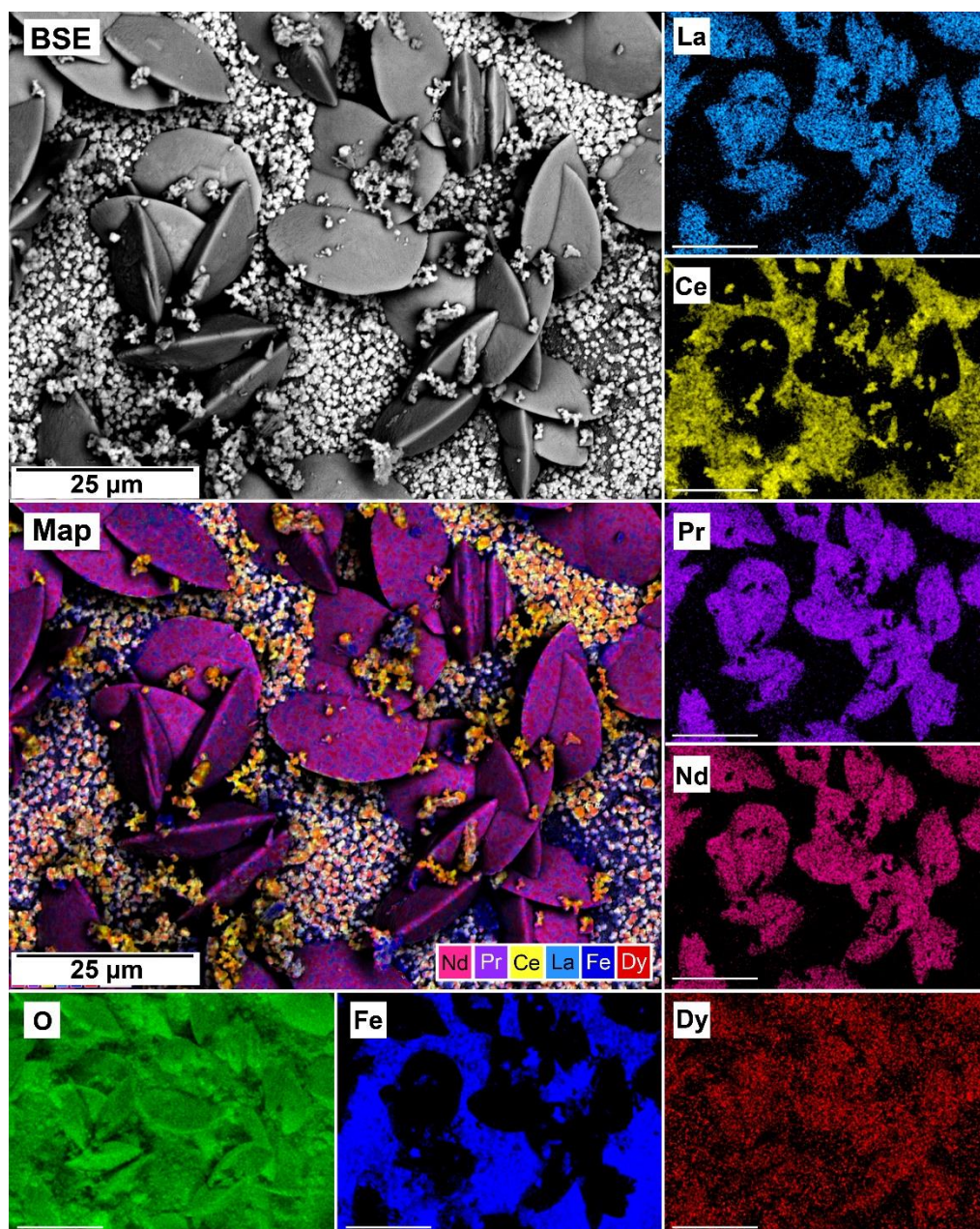


Figure 13. SEM-BSE image of siderite grain being replaced with bastnasite in the equal concentration experiments at 205 °C after 24 hours and EDS maps showing the almost homogenous distribution of REE. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.09574 μm, image width: 98 μm, image height: 73.5 μm, accelerating voltage 20.0 kV, magnification: 2819 x, working distance 15.0 mm.

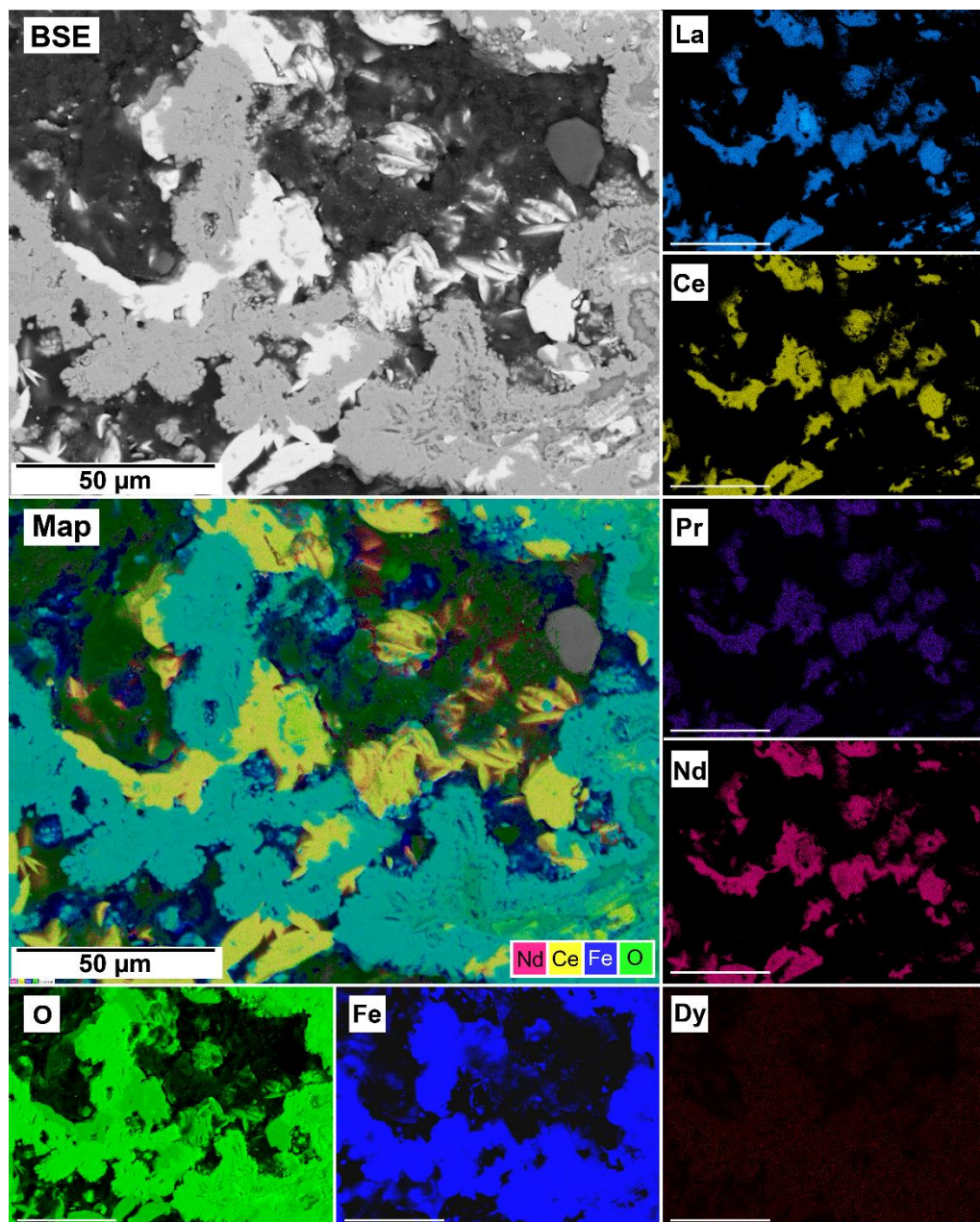


Figure 14. SEM-BSE image of siderite grain being replaced with kozoite in PAAS solution at 165 °C after 24 hours and EDS maps showing the almost heterogenous distribution of REE. Resolution (width): 2048 pixels, resolution (height): 1536 pixels, pixel size: 0.1592 μm , image

width: 163 μm , image height: 122 μm , accelerating voltage: 20.0 kV, magnification: 1693 x, working distance: 15.0 mm.

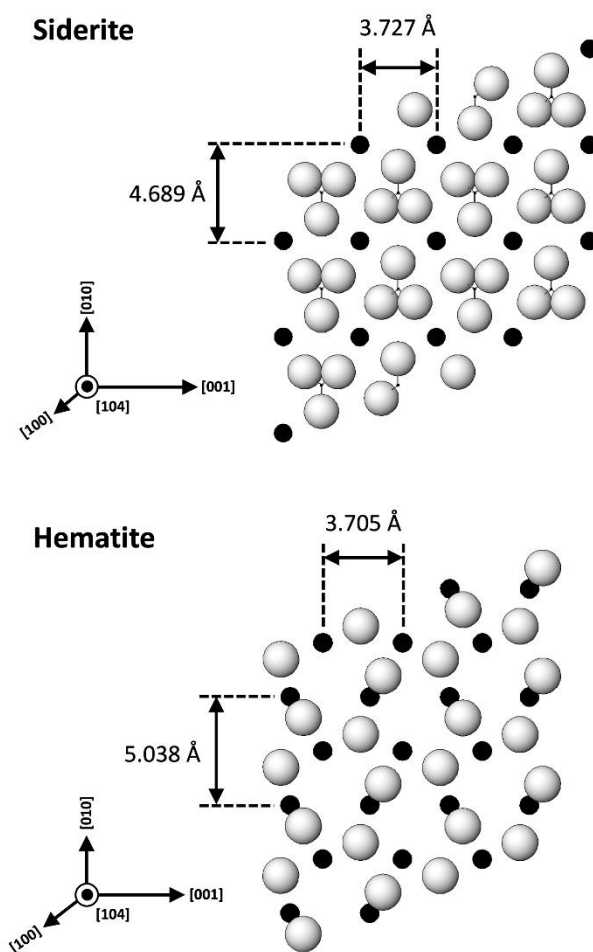


Figure 15. Projection of the atomic structures of a (104) slices of hematite and siderite showing the main directions of epitaxy and repeating periods.

4. Discussion

The interaction of siderite with our REE-bearing aqueous solutions resulted in the initial dissolution of the host grain, releasing Fe^{2+} and CO_3^{2-} ions into the aqueous solution. As temperature increased, siderite broke down (40) and the aqueous Fe^{2+} ions then became oxidized and precipitated as iron oxides goethite and hematite. The CO_3^{2-} interacted with the REE in solution leading to the crystallisation of rare earth minerals kozoite and hydroxylbastnäsite, which then subsequently transformed into the oxide cerianite due to the oxidation of Ce^{3+} . The resulting textures and mineralogy are consistent with the solvent-mediated surface precipitation and subsequent pseudomorphic mineral replacement produced by the interaction of the hydrothermal fluids with the primary siderite.

4.1. The formation of iron oxides as a function of temperature and pH

Siderite is a ferrous mineral found in oxygen-free environments, such as lakes, rivers, and marine sediments (41–43). Its stability, dissolution, and the subsequent precipitation of iron oxides are temperature- and pH-dependent processes that significantly influence the kinetics of siderite breakdown (44–46). Ferrous iron in aqueous solutions readily reacts with dissolved oxygen, oxidizing to ferric iron (Fe^{3+}) and precipitating as iron oxides and/or oxyhydroxides such as goethite, hematite, magnetite, maghemite, and ferrihydrite (41,47,48).

Many studies have shown that a poorly-ordered nanoparticulate phase, two-line ferrihydrite, is a predominant precursor to several iron oxides (49–51). Under oxic

conditions, two-line ferrihydrite gradually transforms to more thermodynamically stable phases, such as goethite and hematite (49,51). It was Bohm (1925) who first demonstrated that an “amorphous Fe(III) hydroxide” rapidly transformed to pure goethite when maintained under 2 M KOH at 150 °C for 2 hours, whereas hematite was the main end product if the material was subjected to hydrothermal conditions (50). This demonstrated that this ferrihydrite-goethite transformation is highly temperature- and pH-dependent. The rate of transformation of ferrihydrite is relatively slow at ambient temperature. For example, Schwertmann & Murad recorded 19% of the initial concentration of ferrihydrite remained after 970 days at $\text{pH} \leq 6$. However, at a temperature of 92 °C, crystallization occurs faster, with hematite formation beginning within 10 minutes and a complete transformation occurring after 116 hours. Our experiments did not reveal the presence of ferrihydrite in the XRD patterns. However, we cannot fully disregard the possibility of its formation. Due to the rapidity of its transformation in the temperature and pH parameters of our experiments, we cannot discard the possibility that it may have been present as a transient phase during the very early stages of the reaction, quickly crystallising to the more thermodynamically stable goethite and hematite.

In our experiments, temperature significantly influenced the oxidation processes of siderite, affecting the kinetics, polymorph selection, and formation of chemical textures during the replacement reactions due to increased dissolution rates and differences in solubilities. At the lowest temperature of 50 °C, we recorded the initial dissolution of siderite and the crystallization of a thin layer of goethite that covered the entire surface of the siderite grain (Figure 4). However, the transformation did not progress further once the siderite surface had been covered by goethite. Our PHREEQC calculations revealed that even during the earliest stages of dissolution of siderite ($\text{SI}_{\text{siderite}} = -15$), the aqueous

solution can become supersaturated in goethite ($SI_{\text{goethite}} = +2.78$), showing that the dissolution of just a few monolayers of the siderite surface would result in a fluid boundary layer that would allow the crystallisation of this iron oxide. We propose that this coating of goethite on the siderite grains isolated the host from the aqueous solution, halting any further dissolution of siderite, and promoting a state of partial equilibrium (38,52,53) which inhibited further recrystallisation and formation of REE carbonates. A similar result was observed by Yu et al., 2023, 2024 who investigated the effects of dissolved oxygen (DO) concentrations on As(V) adsorption onto siderite. They found that while As(V) adsorption capacities increased with an increase in DO concentration, excess DO caused fast oxidation of siderite, constraining As(V) adsorption. This was due to the production of a coating of Fe(III) oxides on the surface of the pristine siderite that prevented any further oxidation of the host (54,55).

At 165 °C we observed an increase in the amount of goethite precipitation as well as its subsequent transformation to hematite (TABLE 1). Parallel to the Fe^{2+} oxidation processes we also observed the crystallisation of REE carbonates. The transformation of goethite to hematite is strongly influenced by temperature and pH, (56–59). It is known that the transformation from goethite to hematite can occur at temperatures ranging from 160-300 °C (50,58,60). There is also a relationship between temperature and pH, with faster transformation rates at higher temperatures coinciding with higher pH. For example, Das et al. (2010) reported the formation of goethite and hematite at 50 °C and pH 2 after 7 days, while similar peak intensities were evident on after 5 days at pH 7 and after only after 21 hours at pH 10. Concomitantly, the transformation of goethite to hematite was also observed with extended reaction time. Hematite formation was also promoted at near neutral pH (7-8) conditions, while goethite formation was favour acidic (~ 4) or highly alkaline (~ 12) conditions (49,50). This is consistent with the evolution of

our experiments: Our REE solution had an initial pH of ~ 5.5 , promoting the formation of goethite. As the siderite dissolved and REE carbonates formed, the pH gradually became more basic, moving towards a pH of ~ 8.2 , promoting the transformation from goethite to hematite.

The solubility of siderite and the rate of its dissolution are highly dependent on temperature and pH Bénézet, Dandurand and Harrichoury (61) investigated the solubility of natural siderite from 25 to 250 °C. Their experimental work showed that the values for $\log_{10}K_{sp-siderite}$ decrease with increasing temperature. For example, at 50 °C $\log_{10}K_{sp-siderite} = -10.19$ compared to $\log_{10}K_{sp-siderite} = -12.19$ at 200 °C. Concomitantly, and similar to other divalent cation carbonates, the dissolution rate of siderite decreases with an increase in pH (40). Golubev et al., experimentally demonstrated that this decrease follows a linear trend, spanning approximately 1.5 orders of magnitude between pH 1 and 5. Furthermore, the dissolution rate is strongly temperature-dependent, exhibiting a variation of approximately 2 orders of magnitude between 25 and 100 °C. Taking the initial pH of the REE-bearing aqueous solution (5.1) into consideration, at 50 °C the solubility of siderite would be $\sim 10^{-10.0} - 10^{-11.1} \text{ mol}\cdot\text{cm}^{-2}\text{sec}^{-1}$ and at 100 °C the value would be $\sim 10^{-10.0} - 10^{-9.9} \text{ mol}\cdot\text{cm}^{-2}\text{sec}^{-1}$. Although no dissolution rates have been reported for temperatures above 100 °C, the observed trend suggests that the dissolution rate would increase $\sim 1.5\text{-}2.0$ orders of magnitude at 200 °C.

At low pH values, particularly in acidic conditions ($\text{pH} < 5$), the dissolution of siderite is promoted due to the increased activity of hydrogen ions in the solution. The adsorption of H^+ onto the mineral surface enhances the dissolution process, leading to higher concentrations of dissolved Fe^{2+} in the aqueous phase (62). Studies have shown that siderite dissolution rates increase significantly at pH levels around 2 to 5, where the mineral becomes more reactive (62). This increased dissolution can facilitate the release

of Fe ions, which can subsequently precipitate as iron oxides such as magnetite or hematite, depending on the redox conditions present (63).

Conversely, at neutral to alkaline pH levels ($\text{pH} \geq 7$), the solubility of siderite decreases, resulting in slower dissolution rates. In circumneutral conditions, the stability of siderite is enhanced, making it more resistant to dissolution (64). In environments with circumneutral pH, siderite can persist due to the buffering capacity of the surrounding media, which limits the availability of H^+ ions necessary for dissolution (64). This resistance to dissolution can hinder the formation of iron oxides and REE-bearing minerals, as the necessary precursor ions may not be sufficiently available in the solution.

Furthermore, carbonate species HCO_3^- and CO_3^{2-} can also influence the dissolution kinetics of siderite. These species can act as inhibitors of dissolution at higher pH levels, as they compete with H^+ ions for adsorption sites on the mineral surface (19). This competition can further reduce the rate of siderite dissolution and, consequently, the availability of iron for subsequent mineral formation.

The formation of REE-bearing minerals is also pH-dependent. In acidic conditions, the increased solubility of siderite can lead to higher concentrations of Fe^{2+} in solution. For example, the presence of dissolved REE in acidic brines can facilitate their incorporation into iron oxides precipitating from the dissolved siderite (65). However, in neutral to alkaline conditions, the reduced dissolution of siderite limits the availability of Fe^{2+} , thereby slowing the formation of the iron oxide minerals.

4.1. Siderite-hematite epitaxial overgrowth

An interesting feature observed in the 165 °C experiments was the presence of oriented overgrowths of the newly formed hematite on the surface of siderite (Figure 6). This epitaxial overgrowth is not unexpected, given that hematite and siderite share the same crystal system (trigonal) and space group ($R\bar{3}c$). Siderite has lattice parameters of $a = b = 4.6916 \text{ \AA}$, and $c = 15.3796 \text{ \AA}$ (66), while hematite lattice parameters are $a = 5.038 \text{ \AA}$ and $c = 13.772 \text{ \AA}$ (67). These structural similarities suggest a favourable fit for epitaxial growth (Figure 15). The misfit values have been calculated using the expression (68):

$$mf(\%) = \frac{t_{[uvw]sub} - t_{[uvw]over}}{t_{[uvw]over}} \times 100$$

These can be used to quantify the degree of lattice mismatch between the epitaxial overgrowth and the substrate. In this expression, $t_{[uvw]sub}$ and $t_{[uvw]over}$ correspond to the repeating periods along the matching directions $[uvw]$ of the substrate (siderite) and the overgrowth (hematite), respectively (68).

The calculated misfit values for the $(104)_{sid}[010]_{sid}|| (104)_{hem}[010]_{hem}$ and the $(104)_{sid}[001]_{sid}|| (104)_{hem}[001]_{hem}$ alignments are -6.93 and +0.59% respectively, falling well below the generally accepted limits (15-20 %) required for epitaxial overgrowth to occur (69). The negative value indicates that the unit cell of hematite is very slightly contracted along the $[010]$ direction of epitaxy of siderite, while the small positive value shows an almost perfect match (with a slight expansion) of the unit cell of goethite with respect to the siderite in the $[001]$ direction.

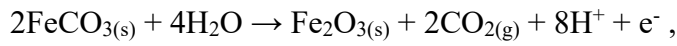
As hematite forms as a consequence of the hydrothermal alteration and Fe^{2+} to Fe^{3+} oxidation process, there are two factors that need to be taken into account: First is the slightly larger molar volume of hematite ($30.39 \text{ cm}^3 \cdot \text{mol}^{-1}$) (70) compared to siderite

($29.33 \text{ cm}^3 \cdot \text{mol}^{-1}$) (70), which is likely contributing to the loss of orientation once the hematite crystals grow and coalesce. Second is the dissolution and breakdown of siderite due to the hydrothermal replacement by REE carbonates and the Fe^{2+} to Fe^{3+} oxidation process, contributing to the subsequent detachment of the newly formed hematite crystals from the host (Figure 7). However, it is important to consider that although the ideal composition of pure siderite is FeCO_3 , this mineral is an end member of a complex solid solution (CaCO_3 - MgCO_3 - FeCO_3) and therefore can contain other divalent ions such as Ca^{2+} , Mg^{2+} or Mn^{2+} , alongside impurities such as Zn^{2+} , Co^{2+} , or Cd^{2+} (71). These chemical variations have the potential to influence the matching unit cells and subsequently impact the kinetics of siderite replacement processes, as well as the final solid morphology of hematite.

4.2. Formation of rare earth carbonates and their secondary replacement by cerianite

Our $165 \text{ }^\circ\text{C}$ experiments resulted in the partial replacement of the siderite host with the rare earth carbonates kozoite and hydroxylbastnasite (Figures 10,13). The reaction sequence for REE carbonates was found to be time-and temperature-dependent (39), with the initial formation of kozoite between 50 and $165 \text{ }^\circ\text{C}$ and its subsequent transformation to the more stable hydroxylbastnasite at temperatures $\geq 165 \text{ }^\circ\text{C}$. The rate of crystallization and composition of the REE-bearing phases is known to be controlled by the solubilities and dissolution rates of the host grain, the REE ratio in solution, as well as the evolving fluid composition during the replacement process (39). The dissolution of siderite and its subsequent replacement from the periphery inwards was a consequence of the lower solubilities of REE carbonates compared to the siderite host. The solubility products for pure Nd-hydroxylbastnasite and Nd-Kozoite have been calculated to be $\log(K_{\text{sp}}) = -$

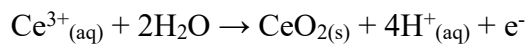
23.8±0.1 and $\log(K_{sp}) = -22.3\pm0.2$, respectively (36), while the solubility product of siderite, $\log(K_{sp}) = -10.94\pm0.4$ (61) is much higher. Our PHREEQC calculations show that high supersaturation levels for kozoite and bastnasite ($SI > 1-3$) as well as cerianite ($SI > 11$) are reached when the REE-bearing solutions (equal concentration or PAAS) are equilibrated with siderite at 165-205 °C, also even if the solution has not fully reached saturation for the host. Siderite dissolution rates have also been shown to increase with temperature (40). Besides, the siderite transformation to hematite due to the Fe^{2+} to Fe^{3+} oxidation,



was translated into the release of CO_2 and therefore in the gradual acidification of the aqueous solution, which promoted the subsequent dissolution of all carbonates after 1 week in equal concentration experiments and 24 hours in PAAS experiments (Table 1).

Point analysis of the EDS maps showed that the uptake and incorporation of the REE in the newly formed carbonates was dependent on the initial concentration in solution. In the equal concentration experiments, the uptake of REE by the crystallising carbonate occurs in the same ratio as their composition in the aqueous solution, indicating that the crystallising carbonate mirrors the REE composition of the surrounding solution (SI-4a). Conversely, in the PAAS solution experiments, the REE ratio is different compared to the equal concentration, but still reflects the higher concentration of La, Ce, and Nd in the original solution (SI-4b). On one hand, this aligns with the typical composition of the REE carbonates bastnasite and kozoite. Bastnasite has a hexagonal structure that tends to uptake the light REE (La to Nd) which are in a 9-fold coordination with oxygen (17,72), with the heavier Dy only entering as impurities. Heavier REE could potentially be incorporated into the bastnasite structure, however, this would require higher pressure

conditions that are outside of our experimental range. In contrast, the intermediate phase kozoite is orthorhombic and it can include both lighter and heavier REE (17), perfectly accommodating Dy. On the other side, the mirroring of the REE ratios of the initial aqueous solution (equal concentration and PAAS experiments) could be explained by assuming that kozoite and bastnasite are both primary phases forming in their respective reactions and have not formed via metastable intermediate precursors (e.g., lanthanite and tengerite (17,37,38). This would also explain why we did not observe any zoning in the REE carbonates as reported in Maddin et al., (2024). At 205°C siderite was fully replaced by hematite and the rare earth carbonates by cerianite. The solution-mediated oxidation of Ce^{3+} to Ce^{4+} initiates cerianite, as described by this reaction:



The oxidation of Ce^{3+} to Ce^{4+} is triggered by several factors. First, Ce^{4+} has the electron structure of a noble gas, making it more stable than Ce^{3+} , and the higher temperatures provide the energy needed to facilitate the loss of an electron. Second, as stated earlier, as our system progressed towards equilibrium, the pH would increase from ~ 5 towards ~ 8.2 . The higher concentration of OH^{-} ions allow the formation of Ce-hydroxo-complexes which facilitate the Ce^{3+} to Ce^{4+} oxidation process (73), especially at the surface-solution interface of the REE minerals (74). As Ce^{4+} is incompatible within the carbonate structure, it combines with oxygen, forming the cerianite (CeO_2) oxide.

Our experimental data shows that the Fe^{2+} to Fe^{3+} oxidation initiated prior to the Ce^{3+} to Ce^{4+} oxidation process, revealing a lower energy barrier required for the former compared to the later under our experimental conditions. However, both processes happened simultaneously during most of the duration of the experiment. As both oxidation processes progressed, the pH lowered, dissolving the host and the REE carbonates. At the

end of the reaction, the only REE remaining in solid-state was Ce in the cerianite, as well as a small amount of Dy present as impurities in the structure of cerianite. Our experimental design (sealed hydrothermal reactors containing a limited atmosphere, under conditions of autogenous pressure) created an oxidizing environment that favoured the oxidation of Ce^{3+} to Ce^{4+} reaction. Had our experiments been conducted using anoxic water and a pure N_2 atmosphere, the presence of carbonates such as siderite would have also buffered the pH of the aqueous solution, increasing the stability of the HCO_3^- ions relative to CO_2 . However, these changes would not have a significant influence on the redox state and the formation of Fe and Ce oxides (goethite, hematite and cerianite) would most likely not have occurred. Consequently, Ce would have been incorporated into the newly formed kozoite and bastnasite as Ce^{3+} along with the other REEs in the system. However, in the studied conditions, Ce had a significant impact on the kinetics of the replacement reactions, showing that the rate of decarbonation is dependent on the ratio of Ce relative to other REE in solution. In the PAAS solution, where Ce is dominant compared to the other REE, the higher concentration of Ce leads to a faster release of CO_2 , resulting in quicker decarbonation and dissolution of all the carbonates. Consequently, the full decarbonation process can occur in less than 24 hours. In contrast, in the equal concentration experiments (where REE are present in equal concentrations) all carbonates dissolved after 24 hours.

The replacement of kozoite and bastnasite is also enhanced by the smaller molar volume of cerianite ($23.86 \text{ cm}^3 \text{ mol}^{-1}$) compared to kozoite ($45.59 \text{ cm}^3 \text{ mol}^{-1}$) or bastnasite ($44.91 \text{ cm}^3 \text{ mol}^{-1}$) which increased the porosity of the parent phase (70). This porosity helps maintain supersaturation levels at the carbonate-solution interface, allowing the replacement reaction to continue and releasing REE back into the solution. Some REE, such as Dy^{3+} and Nd^{3+} , have ionic radii similar to Ce^{4+} and can be incorporated into

cerianite as impurities. Depending on the Ce concentration in the fluid, the crystallization of cerianite could trigger the formation of symplectic textures, as described by Maddin et al. (2024)(39). In these textures, cerianite grows into the nanometer-sized pores created by the dissolution of the REE carbonate (75). Figures 9 and 14 may indicate the early development of these symplectic textures at the nanoscale.

In natural systems, REE-bearing-carbonatites form through the immiscibility of carbonate-silicate magma and through the fractional crystallization of carbonate minerals from carbonatite magma. The REE form complexes and the magmatic hydrothermal system enables their migration. REE circulation is further promoted by fractures in the deposit, which also provide the space necessary for REE-mineral precipitation. Our hydrothermal replacement experiments in REE-aqueous solutions offers insight into the potential mechanisms and conditions needed for the possible formation of REE-minerals. The differences in molar volumes observed in our experiments, along with the increasing porosity they created, can be correlated to the fractures found in natural ore deposits. As many of the world's carbonatites also host hematite-bearing ores, the use of siderite as our reactant was ideal. The REE uptake by the iron oxides formed was negligible in our experiments; however, further investigation into the use of oxidation processes to separate Fe from REE-bearing ores could have significant potential for improving ore processing techniques and enhancing the economic viability of mining operations.

5. Conclusion

The interaction between siderite and multi-component rare earth element (La, Ce, Pr, Nd and Dy) – bearing aqueous solutions resulted in the formation of iron oxides, goethite (α -Fe³⁺O(OH)) and hematite (Fe₂O₃), metastable REE-bearing minerals kozoite

(REE(CO₃)(OH) and bastnasite (REE(CO₃)(OH,F), and the rare earth oxide cerianite (CeO₂). The newly formed phases were the consequence of two oxidation processes, Fe²⁺ to Fe³⁺, promoting goethite and hematite crystallisation, and Ce³⁺ to Ce⁴⁺, resulting in cerianite formation. Both processes were found to be highly dependent on temperature. At low temperatures, the formation of REE carbonates was inhibited due to a coating of goethite layer that isolated the siderite and created a situation of partial equilibrium. At higher temperatures, the dissolution of siderite was promoted and differences in solubility allowed for the formation of kozoite and bastnasite. However, the continuing oxidation processes acidified the solution, initiating the dissolution of all carbonates and resulted in hematite and cerianite being the final phases in our system.

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Supplementary Information

Transient crystallisation of rare earth carbonates during the hydrothermal oxidation of siderite

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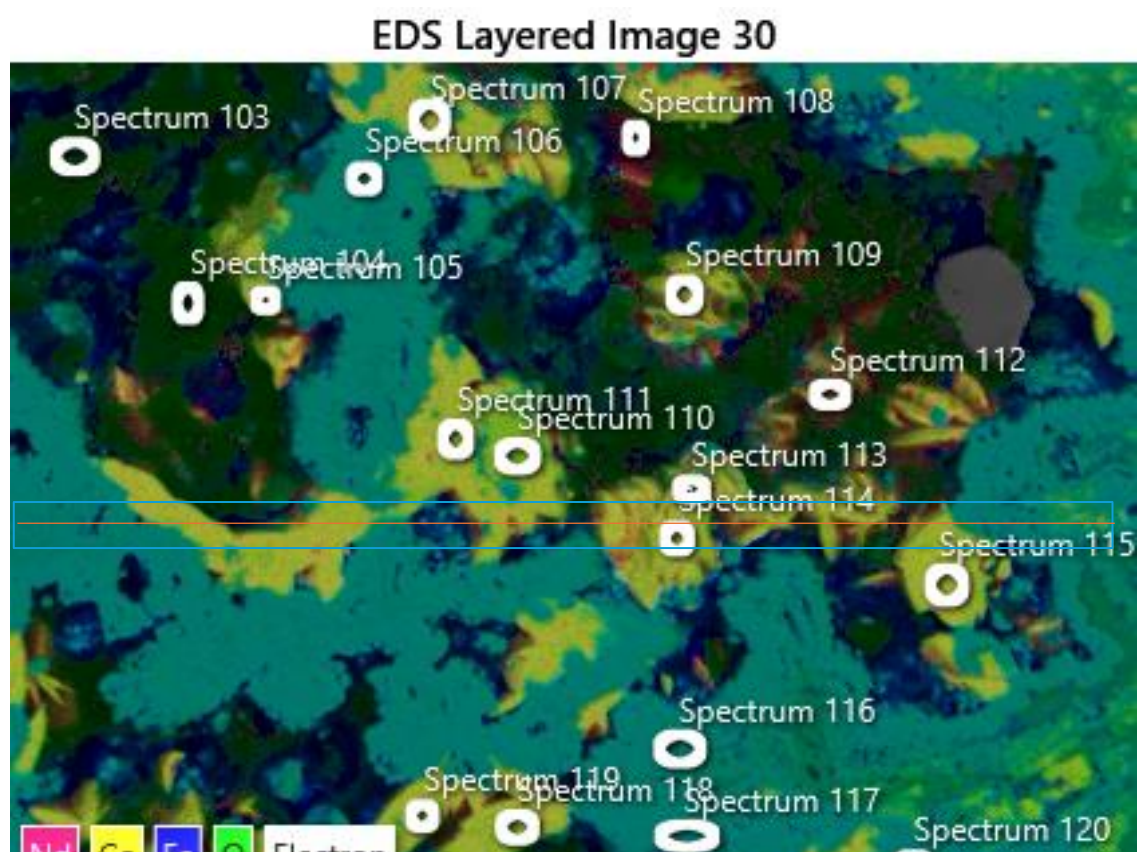
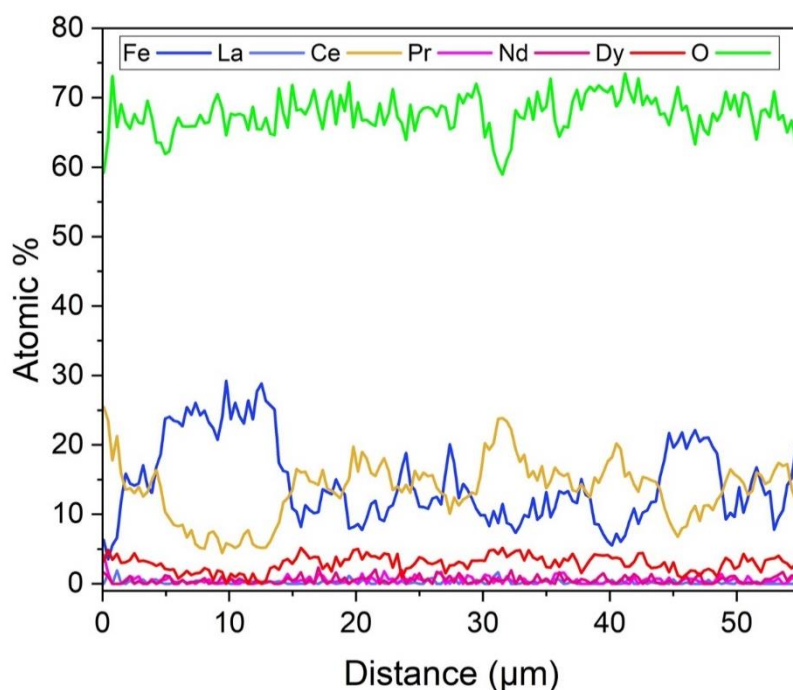


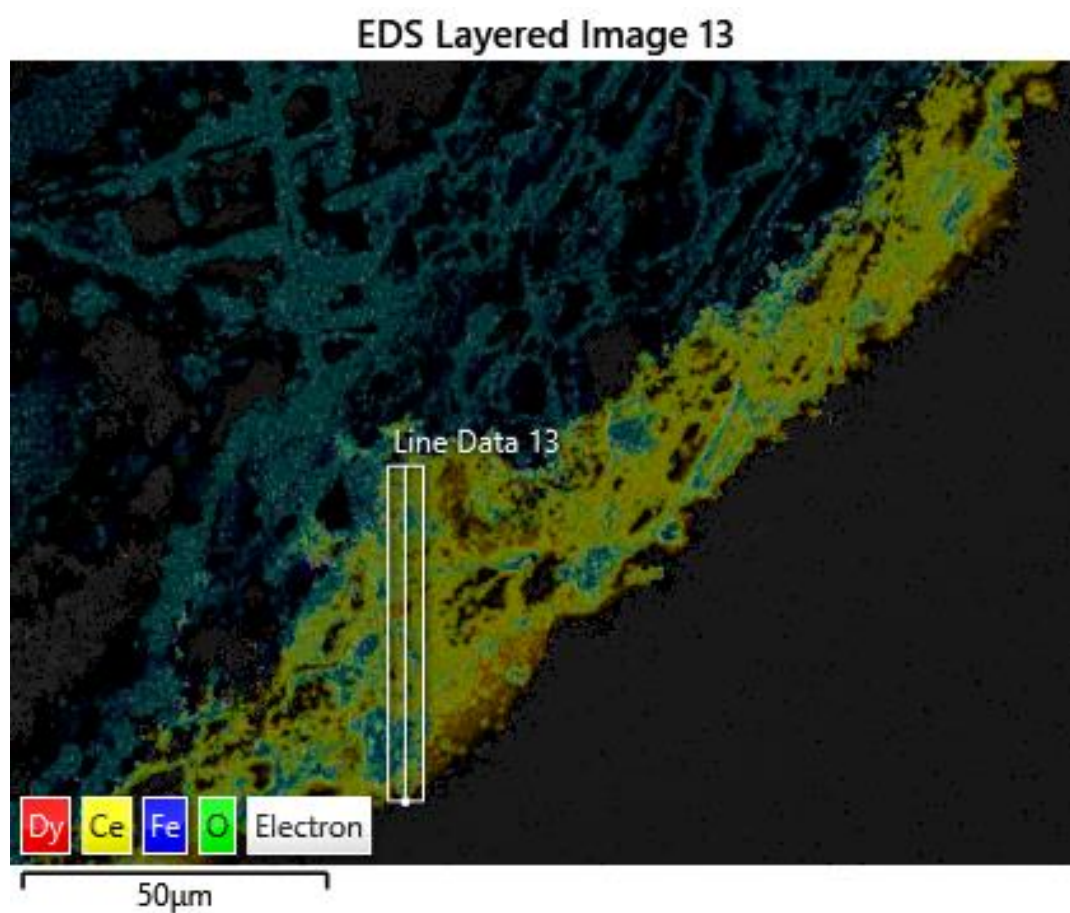
Figure SI-1a. SEM-EDS map showing acquisitions for point analysis. A preferential uptake of Nd and La with Ce in the PAAS solution was observed at 165 °C after 24 hours (see Figure SI-1b).



PAAS 165 °C 24 hrs	C	O	Fe	La	Ce	Pr	Nd	Dy	Total
Spectrum 103	0.00	75.27	23.87	0.08	0.76	0.00	0.00	0.20	100.00
Spectrum 104	29.68	59.36	9.15	0.29	0.89	0.19	0.40	0.03	100.00
Spectrum 105	28.86	57.73	1.64	2.14	5.86	0.69	2.78	0.30	100.00
Spectrum 106	25.13	50.25	23.85	0.14	0.37	0.05	0.19	0.01	100.00
Spectrum 107	28.93	57.86	0.95	2.34	6.14	0.69	2.77	0.32	100.00
Spectrum 108	17.07	34.14	12.82	6.22	17.89	2.23	8.72	0.90	100.00
Spectrum 109	28.35	56.70	1.37	2.56	6.76	0.80	3.11	0.35	100.00
Spectrum 110	29.09	58.18	1.03	3.60	5.43	0.48	1.94	0.25	100.00
Spectrum 111	28.98	57.96	0.99	2.68	6.02	0.56	2.50	0.32	100.00
Spectrum 112	22.43	44.85	6.66	4.85	13.09	1.48	6.04	0.61	100.00
Spectrum 113	28.47	56.93	1.68	2.40	6.43	0.77	3.01	0.31	100.00
Spectrum 114	29.01	58.03	0.64	2.67	6.11	0.67	2.54	0.32	100.00

Spectrum 115	28.93	57.86	0.73	2.59	6.23	0.64	2.69	0.33	100.00
Spectrum 116	24.66	49.32	25.46	0.13	0.29	0.04	0.08	0.03	100.00
Spectrum 117	24.82	49.64	25.18	0.07	0.18	0.02	0.07	0.02	100.00
Spectrum 118	28.83	57.66	2.02	2.47	5.63	0.59	2.47	0.33	100.00
Spectrum 119	29.07	58.14	0.61	2.62	6.03	0.61	2.61	0.32	100.00
Spectrum 120	24.83	49.67	24.87	0.11	0.30	0.05	0.13	0.04	100.00

Figure SI-1b. Line graph and point analysis data (from Figure SI-1a map) showing the preferential uptake of Nd and La with Ce in the PAAS solution was observed at 165 ° C after 24 hours.



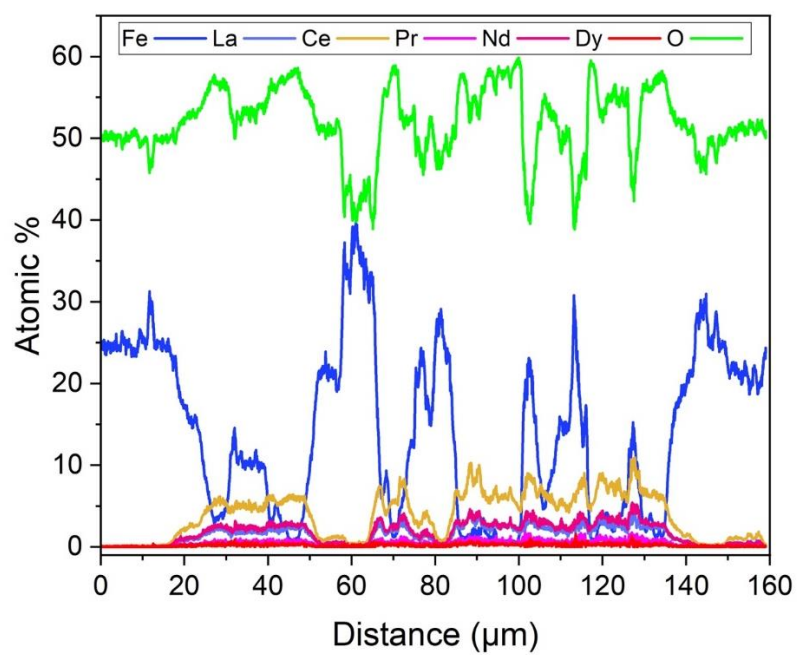
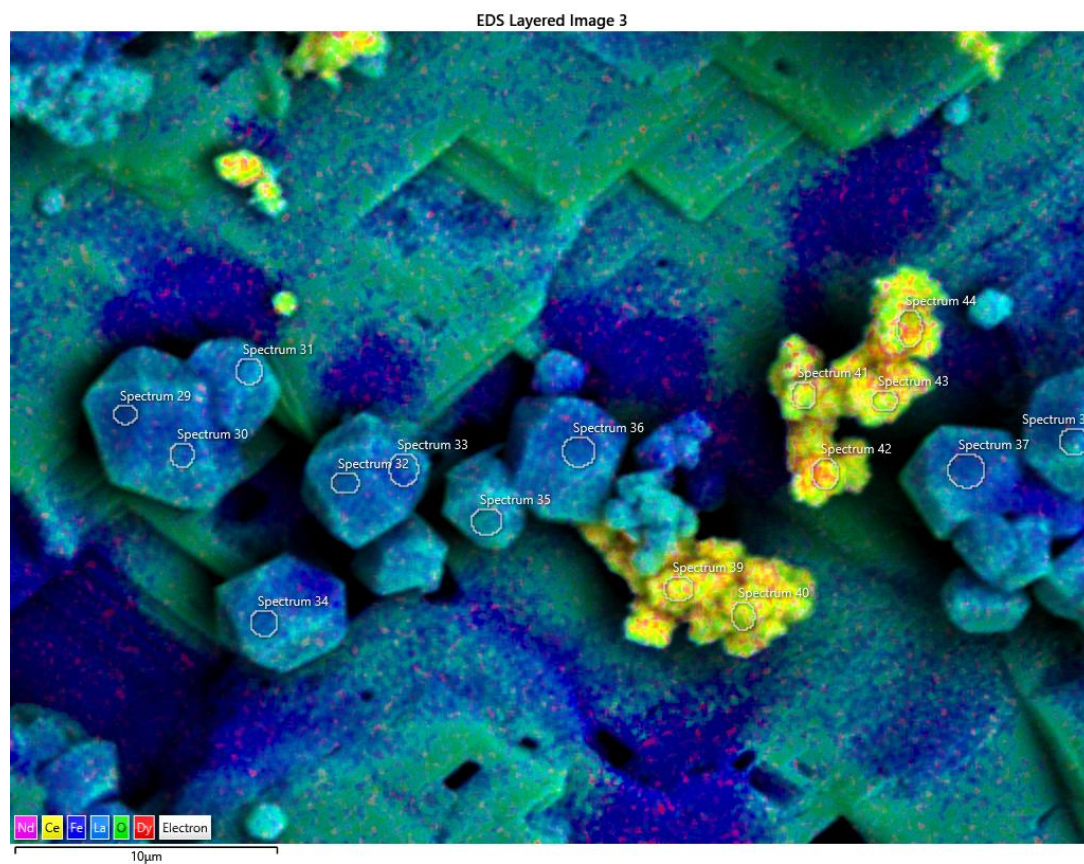
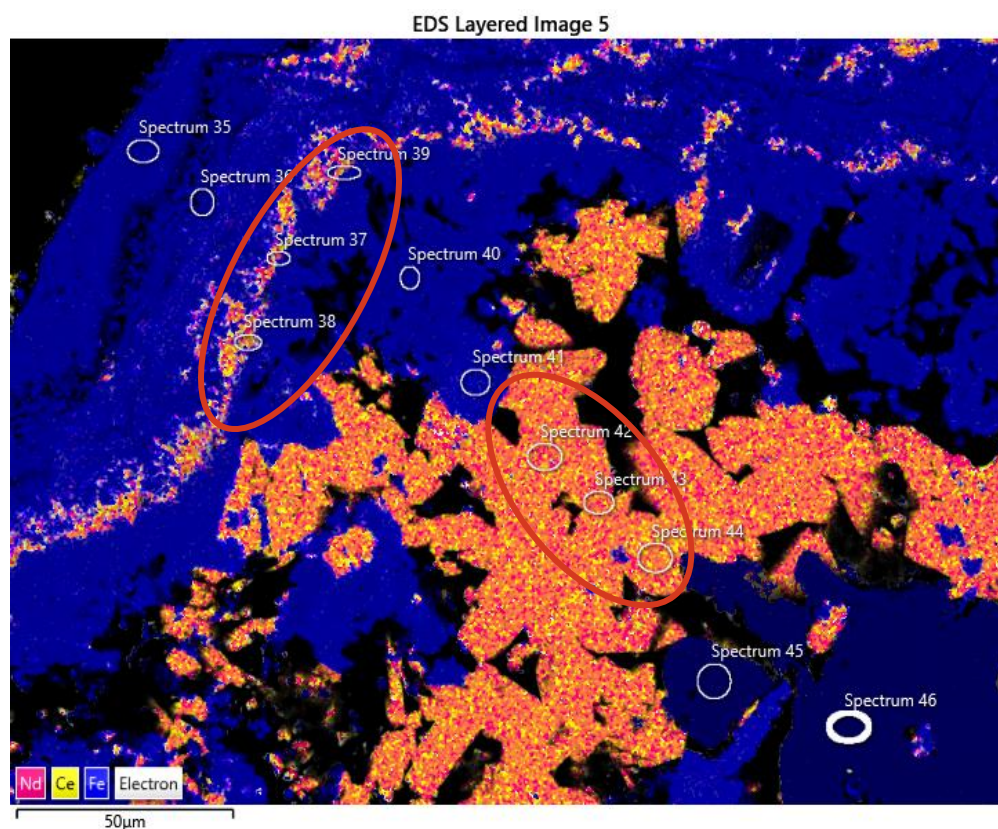


Figure SI-2. SEM-EDS map showing the Dy incorporation into cerianite in the PAAS solution at 205 °C after 1 week and in the non-PAAS solution at 205 °C after 24 hours



Equal Conc. 205 °C 24 hrs	C	O	Fe	La	Ce	Pr	Nd	Dy	Total
Spectrum 29	18.48	36.96	44.64	0.00	0.06	0.05	0.00	0.00	100.00
Spectrum 30	19.53	39.06	41.21	0.10	0.05	0.08	0.04	0.00	100.00
Spectrum 31	20.30	40.60	38.92	0.01	0.11	0.02	0.00	0.04	100.00
Spectrum 32	19.77	39.54	40.37	0.01	0.14	0.04	0.00	0.15	100.00
Spectrum 33	18.74	37.47	43.31	0.03	0.08	0.00	0.02	0.39	100.00
Spectrum 34	19.25	38.49	42.21	0.06	0.14	0.02	0.04	0.00	100.00
Spectrum 35	22.89	45.79	30.91	0.00	0.22	0.12	0.02	0.09	100.00
Spectrum 36	18.84	37.68	43.26	0.05	0.33	0.07	0.00	0.00	100.00
Spectrum 37	18.59	37.17	43.90	0.00	0.40	0.09	0.03	0.00	100.00
Spectrum 38	20.87	41.73	36.86	0.06	0.31	0.09	0.00	0.13	100.00
Spectrum 39	24.39	48.78	11.84	0.00	11.49	0.57	0.64	2.48	100.00
Spectrum 40	24.29	48.58	14.21	0.03	10.11	0.13	0.21	2.44	100.00
Spectrum 41	23.68	47.36	15.76	0.13	9.83	0.64	0.55	2.06	100.00
Spectrum 42	21.08	42.17	16.23	0.40	16.14	0.04	0.38	3.56	100.00
Spectrum 43	22.61	45.21	17.30	0.29	11.33	0.22	0.35	2.70	100.00
Spectrum 44	21.36	42.72	18.61	0.00	14.05	0.28	0.25	2.95	100.00

Figure SI-3. SEM-EDS map showing the Dy incorporation into cerianite in the equal concentration solution at 205 °C after 24 hours, REE concentration in the iron oxides was below the SEM-EDS detection limit, at <0.1%



A. Equal Conc. 165 °C 24 hrs	O	Fe	La	Ce	Pr	Nd	Dy	Total
Spectrum 35	60.68	39.11	0.00	0.12	0.08	0.10	0.00	100.00
Spectrum 36	61.95	36.94	0.19	0.21	0.21	0.15	0.34	100.00
Spectrum 37	69.73	22.60	1.37	1.02	1.21	1.57	2.50	100.00
Spectrum 38	70.56	18.75	1.91	2.91	2.47	2.22	1.18	100.00
Spectrum 39	66.27	27.92	0.82	1.04	1.17	1.27	1.50	100.00
Spectrum 40	60.89	39.07	0.14	0.14	0.00	0.05	0.00	100.00
Spectrum 41	64.08	33.32	0.28	0.53	0.46	0.38	0.95	100.00
Spectrum 42	77.41	3.16	4.22	3.52	3.95	4.42	3.33	100.00
Spectrum 43	78.47	1.00	4.04	3.78	5.16	4.80	2.75	100.00
Spectrum 44	78.89	0.65	4.38	4.13	5.04	4.42	2.49	100.00
Spectrum 45	71.56	28.27	0.03	0.10	0.01	0.00	0.12	100.00
Spectrum 46	71.25	28.59	0.04	0.14	0.03	0.00	0.04	100.00

Figure SI-4a. SEM-EDS map showing that in the equal concentration experiments (A), the uptake of REEs by the crystallising carbonate occurs in the same ratio as their composition in the aqueous solution, indicating that the crystallising carbonate mirrors the REE composition of the surrounding solution.

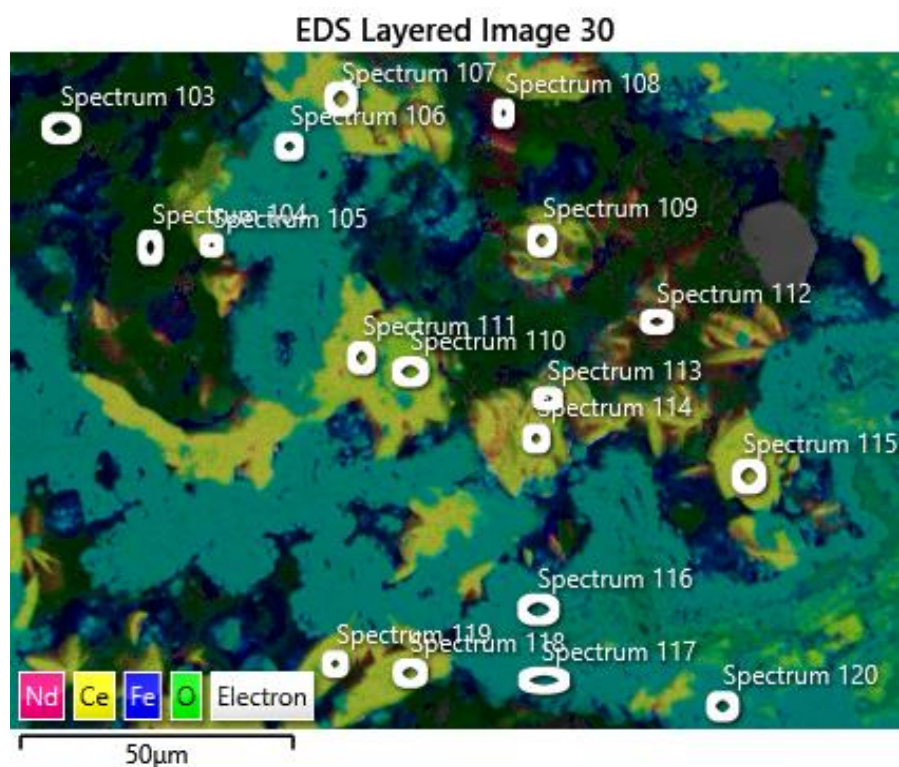


Figure SI-4b. SEM-EDS map showing that in the PAAS solution experiments the REE ratio is different compared to the equal concentration, but still reflects the higher concentration of La, Ce and Nd in the original solution.

B. PAAS 165 °C 24 hrs	C	O	Fe	La	Ce	Pr	Nd	Dy	Total
Spectrum 103	0.00	75.27	23.87	0.08	0.76	0.00	0.00	0.20	100.00
Spectrum 104	29.68	59.36	9.15	0.29	0.89	0.19	0.40	0.03	100.00
Spectrum 105	28.86	57.73	1.64	2.14	5.86	0.69	2.78	0.30	100.00
Spectrum 106	25.13	50.25	23.85	0.14	0.37	0.05	0.19	0.01	100.00
Spectrum 107	28.93	57.86	0.95	2.34	6.14	0.69	2.77	0.32	100.00
Spectrum 108	17.07	34.14	12.82	6.22	17.89	2.23	8.72	0.90	100.00
Spectrum 109	28.35	56.70	1.37	2.56	6.76	0.80	3.11	0.35	100.00
Spectrum 110	29.09	58.18	1.03	3.60	5.43	0.48	1.94	0.25	100.00
Spectrum 111	28.98	57.96	0.99	2.68	6.02	0.56	2.50	0.32	100.00
Spectrum 112	22.43	44.85	6.66	4.85	13.09	1.48	6.04	0.61	100.00
Spectrum 113	28.47	56.93	1.68	2.40	6.43	0.77	3.01	0.31	100.00
Spectrum 114	29.01	58.03	0.64	2.67	6.11	0.67	2.54	0.32	100.00
Spectrum 115	28.93	57.86	0.73	2.59	6.23	0.64	2.69	0.33	100.00
Spectrum 116	24.66	49.32	25.46	0.13	0.29	0.04	0.08	0.03	100.00
Spectrum 117	24.82	49.64	25.18	0.07	0.18	0.02	0.07	0.02	100.00
Spectrum 118	28.83	57.66	2.02	2.47	5.63	0.59	2.47	0.33	100.00
Spectrum 119	29.07	58.14	0.61	2.62	6.03	0.61	2.61	0.32	100.00
Spectrum 120	24.83	49.67	24.87	0.11	0.30	0.05	0.13	0.04	100.00

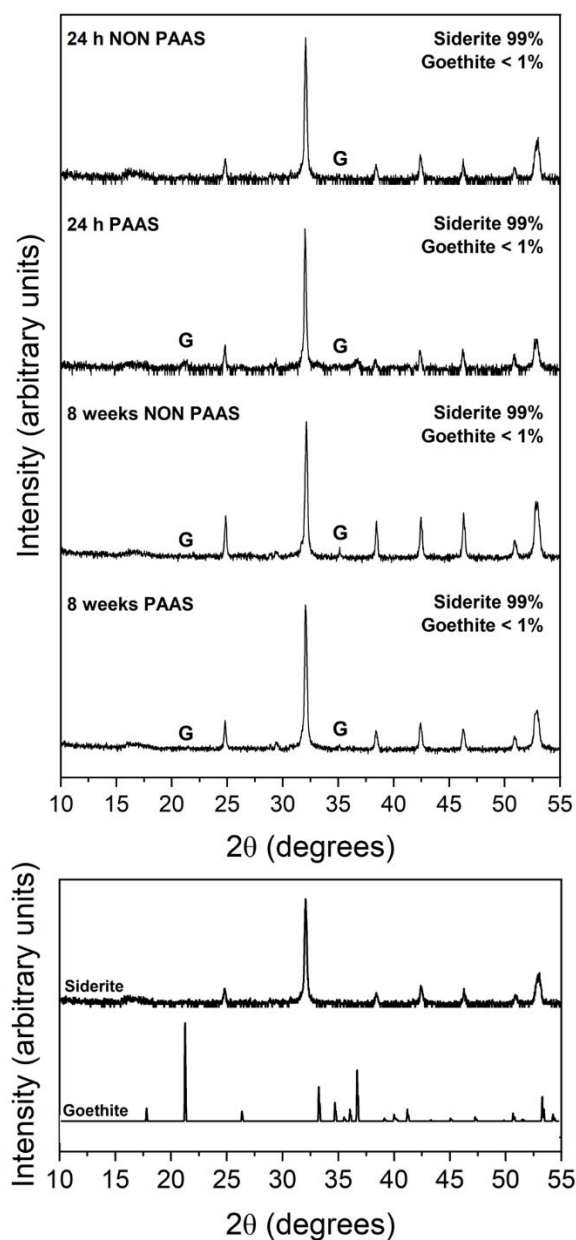


Figure SI-5. Powder XRD patterns of goethite (G) in the equal concentration (non-PAAS) and PAAS experiments at 50 °C after 24 hours and 8 weeks (*Bragg peaks that have not been assigned to any phase correspond to siderite). The diagram in the bottom area shows the standard XRD patterns of the phases found in these experiments.

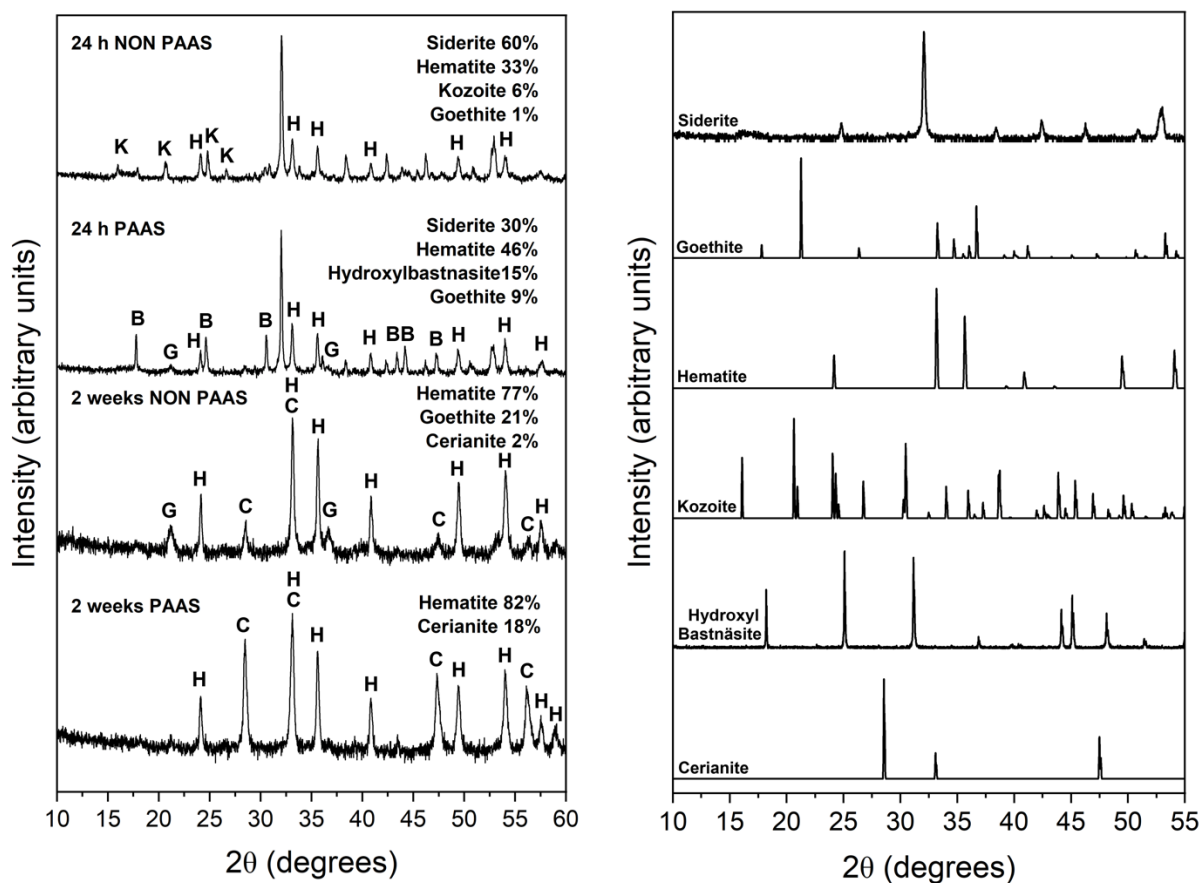


Figure SI-6. Powder XRD patterns of goethite (G), hematite (H), kozoite (K), hydroxylbastnasite (B) and cerianite (C) in the equal concentration (non-PAAS) and PAAS experiments at 165 °C after 24 hours and 2 weeks (*Bragg peaks that have not been assigned to any phase correspond to siderite) The diagram in the right area shows the standard XRD patterns of the phases found in these experiments.

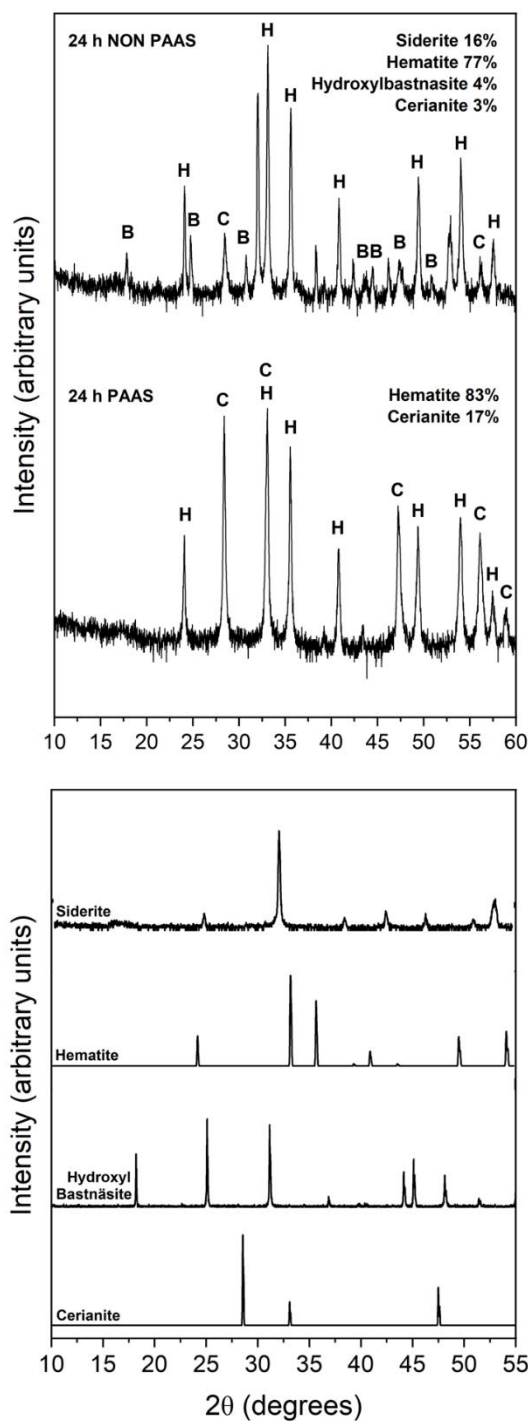


Figure SI-7. Powder XRD patterns of, hematite (H), hydroxylbastnasite (B) and cerianite (C) in the equal concentration (non-PAAS) and PAAS experiments at 205 °C after 24 hours (*Bragg peaks that have not been assigned to any phase correspond to siderite). The diagram in the bottom area shows the standard XRD patterns of the phases found in these experiments.

Chapter 4. Nanophase REE Phosphate Crystallization Induced by Vivianite Oxidation: Mechanistic Insights and Mineralogical Implications

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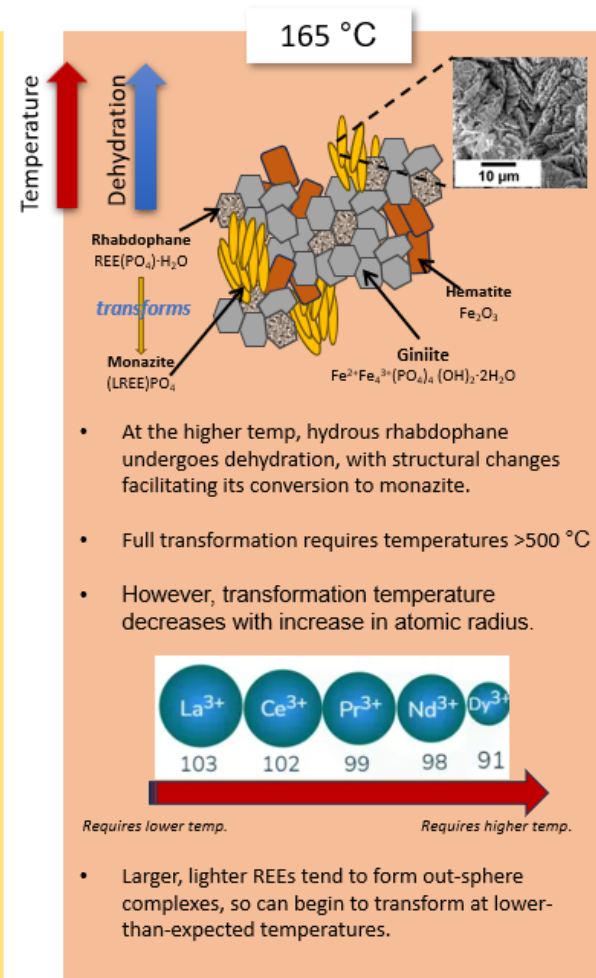
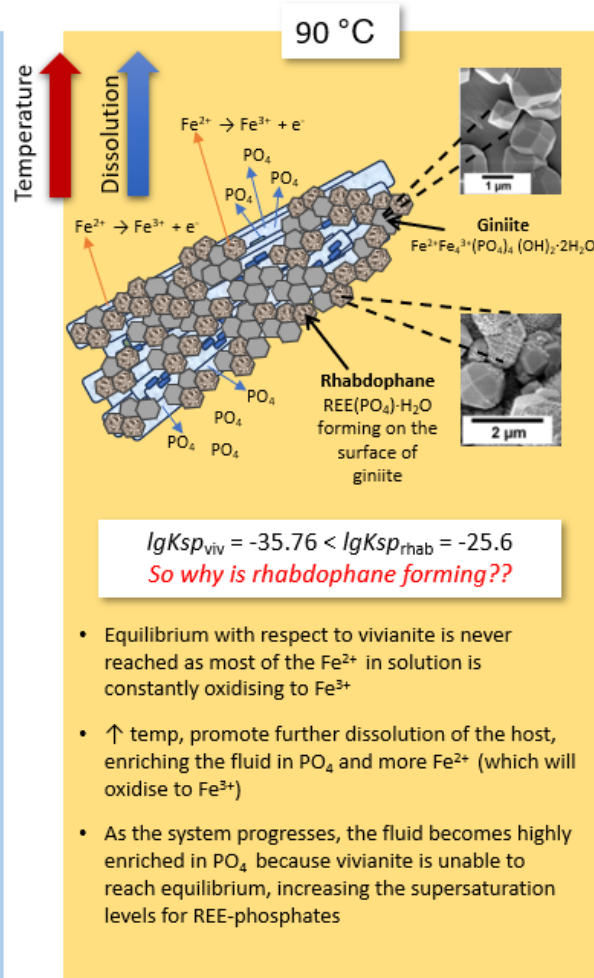
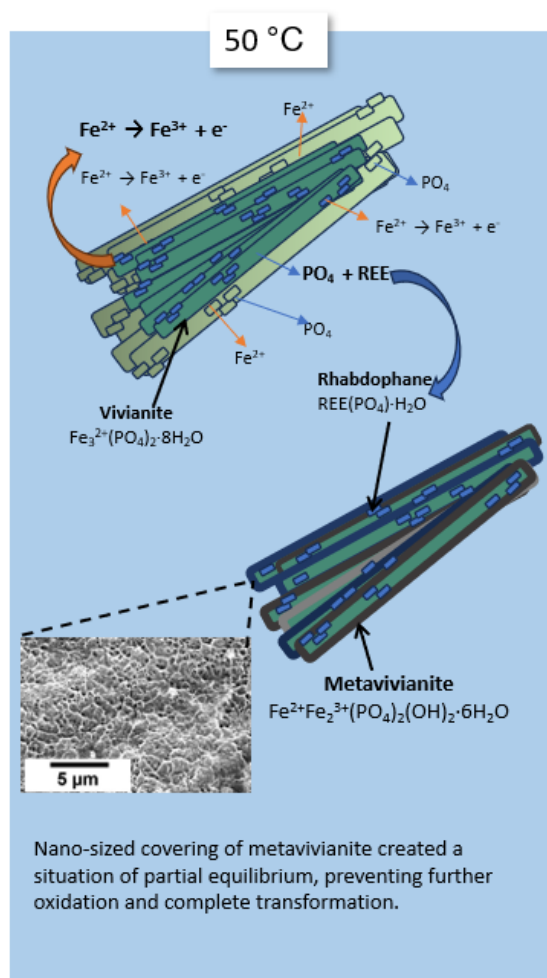
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This chapter is in review with the journal RSC Advances.

Abstract

Our study investigates the interaction between multi-component rare earth element (REE; La, Ce, Pr, Nd, Dy)-bearing aqueous solutions with vivianite ($\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) grains under hydrothermal conditions (50-165 °C). The results revealed the solution-mediated, progressive oxidation and dissolution of vivianite. This resulted in the formation of iron phosphates, metavivianite [$\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$], and giniite [$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{PO}_4)_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$], iron oxide hematite [Fe_2O_3], and rare earth phosphates, rhabdophane [$\text{REE}(\text{PO}_4) \cdot \text{H}_2\text{O}$] and monazite [$(\text{LREE})\text{PO}_4$]. The extent of the reactions was found to be dependent on temperature, pH, as well as the concentration and ionic radii of the rare earths in solution. The rate of vivianite oxidation and dissolution increased with increased temperature, with 50% of vivianite transformed after 32 days at 50 °C, and 100% transformed after 28 days and 4 hours at 90 and 165 °C respectively. The pH of the solutions at all three temperatures maintained the stability of rhabdophane, and only at

the highest temperature of 165 °C it began to transform to monazite. Understanding the stability of iron



Graphical Abstract Depicting the reaction of vivianite with multi-component rare earth element bearing solutions

phosphates, their transformation products, and their capacity to incorporate REEs is crucial for resource recovery, especially in the extraction of REEs from waste materials.

1. Introduction

Phosphate rocks are considered to be an essential resource as they provide the raw material for phosphoric acid and fertilizers utilized in agriculture, thereby contributing to the sustainability of the world's food supply. They are also gaining increased interest as a potential rare earth element (REE) source (1). With their unique optical, magnetic, and catalytic properties, REEs are becoming more and more essential in modern technologies and are considered critical metals (2,3). However, as minable concentrations of REEs are limited, there is a substantial risk to their supply and availability (4). REE deposits that contain iron phosphates are of significant interest due to their potential economic value and strategic importance. One example is the Mount Weld carbonatite deposit in western Australia, which has been identified as a secondary rare earth phosphate deposit where phosphates, such as monazite, are enclosed within iron oxide minerals (5). The deposit, which is enclosed within a weathering cap of an intrusive plug (6) contains an average REE grade of 9.8 wt% $\sum \text{REE}_2\text{O}_3$ and REE concentrations up to 45 wt% $\sum \text{REE}_2\text{O}_3$, is now considered one of the richest deposits in the world (7). Phosphorite-type rare earth deposits, such as the early Cambrian Zhijin Phosphorite, China, are also known for their high concentrations of REEs including yttrium (REEY) (8), as well as heavy REE enrichment (9) During its formation, which was initiated by the breakup of supercontinent

Rodinia, the local reducing environment promoted the release of REEY from hydroxides which dramatically increased the concentration of REEY in the seawater. As the supercontinent continued to break apart, there was an upwelling of hydrothermal fluids which carried phosphorous-rich materials. The upwelling processes contributed to the reducing environment and concomitantly to the dissolution of REEs. The upwelling currents carried the P-and REE-rich complexes to the upper oxidising surface waters, where they were able to mix and form REEY-rich apatite (8). Studies have also shown a correlation between REE distribution and phosphorous in sedimentary phosphate deposits (10), with particular interest in the microdistribution of REEs in specific mineral phases and their locations. Further analysis of the Zhijin deposit by Xiong et al. (2024) revealed that the REE distribution was highly correlated with that of phosphorous and that they occur as lattice defects in apatite via isomorphic substitution. Lastly, an association of Fe with P and REEs has been observed in high-P ooidal iron ores, with some of the largest resources located in Morocco (1). Current research indicates that their formation is linked to large igneous provinces, upwelling, marine hypoxia, and rifting (11,12). The recent discovery by the state-owned Swedish mining company LKAB of a significant REE deposit in the Kiruna iron ore mine in north Sweden has the potential to provide a substantial REE source for Europe. LKAB has reported mineral resources of rare earth metals exceeding one million tonnes of oxides, making it the largest known deposit of its kind in Europe. The rare earths at Kiruna occur together with phosphorous in apatite in an iron ore deposit.

In order to better understand the relationship and mineralization pathways between iron phosphates and REEs we chose to react the mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) with multi component REE-bearing aqueous solutions at hydrothermal conditions. Vivianite is a common Fe(II)-phosphate mineral found globally in marine, freshwater, and

terrestrial systems (13). Its formation in natural deposits is a complex process influenced by redox conditions, sedimentary deposits, porewater interactions, and the presence of key elements such as Fe, P and S. The aim of this study is to investigate whether the interaction of vivianite with rare earth-bearing aqueous solutions would lead to the various processes and/or transformations such as dissolution-recrystallization and oxidation. With REEs present in the aqueous solution, their interaction with vivianite has the potential to result in the formation of rare earth phosphate compounds or solid solutions. These reactions could involve the precipitation of rare earth phosphates or the incorporation of REEs into the crystal structure of vivianite. It is well known that vivianite has the capability to uptake elements from aqueous solution (14). Therefore, the interaction between vivianite and REEs in aqueous solution could potentially lead to the adsorption or complexation of the REEs onto the vivianite surface (3). The formation of such compounds could impact the speciation and mobility of the REEs in the aqueous solution. Further research into the specific mechanisms and outcome of these interactions could provide valuable insights into the behaviour of REEs and iron phosphates in natural aquatic and hydrothermal environments. The replacement of iron phosphates by REE-phosphates like rhabdophane, monazite or xenotime would have important implications for resource recovery, particularly in the context of REE from waste materials. Transforming iron phosphates into stable rare earth phosphates can significantly enhance the recovery of economically valuable REEs from sources such as industrial waste and contaminated soils, supporting their critical role in high-tech and green energy industries.

2. Methods

The interaction of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) grains with multi-component REE (La, Ce, Pr, Nd, Dy) aqueous solutions was investigated at hydrothermal conditions (50-165 °C). Vivianite crystals were crushed in a ceramic mortar and sieved to extract 0.5-1.0 mm clasts. Five single REE bearing solutions were prepared, La, Ce, Pr, Nd and Dy, with a total concentration of 50 mM. These solutions were produced via the dissolution of single REE nitrate salts, $\text{REE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.9% purity), in de-ionized water (18.18 $\text{M}\Omega \cdot \text{cm}$). These five specific REE were chosen as they are representative of both light (La, Ce, Pr, and Nd) and heavy (Dy) REE. This group of REE from La to Dy also represent 72% of the ionic radii of the lanthanides as well as being some of the most abundant REE in the earth's crust (Taylor, 1964)(Taylor, 1964). To better understand the effect of ionic radii of the five REEs and to what extent these ions are taken up by the vivianite host, two different sets of experiments were conducted, one with equal concentrations of the five REEs and one with the concentrations of the five REEs normalized to the commonly used Post Archean Australian Shale standard (PAAS) (16), to mimic the REE concentrations found in continental crust and in natural geological fluids. For the equal concentration experiments, 4 mL of each of the five REEs were used to give a total solution volume of 20 mL for each experiment. For the PAAS experiments, a 1 L bulk solution was made and 20 mL, comprised of 11.8 mM $\text{La}(\text{NO}_3)_3$, 24.3 mM $\text{Ce}(\text{NO}_3)_3$, 2.70 mM $\text{Pr}(\text{NO}_3)_3$, 10.0 mM $\text{Nd}(\text{NO}_3)_3$, and 1.20 mM $\text{Dy}(\text{NO}_3)_3$, of this was used for each experiment.

For each experiment, 0.1 g of vivianite grains were added to 20 mL of each of the 50 mM REE-bearing solutions and placed in 25 mL Teflon-lined and capped stainless-steel autoclaves. The reactors were then placed in a pre-heated oven at 50, 90, and 165 °C.

Solid samples were then extracted using a sterilized metal spatula at increasing time intervals from 4.5 hours to 7 weeks. The samples were then placed in plastic Eppendorf tubes and dried in a 30 °C oven for at least one hour.

In order to identify and quantify the formation of crystalline solids present in our samples, several grains were selected from each experiment ensuring that each time and temperature variable was represented. The selected grains were ground to a consistently fine powder using an agate pestle and mortar. The minerals were identified and quantified with powder X-ray diffraction (XRD). Conventional powder XRD patterns were collected using a Siemens/Bruker D5000 powder X-ray diffractometer (Cu K α radiation, 0.01° step⁻¹ from 5 to 60° 2 θ at 0.2° min⁻¹; 4.5 hours scans per sample, with a detection limit of ~1%). Identification of crystalline phases was carried out with the Diffract Suite EVA software from Bruker in combination with the Powder Data File (PDF-4, the International Centre for Diffraction Data) (Gates-Rector and Blanton, 2019)(Gates-Rector and Blanton, 2019). Pattern-matching refinement and quantification of crystalline phases were carried out with the Rietveld refinement software TOPAS (18). Finally, scanning electron microscopy (SEM) was used to obtain high resolution images to characterize changes in the morphology of the vivianite host grains and identify newly formed phases. Analyses were conducted in the iCrag Lab at Trinity College Dublin using a TIGER S8000 FEG-SEM operating under high vacuum conditions and equipped with two Oxford X-Max 170 mm² EDS detectors and an X4 pulse processor running the Oxford Aztec analysis software version 5.1 and subsequently version 6.1. Analysis at a working distance of 15 mm was performed using an accelerated voltage of 20kV, a 4.5 nm wide beam with a beam current of 300pA, and a process time of five, following the SEM-EDX protocol defined in Ubide et al., 2017 (19). Beam current drift was controlled by analysis of cobalt after each sample change (20) while imaging carried out at a working distance of 5mm was performed

using an accelerating voltage of 10kV. X-ray peak energies for each peak were calibrated to concentrations using a range of mineral and glass standards. The following phases on the Astimex MINM25-53 standard mount for standardization were used: apatite, chromite, diopside, kaersutite, magnetite, olivine, orthoclase, pentlandite, rhodonite, rutile and tugtupite. Standard phases were analysed for 2M counts.

Saturation indexes of solid phases during the equilibration of the REE-bearing aqueous solutions with respect to vivianite were calculated with the hydrogeochemical code PHREEQC (Parkhurst and Appelo, 1999)(Parkhurst and Appelo, 1999) using the LLNL database and the solubility products of REE-bearing phosphates and Fe oxides determined by Essington et al., (Essington and Mattigod, 1985)(Essington and Mattigod, 1985).

3. Results

Analysis of all solid samples obtained from the replacement reactions showed the formation of surface precipitates that either partially or totally replaced the vivianite host grain. The combination of powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) allowed us to identify and quantify the newly formed phases and interpret the mechanisms responsible for the alteration and decomposition of vivianite and the precipitation of the newly formed phases.

3.1. Powder X-ray diffraction (XRD)

The interaction between vivianite and multi-component rare earth element (La, Ce, Pr, Nd and Dy)-bearing aqueous solutions resulted in the formation of iron phosphates, metavivianite ($\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$; PDF 00-030-062) and giniite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{PO}_4)_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$; PDF 00-033-0669), iron oxide, hematite (Fe_2O_3 ; PDF 00-013-0534), and rare earth phosphates, rhabdophane ($\text{REE}(\text{PO}_4) \cdot \text{H}_2\text{O}$; PDF 00-035-0614) and monazite ($\text{LREE}(\text{PO}_4)$; PDF 00-029-0403) (FIGURE 1). Full quantitative data is available in table 1.

The extent of the replacement reaction was found to be time and temperature dependent. At 50 and 90 °C we observed the gradual transformation of vivianite to metavivianite and the subsequent precipitation of rhabdophane (TABLE 1). At 90 °C the formation of giniite was recorded after 28 days. At 165 °C, the vivianite to metavivianite transformation was not observed due to the extremely fast transformation rate, and all of the host vivianite recrystallizing in less than 4 hours.

The observed mineralogy was also found to be temperature-and REE ratio-dependent. At 50 °C, transformation of vivianite to metavivianite proceeded at a faster rate in the equal concentration solutions compared to the PAAS solution. For example, 28 % of the vivianite was consumed after one day in the equal concentration compared to 12 % in the PAAS solution. At the end of the experiment (32 days), 60 % of the vivianite had been consumed in the equal concentration solution compared to 45% in the PAAS solution.

At 90 °C, transformation of vivianite to metavivianite was slower compared to 50 °C, with less than 1 % of vivianite consumed in the first 2 days. However, in contrast to the 50 °C experiments, it was observed that the PAAS solution experiments progressed at a slightly increased rate with 9 % of vivianite consumed after 5 days compared to less than 1 % in the equal concentration solution. There were also minor amounts of rhabdophane

(1-4 %) precipitation in the early stages (1-5 days) of the PAAS solution experiments compared to no rhabdophane detected in the equal concentration experiments after the same time.

At 165 °C, the initial solution concentrations played a less critical role. Similar consumption rates (< 4 hours) of vivianite were recorded in both equal concentration and PAAS solutions. The subsequent transformation of vivianite to metavivianite, giniite and hematite as well as the precipitation of rhabdophane and its transformation to monazite occurred almost in parallel when comparing the equal concentration and PAAS solution experiments.

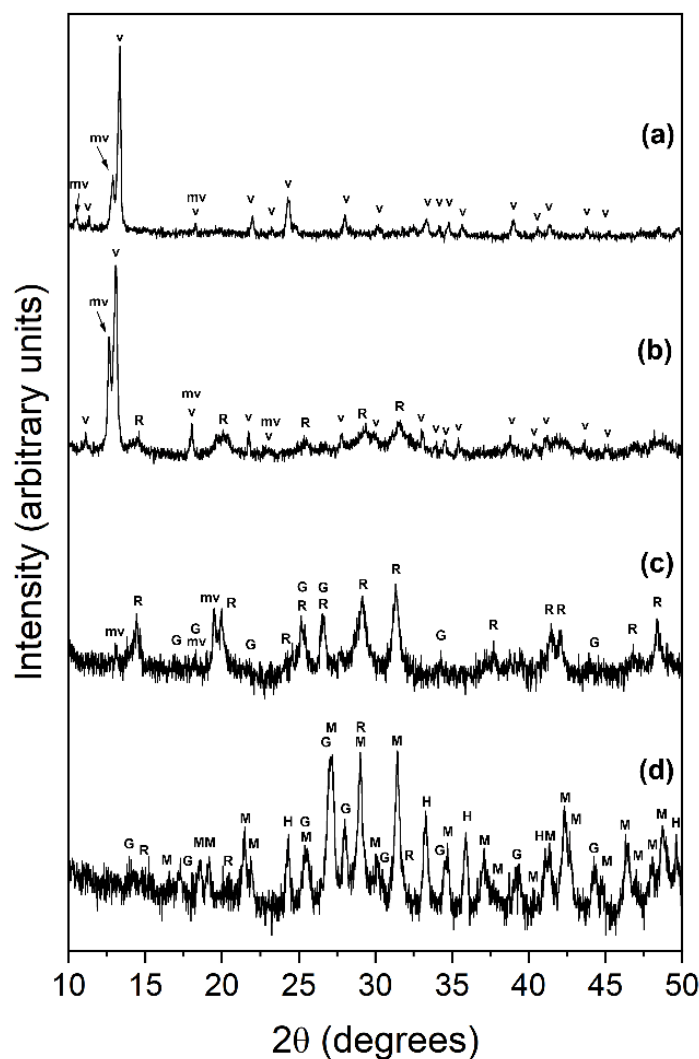


Figure 1: Powder XRD diagrams from samples obtained at (a) 50 °C equal concentration experiments, 24 hours; (b) 50 °C, equal concentration experiments, 32 days; (c) 90 °C, PAAS experiments, 28 days; (d) 165 °C PAAS experiments, 1 week. Bragg peaks have been assigned to the following phases: vivianite (v), metavivianite (mv), rhabdophane (R), giniite (G), monazite (M), hematite (H).

Table 1. Experimental conditions, identities and morphologies of the solid iron phosphates, rare earth phosphates and iron oxides formed during the interaction of vivianite with multi-component (La, Ce, Pr, Nd, and Dy) REE-bearing aqueous solutions (equal concentration and PAAS experiments) at 50, 90, and 165 °C [metavivianite (metaviv.), rhabdophane (rhab.), giniite (gin.), monazite (mon.), hematite (hem.)]

EQUAL CONCENTRATION					PAAS			
T(°C)	Time (days)	% Phase consumed	Phase formed	Morphology	Time (days)	% Phase consumed	Phase formed	Morphology
50	1	28	metavivianite	bladed flaky crystals	1	12	metavivianite	bladed flaky crystals
	3	30	metavivianite		3	21	metavivianite	
	9	16	9% metaviv., 7% rhab	metaviv: bladed flaky crystals Rhab: flakes & needle-like	9	44	32 metaviv., 12 rhab.	metaviv: bladed crystals Rhab: flakes & needle-like
	18	47	13% metaviv., 34% rhab.		18	21	<1% metaviv., 21% rhab.	
	25	57	31% metaviv., 27% rhab.		25	33	<1% metaviv., 33% rhab.	
	32	60	24% metaviv., 36% rhab.		32	45	3% metaviv., 42% rhab.	
90	1	<1%	metavivianite	Bladed flaky crystals	1	1	<1% metaviv., <1% rhab.	metaviv: bladed flaky crystals Rhab: flakes & needle-like
	2	<1%	metavivianite		2	1	<1% metaviv., <1% rhab.	
	5	<1%	metavivianite		5	9	5% metaviv., 4% rhab.	
	28	100	64% rhab., 32% giniite, 4% monz.	Rhab: flakes & Nano spherulites Gin: polygonal prisms, Monz: polygonal composite prisms	28	100	5% metaviv., 57% rhab., 38% giniite	metaviv: bladed flaky crystals Rhab: flakes, needle-like & nano-spherulites
165	0.2	99	94% ginnite, 4% rhab., 2% hema.	Gin: polygonal prisms; Rhab flakes & Nano spherulites Hem: nm polygonal prism aggregates	0.2	100	81% giniite, 16% rhab., 3% hema.	Gin: polygonal prisms; Rhab: flakes & Nano spherulites Hem: nm polygonal prism aggregates
	2	100	85% giniite, 10% rhab., 3% hema., 2% monz	Gin: polygonal prisms flakes & Nano spherulites Hem: nm polygonal prism aggregates Monz: polygonal composite prisms	2	100	74% giniite, 5% rhab., 7% hema., 13% monz	Gin: polygonal prisms flakes & Nano spherulites Hem: nm polygonal prism aggregates Monz: polygonal composite prisms
	7	100	50% giniite, 11% rhab., 19% hema., 20% monz	Gin: polygonal prisms flakes & Nano spherulites Hem: nm polygonal prism aggregates Monz: polygonal composite prisms	7	100	40% giniite, 8% rhab., 19% hema., 33% monz	Gin: polygonal prisms flakes & Nano spherulites Hem: nm polygonal prism aggregates Monz: polygonal composite prisms

3.2. Scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS)

SEM imaging revealed the formation of crystalline phases on the surface of the vivianite grains. These newly formed phases were observed as surface precipitates that partially or fully covered the vivianite host grains. In some experiments, vivianite was fully replaced from the periphery inwards (Figure 2). SEM photomicrographs showed that metavivianite initially formed in the dissolution pits of vivianite and consisted of acicular aggregates with individual needles not exceeding lengths larger than 1 μm and thicknesses of ~ 50 nm. While at 50 $^{\circ}\text{C}$ the crystals looked acicular, at higher temperatures their morphology during the early stages of crystallization consisted mainly of clusters of irregular flakes with random orientation. At 50 $^{\circ}\text{C}$ we also observed the growth of nanometric flakes and acicular crystals of rhabdophane on the surface of metavivianite (Figure 3d,e,f). The rhabdophane crystals were needle-like and sometimes formed a radiating pattern around a central point. However, these showed a less than perfect symmetrical orientation resulting in a slightly irregular, but still overall radiating appearance (Figure 4g,h). Each individual crystal from the radiating structure had a length < 1 μm and a thickness of no more than 100 nm. At 90 $^{\circ}\text{C}$ we observed the growth of giniite crystals along with metavivianite on the surface of vivianite (Fig 4c,d). The giniite crystals consisted of individual equant polygonal prisms with sizes between 600 nm and 2 μm . At 165 $^{\circ}\text{C}$ nanorods of rhabdophane began to cover the surface of giniite (Fig 5a), sometimes forming spherulitic-type structures (Fig 5c). Nanocrystals of hematite were also observed on the surface of rhabdophane. These consisted of nm polygonal prism aggregates with sizes < 200 nm (Fig 5d). Finally, monazite presented as elongated composite prisms with polygonal consisting of acicular or flaky subunits. These subunits were aligned parallel or subparallel to the prism's elongation, giving the overall crystal a textured or layered appearance. The subunits had lengths between 500

nm and 2 μm and created a fibrous or platy surface on the prism's faces, reflecting their acicular or flaky nature (Fig 5e,f).

SEM-EDS maps showed relatively homogenous uptake of the five REEs in the equal concentration solution experiments (Supplementary Info – Image 1). In contrast, in the PAAS solution experiments the uptake of REE reflect their original concentration in the aqueous solution, with higher concentrations of La, Ce, and Nd (Supplementary Info – Image 2).

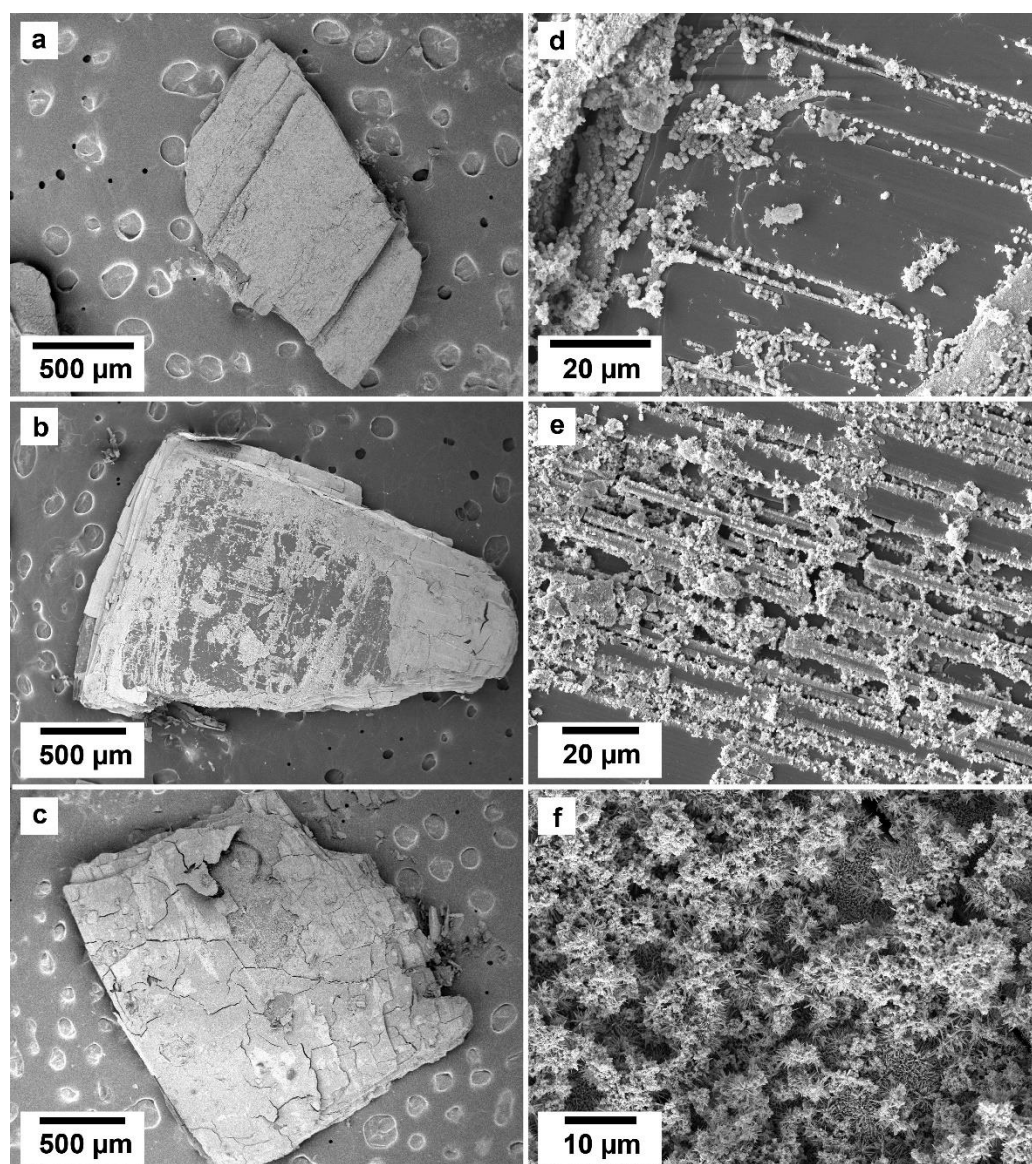


Figure 2: SEM micrographs of the surface of vivianite grains exposed to equal concentration REE-bearing solutions at 50 °C showing (a-c) the surface appearance due to the replacement of the vivianite by newly formed crystals; images (d-f) show details of the micro- and nano-crystalline materials gradually covering the host grain.

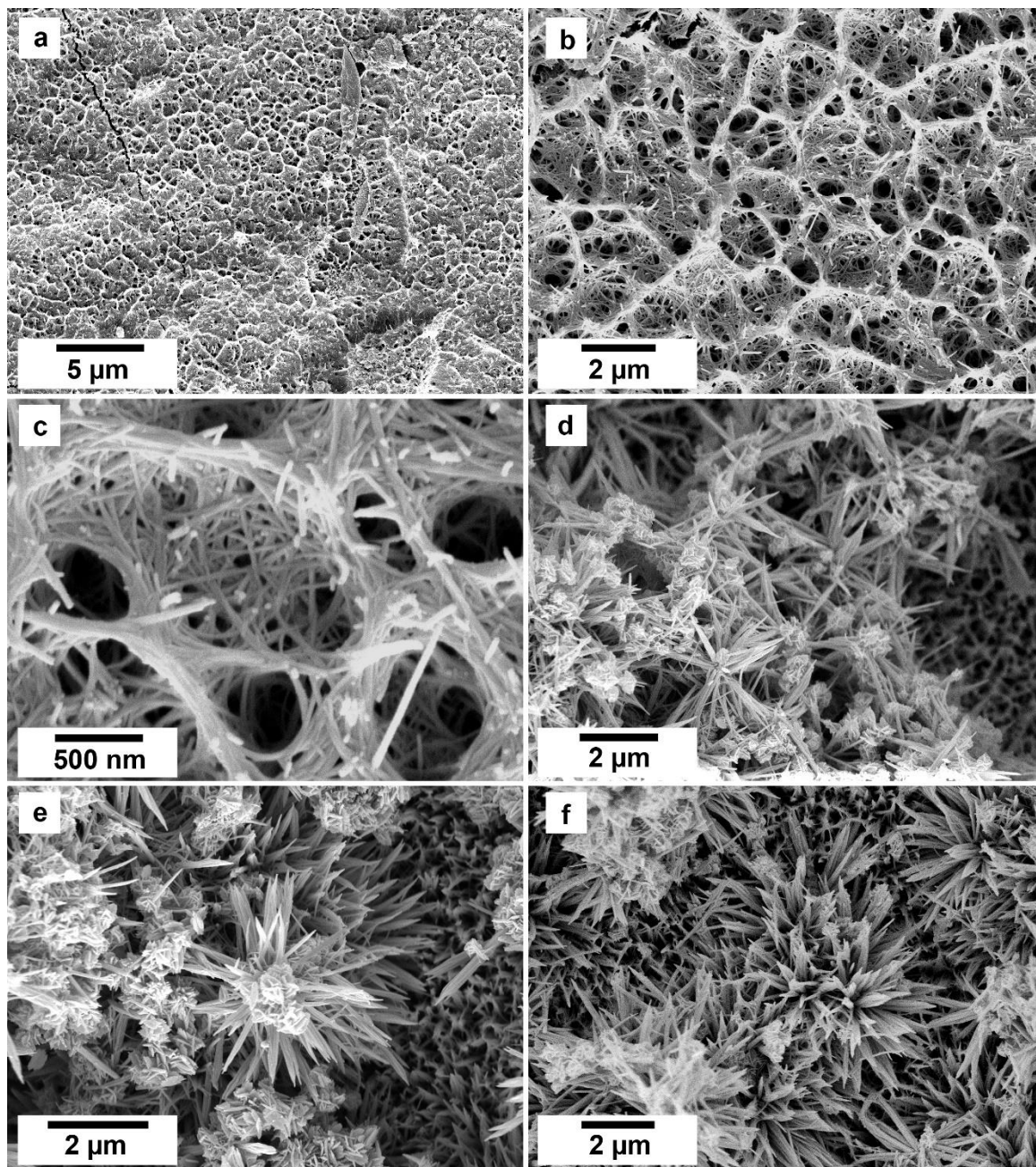


Figure 3: SEM photomicrographs showing the nanophases obtained in the experiments using equal concentration of REEs at 50 °C. (a,b,c) Surface of vivianite covered by metavivianite nanoaggregates; (d,e,f) growth of rhabdophane needle aggregates on the surface of the metavivianite.

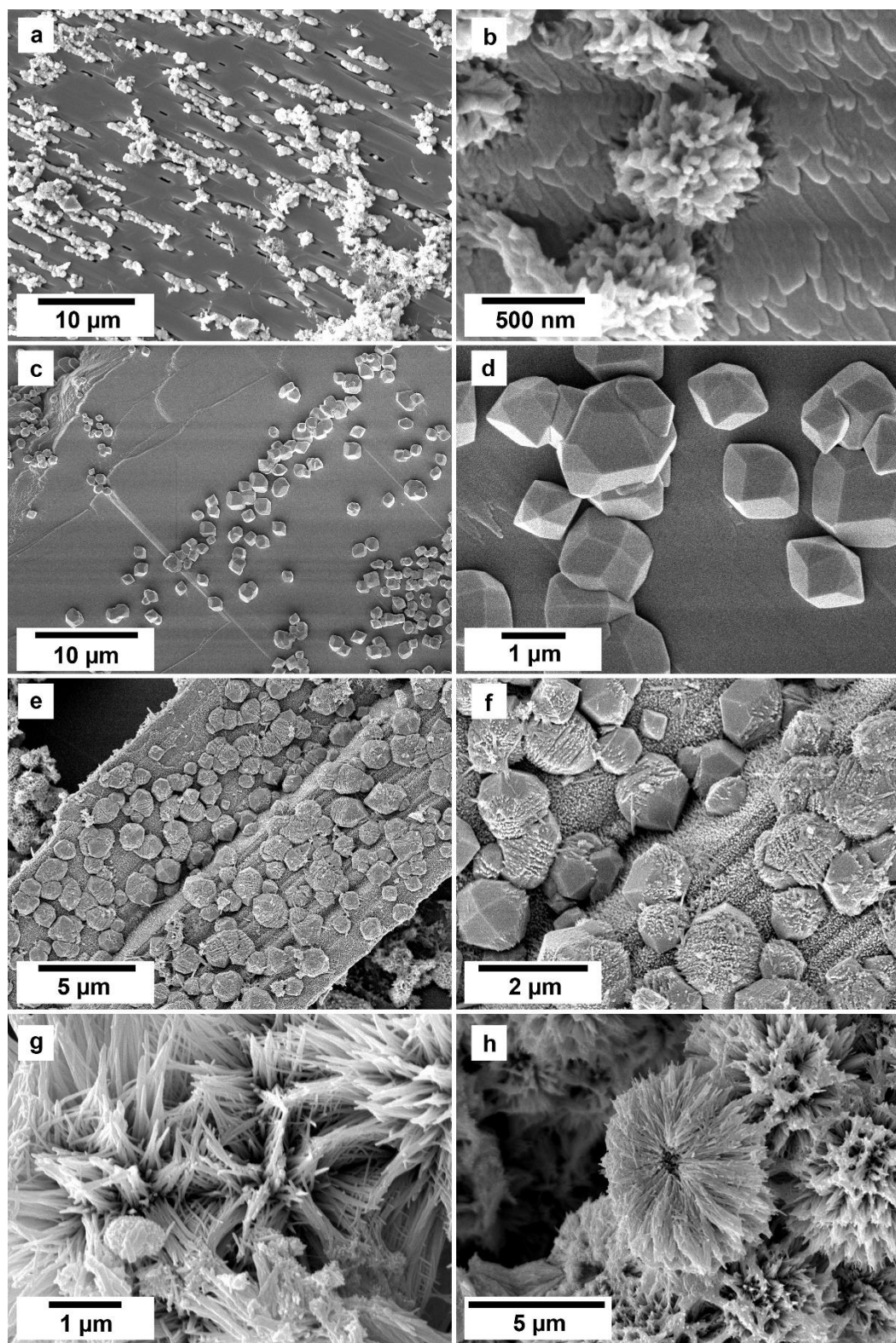


Figure 5: SEM photomicrographs showing the nanocrystals obtained in the experiments at 165 °C in the PAAS solution experiments. (a) Surface of giniite becoming covered by rhabdophane nanorods; (b, c) growth of rhabdophane nanocrystals on the surface of the host, sometimes forming spherulitic-type aggregates (c); (d) nanocrystals of hematite on rhabdophane. (e, f) Monazite and rhabdophane aggregates.

4. Discussion

The dissolution of vivianite and the subsequent formation of iron phosphates metavivianite and giniite, iron oxide hematite and REE-phosphates rhabdophane and monazite were the result of three simultaneous processes: (i) the solution-mediated oxidation of vivianite during its dissolution, coupled with the formation of secondary iron phosphates, (ii) the replacement of the iron phosphates by REE phosphates, and (iii) REE phosphate mineral transformation reactions. In fact, all three processes were mediated by the aqueous solution, with pH, temperature, and the ionic radius of the rare earths present in solution, playing key roles in the extent and rate of the replacement reactions.

4.1. The progressive and concurrent oxidation and dissolution of vivianite

Under oxic conditions, vivianite is unstable, and structural Fe^{2+} oxidizes rapidly to Fe^{3+} . While the vivianite crystal structure seems to maintain stability until an oxidation degree of $\sim 50\%$ (23), the additional positive charge of the Fe^{3+} needs to be balanced by the conversion of a H_2O ligand into an OH^- group and the release of a H^+ . Therefore, upon further oxidation of Fe^{2+} above the 50% threshold, the crystal structure is impacted, leading to significant surface modification, structural distortion, and phase changes (24–26). In our experiments, the progressive oxidation of vivianite resulted in the formation of metavivianite and giniite, where 66% and 80% of the Fe is Fe^{3+} respectively, and hematite (100% Fe^{3+}). Crystallisation of these phases was the result of the solution-mediated coupled oxidation and dissolution of vivianite. This is a complex process that involves the interplay between oxidation reactions and the solubility of vivianite in

aqueous environments and is strongly influenced by the aqueous solution chemistry, pH, and temperature.

The oxidation of vivianite crystals occurs more rapidly in solution compared to exposure to air due to enhanced availability of reactants, favourable environmental conditions, and different kinetic mechanisms that facilitate faster oxidation rates. In aqueous environments, the presence of dissolved oxygen (DO) significantly enhances the oxidation kinetics of Fe^{2+} ions in vivianite. Several studies indicate that the oxidation of Fe^{2+} to Fe^{3+} is also facilitated in solution due to the higher concentration of reactive species, which can lead to faster reaction rates compared to the limited diffusion of oxygen in air (27,28). Additionally, the kinetics of oxidation in solution are governed by different mechanisms than those occurring in air. In air, the oxidation process is primarily limited by the diffusion of oxygen in the mineral structure, which can create a slower reaction environment. In contrast, in solution, the oxidation can occur through direct contact with dissolved oxygen, leading to a more rapid dissolution and transformation of vivianite (29,30). Furthermore, the layered structure of vivianite, which is stabilized by hydrogen bonds, can be disrupted more easily in solution, allowing for easier access of oxidizing agents to the Fe^{2+} sites (30,31). The interaction of vivianite with water creates a dynamic environment where the solubility of oxygen is higher, allowing for more efficient oxidation processes. The aqueous medium also allows for better thermal management, as temperature fluctuations can be more easily controlled, thereby influencing the rate of oxidation reactions (13).

The kinetics of oxidation were found to be temperature-dependent with metavivianite more abundant at 50 °C. At 90 °C, small amounts of metavivianite were recorded, however, after 28 days all metavivianite had transformed to giniite, a phase that was not seen at 50 °C. At the highest temperature of 165 °C, no metavivianite was detected,

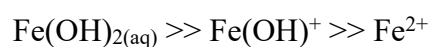
giniite was the main phase with around 20 % transformed to hematite. Increased temperature significantly affects the oxidation of vivianite in aqueous environments by accelerating the reaction kinetics and altering the mineral's stability. As temperature rises, the solubility of gases, including oxygen, decreases, but the diffusion rate of oxygen in water increases, which enhances the oxidation rate. This can lead to enhanced oxidation rates of Fe^{2+} ions present in vivianite. At elevated temperatures (155-185 °C), such as those observed by Wang et al (32)., vivianite will undergo partial transformation into various iron phosphate phases such as strengite and giniite. This auto-oxidation is facilitated by the decomposition of water at higher temperatures (32). The increased thermal energy not only enhances the mobility of ions but also promotes the breaking of chemical bonds within the vivianite structure, thereby accelerating the oxidation process (33). Studies have shown that even moderate increases in temperature can compromise the structural integrity of vivianite leading to significant alterations in the crystal structure, subsequently enhancing its susceptibility to oxidation (13). For example, the presence of bound water in the vivianite crystal plays a crucial role in stabilizing the structure, however, as temperature rises, the hydration layer can be disrupted, making the Fe^{2+} ions more accessible to oxidizing agents (34). In our experiments, vivianite partially dissolved at 50 °C, however at higher temperatures, vivianite was fully replaced by giniite and rhabdophane (90 °C) and giniite, hematite, rhabdophane, and monazite (165 °C). This is in agreement with Metz, et al., 2024 (31) who experimentally demonstrated that the maximum temperature at which vivianite is stable under oxic conditions is between 65 and 75 °C.

The slower transformation kinetics at 50 °C could also be explained by a partial equilibrium situation in which a crust of nano-sized metavivianite covering the vivianite host hinders further oxidation and dissolution (35–37). Similar results were recorded by

Yu et al., 2023(38) in their investigation of the effects of dissolved oxygen (DO) concentrations on As(V) adsorption onto the iron carbonate siderite. They found that excess DO caused fast oxidation of siderite which in turn constrained As(V) adsorption. This was due to the production of a coating of Fe(III) oxides on the surface of the siderite that prevented any further oxidation of the host (38,39).

The oxidation of vivianite in water is also significantly influenced by pH, which affects both the stability of the mineral as well as the kinetics of oxidation reactions through the alteration of iron and phosphate speciation. When vivianite is oxidised, the Fe^{2+} and phosphate ions present in its structure can be released into the aqueous phase, leading to the dissolution of vivianite. The oxidation of Fe^{2+} to Fe^{3+} results in the release of protons (H^+) into the solution, which will initially lower the pH. At low pH, extensive protonation at the vivianite surface results in the weakening of structural Fe-(PO_4) bonds due to polarization of water molecules promoting Fe detachment (40). The Fe can then undergo hydrolysis and lead to the formation of various hydrolysed ferrous species, such as $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})_2^+$. This has been experimentally shown to be dependent on the pH of the solution. Morgan and Lahav (41) described the fundamental equilibrium and thermodynamic principles governing the kinetics of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). They propose a pH dependent range of $\sim 5 < \text{pH} < \sim 8$ and a pH independent range of $\sim 5 > \text{pH} > \sim 8$. In other words, the overall oxidation rate depends on the distribution of these three species in the aqueous phase, which is pH dependent. At pH below ~ 4 , Fe^{2+} concentration dominates, and the rate is independent of pH. At pH above ~ 5 , $[\text{Fe}(\text{OH})_2]$ determines the rate because it is far more readily oxidised than both Fe^{2+} and FeOH^+ . Between pH 5 and 8, the $\text{Fe}(\text{OH})_2$ concentration rises steeply with pH and the overall oxidation rate increases accordingly. Finally, at pH $> \sim 8$ $[\text{Fe}(\text{OH})_2]$ no longer varies with pH and the oxidation is again independent of pH (41). This is in agreement with Luther,

1995 (42) who used molecular orbital theory to show that hydrolysed ferrous iron species are more readily oxidised than non-hydrolysed ferrous species:



However, as the oxidation progresses and ferric iron precipitates, the overall effect can lead to an increase in pH due to the consumption of protons during the formation of insoluble iron oxides (43).

In our experiments, our initial solution pH was ~ 5.1 , laying just above the threshold for pH-dependent oxidation. According to PHREEQC calculations, as our system progressed at 50 °C, the pH would have risen to ~ 6.93 which promoted the hydrolysis of Fe and the subsequent oxidation of Fe(OH)_2 . Also, as mentioned above, vivianite is still quite stable at 50 °C, which is why we did not observe its complete dissolution and replacement by metavivianite and rhabdophane. At 90 °C, the pH would remain relatively stable with respect to 50 °C and is estimated to be just slightly lower at ~ 6.90 . However, here the temperature is now higher than the vivianite stability zone mentioned above of 65-75 °C, and after 28 days all vivianite had oxidized and dissolved. Finally, at 165 °C, the pH would have been ~ 6.50 , therefore still within the pH dependent range for Fe hydrolyses and oxidation, however it is the higher temperature that mainly contributed to the rapid and complete oxidation and dissolution of vivianite. Also, at 165 °C any of the Fe^{3+} that did not combine with REE to form rhabdophane and monazite, precipitated as hematite.

4.2. Replacement of iron phosphates by rare earth element phosphates

The replacement of iron phosphates by rhabdophane, a hydrated rare earth phosphate, can occur through several mechanisms, including dissolution-precipitation reactions.

When iron phosphates, like vivianite, metavivianite and giniite dissolve in the presence of rare earth-bearing solutions, the released phosphate ions can react with dissolved REE ions to form rhabdophane. The presence of REEs has been shown to stabilize the formation of rhabdophane through ionic interactions. The effect of the REE^{3+} ionic radius on the formation and stability of rhabdophane is a significant factor in understanding its crystallization behaviour and thermodynamic properties. One key observation is that the ionic radius of the rare earth ion directly affects the stability of rhabdophane. Larger lanthanide ions, such as La^{3+} - Gd^{3+} , are more favourable for the formation of rhabdophane due to their ability to stabilize the crystal lattice (44). Smaller lanthanide ions (Gd^{3+} - Lu^{3+}) tend to destabilize the rhabdophane structure. The incorporation of smaller ions can lead to an increased lattice strain and reduced stability, making the rhabdophane more susceptible to transformation into other phosphate structures, such as monazite or xenotime (45).

With time, we recorded the replacement of the iron phosphates, metavivianite and giniite, with REE-phosphates rhabdophane and monazite. As the vivianite dissolution progressed, releasing phosphate ions into the solution, it created conditions favourable to REE-phosphate precipitation. Normally these conditions would be governed by the solubility products of the initial vivianite and the subsequent newly formed rhabdophane and monazite. However, the solubility products for vivianite are $\log K_{sp} = -35.76 \pm 0.076$ (46) and range for rhabdophane from $\log K_{sp} = -25.6 \pm 0.8$ (Pr) to -24.9 ± 1.7 (Eu) (47). As rhabdophane is more soluble than vivianite, it should not be forming in these conditions. We, therefore, propose that the crystallization processes happening in our experiments are driven by the oxidation of vivianite and secondary Fe^{2+} -bearing phosphates. Equilibrium with respect to vivianite is never reached as the majority of Fe^{2+} in solution is constantly oxidising to Fe^{3+} . The process is enhanced by the higher

temperatures, which promotes further dissolution of the host, enriching the fluid with PO_4 and more Fe^{2+} , which, again, will oxidise to Fe^{3+} . As the oxidation process is progressive and not instantaneous, some of the Fe^{2+} will incorporate in the metastable phases metavivianite and giniite. As the system progresses, the fluid becomes highly enriched in PO_4 because vivianite is unable to reach equilibrium with the aqueous solution, increasing the supersaturation levels for the REE phosphates. The PO_4 will therefore combine with the REE in solution to form rhabdophane which at some point will transform to monazite as temperatures increased from 90 to 165 °C, contributing to the depletion of phosphate in the aqueous solution and the crystallisation of iron oxides. The observed behaviour is in agreement with Gausse et al., 2016 (48), who noted that the solubility of rhabdophanes is influenced by thermodynamic equilibria, which can shift in favour of rhabdophane precipitation when iron phosphates are dissolved. They demonstrated that in aqueous environments at temperatures below 90 °C, rhabdophane is more stable than the corresponding monazite-type phase.

Supersaturation levels at the host-mineral - solution interface would also contribute to the rapid crystal nucleation of secondary REE-phosphates. The dissolution of only a few monolayers of the surface host is sufficient enough to initiate the formation of a fluid boundary layer near the surface of the host seed, resulting in the development of a surface precipitate (49). The high concentration of PO_4 ions at the fluid boundary layer of the vivianite, metavivianite and giniite compared to the bulk solution promoted the high supersaturation levels required for the spherulitic crystals of rhabdophane that we observed in our 165 °C experiments.

It has also been shown that the presence of iron oxyhydroxides play a role in the adsorption and desorption processes that govern the availability of REE and phosphates

in solution. Belogub et al., 2021(50) discussed how the interaction between iron oxyhydroxides and phosphate ions can influence the formation of rhabdophane, as these interactions can affect the mobility and concentration of REE in the environment. It is the sorption of REE on iron oxyhydroxides that cause early REE scavenging from solutions, with a pH >5 (50). Sorption and desorption of REEs on iron oxyhydroxides depend on particle size and morphology, crystallographic defects, composition, and purity of the sorbent surface (51). Concomitantly, adsorption capacity also strongly depends on the pH and the ionic strength of the solution. The combination of these properties determines whether adsorption takes place via the formation of outer-sphere or inner-sphere complexes (52,53). REE adsorption on iron oxyhydroxides, occurring before rhabdophane formation, can involve both inner-sphere and outer-sphere complexation mechanisms. The specific type of complexation plays a key role in determining the thermodynamic stability and crystal properties of rhabdophane. Inner-sphere complexes are characterized by direct coordination between the rare earth ions and the surface hydroxyl groups of iron oxyhydroxides. This type of complexation typically results in stronger chemical bonds, leading to enhanced stability of the adsorbed species. Studies have shown that the inner-sphere complexes are less sensitive to changes in ionic strength of the aqueous solution, making them more stable under varying environmental conditions (54). For example, Li et al., (55) indicated that inner-sphere adsorption sites are strong and stable, which is crucial for the retention of REEs in solid phases such as rhabdophane. The formation of inner-sphere complexes on iron oxyhydroxides can also contribute to the overall stability of rhabdophane by reducing the mobility of REEs, thereby limiting their release back into solution (56). In contrast, outer-sphere complexes involve weaker electrostatic interactions where REE ions are held at the surface of the iron oxyhydroxides via water molecules without forming strong chemical bonds. This

type of complexation is more sensitive to ionic strength. As ionic strength increases, the stability of the outer-sphere complexes can decrease due to competition with other ions in solution (57). The lower stability of outer-sphere complexes can lead to higher desorption rates and reduced retention of REEs in the environment (54). The presence of both types of complexes in the formation of rhabdophane suggests that the stability of the mineral can be influenced by the conditions in which it forms. For example, at lower pH values ($\sim 4-7$), the competition between REEs and protons can lead to increased outer-sphere complexation, while higher pH levels ($\sim 7-9$) promote inner-sphere complexation due to the availability of hydroxyl groups for coordination (58). For each of our temperature parameters, 50, 90, and 165 °C, the pH of the aqueous solution evolved from an initial value of 5.1 (before vivianite was added to the aqueous solution) to ~ 6.93 , 6.90, and 6.50 respectively. These pH values would allow for the more stable inner-sphere complexation, and this would be consistent with the formation of rhabdophane at all temperatures. Also, the slightly lower value of the pH 6.50 at 165 °C (compared to 6.90 at 90 °C) could also promote for the initiation of rhabdophane transformation to monazite.

4.3. Transformation of rhabdophane to monazite

Rhabdophane, a hydrated rare earth phosphate, can transform to monazite, an anhydrous rare earth phosphate. The transformation of rhabdophane to monazite is influenced by several factors, including temperature, pH and REE speciation, hydration state, and differences in solubility (59). At higher temperatures hydrous rhabdophane will undergo dehydration, and the structural changes will facilitate its conversion to the more thermodynamically stable anhydrous monazite (60). Full dehydration towards anhydrous

rhabdophane takes place between 190 – 240 °C, with the irreversible transformation into monazite in aqueous solution occurring at temperatures above 500 °C (61). The rhabdophane crystal structure presents as hexagonal symmetry and consists of alternating PO₄ tetrahedra and LnO₈ polyhedral linked together in chains along the [100] direction creating large one-dimensional channels, which accommodate the water molecules. Monazite presents as monoclinic symmetry with a crystal structure comprised of PO₄ tetrahedra and LnO₉ polyhedral also linked together in chains along the c-axis, but in a much more compact way (62). The transformation process involves the progressive loss of water from larger channels along the c-axis of the rhabdophane structure, leading to the conversion to monazite (63,64). This loss of water molecules is crucial for stabilizing the monazite structure and can commence within the temperature range of 110 – 400 °C. This leads to the formation of anhydrous hexagonal CePO₄, before transitioning to the monoclinic form of CePO₄, monazite (65). The thermal stability of monazite at high temperatures is well documented, with full transformation from rhabdophane completed at temperatures > 900 °C when heated in air (66). However, it has been reported that the process can be initiated at significantly lower temperatures, particularly in the presence of water (66) and can also occur in samples that have been heat-treated during synthesis (63). While solubility values vary in the literature for monazite at our experimental conditions, all are in agreement that monazite is less soluble than rhabdophane at temperatures of 165 °C (45,67–69) also demonstrate that the solubility of monazite end members, LaPO₄, PrPO₄, NdPO₄, and EuPO₄, decrease sharply with increasing temperatures between 100 – 250 °C.

The transformation kinetics from rhabdophane to monazite can also be influenced by the ionic radius of the rare earth elements involved. Shelyug et al.(45) demonstrated that the transformation temperature decreases with an increase in the ionic radius of the

lanthanides. For example, when heated in air, the temperature required to transform the larger La-bearing rhabdophane to monazite is ~ 750 °C, compared to 900 °C to fully transform the smaller Gd-bearing rhabdophane (45). This is in agreement with (70) who demonstrated that the smaller, heavier REEs tend to form inner-sphere complexes. The formation of inner-sphere complexes typically results in a more stable adsorption site, requiring higher heat for transformation.

In our experiments at 165 °C, we recorded the initiation of the transformation of rhabdophane to monazite. However, as the temperature is well below the reported temperature range of 700-900 °C for complete transformation in air and 500 °C in aqueous solution, we observed only a 20 and 30% transformation in the equal concentration and PAAS solutions respectively. We propose that while the transformation was initiated by the dehydration of rhabdophane, it is the solution chemistry containing mainly larger REE ions (La, Ce, Pr, Nd) that helped to facilitate the transformation at relatively lower temperatures. As stated above, larger, lighter REEs tend to form outer-sphere complexes, and can begin to transform at lower than expected temperatures. SEM-EDS maps showed a relatively homogenous uptake of the REEs in the equal concentration experiments. However, in the PAAS solution experiments there was a preferential uptake of the larger, lighter REE which also correlated to their original concentration in the aqueous solution, with higher concentrations of La, Ce, and Nd. In contrast, point analysis revealed no Dy incorporation into the rhabdophane. This could be the result of its low concentration in the PAAS solution as well as its incompatible smaller ionic radii (Supplementary images, 1 & 2).

5. Conclusion

The interaction of vivianite grains with multi-component REE-aqueous solution resulted in the progressive oxidation and dissolution of vivianite and its transformation to iron phosphates, metavivianite and giniite and iron oxide hematite. The rate of vivianite dissolution increased with increasing temperature, with metavivianite and giniite being replaced by the rare earth phosphate rhabdophane. The pH range of ~ 6.5-6.93 maintained the stability of rhabdophane for all three experimental temperatures (50, 90, and 165 °C). At the highest temperature of 165 °C we observed the partial transformation of rhabdophane to monazite. The transformation initiated below the documented temperature of 500 °C for complete transformation. Therefore, we propose that it is the incorporation of larger REE and their tendency to form more weakly bound outer-sphere complexes. The transformation of iron phosphate, such as vivianite, into more stable and less soluble REE-phosphates has potential applications in REE recovery, particularly in waste materials, contaminated soils, and mine waste waters.

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Supplementary Information

Nanophase REE phosphate crystallisation induced by vivianite oxidation: mechanistic insights and mineralogical implications

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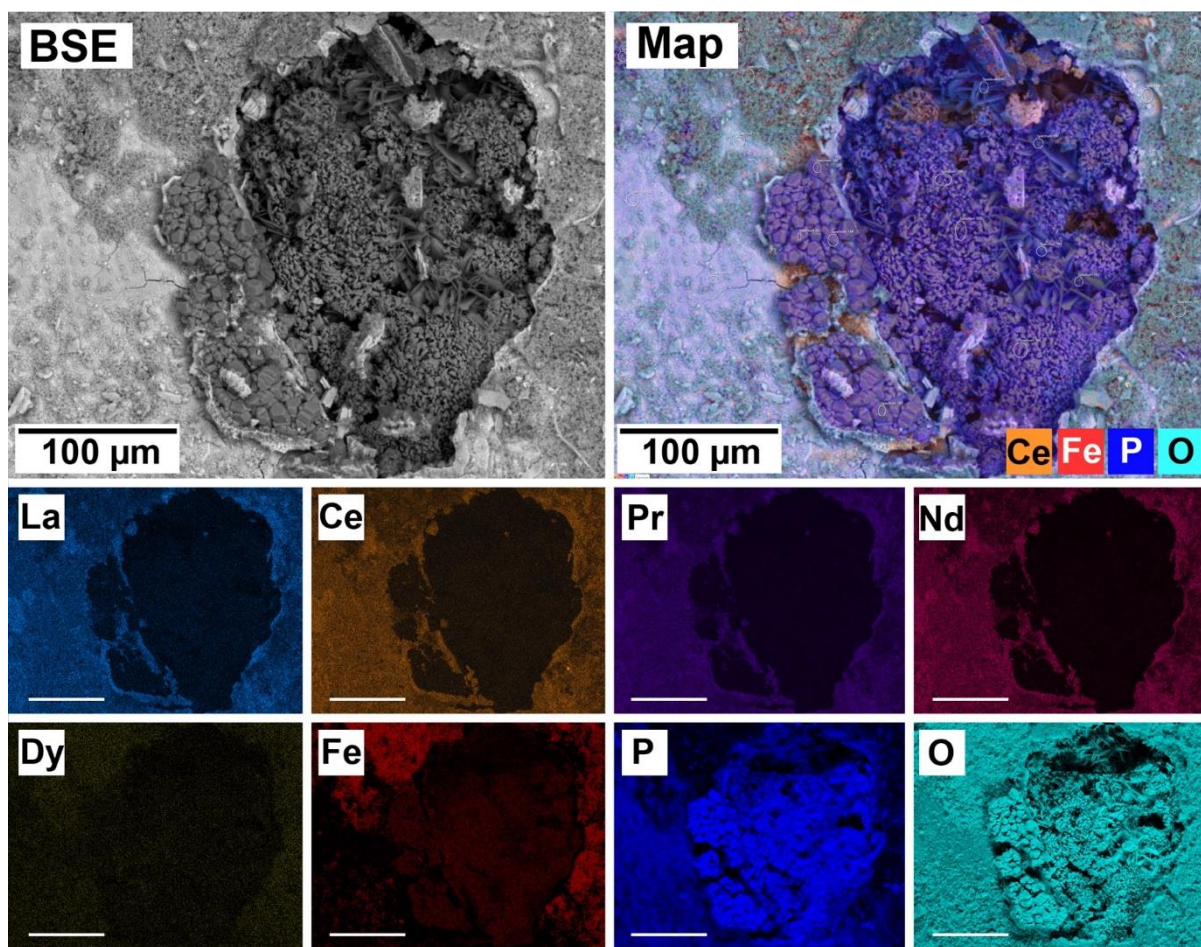


Figure SI-1: SEM-EDS elemental maps of sample obtained after 148 hours in the equal concentrations experiment at 165 °C. Resolution (width): 2048 pixels, resolution (height): 1600 pixels, pixel size: 0.39155 μm , image width: 401 μm , image height: 313 μm , accelerating voltage: 20.0 kV, magnification: 683 x, working distance: 15.0 mm.

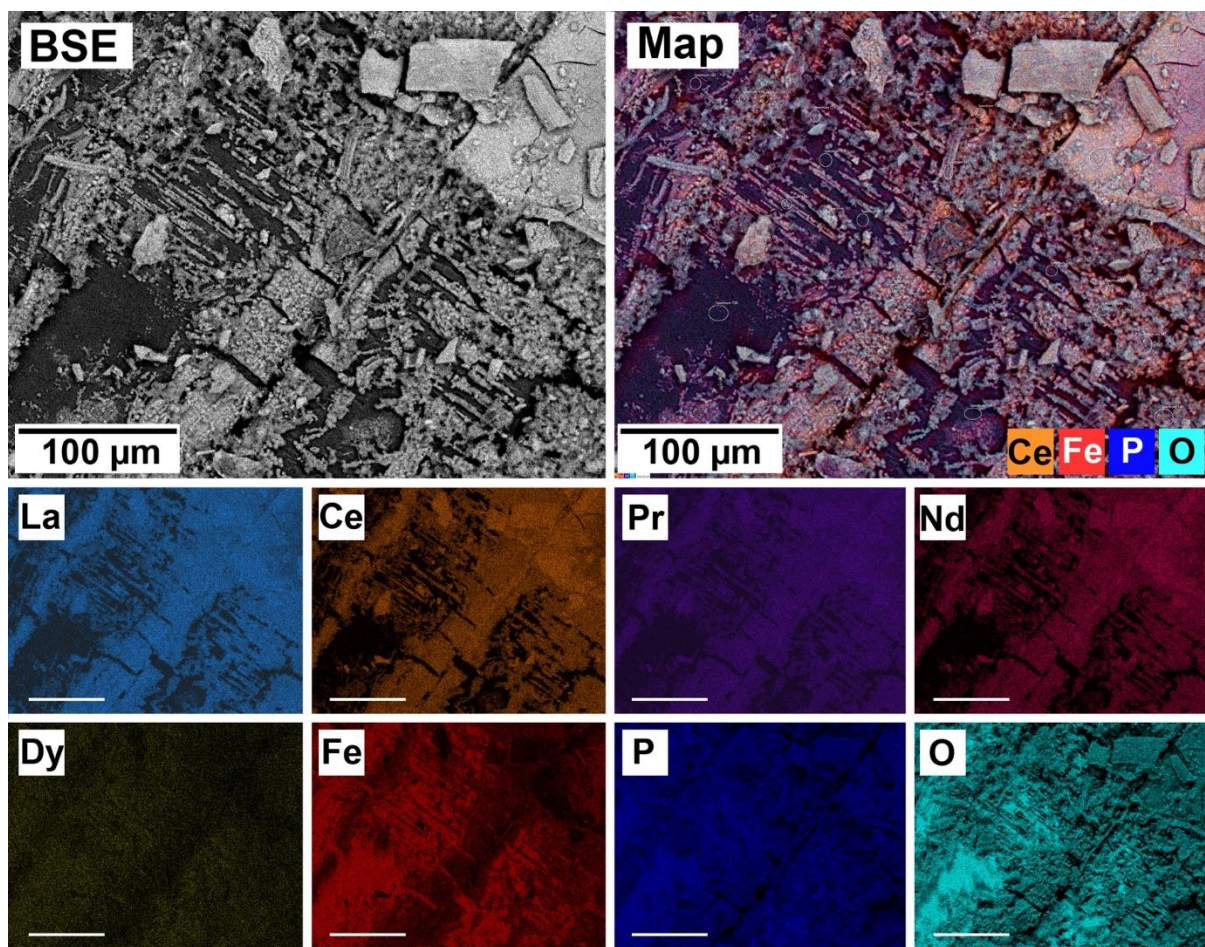


Figure SI-2: SEM-EDS elemental maps of sample obtained after 48 hours in the PAAS experiment at 90 . Resolution (width): 2048 pixels, resolution (height): 1600 pixels, pixel size: 0.39155 µm, image width: 401 µm, image height: 313 µm, accelerating voltage: 20.0 kV, magnification: 683 x, working distance: 15.0 mm.

```

PHREEQC PROGRAM

SOLUTION 1
Temp.          25      adjusted per experiment
pH             11
pe             4
redox          pe
units          mmol/l
density        1
(-) water      1 # kg

REACTION 1          # this is for equal concentration, for PAAS, the "1" was changed to appropriate ratio as follows
La(NO3)3          1          11.8
Ce(NO3)3          1          24.3
Pr(NO3)3          1          2.7
Nd(NO3)3          1          10
Dy(NO3)3          1          1.2

EQUILIBRIUM_PHASES
calcite        0 10      # or aragonite, dolomite, siderite, vivianite

END

```

Figure S1-3. PHREEQC Calculations general program

Chapter 5: Synthesis

The main objective of this PhD thesis was to acquire information on the interaction between multi-component rare earth-bearing aqueous solutions with Ca-Mg-Fe-carbonates and Fe-phosphates under hydrothermal conditions and to better understand the effect of ionic radii. Concomitantly, we aspired to gain insight into the mechanisms and crystallisation pathways that lead to the formation of rare earth carbonates and rare earth phosphates with particular focus on inferences for natural systems containing carbonate and phosphate minerals in the presence of REE-rich fluids.

A summary of our main findings is listed below:

1. The interaction of carbonate minerals and REE-bearing (La, Ce, Pr, Nd and Dy) hydrothermal fluids results in the replacement of the host carbonates by newly formed REE-bearing minerals and follows the crystallisation sequence lanthanite $\rightarrow$ kozoite $\rightarrow$ bastnäsite $\rightarrow$ cerianite. The preferential incorporation of REE into the growing minerals, and their crystallisation pathways and formation kinetics are dependent on REE concentrations and ratio, ionic radii, temperature, time, and host grain solubility.
2. The secondary replacement of rare earth carbonates, kozoite and bastnäsite, by rare earth oxide cerianite is facilitated by higher temperatures and porosity created by differences of their molar volumes. This solution-mediated mineral replacement results in the formation of symplectic textures comprising of vermicular intergrowths of Ce and Nd.
3. The interaction between the Fe-carbonate siderite and REE-bearing (La, Ce, Pr, Nd and Dy) hydrothermal fluids results in the solution-mediated replacement of

siderite that occurs via a multi-step crystallisation pathway involving the formation of iron oxides, goethite and hematite, metastable REE-minerals, kozoite and bastnäsite, and rare earth oxide cerianite. The redox behaviour of Fe and Ce, temperature, and pH are crucial for the sequential formation and stability of the newly formed phases. The oxidation of Fe^{2+} to Fe^{3+} results in the formation of goethite and hematite, while the oxidation of Ce^{3+} to Ce^{4+} results in cerianite formation. At low temperature (50 °C), dissolution is initiated, however the complete covering of the host grain by a thin layer ($< 2 \mu\text{m}$) of goethite promotes a state of partial equilibrium, thereby inhibiting further dissolution/recrystallisation and the formation of REE-carbonates. At higher temperatures (165 °C), the dissolution of siderite is promoted, and differences in solubility allow for the crystallisation of kozoite and bastnäsite.

4. The interaction between Fe-phosphate vivianite and REE-bearing (La, Ce, Pr, Nd and Dy) hydrothermal fluids results in the solution-mediated progressive oxidation and dissolution of vivianite with subsequent formation of iron phosphates metavivianite and giniite, iron oxide hematite, and rare earth phosphates rhabdophane and monazite. Transformation is accelerated with higher temperatures ($>165 \text{ °C}$), with rhabdophane transitioning to the more thermodynamically stable monazite.
5. The chemistry of the REE-bearing minerals is dependent on the REE ratio in the initial aqueous solution, with more homogenous distributions in the equal concentration solutions and more heterogenous distributions with PAAS solution. The use of PAAS solution also results in more pronounced chemical variations in the composition of the overgrowths as well as in localized differences in

individual crystals. There are early indications of possible zoning, with the lighter REE more concentrated in the centre and the heavier REE in the rims of the crystals. Similarly, the replacement coronas surrounding the carbonate hosts display compositional gradients, also with lighter REE in the inner rim and heavier REE in the outer rim.

Future Work

There are several promising avenues for future experimental work. Listed below are some of the key directions that could be explored. These areas have immediate relevance as they align with existing industrial and technological challenges and enable advancements in material sciences and resource utilization.

1. Expansion of REE Systems and Solution Chemistry

- **Inclusion of more rare earth elements:** By extending the experiments to include the full suite of lanthanides (e.g., Sm, Eu, Gd, Tb, etc.) including the HREEs could help clarify trends in crystallisation and substitution behaviour.
- **Complex aqueous solution chemistries:** Simulating more realistic geochemical conditions, such as the addition of ligands (e.g., F^- , Cl^- , SO_4^{2-}) could provide insights into natural processes influencing REE precipitation.

2. Variations in Host Substrate Materials

- **Alternative hosts:** Examine the interaction of REE solutions with multiple Ca-Mg-Fe carbonates simultaneously (or silicates in hydrothermal experiments) to assess their reactivity and replacement patterns. A better understanding of REE partitioning in alternative hosts could help identify new economic deposits or enhance the value of existing ones.
- **Synthetic Substrates:** The use of engineered materials with controlled porosity or crystal orientation could help isolate specific factors influencing nucleation and growth. Insights into reactivity with synthetic substrates could be translated into material engineering for selective REE capture and separation.

3. Mechanistic Insights into Phase Transitions

- **In Situ Monitoring:** As some phase transitions occur rapidly, the employment of real-time techniques such as synchrotron X-ray diffraction (SXRD) or laser Raman spectroscopy (LRS) under hydrothermal conditions would be useful to track transient phase formation and transformation kinetics. Compared to laboratory X-rays, which are produced by colliding electrons on a metal target, SXRD are emitted by bending the path of electrons travelling in circular path. This, combined with their high intensity, high spatial and temporal resolution, allow for rapid data collection on highly detailed structural information (1). LRS is another powerful tool for the study of materials and surfaces under working conditions and can be carried out at temperatures up to 1000 K (2).
- **High-Resolution Imaging:** By utilizing advanced microscopy techniques, such as transmission electron microscopy (TEM) and cryogenic electron microscopy (cryo-EM), nanoscale mechanisms responsible for phase evolution and epitaxial relationships could be investigated. TEM, which is used to characterize materials, can provide detailed information on morphology, structure, chemistry, and nature of bonds. Its ability to form images of atomic arrangements provides a view of the microstructure (3). Cryo-EM, is the technique by which fragile biomolecules are frozen and stabilized to allow for near atomic-resolution imaging in their native states (4). This offers the potential for material characterisation in systems that would normally be considered too sensitive, and for materials that are weakly bonded, as well as reactive materials that historically have shown to degrade under electron irradiation (4).

4. Exploration of Texture and Morphology Control

- **Additives and inhibitors:** The incorporation of organic molecules, surfactants, and inhibitors into solution can profoundly affect the textures and morphologies of crystallising solids. These compounds influence the adsorption processes on metal surfaces, modify surface energies, and alter crystallisation pathways, leading to varied and often desirable outcomes in material properties and performance. For example, the presence of surfactants can modify the surface energy of precipitates, consequently leading to changes in morphology, such as smaller and more uniform particles (5). Surfactants can also stabilize certain morphologies by acting as capping agents and control crystal growth, also through the modification of surface energies (6). It has also been shown that the crystallisation of calcium phosphates can be significantly altered by the presence of citrate ions, which inhibits crystallisation and modifies the size and morphology of the precipitates formed (5). Therefore, through the addition of organic molecules, surfactants, or inhibitors to the solutions, the effects on chemical textures and morphologies could be explored. This would be highly relevant for material synthesis applications. The ability to control morphologies is critical for applications in catalysts, optics, and magnets. Also, by tailoring crystal textures during formation, downstream processes, like milling, separation, or leaching, can be improved.

5. Industrial Applications and Resource Recovery

- **Leaching and extraction studies:** The selective extraction of REEs from experimental products is a critical area of research due to the increasing demand for these materials. The extraction processes typically involve leaching, followed

by solvent extraction. Recent studies have highlighted various methods and materials that enhance the selectivity and efficiency of REE extraction. For example, the use of diglycolamide (DGA) ligands, has been shown to exhibit high selectivity for REEs over other matrix ions (7). Therefore, it would be interesting to test how REEs can be selectively extracted from our experimental products. This could potentially enhance extraction efficiencies from alternative and unconventional REE sources, such as laterites, phosphates, and iron ores.

- **Scaling-Up Processes:** replicate our experiments at larger scale to evaluate their applicability in industrially relevant conditions, particularly for REE recycling and sustainable mining technologies.

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Chemical Textures on Rare Earth Carbonates: An Experimental Approach to Mimic the Formation of Bastnäsité

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The interaction between multi-component rare earth element (REE) aqueous solutions and carbonate grains (dolomite, aragonite, and calcite) are studied at hydrothermal conditions (21–210 °C). The effect of ionic radii of five REEs (La, Ce, Pr, Nd, Dy) on solid formation are analyzed using two solution types: equal REE concentrations and concentrations normalized to Post Archean Australian Shale Standard (PAAS). The interaction replaces the host Ca–Mg carbonate grains with a series of REE minerals (lanthanite → kozoite → bastnäsité → cerianite). At 165 °C, equal concentration solutions promote kozoite crystallization, maintaining similar REE ratios in solids and solution. PAAS solutions result in zoned REE-bearing crystals with heterogeneous elemental distributions and discrete REE phases (e.g., cerianite). Chemical signatures indicate metastable REE-bearing phases transforming into more stable polymorphs, along with symplectite textures formed by adjacent phase reactions. Overall, experiments highlight the dependence of polymorph selection, crystallization pathway, mineral formation kinetics, and chemical texture on REE concentrations, ionic radii, temperature, time, and host grain solubility.

1. Introduction

As rare earth elements (REE) are essential in many green technologies, they play a critical role in a more sustainable future. However, there is a substantial risk to their supply as the availability of REE deposits with minable concentrations are limited. A better understanding of the mechanisms controlling REE concentration in minerals would have applications in more efficient

mining practices as well as REE separation techniques and recycling.

REES are critical materials with their applications spanning a wide range including hybrid vehicles, rechargeable batteries, and wind turbines, as well as medical and military technologies.^[1,2] With increased demand from the green energy market as well as REE applications migrating into common domestic items such as computer parts and television screens, the pressure is building on the current global REE supply chain. Presently, REE processing is dominated by China (≈85%).^[3] However, in recent years, a significant reduction in export quotas from China is leading to supply chain instability.^[4]

REE deposits can be categorized as either primary or secondary deposits. Magmatic, hydrothermal, and/or metamorphic processes are responsible for the formation of primary deposits which are

generally associated with alkaline igneous rocks and carbonates. Some examples of these types of deposits include Mountain Pass, California and China's Bayan Obo, which is the world's largest REE deposit. In secondary deposits, formation occurs as a consequence of weathering and erosion, such as placers, laterites, and bauxites.^[5] For example, the weathering of tin granite in south China has resulted in REE-laterite. Also, the humid, subtropical climatic conditions in northeast India have also promoted the formation of a thick laterite profile offering a promising alternative for this type of REE deposit.^[6] Presently, the world reserves of REE amount to ≈130 million tonnes and are under the control of China, Brazil, Vietnam, Russia, and India.^[7] However, China holds one-third of the world's REE reserves and dominates in REE exploration and production. Bastnäsité, monazite, and xenotime are currently the principal economic resources of REE minerals and can be sourced from these geological deposits.^[8]

In our study, we focussed on bastnäsité as it is one of the major sources of REE found in commercial deposits such as Bayan Obo, China.^[9] Three natural carbonate-fluoride minerals comprise the bastnäsité family each with varying amounts of REE. These include (Ce)-bastnäsité; (Ce,La)[CO₃]F, which is the most abundant, (La)-bastnäsité; (La,Ce)[CeO₃]F, and (Y)-bastnäsité; (Y,Ce)[CO₃]F. Synthetic bastnäsites are gaining increased

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attention as they can be used as precursors for rare earth oxy-carbonate ($\text{RE}_2\text{O}_2\text{CO}_3$) and oxyfluorides (REOF) synthesis, both of which can be utilized as host lattices for phosphors. (Ce)-bastnäsite together with the phosphate mineral (Ce)-monazite ($\text{Ce,La,Nd,Th}[\text{PO}_4]$), make up our major source of Ce as well as additional REE such as La, Nd, and Y.^[10]

When studying natural ore deposits, researchers will generally only characterize the final mineralogical assemblage. However, the aim of this study is to better understand the reaction pathways and crystallization sequence that leads to some rare earth carbonates. A better understanding of the mechanisms controlling the REE concentration in minerals would have applications in more efficient practices as well as separation techniques and recycling. Therefore, we have mimicked natural systems by carrying out replacement experiments using multi-component REE aqueous solutions and carbonate host grains of dolomite, aragonite and calcite, which are commonly found in carbonatite ore deposits. All of the products obtained in our experiments were characterized with high resolution electron microscopy and powder X-ray diffraction, allowing us to show that temperature as well as aqueous chemistry are key in controlling the mineralogy and distribution of REE in carbonate rocks.

2. Results

The analysis of all solid samples obtained from the replacement experiments resulted in the formation of a series of surface precipitates that partially or totally replaced the host carbonate grain. The combination of powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) allowed us to identify and quantify the newly formed phases and interpret the mechanisms responsible for some of the chemical textures exposed in the polished resin pucks.

2.1. Powder X-ray Diffraction

The interaction of calcite, dolomite and aragonite with multi-component rare earth element (La, Ce, Pr, Nd, and Dy) -bearing aqueous solutions resulted in the formation of secondary REE-bearing minerals. The characterization with powder X-ray diffraction (XRD) revealed the formation of a series of rare-earth bearing carbonate minerals: lanthanite ($\text{REE}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$), kozoite ($\text{REE}(\text{CO}_3)(\text{OH})$), hydroxylbastnäsite ($(\text{REE}(\text{CO}_3)(\text{OH},\text{F}))$) (Figure 1) and a REE oxide, cerianite (CeO_2). These newly formed phases presented as surface precipitates that partially replaced the host mineral. In some experiments, the host carbonate minerals were fully replaced. The extent of the replacement reaction was found to be temperature and time dependent (Figure 2). At certain temperatures, the formation of specific crystalline polymorphs was hindered during reaction. Lanthanite was found to be present and stable at low temperature only (21 °C), with minor amounts found in the aragonite experiments at 50 °C. Kozoite precipitated and remained stable at 50 and 80 °C. At 165 and 205 °C, kozoite also formed but it quickly transformed to hydroxylbastnäsite and cerianite. At 205 °C, hydroxylbastnäsite and cerianite precipitated after short reaction times (i.e., within 24 h). In

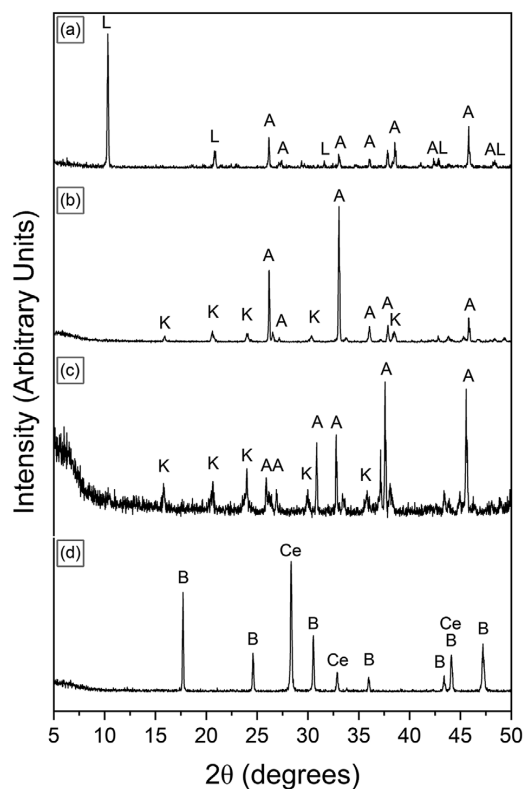


Figure 1. (Powder XRD patterns of lanthanite (L), kozoite (K), hydroxylbastnäsite (B) and cerianite (Ce) obtained from experiments reacting a) aragonite at 21 °C (non-PAAS), b) 80 °C (non-PAAS), c) 80 °C (PAAS) and d) dolomite at 165 °C (PAAS).

some cases, the host mineral (e.g., calcite) was fully consumed by cerianite and/or hydroxylbastnäsite. Cerianite was the end product of the higher temperature experiments, replacing the host and the REE carbonates. The formation of the REE carbonates in the reaction sequence was also found to relate to the nature of the host mineral (e.g., at 165 °C, hydroxylbastnäsite and cerianite precipitated faster in the aragonite experiments compared to the dolomite and calcite experiments). The REE concentration in the initial solution also played a key role, an example being the 21 °C experiments with lanthanite precipitating in the Post Archean Australian Shale (PAAS) solution experiments for all three host grains, however, in the non-PAAS experiments, lanthanite only formed on the surface of aragonite, with no additional phases being detected by XRD on the surface of calcite or dolomite. There was a small amount of lanthanite precipitated in the aragonite experiments at 50 °C in the PAAS solution, compared to only kozoite in the dolomite and calcite experiments. At 80 °C, kozoite was the sole main stable phase in both the non-PAAS and PAAS experiments. At 165 and 210 °C, kozoite quickly transformed to hydroxylbastnäsite and cerianite, with only slightly prolonged stability in the non-PAAS solutions with dolomite and calcite grains.

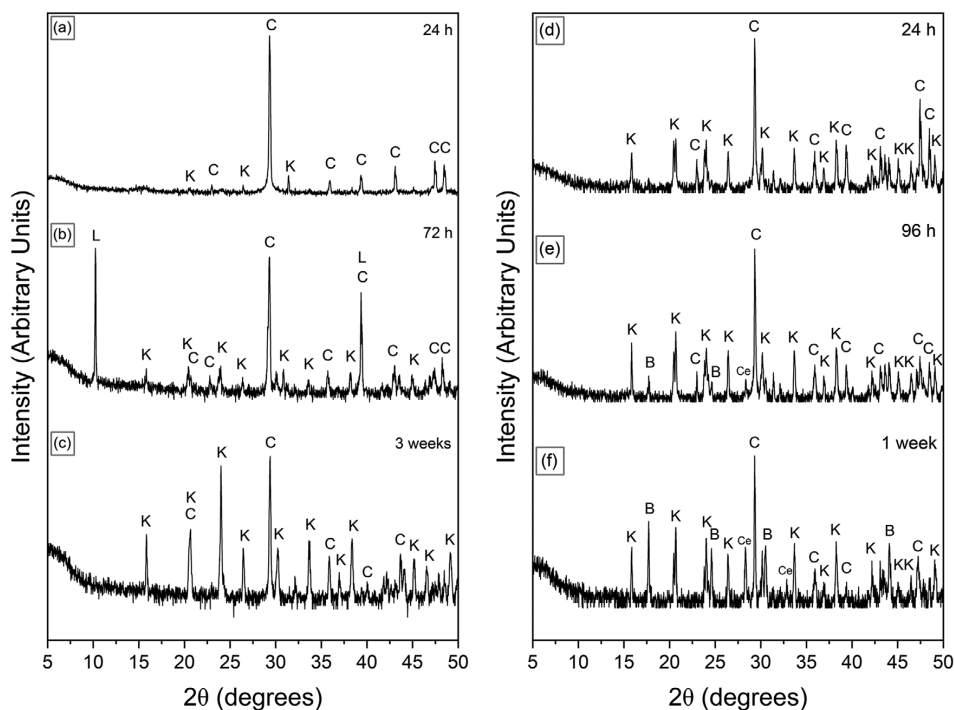


Figure 2. Powder XRD patterns of calcite in PAAS solution at 80 °C a) 24 h, b) 72 h, c) 3 weeks, and 165 °C, d) 24 h, e) 96 h, f) 1 week, *calcite (C), kozoite (K), bastnäsite (B)]. The extent of the replacement reaction was found to be time and temperature dependent, with 40% of calcite consumed after 3 weeks at 80 °C (c), and 37% of calcite consumed after just one week (f) at 165 °C.

Also, at 165 and 210 °C, the amount of cerianite that formed in the non-PAAS solution ranged from <1% to 5%, while in the PAAS solutions, Ce was the most highly concentrated element and resulted in cerianite replacing the host by 17–46%.

2.1.1. Scanning Electron Microscopy–Energy Dispersive Spectroscopy (SEM–EDS)

SEM imaging revealed the formation of precipitates on the surface of the calcite, dolomite and aragonite grains. The extent to which these newly formed precipitates covered and replaced the host carbonate grain was found to be time and temperature dependent. The type of carbonate host as well as the REE concentration in solution also played a key role in the rate of replacement. For example, at ambient temperature, and in the equal concentration solutions, only the aragonite grains were seen to be fully covered by large (50–100 μm) platy lanthanite crystals, while the dolomite and calcite grains experienced only minor replacement (<1%) and few visible small (<10 μm) elongate lanthanite crystals (Tables 1–3). Comparatively, in the PAAS solution, both aragonite and calcite were both fully encased in a crust of lanthanite, while the dolomite still showed some surface area without any replacement, albeit with dissolution textures. At 50 and 80 °C, all three hosts were completely encapsulated by the REE carbon-

ate kozoite (Figure 3). Morphologies of the newly formed crystals consisted of small, elongate prisms of ≈10 μm were found on all three hosts along with spherulitic aggregates in the aragonite experiments in both the equal concentration solution (after 8 weeks) and the PAAS solution (after 24 h). In the higher temperature experiments (165–210 °C) crystal morphologies consisted of triangular prisms of hydroxy-bastnäsite along with small octahedron of cerianite (Figure 4).

The polished epoxy resin pucks were subjected to energy dispersive spectroscopy (EDS). By mapping the cross section of the grains, differences in the spatial distribution of the REEs as they replaced the carbonate host grains were recorded. The replacement trends were found to be dependent on the initial concentration of REE in solution, with a more homogenous distribution in the equal concentration solution (Figure 5), and a more heterogeneous distribution in the PAAS solution (Figure 6). The SEM-EDS analyses of the REE within the overgrowth revealed intriguing differences between the PAAS and non-PAAS samples, showing variations in the composition of both the complete overgrowth and localized differences in individual crystals. Although this trend is consistent across all experiments, both SEM-EDS and SEM-BSE analyses showed more pronounced chemical variations in the PAAS samples compared to the non-PAAS samples. In all instances, these compositional variations indicate two main trends: the first involves potential zoning, with lighter elements

Table 1. Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of dolomite with multi-component (La, Ce, Pr, Nd, and Dy), REE-bearing aqueous solutions (non-PAAS, and PAAS). *kozoite (koz), hydroxylbastnäsite (HB), cerianite (Cer).

DOLOMITE							
NON-PAAS					PAAS		
T [°C]	Time [days]	% Phase consumed	Phase formed	Morphology	% Phase consumed	Phase formed	Morphology
21	14	0			6	Lanthanite	Thin platy crystals
	28	0			1		
	42	0			3		
	56	0			1		
	84	0			4		
50	1	0			0		
	3	<1	Kozoite		3	Kozoite	small prisms, elongated prisms
	7	6		small prisms, elongated prisms	5		
	21	7			19		
	28	14			11		
80	42	25			20		
	56	19			44		
	1	0			3	Kozoite	small prisms, elongated prisms
	3	7	Kozoite	small prisms, elongated prisms	9		
	7	14			24		
165	21	17			24		
	28	19			15		
	42	48			20		
	56	18			36		
	1	23	Kozoite	Koz: small prisms, elongated prisms	22	12% Koz, 8% HB, 2% Cer	Koz: small prisms, elongated prisms
210	2	16	Kozoite		17	6% Koz, 7% HB, 2% Cer	
	3	18	17% Koz, <1% Cer	Cer: small	40	5% Koz, 29% HB, 6% Cer	Cer: small
	4	28	27% Koz, <1% Cer	octahedron HB: triangular prisms	31	2% Koz, 25% HB, 4% Cer	octahedron HB: triangular prisms
	7	22	21% Koz, <1% Cer		100	73% HB, 27% Cer	
	14	23	19% Koz, 3% HB, <1% Cer		100	43% HB, 57% Cer	
210	1	24	14% Koz, 5% HB, 5% Cer	Koz: small prisms, elongated prisms	42	25% HB, 17% Cer	Koz: small prisms, elongated prisms
	2	27	16% Koz, 10% HB, <1% Cer		38	21% HB, 17% Cer	
	3	37	13% Koz, 22% HB, 2% Cer	Cer: small	42	24% HB, 18% Cer	Cer: small
	7	34	33% HB, 1% Cer	octahedron HB: triangular prisms	41	25% HB, 16% Cer	octahedron HB: triangular prisms

concentrated in the centre and heavier elements in the rims of the crystal (Figures 7 and 8; Figure S2, Supporting Information), similar to the observations of Miyawaki et al.^[11] Similarly, the second trend comprises a general compositional gradation in the replacement corona surrounding the Ca–Mg carbonate host, also featuring lighter REE elements in the inner rim and heavier elements in the outer rim (Figure 9; Figure S3, Supporting Information). Despite the occurrences of these chemical variations, there are limitations in our quantitative determinations which arise from the small size of individual kozoite/bastnäsite crystals (<20 µm) within the replacement corona, impeding detailed scrutiny, coupled with the subtle nature of compositional REE variations. These factors constrain the ability to carry out a precise quantification of these compositional variations.

Another feature observed in the cross-section EDS maps was symplectic textures, particularly in the PAAS samples subjected

to the highest temperature of 210 °C. In the aragonite grains, we can see La, Pr-rich areas surrounded by vermicular intergrowths of Nd and Ce, radiating outwards (Figure 10), further supporting the idea that the heterogenous distribution of REEs is dependent on the REE initial concentration in solution. In addition to the symplectic textures, we also observed areas with a significant accumulation of cerianite, seemingly having fully replaced the rare earth carbonate minerals, with Dy being associated with Ce. (Figures 10 and 11).

3. Discussion

The interaction of the Ca–Mg carbonates with the REE-bearing solutions resulted in the initial dissolution of the host grain, releasing Ca^{2+} and CO_3^{2-} (and Mg^{2+} from dolomite) into the aqueous solution. This dissolution of the host Ca(-Mg) carbonates

Table 2. Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of aragonite with multi-component (La, Ce, Pr, Nd, and Dy), REE-bearing aqueous solutions (non-PAAS, and PAAS). * lanthanite (lan), kozoite (Koz), hydroxylbastnäsäsite (HB), cerianite (Cer).

ARAGONITE							
NON-PAAS					PAAS		
T [°C]	Time [days]	% Phase consumed	Phase formed	Morphology	% Phase consumed	Phase formed	Morphology
21	14	0			13	Lanthanite	Thin platy crystals
	28	7	Lanthanite	Thin platy crystals	11		
	42	11			22		
	56	8			15		
	84	18			13		
50	3	12	Kozoite	small prisms, elongated prisms	4	3%Koz, 1% Lan	Lan: Thin platy crystals
	7	8			12	Koz	Koz: Small prisms, Elongated prisms
	21	68			11	Koz	
	28				14	Koz	
	42	100			27	25% Koz, 2% Lan	
80	56	16			50	48% Koz, 2% Lan	
	1	11	Kozoite	small prisms, elongated prisms	16	Koz	Koz: small prisms, elongated prisms HB: Triangular prisms
	3	6			9		
	7	9			21		
	21	25			28	23% Koz, 5% HB	
165	28	57			23	Koz	
	42	37			42		
	56	50			54		
	1	13	Koz	Koz: small prisms, elongated prisms Cer: small octahedron HB: triangular prisms	17	14% Koz, 2% HB, 1% Cer	Koz: small prisms, elongated prisms Cer: small octahedron HB: triangular prisms
	2	15	13% Koz, <1% Cer, <1% HB		19	13% Koz, 4% HB, 2% Cer	
210	3	18	17% Koz, <1% Cer		29	11% Koz, 15% HB, 3% Cer	
	4	25	24% Koz, 1% Cer		34	12% Koz, 19% HB, 3% Cer	
	7	39	37% Koz, 2% Cer		60	2% Koz, 45% HB, 13% Cer	
	14	25	23% Koz, <1% Cer, <1% HB				
	1	9	7% Koz, 1% Cer		43	3% Koz, 23% HB, 17% Cer	
	2	11	6% Koz, 4% HB, 1% Cer		45	29% Hb, 16% Cer	
	3	31	12% Koz, 16% HB, 3% Cer		48	30% HB, 18% Cer	
	7	38	8% Koz, 28% HB, 2% Cer		64	49% HB, 15% Cer	

rapidly increased the supersaturation of the solution, especially at the carbonate surface/solution interface, triggering the surface precipitation of REE-bearing carbonates, with some grains being fully replaced from the periphery inwards. Also, at the highest temperatures (210 °C), a secondary replacement occurred, with the REE-carbonate minerals being partially or totally replaced by cerianite. The reaction sequence (lanthanite → kozoite → hydroxylbastnäsäsite → cerianite) was time- and temperature-dependent, with some of the intermediate, metastable phases not forming at higher temperatures (≥ 165 °C) (Figure 12). The rate of crystallization and composition of the main REE-bearing phases as well as the observed textures (Figures 5–11) were controlled by the solubilities and dissolution rates of the host grains and the REE ratio in solution, combined with the evolving fluid composition during the gradual replacement process. The influence of temperature is also a key factor, as it affects the dehydration of specific REE³⁺

before being incorporated into the growing crystals as well as the oxidation of Ce³⁺ to Ce⁴⁺ in solution.

3.1. Solubility, Dissolution Rate and Chemical Textures

In all of our experiments we observed a centripetal replacement of the host mineral, as they were replaced from the periphery inwards by the newly formed REE carbonates. This is a consequence of the lower solubilities of REE carbonates compared to the host minerals at the specific pressure-temperature conditions studied.^[12–14] For example, the solubility products for pure Nd-hydroxylbastnäsäsite, La-hydroxylbastnäsäsite, and Nd-Kozoite have been calculated to be $\log(K_{sp}) = -23.8 \pm 0.1$, $\log(K_{sp}) = -24.1 \pm 0.3$, and $\log(K_{sp}) = -22.3 \pm 0.2$, respectively,^[13] while the solubility products of calcite, $\log(K_{sp}) = -8.480 \pm 0.020$,

Table 3. Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of calcite with multi-component (La, Ce, Pr, ND, and Dy), REE-bearing aqueous solutions (non-PAAS, and PAAS). *lanthanite (Lan), kozoite (Koz), hydroxylbast-näsite (HB), cerianite (Cer).

CALCITE							
NON-PAAS					PAAS		
T [°C]	Time [days]	% Phase consumed	Phase formed	Morphology	% Phase consumed	Phase formed	Morphology
21	14	0			6	Lan	Thin platy crystals
	28	0			0		
	42	0			0		
	56	0			0		
	84	0			10		
50	1	0			0		
	3	0			0		
	7	3	Kozoite	small prisms, elongated prisms	1	Kozoite	small prisms, elongated prisms
	21	7			7		
	28	7			11		
80	42	12			37		
	56	14			29		
	1	0			<1	Koz	small prisms, elongated prisms
	3	7	Kozoite	small prisms, elongated prisms	11	6% Koz, 5% Lan	
	7	10					
165	21	36			40	Koz	
	28	67					
	42	76			17	Koz	
	56	53			41	Koz	
	1	41	Koz	Koz: small prisms, elongated prisms Cer: small octahedra HB: triangular prisms	28	25% Koz, 2% HB, <1% Cer	Koz: small prisms, elongated prisms Cer: small octahedra HB: triangular prisms
210	2	25	Koz		32	30% Koz, <1% HB, <1% Cer	
	3	49	Koz		35	31% Koz, 3% HB, 1% Cer	
	4	54	52% Koz, <1% Cer, <1% HB		29	25% Koz, 3% HB, 1% Cer	
	7	38	35% Koz, 1% Cer, 2% HB		37	19% Koz, 13% HB, 5% Cer	
	14	38	35% Koz, <1% Cer, 2% HB				
210	1	20	16% Koz, 4% Cer	Koz: small prisms, elongated prisms Cer: small octahedra HB: triangular prisms	72	37% HB, 35% Cer	Koz: small, elongated prisms Cer: small octahedra HB: triangular prisms
	2	13	11% Koz, 1% HB, <1% Cer		100	54% HB, 46% Cer	
	3	17	14% Koz, 3% HB		95	58% HB, 37% Cer	
	7	100	Cerianite		80	47% HB, 33% Cer	

aragonite, $\log(K_{sp}) = -8.336 \pm 0.020$ ^[15] and dolomite, $\log(K_{sp}) = -18.14$ ^[16] are much higher. Determining the solubility of solid phases with intermediate compositions is not feasible due to the absence of relevant data. Existing literature suggests that lighter REE carbonates are more soluble than their heavier counterparts.^[12] However, conflicting trends and discrepancies have been reported by other researchers,^[13,14] highlighting the complexity of this system, with some reported variations potentially arising from the occurrence of different crystalline (nano)phases during synthesis, each possessing different solubility products and different kinetics of crystallization.^[17,18] Also, measuring the solubility products at elevated temperatures is challenging because of insufficient availability of reliable data pertaining to the stability of diverse aqueous complexes formed by REEs with carbonate and hydroxyl ions.^[13]

While these large differences in solubility influence the polymorph selection and its chemistry, it is the dissolution rate of the host mineral that determines the rate at which the new phase can precipitate. For example, the dissolution rates of calcite, aragonite and dolomite at 25 °C have been calculated to be $\log R_{cal} = -8.8 \text{ mol}^{-2} \text{ s}^{-1}$, $R_{arg} = -9.2 \text{ mol}^{-2} \text{ s}^{-1}$ and $\log R_{dol} = -10.1 \text{ mol}^{-2} \text{ s}^{-1}$ ^[19] meaning that, e.g., aragonite will dissolve almost an order of magnitude faster than dolomite at the initial pH of 5.1. This is particularly evident in our ambient and 50 °C experiments, with replacement of aragonite commencing after 3 days compared to the replacement of calcite and dolomite initiating after 7 and 21 days respectively. The higher dissolution rates of aragonite and calcite mean that carbonate ions are released faster into the aqueous solution compared to the dolomite experiments, resulting in higher supersaturation levels needed to

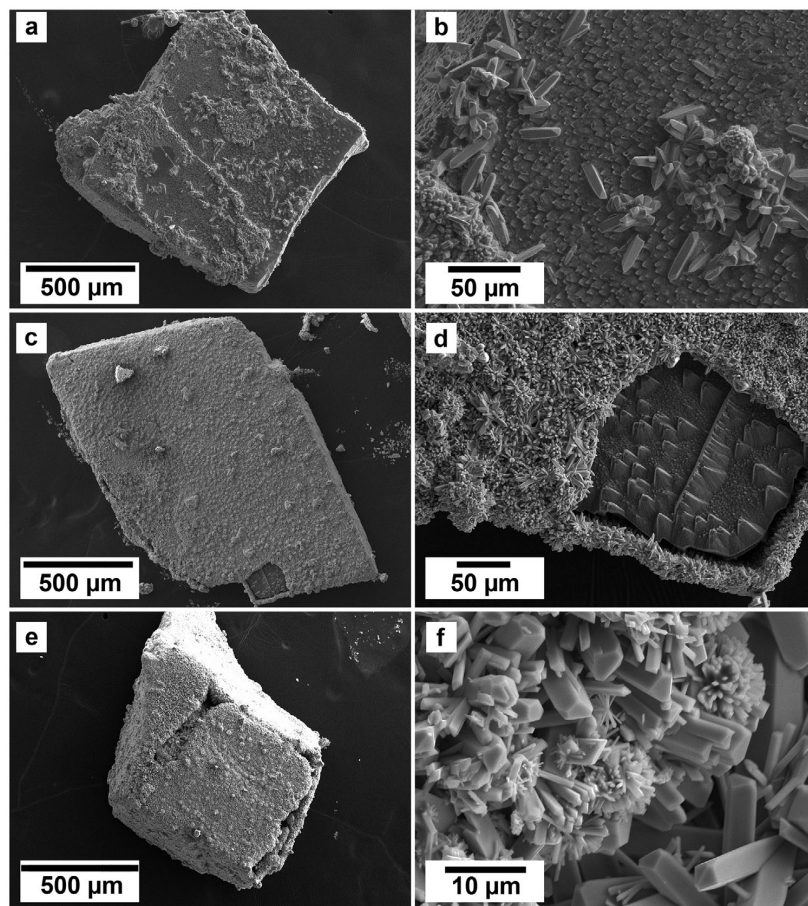


Figure 3. Secondary electron SEM images of the surface of calcite grains reacted with the PAAS solution at 80 °C showing the progressive replacement by REE carbonates (left: grain view, right: detailed view), after a,b) 24, c,d) 72 h, and e,f) 4 weeks.

initiate the nucleation of the REE carbonates. Using calcite as an example, PHREEQC calculations show that even when the saturation index for calcite is -5 , the concentration of Ca^{2+} and CO_3^{2-} released into the aqueous solution is high enough to allow the supersaturation with respect to REE carbonate minerals. Therefore, at ambient temperature, even small amounts of the host mineral dissolution would promote the precipitation and growth of REE carbonates (e.g., lanthanite in our ambient temperature experiments). Another factor to consider is that we did not stir our experiments, meaning that our grains remained static inside the reactors. As a consequence, the concentrations of Ca^{2+} , Mg^{2+} , and CO_3^{2-} at the interface between the host mineral and the aqueous solution should have been even higher, resulting in higher supersaturation levels with respect to REE carbonates. This means that dissolving just a few monolayers of the host grain would sufficiently promote the nucleation and surface crystallization of the REE carbonates. This process, in turn, would lower the concen-

tration of CO_3^{2-} in the solution, further enhancing the dissolution of the host grain.

Additionally, it is important to emphasize the role of ionic potentials of the REE^{3+} cations in this process.^[20] Lighter trivalent ions require lower energy for dehydration from solution compared to heavier ones,^[17,18] kinetically favoring the formation of La-rich crystals in the initial stages of the replacement reaction. As the lighter elements are gradually consumed, the solution becomes enriched in heavier ions, resulting in the development of crystals characterized by heavier-REE rims.

Although our SEM-BSE-EDS analyses of REE carbonates (Figures 5–9; Figures S2 and S3, Supporting Information) would suggest lighter REE carbonates exhibiting lower solubility compared to their heavier counterparts, it is crucial to emphasize that these replacement reactions present a multi-variable challenge. The chemical textures observed in kozoite may be subject to local reorganization during its transformation to sec-

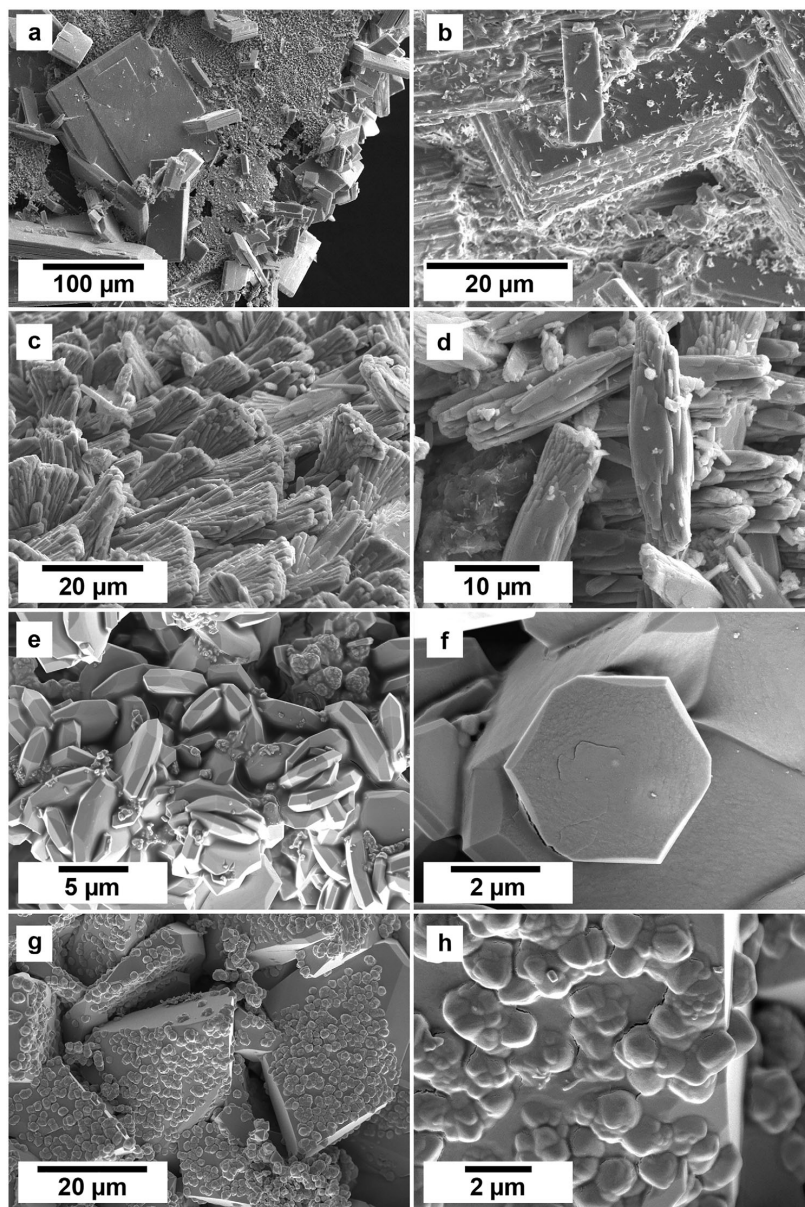


Figure 4. Secondary electron SEM images showing the series of replacement REE-bearing minerals observed on the surface of the host carbonate grains. a) Thin, platy lanthanite crystals on calcite at 21 °C after 12 weeks in PAAS solution. b) Detail of lanthanite with small (<1 µm) secondary kozoite crystals on aragonite at 21 °C after 8 weeks in PAAS solution. c) Spherulitic kozoite on aragonite at 80 °C after 1 week in PAAS solution. d) Detail of kozoite on aragonite at 80 °C after 1 week in non-PAAS solution. e) Hydroxylbastnäsite on aragonite at 210 °C after 24 h in non-PAAS solution. f) Detail of hydroxylbastnäsite on dolomite at 210 °C after 48 h in non-PAAS solution. g) Secondary replacement of hydroxylbastnäsite by cerianite on calcite at 210 °C after 24 h in non-PAAS solution. h) Detail of the early stages of nanocerianite formation on calcite at 210 °C after 24 h in non-PAAS solution.

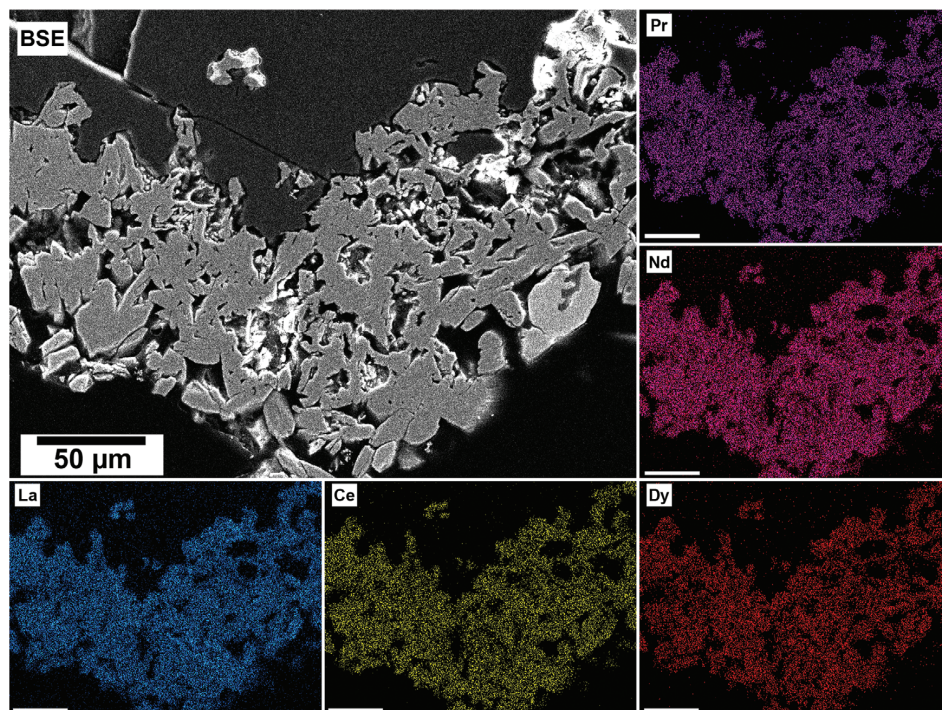


Figure 5. SEM-BSE image of calcite grain at 165 °C after 48 h in non-PAAS solution and EDS maps of La (blue), Ce (yellow), Pr (purple), Nd (pink), and Dy (red) showing the homogenous distribution of the REE.

ondary bastnäsäsite. This gradual process observed in our experiments (Tables 1–3, Figure 2), is known to occur via dissolution-recrystallization^[17,18,21–23] and introduces an additional layer of complexity, potentially influencing the complex chemical variations occurring in the replacement rim at the micro- and nanoscale. Overall, the intricate interplay of crystal structures, variable solid-solution compositions and solubilities, ionic potentials, temperature, evolving solution composition, available reactive surface, as well as temperature-dependent dissolution-recrystallization processes, collectively contribute to the observed chemical variability within the single crystals and in the replacement ring. Quantifying the preferential incorporation of REEs in our samples is also highly complicated due to the small size and random orientation of the individual kozoite or bastnäsäsite crystals within the replacement corona. Therefore, a more comprehensive examination would require the production of larger or isolated single crystals, a task that exceeds the scope of the current study.

3.1.1. The Effect of Molar Volume

With the exception of two of our experiments (e.g., dolomite, PAAS solution at 165 °C, and calcite, non-PAAS solution at 210 °C), none of the experiments resulted in the complete replacement of the host grain. This can be explained by difference

in molar volume between the minerals in the host grain and the overgrowth. If the newly forming REE carbonate overgrowth has a larger molar volume compared to the host mineral, it will begin to encapsulate the host. As the host is being covered, its dissolution rate will decrease, triggering a decrease in REE carbonate precipitation as there are less CO_3^{2-} ions entering the aqueous solution. When this overgrowth is large and dense enough, and completely isolates the host grain from the aqueous solution, the dissolution of the host stops and a 'partial equilibrium' with respect to the REE carbonates is reached.^[24] We can use the reaction of calcite (molar volume of $36.93 \text{ cm}^3 \text{ mol}^{-1}$) being replaced by lanthanite (molar volume $216.70 \text{ cm}^3 \text{ mol}^{-1}$) as an example:



The difference between the molar volumes of the reagents and the products is so great that the lanthanite replacement can fully encapsulate the host. In our ambient temperature experiments, the maximum consumption of the host phase was only 18%, even after a duration of 84 days (Tables 1–3). Comparatively, we can look at the replacement of calcite by kozoite or bastnäsäsite (molar volumes 45.48 and $44.91 \text{ cm}^3 \text{ mol}^{-1}$ respectively):



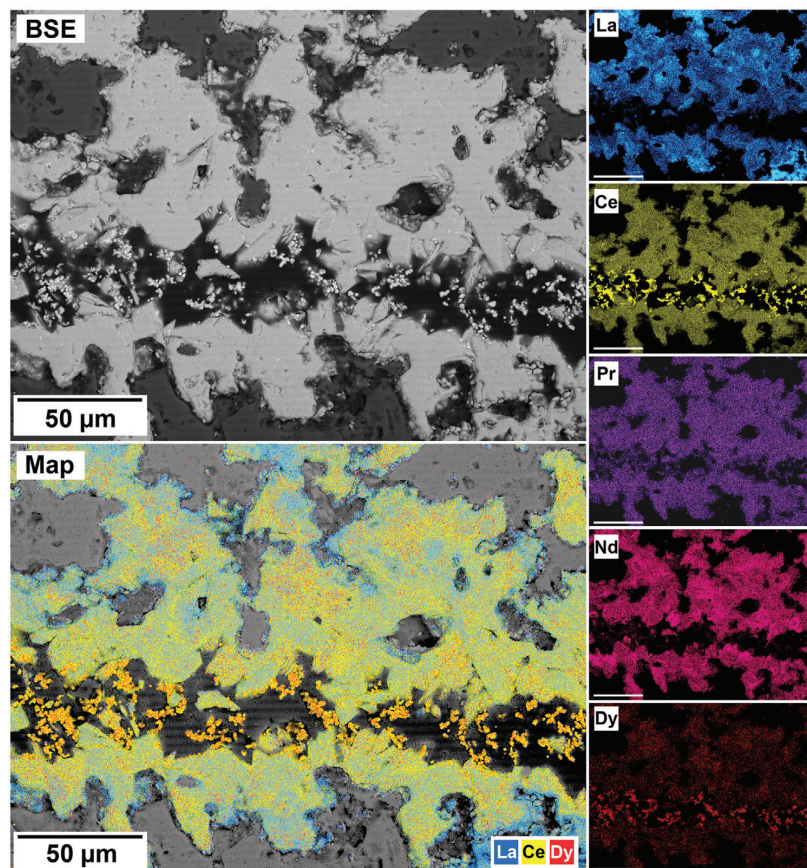


Figure 6. SEM-BSE image and EDS elemental maps of an aragonite grain at 165 °C after 24 h in PAAS solution showing the heterogenous distribution of the REE and the association of cerianite (yellow) and Dy (red).

Here, the difference in molar volumes also results in the encapsulation of the host, however, the difference is not substantial compared to the difference between lanthanite and calcite. This very small difference in molar volume, combined with the morphology of kozoite and bastnäsité consisting of many small micrometric crystals, allows for the development of microporosity during the replacement process. This causes some fluid to remain in contact with the host grain, enabling its dissolution and the potential full replacement of the host grain, as seen in our high temperature (>165 °C) experiments.

Secondary replacement of the REE carbonates with cerianite and formation of symplectic textures

In all of our experiments above 165 °C we observed a secondary replacement of kozoite and hydroxylbastnäsité by cerianite (Figure 10). The onset of cerianite formation is a consequence of the oxidation of Ce^{3+} to Ce^{4+} , with several factors promoting this transition. First, Ce^{4+} has the electron structure of a noble gas, making it more stable than Ce^{3+} , and the higher temperatures provide the energy needed to facilitate the loss of an electron. Also, as our systems progressed toward equilibrium, the

pH would increase from ≈ 5 to 8.1–8.2. The higher concentration of OH^- ions allows the formation of Ce-hydroxo-complexes which facilitate the Ce^{3+} to Ce^{4+} oxidation process,^[21,25] especially at the surface-solution interface of the REE or Ca-Mg-carbonate minerals.^[21,25] As Ce^{4+} is incompatible within the carbonate structure, it combines with oxygen, forming the oxide cerianite (CeO_2), which is the most insoluble and the most thermodynamically stable phase in our system. Our experimental setup (sealed hydrothermal reactors containing a limited atmosphere, under conditions of autogenous pressure) inherently creates an oxidising environment favoring the oxidation of Ce^{3+} to Ce^{4+} reaction. Had we conducted the experiments using anoxic water and a pure N_2 atmosphere, the presence of carbonates like calcite and dolomite would have also buffered the pH of the aqueous solution, increasing the stability of the HCO_3^- ions relative to CO_2 , but these changes would have a negligible influence on the redox state. This means that the formation of cerianite would likely not have occurred and Ce would have been incorporated to the newly formed carbonates as Ce^{3+} along with the other REEs in the system.

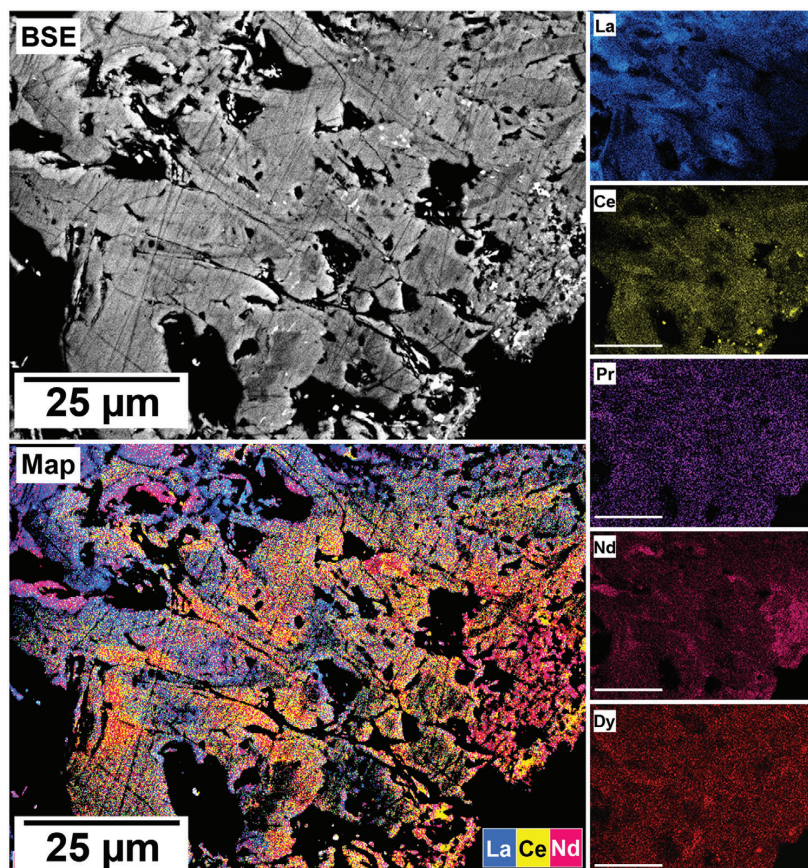
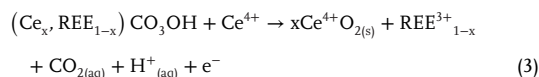


Figure 7. SEM-BSE image and EDS elemental maps of a calcite grain at 165 °C after 96 h in PAAS solution showing potential zoning in kozoite crystal, with lighter REE concentrated in the centre and heavier REE in the outer edges of the crystals.

The SEM-EDS images and maps (Figures 10 and 11) show a very specific intergrowth of the REE carbonates and cerianite at high temperatures (>165 °C), a textural feature known as a symplectite. These textural features are common in metamorphic rocks that have undergone high pressure-temperature conditions^[26] and have also been found in REE-bearing deposits.^[27] The exact mechanisms behind the formation of symplectites can vary depending on the specific mineral assemblages and geological conditions. However, we propose that in our experiments this texture results from a fluid-mediated mineral replacement, driven by dissolution-precipitation mechanisms and intra-mineral diffusion processes.^[28] In all of our experiments, all of the REE carbonates formed prior to cerianite and the latter always crystallized exclusively in association with the surface of the pre-existing REE carbonates, indicating that this process takes place at the solution-surface interface, in agreement with Szucs et al (2023). As cerianite is more insoluble ($\log(K_{sp}) = -59.3 \pm 0.3$;^[29] compared to kozoite ($\log(K_{sp}) = -22.3 \pm 0.2$) or bastnäsité ($\log(K_{sp}) = -23.8 \pm 0.1$) or the host Ca–Mg carbonates, it can replace any carbonate crystals in our

system until the Ce^{4+} is depleted from the aqueous solution. This replacement is also enhanced by the smaller molar volume of cerianite ($23.86 \text{ cm}^3 \text{ mol}^{-1}$) compared to kozoite ($45.59 \text{ cm}^3 \text{ mol}^{-1}$) or bastnäsité ($44.91 \text{ cm}^3 \text{ mol}^{-1}$) which increases the porosity of the parent phase.^[30] The kozoite / bastnäsité replacement by cerianite can be expressed by the following reaction:



As the molar volume of cerianite is the smallest of all phases present in our system, when this oxide replaces any REE carbonate, or the host, it creates porosity. This allows fluid access to the pre-existing REE carbonates, and the continuation of the replacement reaction, releasing previously immobilized REEs from the carbonate minerals back into the solution. As some of the REE have similar ionic radii to Ce^{4+} , in particular Dy^{3+} , and to a slightly lesser extent, Nd^{3+} , they can be incorporated into cerianite as impurities. If there is enough Ce in the system, cerianite

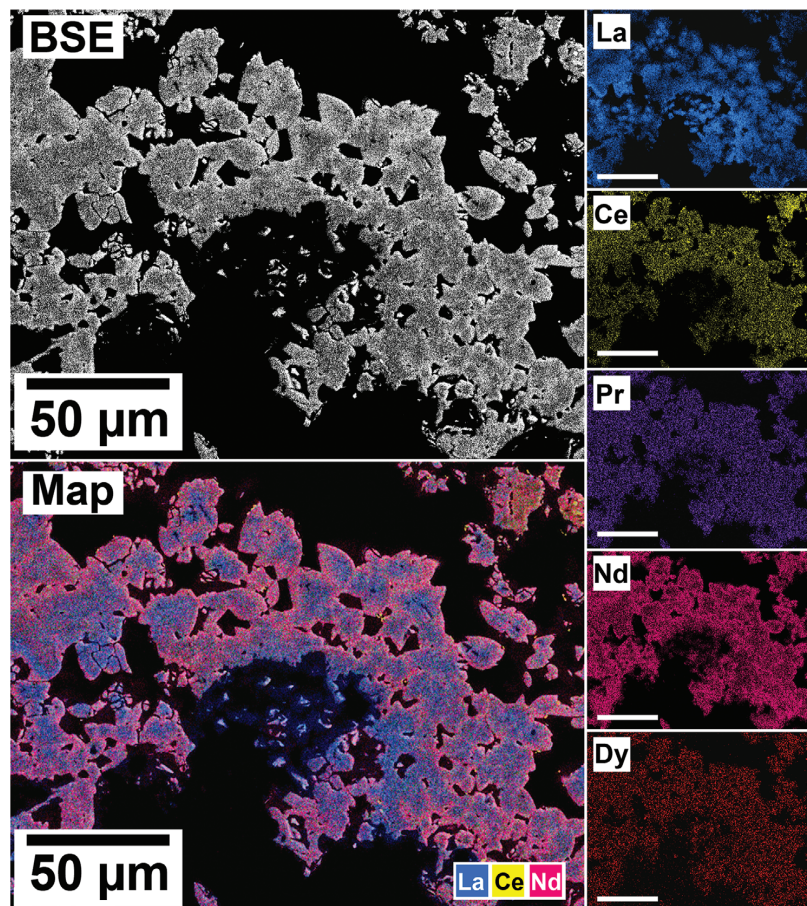


Figure 8. SEM-BSE image and EDS elemental maps of an aragonite grain at 165 °C after 72 h in PAAS solution showing potential zoning in kozoite crystal, with lighter REE concentrated in the centre and heavier REE in the outer edges of the crystals.

has the potential to fully replace all of the other mineral phases, with the remaining incompatible REE^{3+} ending up in the aqueous solution.

Concomitantly, any Ce^{3+} located in the non-replaced kozoite or bastnäsité structures will also tend to oxidize to Ce^{4+} . Assuming an REE-O coordination of 9 in kozoite and bastnäsité, the Ce^{3+} to Ce^{4+} oxidation is also translated into a decrease in the ionic radius from 1.33 to 1.16 Å,^[20] making Ce^{4+} incompatible with these REE carbonates. Therefore, the oxidation process would trigger a solid-state phase transformation from REE-carbonates to cerianite at the local scale. This process would involve the migration of Ce^{4+} ions through the existing REE carbonate structure, leading to their accumulation at the nanoscale, triggering the nucleation of nm-sized cerianite. Our EDS maps (Figures 10 and 11) reveal a depletion of Ce in the REE carbonate phases and the accumulation of this element as a discrete phase (cerianite), while the rest of the REEs tend to concentrate in the carbonate crystals.

Both our SEM-BSE images and EDS maps (Figures 10 and 11) show that the location of cerianite defines the boundaries between pre-existing spindle-shaped kozoite crystals. This indicates that the formation of these symplectic textures has been favored by the boundaries of the original polycrystalline material, as it is easier for ions to migrate through crystal imperfections. Therefore, the local boundaries between the parent kozoite single crystals provide the ideal starting point to initiate the formation of the symplectic texture, in turn creating the visible “ghosts” textures of the pre-existing kozoite.

4. Conclusion

The reaction between each of the carbonate host grains, dolomite, aragonite and calcite, with multi-component REE-bearing (La, Ce, Pr, Nd, and Dy) aqueous solutions resulted in the replacement of the carbonate host and the formation of secondary REE-bearing minerals. The reaction followed the multi-step crystal-

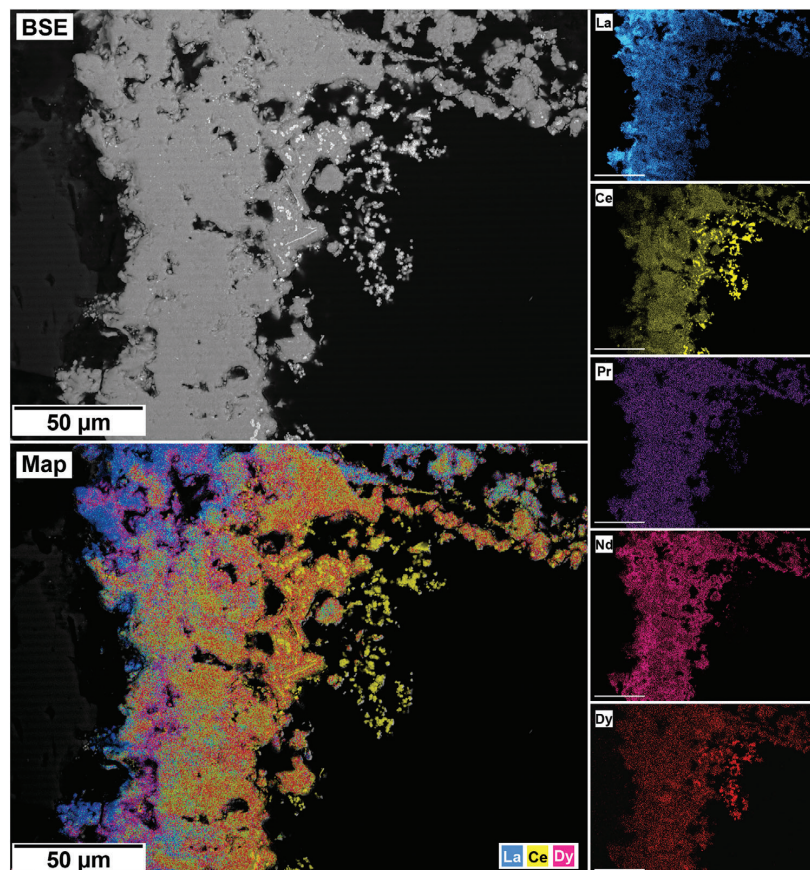


Figure 9. SEM-BSE image and EDS elemental maps showing the compositional gradation of REE in the replacement corona surrounding the aragonite host at 165 °C after 96 h in PAAS solution, with lighter REE accumulated toward the inner rims and heavier REE in the outer rim.

lization sequence: lanthanite → kozoite → hydroxylbastnäsite → cerianite. The REEs were preferentially incorporated into the growing REE-minerals, likely because of the combination of several factors including the solubility and dissolution rate of the carbonate host compared to the REE minerals, time, temperature, ionic radius and ionic potential of the REE as well as its concentration in solution. At higher temperatures (>165 °C) a secondary replacement of kozoite and bastnäsite by the rare earth oxide, cerianite, was observed. Differences in molar volumes between cerianite and kozoite/bastnäsite generated porosity in the newly formed mineral and allowed for solution-mediated mineral replacements, producing symplectic textures. Our study sheds light on the uptake of multiple REEs by various carbonate minerals and provides insight into the potential zoning of REEs in rare earth minerals. A broader knowledge of REE zoning will have potential applications in rare earth separation techniques, beneficiation, and recycling.

5. Experimental Section

The interaction of calcite, dolomite and aragonite with multi-component REE (La, Ce, Pr, Nd, and Dy) aqueous solutions was investigated at ambient and hydrothermal conditions (21–210 °C). Calcite (Iceland spar), aragonite (Sputnik variety) and light-pink dolomite (Morocco) crystals were crushed in a ceramic mortar and sieved to extract 0.5–1.0 mm clasts. Five single REE bearing solutions were prepared, (La, Ce, Pr, Nd, and Dy), with a REE concentration of 50 mM. These solutions were produced via the dissolution of single rare earth element nitrate salts, $\text{REE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, 99.9% purity), in de-ionized water (18.18 MΩ cm). These five specific REE were chosen as they were representative of both the light (La, Ce, Pr, and Nd) and heavy REE (Dy). This suit of REE from La to Dy also represents 72% of the ionic radii of the lanthanides as well as being some of the most abundant REE in the earth's crust.^[31] In order to understand the effect of ionic radii of the five REEs and to what extent these ions were taken up by the carbonate host, two different sets of experiments were conducted, one with equal concentrations of the five REEs and one with the concentrations of the five REEs normalized to the commonly used Post Archean Australian Shale standard (PAAS)^[32] to mimic the rare earth element concentrations found in continental crust and natural geo fluids. For the equal concentration experiments 4 mL of each of the five REEs were used to give a total solution volume of 20 mL

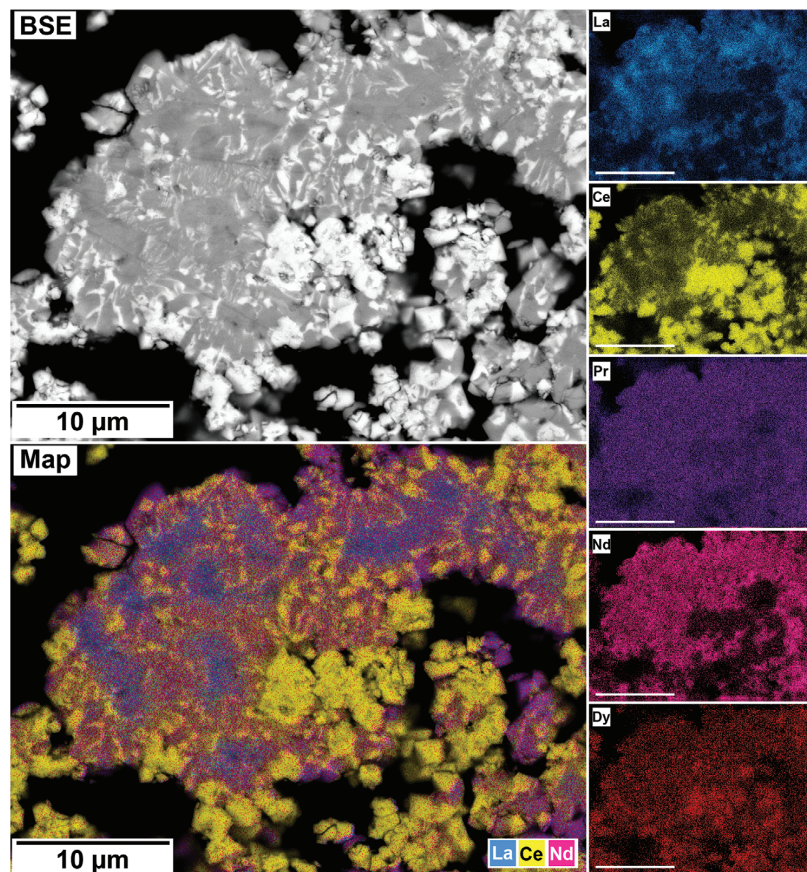


Figure 10. SEM-BSE image and EDS elemental maps of an aragonite grain at 210 °C after 24 h in PAAS solution. Areas of La-rich areas surrounded by vermicular intergrowths of Nd and Ce radiating outwards form the symplectic textures.

for each experiment. For the PAAS experiments, a 1 L bulk solution was made and 20 mL of this was used for each experiment.

For each experiment, 0.1 g of either calcite, dolomite, or aragonite grains were added to 20 mL of each of the 50 mm REE-bearing solutions and placed in 25 mL Teflon-lined and capped stainless-steel autoclaves (for the 80, 165, and 210 °C experiments). For the lower temperatures (21 and 50 °C), narrow-mouth Nalgene polypropylene PPCO bottles (Thermo Fisher Scientific) were used. The reactors were then placed in a pre-heated oven at 50, 80, 165, and 210 °C. The room temperature experiments were kept undisturbed in a laboratory cupboard. Solid samples were then extracted using a sterilized metal spatula at increasing time intervals from 24 h to 8 weeks. The samples were placed in plastic Eppendorf tubes and dried in a 30 °C oven, with the exception of the 21 °C samples, which were dried at room temperature. A summary of the experimental protocol is presented in Figure S1 (Supporting Information).

In order to identify and quantify the formation of crystalline solids present in our samples, several grains were selected from each experiment ensuring that each time and temperature variable was represented. The selected grains were ground to a consistently fine powder using an agate pestle and mortar. The powders were analyzed, and minerals characterized with powder X-ray diffraction (XRD). Conventional powder XRD patterns were collected using a Siemens/Bruker D5000 powder X-ray diffractometer (Cu K α radiation, 0.01° step⁻¹ from 5 to 60° 2 θ at 0.2° min⁻¹, 4.5 h

scans per samples). Identification of crystalline phases was carried out with the Diffract Suite EVA software from Bruker in combination with the Powder Data File (PDF-4, the International Centre for Diffraction Data).^[33] Pattern-matching refinement and quantification of crystalline phases were carried out with the Rietveld refinement software TOPAS.^[34] Finally, scanning electron microscopy (SEM) was used to obtain high resolution images to characterize changes in the morphology of the carbonate host grains and identify newly formed phases. Analyses were conducted in the iCrag laboratory at Trinity College Dublin using a TIGER S8000 FEG-SEM operating under high vacuum conditions and equipped with two Oxford X-Max 170 mm² EDS detectors and an X4 pulse processor running the Oxford Aztec analysis software.

Two methods of sample preparation were employed, i) standard SEM sample stubs with intact grains mounted to examine surface morphology, and ii) polished epoxy resin pucks that provided a cross section of the grains, allowing for the identification of potential differences in spatial distribution and internal chemical textures. The epoxy mounts (2.5 cm wide) were made using Epoxy resin (Struers Epofix) mixed with the accompanying hardener and then polished using a three-step process (Struers Diapro, 6 and 1 μ m) to expose the internal cross section of the grains. The pucks were then cleaned in an ultrasonic bath of deionized water to remove any residual polishing fluid and then dried. Both the stubs and the pucks were then coated with either carbon (for elemental mapping

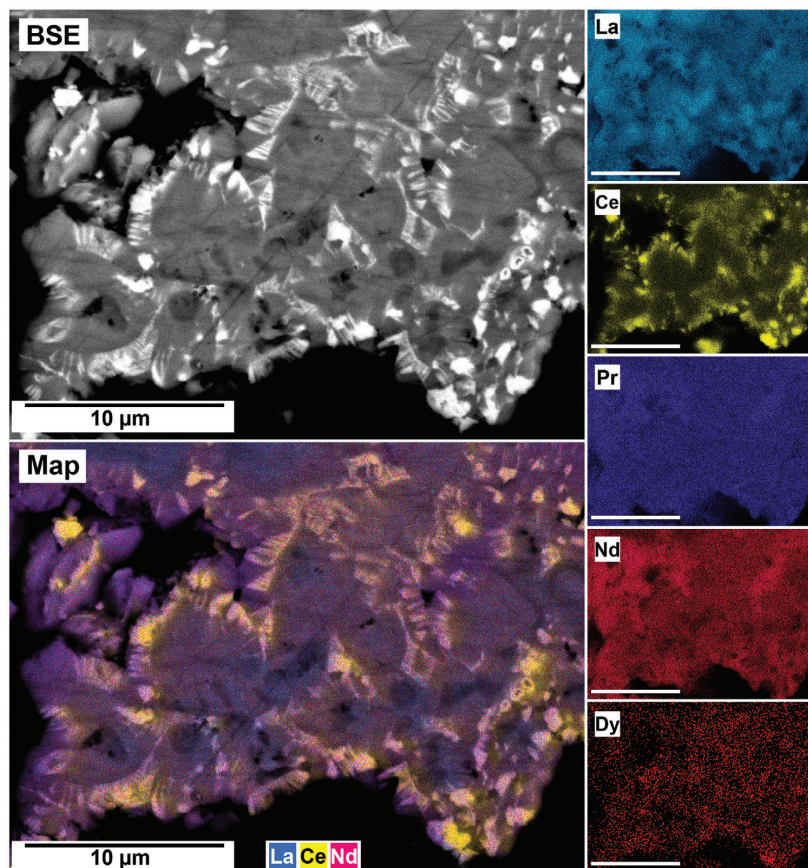


Figure 11. SEM-BSE image and EDS elemental maps of an aragonite grain at 210 °C after 24 h in PAAS solution showing how the location of cerianite defines the boundaries between pre-existing spindle-shaped kozoite crystals.

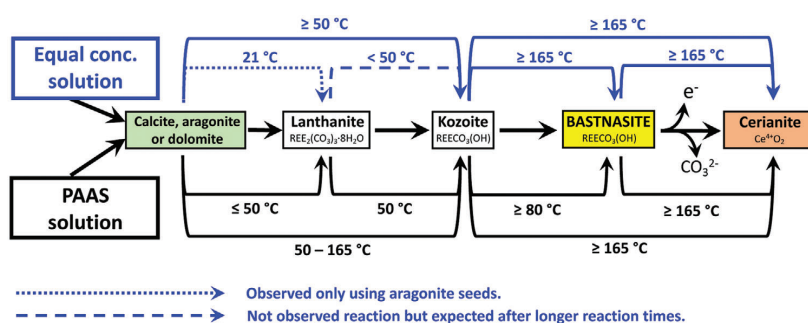


Figure 12. Reaction pathways during the replacement of Ca(-Mg) carbonates by rare earth carbonates and cerianite. Continuous lines correspond to observed reactions, dotted lines to observed reactions only using aragonite seeds, while dashed lines correspond to expected reactions that were not observed in our experiments. Each line shows the temperature at which the reaction takes place.

and analysis) or gold (for high resolution imaging). Analysis at a working distance of 15 mm was performed using an accelerated voltage of 20 kV, while imaging carried out at a working distance of 5 mm was performed using an accelerating voltage of 10 kV. The images and maps were processed using the AZtec v6.1 X-ray microanalysis software suit (Oxford Instruments).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cerianite, crystallization, hydroxylbastnasite, kozoite, rare-earth-carbonates

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PAPER

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Transient crystallisation of rare earth carbonates during the hydrothermal oxidation of siderite†

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The researchers investigated the interaction between multi-component rare earth element-bearing aqueous solutions and siderite grains under hydrothermal conditions. Our study investigates the interaction between multi-component rare earth element (REE; La, Ce, Pr, Nd, Dy)-bearing aqueous solutions and siderite (FeCO_3) grains under hydrothermal conditions (50–205 °C). The results revealed a solution-mediated mineral replacement reaction that occurs via a multi-step crystallisation pathway involving the formation of iron oxides (goethite, $\alpha\text{-FeO(OH)}$, and hematite, Fe_2O_3), metastable REE-bearing minerals (kozoite, $\text{REE}(\text{CO}_3)(\text{OH})$, and bastnasite, $\text{REE}(\text{CO}_3)(\text{OH},\text{F})$), and cerianite (CeO_2). Siderite stability, dissolution, and subsequent mineral formation are temperature and pH-dependent. At low temperatures, REE carbonate formation is inhibited by a goethite coating, creating a partial equilibrium situation. Higher temperatures increase dissolution rates and enable kozoite and bastnasite formation. The redox behaviour of Fe and Ce combined with the temperature, and the availability of CO_3^{2-} govern this crystallisation sequence. Continued oxidation promotes decarbonation processes by acidifying the aqueous solution, dissolving all carbonates, and resulting in hematite and cerianite crystallisation as thermodynamically stable phases. Understanding iron carbonate, oxide and REE interactions can inform new resource targets and improve recovery and separation techniques.

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Introduction

Due to their application in a range of green technologies and renewable energy, the demand for rare earth elements (REE) is ever increasing.^{1,2} While the development of recycling REE from end-products has progressed, we are still heavily reliant on natural, mineable sources.³ Currently, China is host to one-third of all known REE deposits and processes 97% of the world's REE + Y.^{3,4}

Presently, commercially significant REE deposits are associated with magmatic processes related to alkaline igneous rocks and carbonatites.⁵ As of 2016, there were approximately 50 advanced REE exploration projects active outside of China, 20 of which are targeting carbonate igneous rocks (carbonatites).⁶ Carbonatites and alkaline-carbonatite complexes have been identified as significant sources of REE and Nb, as well as hosting substantial deposits of apatite, vermiculite, copper, fluorite, thorium, uranium, and iron.⁷ The genesis of

carbonatite-associated REE deposits, a vital global REE source, is therefore a subject of strong interest and investigation.⁸

In general, carbonatites are igneous rocks derived from the mantle and have a carbonate mineral volume of >50% and SiO_2 <20 wt%.⁹ Their formation occurs through the immiscibility of carbonate-silicate magma and through the fractional crystallisation of carbonate minerals from carbonatite magma. The main source of these ore-forming elements comes from primitive mantle with an additional contribution from REE carrying crustal materials.⁵ The REE form complexes and migrate through the magmatic-hydrothermal system. Changes in temperature, pressure, pH and fluid composition allow their precipitation and mineralization. The formation of the world's largest REE deposit, Bayan Obo REE-Nb-Fe in China, has been linked to prolonged fluxing of carbonatite by subduction-derived fluids, and highlights the intricate interplay of geological processes involved in REE enrichment.¹⁰ It is characterized by a light rare earth (LREE) enrichment and is also hosted in hematite-bearing iron ores with high REE concentrations.¹¹

Investigations into the magmatic-hydrothermal processes in carbonatite-related REE deposits have offered insights into the enrichment mechanisms of REE, such as the Saint-Honoré carbonatite complex in Canada¹² and the Weishan carbonatite-related REE deposit in China.¹³ For example, in Weishan, two enrichment processes were responsible for the formation of the deposit: (i) the production of mineralized carbonatite and (ii)

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the subsequent enrichment by magmatic-hydrothermal processes. Fractures in the deposit promoted the circulation of ore-forming fluids and provided the space necessary for REE precipitation. Concomitantly, high F^- and SO_4^{2-} concentrations in the ore-forming fluids are thought to have facilitated REE transport and deposition *via* the formation of stable complexes.¹³

The behaviour of fluids under high-pressure conditions can influence the phase transitions of carbonatitic melts and the subsequent formation of hydrothermal brines. It has been demonstrated that under high-pressure and high-temperature conditions, the transition from carbonatitic melts to hydrothermal brines occurs, which can lead to the concentration of REE in these brines.¹⁴ The pressure conditions can also affect the stability of mineral phases, influencing which REE-bearing minerals are formed during the cooling and crystallization processes.

The pH of the fluid environment is another crucial factor influencing REE mineralization. Acidic conditions can enhance the solubility of REE and promote their mobility, while neutral to alkaline conditions may stabilize certain REE-bearing minerals. Anenburg and Mavrogenes highlighted that the transport of REE influenced by the pH of the fluids, with different REE complexes forming under varying pH conditions.¹⁵ Furthermore, the presence of ligands such as F^- , Cl^- , and CO_3^{2-} can significantly affect the solubility and transport of REE, with acidic conditions often favouring the dissolution of REE minerals and their subsequent transport in solution.

If REE carbonates are heated at temperatures up to their melting points, several processes would occur, dependent on the specific REE and temperature. Initially, dehydration would happen if the carbonates contained structural water or $-OH$ groups, with heavier REE requiring temperatures above 700 °C for water release. As temperatures rise, REE carbonates would undergo phase transitions, transforming into anhydrous oxycarbonates and eventually into oxides.^{16,17} This decarbonation process, releasing CO_2 , occurs at around 450–550 °C for oxycarbonates, with heavier REE requiring higher temperatures due to their smaller ionic radii and ability to retain some minor amounts of structural water.¹⁶ Formation of solid solutions is expected, but differences in ionic sizes would lead to distinct hexagonal, monoclinic, or cubic structures.^{16,18} At more elevated temperatures, the REE oxides would melt, and the behaviour of REE in the melt would depend on their partitioning, melt composition, and interactions with other elements from the rock.

The composition of the fluids involved in carbonatite formation is critical for the concentration of REE. Fluids rich in specific ligands (*e.g.*, F^- , Cl^- , SO_4^{2-}) can enhance the mobility of REE and facilitate their precipitation as economically viable minerals. Pokrovsky *et al.*, 2002¹⁹ noted that the fluids involved in REE transport and deposition are characterized by high activities of ligands and brines, which play a significant role in the mineralization processes. Additionally, the presence of carbonate-rich fluids can lead to the formation of REE-bearing minerals through complexation and precipitation reactions.⁵ The interaction of these fluids with the host rocks can also lead

to metasomatic processes that enrich the REE content in carbonatites.²⁰

There are also several examples of REE-rich carbonatite complexes containing high REE concentrations connected to hematite-bearing rocks and iron ores,¹¹ one being the Mountain Pass complex in California. Another example is the Fen complex, Telemark, southeast Norway where REE concentrations of up to 15 000 ppm have been recorded and originate from hematite–carbonatite and iron ores.^{21–23} The Fen complex was formed by the alteration of ankerite ferrocarnatite which included the oxidation of ferrous minerals in the primary ferrocarnatite assemblages.^{21,24–26} One of the largest concentrations of Fe-oxides on Earth is the Olympic Dam Cu–U–Au–Ag iron oxide copper–gold (IOCG-type) deposit, in South Australia,²⁷ with hematite being the most abundant mineral in the deposit.²⁶ REE-rich hematite carbonatites are found in several carbonatite complexes worldwide and are commonly associated with ankerite $[Ca(Fe, Mg, Mn)(CO_3)_2]$ - and siderite ($FeCO_3$)-bearing carbonatites.¹¹

In this experimental study we aim to better understand the formation of rare earth carbonates during the oxidation and replacement of siderite. Of particular interest is the crystallization of REE carbonates in the presence of multiple foreign ions during the oxidation process as well as the extent to which REE are incorporated into the iron oxides that may form. Therefore, we have mimicked natural systems by carrying out replacement experiments using multi-component REE aqueous solutions and iron carbonate host grains of siderite, which are commonly associated with carbonatite ore deposits.

Methods

The interaction of siderite ($FeCO_3$) grains with multi-component REE (La, Ce, Pr, Nd and Dy) aqueous solutions was investigated at hydrothermal conditions (50–205 °C). Siderite crystals were crushed in a ceramic mortar and sieved to extract 0.5–1.0 mm clasts. Five single REE bearing solutions were prepared, La, Ce, Pr, Nd and Dy, with a total REE concentration of 50 mM. These solutions were produced *via* the dissolution of single REE nitrate salts, $REE(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9% purity), in de-ionized water (18.18 MΩ cm). These five specific REE were chosen as they are representative of both light (La, Ce, Pr, and Nd) and heavy (Dy) REE. This suit of REE from La to Dy also represents 72% of the ionic radii of the lanthanides as well as being some of the most abundant REE in the earth's crust.²⁸ In order to understand the effect of ionic radii of the five REEs and to what extent these ions are taken up by the siderite host, two different sets of experiments were conducted, one with equal concentrations of the five REE and one with the concentrations of the five REE normalized to the commonly used Post Archean Australian Shale standard (PAAS)²⁹ to mimic the REE concentrations found in continental crust and natural geologic fluids. For the equal concentration experiments, 4 mL of each of the five REE were used to give a total solution volume of 20 mL for each experiment. For the PAAS experiments, a 1 L bulk solution was made and 20 mL of this was used for each experiment.

For each experiment, 0.1 g of siderite grains were added to 20 mL of each of the 50 mM REE-bearing solutions and placed in 25 mL Teflon-lined and capped stainless-steel autoclaves (for the 165 and 205 °C experiments). For the 50 °C experiments, narrow mouth Nalgene polypropylene PPCO bottles (Thermo Fisher Scientific) were used. The reactors were then placed in a pre-heated oven at 50, 165, and 205 °C. Solid samples were then extracted using a sterilized metal spatula at increasing time intervals from 24 hours to 12 weeks. The samples were placed in plastic Eppendorf tubes and dried in a 30 °C oven for a minimum of 1 hour. The samples were then inspected several days later before preparing them for XRD and SEM analysis.

In order to identify and quantify the formation of crystalline solids present in our samples, several grains were selected from each experiment ensuring that each time and temperature variable was represented. The selected grains were ground to a consistently fine powder using an agate pestle and mortar. The minerals were identified and quantified with powder X-ray diffraction (XRD). Conventional powder XRD patterns were collected using a Siemens/Bruker D5000 powder X-ray diffractometer (CuK α radiation, 0.01° per step from 5 to 60° 2 θ at 0.2° min⁻¹; 4.5 hours scans per sample). Identification of crystalline phases was carried out with the Diffract Suite EVA software from Bruker in combination with the Powder Data File (PDF-4, the International Centre for Diffraction Data).³⁰ Pattern-matching refinement and quantification of crystalline phases were carried out with the Rietveld refinement software TOPAS.³¹ Finally, scanning electron microscopy (SEM) was used to obtain high resolution images to characterize changes in the morphology of the siderite host grains and identify newly formed phases. Analyses were conducted in the iCrag Lab at Trinity College Dublin using a TIGER S8000 FEG-SEM operating under high vacuum conditions and equipped with two Oxford X-Max 170 mm² EDS detectors and an X4 pulse processor running the Oxford Aztec analysis software.

Two methods of sample preparation were employed: (i) standard SEM sample stubs with intact grains mounted to examine surface morphology, and (ii) polished epoxy resin pucks that provided a cross section of the grains, allowing for the identification of potential differences in spatial distribution of elements and any internal chemical textures. The epoxy mounts (2.5 cm wide) were made using Epoxy resin (Struers Epofix) mixed with the accompanying hardener and then polished using a three-step process (Struers Diapro, 6 and 1 μ m) to expose the internal cross section of the grains. The pucks were then cleaned in an ultrasonic bath of deionized water to remove any residual polishing fluid and then dried. Both the stubs and the pucks were then coated with either carbon (for elemental mapping and analysis) or gold (for high-resolution imaging). Analysis at a working distance of 15 mm was performed using an accelerated voltage of 20 kV, while imaging carried out at a working distance of 5 mm was performed using an accelerating voltage of 10 kV. The images and maps were processed using the Aztec v6.1 X-ray microanalysis software suit (Oxford Instruments).

Finally, the saturation indexes of solid phases during the equilibration of the REE-bearing aqueous solutions with respect to siderite were calculated with the hydro-

Table 1 Experimental conditions, identities and morphologies of the solid rare earth carbonate and oxide phases formed during the interaction of siderite with multi-component (La, Ce, Pr, Nd, and Dy) REE-bearing aqueous solutions (equal concentration and PAAS experiments) at 50, 165, and 205 °C^a

Equal concentration experiments				PAAS experiments				
T (°C)	Time (days)	% phase consumed	Phase formed	Morphology	Time (days)	% phase consumed	Phase formed	Morphology
50	1	<1	Goethite	Flakes	1	<1	Goethite	Flakes
	2	<1			2	<1		
	3	<1			3	<1		
	4	<1			4	<1		
	12	<1			12	<1		
165	56	<1			56	<1		
	84	<1			84	<1		
	1	40	33% Hem, 6% Koz, <1% goeth	Koz (spindle-shaped prisms),	1	70	46% Hem, 15% HB, 9% goeth	Hem (pseudohexagonal
	7	100	87% Hem, 3% HB, 9% Cer, <1% goeth	Hem (pseudohexagonal prisms), Cer (cubes, bipyramidal prisms), HB (triangular prisms)	7	100	73% Hem, 20% Cer, 7% goeth	prisms), Cer (cubes, bipyramidal prisms), HB (triangular prisms)
	14	100	77% Hem, 2% Cer, 21% goeth		14	100	82% Hem, 18% Cer	
205	1	84	77% Hem, 4% HB, 3% Cer	Hem (pseudohexagonal prisms)	1	100	83% Hem, 17% Cer	Hem (pseudohexagonal
	7	100	95% Hem, 5% Cer		7	100	94% Hem, 6% Cer	prisms), Cer (cubes, bipyramidal prisms)

^a Goethite (goeth), hematite (Hem), kozoite (koz), hydroxylbastnasite (HB), cerianite (Cer).

geochemical code PHREEQC³² using the LLNL database and the solubility products of REE-bearing carbonates determined by ref. 33 and 34.

Results

The analysis of all solid samples obtained from the replacement experiments resulted in the formation of surface precipitates that partially or totally replaced the siderite host grain. The combination of powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) allowed us to identify and quantify the newly formed phases and interpret the mechanisms responsible for the alteration and decomposition of the siderite grains and the precipitation of the newly formed phases.

Powder X-ray diffraction (XRD)

The interaction between siderite and multi-component rare earth element (La, Ce, Pr, Nd and Dy) – bearing aqueous solutions resulted in the formation of iron oxides, goethite (α -FeO(OH); PDF 00-003-0249) and hematite (Fe_2O_3 ; PDF 00-024-0072), REE-bearing minerals kozoite ($\text{REE}(\text{CO}_3)(\text{OH})$; PDF 04-017-1451) and hydroxylbastnasite ($\text{REE}(\text{CO}_3)(\text{OH},\text{F})$; PDF 00-027-1295) and the rare earth oxide cerianite (CeO_2 ; PDF 00-004-0593). The full quantitative XRD data are presented in Table 1.

These newly formed phases were observed as surface precipitates that partially or fully covered the siderite host mineral. In some experiments, siderite was fully replaced from the periphery inwards.

The extent of the replacement reaction was found to be time- and temperature-dependent. At the lowest temperature (50 °C), REE-bearing mineral formation was not detected in XRD and only the precipitation of minor (<1%) amounts of goethite, below the quantification level of XRD, was recorded after 56 days (Fig. 1). At higher temperatures, the extent and rate of siderite host replacement depended on the REE ratio in the aqueous solution, with faster replacement occurring in experiments using PAAS solutions: At 165 °C in the equal concentration solution, 40% of the siderite was consumed after 24 hours, compared to 70% in the PAAS solution (Table 1). In the 205 °C experiments, full replacement was observed after 1 week in the equal concentration experiments, compared to less than 24 hours in the PAAS solution experiments.

The observed mineralogy was also temperature- and REE ratio-dependent: At 165 °C, a rapid transformation (<24 hours) of goethite to hematite was observed, accompanied by the formation of the rare earth carbonates kozoite and hydroxylbastnasite (Fig. 2). After 14 days in equal concentration solutions and 7 days in PAAS solutions, a secondary replacement of

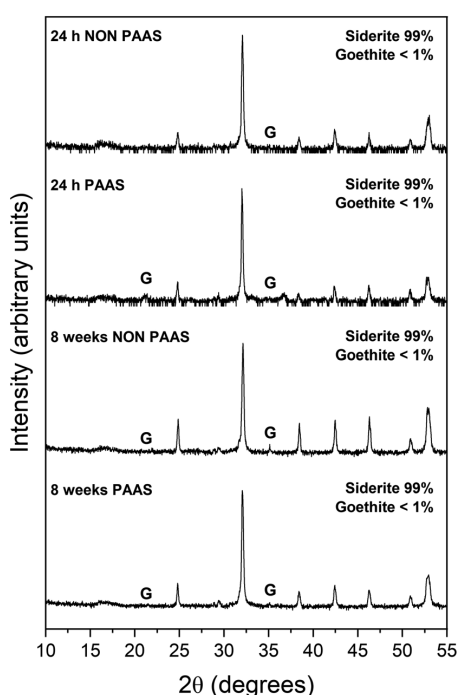


Fig. 1 Powder XRD patterns of goethite (G) in the equal concentration (non-PAAS) and PAAS experiments at 50 °C after 24 hours and 8 weeks (Bragg peaks that have not been assigned to any phase correspond to siderite).

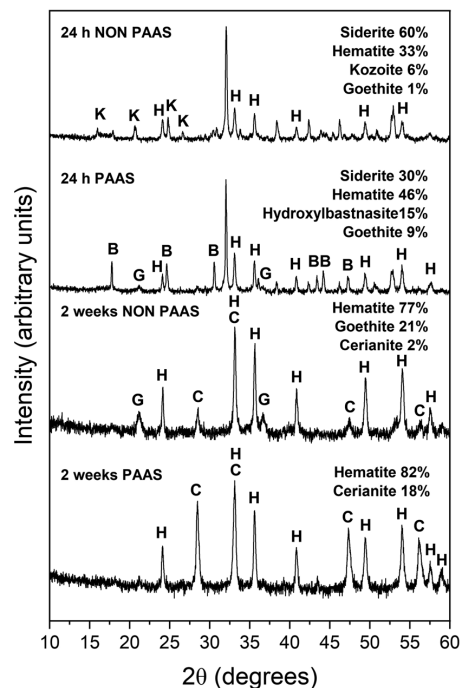


Fig. 2 Powder XRD patterns of goethite (G), hematite (H), kozoite (K), hydroxylbastnasite (B) and cerianite (C) in the equal concentration (non-PAAS) and PAAS experiments at 165 °C after 24 hours and 2 weeks (Bragg peaks that have not been assigned to any phase correspond to siderite).

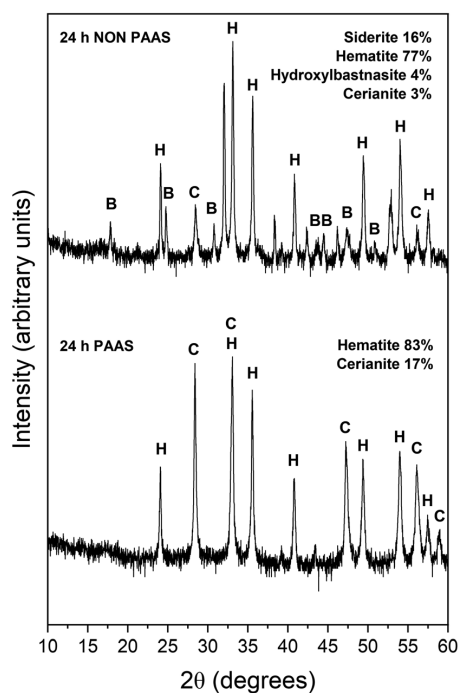


Fig. 3 Powder XRD patterns of, hematite (H), hydroxylbastnasite (B) and cerianite (C) in the equal concentration (non-PAAS) and PAAS experiments at 205 °C after 24 hours (Bragg peaks that have not been assigned to any phase correspond to siderite).

the rare earth carbonates by cerianite was observed. In both the 165 and 205 °C experiments, siderite was fully replaced by hematite and cerianite after 7 days (Fig. 3). While in the equal concentration experiments, not all of the goethite transformed to hematite, in the PAAS solution, hematite and cerianite were the final phases formed. In both 165 and 205 °C experiments, the final amount of cerianite in the system was also higher in the PAAS solution experiments (18% compared to 2%, at 165 °C).

Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)

SEM imaging revealed the formation of precipitates on the surface of the siderite grains. The extent to which the newly formed precipitates covered and replaced the host grain was found to be time- and temperature-dependent. For example, at 50 °C, the surface of the siderite grains became fully covered by a thin (<2 μm) of goethite nanocrystals with flaky morphologies (Fig. 4). Minor amounts of kozoite with similar morphologies reported by Szucs *et al.* (2021),³⁵ Szucs *et al.* (2022)³⁶ and Maddin *et al.* (2024)³⁷ were also observed in images taken after 12 weeks in the equal concentration experiments (Fig. 4d), however, the amount was too small to be detected by XRD. At 165 °C, the newly formed phases consisted of triangular prisms of hydroxylbastnasite, pseudohexagonal prisms of hematite, and cubes and bipyramidal prisms of cerianite (Fig. 5).

SEM imaging also revealed that the early stages of hematite crystallization on the siderite surfaces were characterized by the formation of prismatic nanocrystals with diameters of ~150–200 nm (Fig. 6a and 7). Many of these nanocrystals exhibited

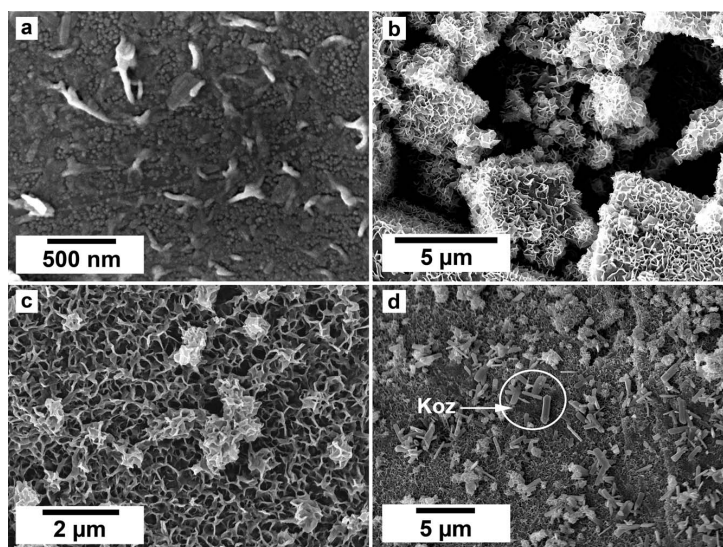


Fig. 4 The gradual and complete covering of siderite by a thin (<2 μm) layer of goethite at 50 °C after (a) 48 hours, equal concentration experiments, (b) 8 weeks, PAAS experiments, (c) 12 weeks, PAAS experiments, and (d) goethite and kozoite (koz) crystals after 12 weeks in equal concentration experiments.

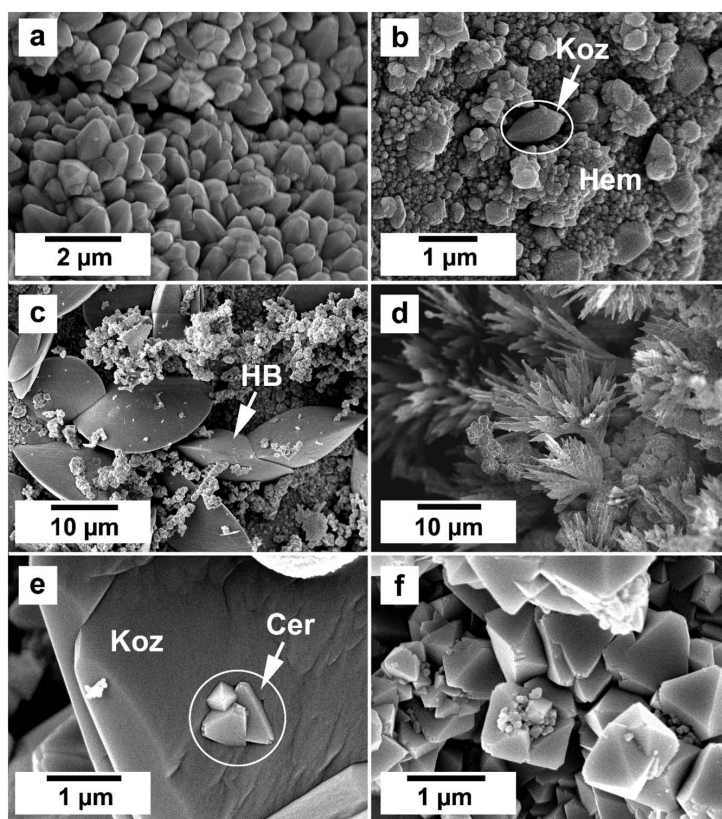


Fig. 5 (a) Hematite prisms covering the surface of siderite in equal concentration solution at 165 °C after 1 week; (b) kozoite prism on hematite in equal concentration solution at 165 °C after 24 hours; (c) hydroxylbastnasite in a matrix of cerianite and hematite in equal concentration solution at 165 °C after 24 hours; (d) hydroxylbastnasite dendrites in PAAS solution 165 °C after 24 hours; (e) cerianite growing on kozoite surface in equal concentration solution at 205 °C after 24 hours; (f) cerianite prisms in equal concentration solution at 205 °C after 1 week.

a transient, non-random orientation on the (104) face of siderite, indicative of epitaxial overgrowth (Fig. 8). Specifically, this hematite–siderite epitaxial relationship was defined by the parallel alignment of the crystallographic axes of the hematite to those of the underlying siderite substrate (Fig. 6b). However, once the hematite crystals grew and coalesced, this orientation was lost (Fig. 6c).

The EDS analyses of the cross section of the grains in the polished epoxy resin pucks revealed differences in spatial distribution of the REEs in the newly formed solids. The chemistry of the REE-bearing minerals was found to be dependent on the REE ratio in the initial aqueous solution, with a more homogenous distribution in the equal concentration solution (Fig. 9 and 10) and a more heterogenous distribution in the PAAS solution (Fig. 11). A preferential uptake of Nd and La with Ce in the PAAS solution was observed at 165 °C after 24 hours (SI-1 Line Analysis, ESI†), as well as Dy incorporation into the cerianite in the PAAS solution at 205 °C after 1 week (SI-2 ESI†), and in the equal concentration at 205 °C after 24 hours (Fig. 12). In general, the composition and ratio of the REE in the bastnasite and kozoite appeared to record the composition of

the original fluid phase (equal concentration and PAAS experiments; Fig. 13 and 14), with almost equal uptake of REEs in bastnasite (Fig. 10) and preferential uptake of La, Ce and Nd in kozoite (Fig. 11). In contrast, REE incorporation in the iron oxides was below the SEM-EDS detection limit, at <0.1%. (SI-3 ESI,† point analysis).

Discussion

The interaction of siderite with our REE-bearing aqueous solutions resulted in the initial dissolution of the host grain, releasing Fe^{2+} and CO_3^{2-} ions into the aqueous solution. As temperature increased, siderite broke down³⁸ and the aqueous Fe^{2+} ions then became oxidized and precipitated as iron oxides goethite and hematite. The CO_3^{2-} interacted with the REE in solution leading to the crystallisation of rare earth minerals kozoite and hydroxybastnaesite, which then subsequently transformed into the oxide cerianite due to the oxidation of Ce^{3+} . The resulting textures and mineralogy are consistent with the solvent-mediated surface precipitation and subsequent

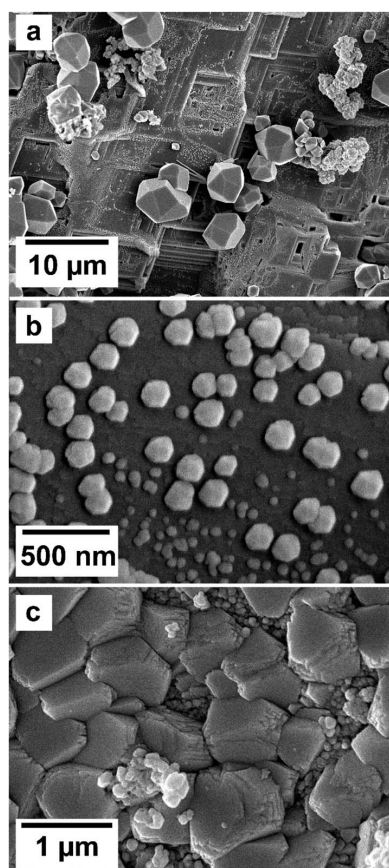


Fig. 6 Growth of hematite on siderite and epitaxial growth. (a) Hematite growing on the surface of siderite, forming μm -sized and nanocrystals on the surface of the host in equal concentration solution at 205 °C after 24 hours. (b) Hematite growing oriented on the surface of siderite in equal concentration solution at 205 °C after 24 hours. (c) μm -sized hematite coating the surface of siderite, showing a loss of their initial non-random orientation in equal concentration solution at 165 °C after 1 week.

pseudomorphic mineral replacement produced by the interaction of the hydrothermal fluids with the primary siderite.

The formation of iron oxides as a function of temperature and pH

Siderite is a ferrous mineral found in oxygen-free environments, such as lakes, rivers, and marine sediments.^{39–41} Its stability, dissolution, and the subsequent precipitation of iron oxides are temperature- and pH-dependent processes that significantly influence the kinetics of siderite breakdown.^{42–44} Ferrous iron in aqueous solutions readily reacts with dissolved oxygen, oxidizing to ferric iron (Fe^{3+}) and precipitating as iron oxides and/or oxyhydroxides such as goethite, hematite, magnetite, maghemite, and ferrihydrite.^{39,45,46}

Many studies have shown that a poorly-ordered nanoparticulate phase, two-line ferrihydrite, is a predominant precursor to several iron oxides.^{47–49} Under oxic conditions, two-line ferrihydrite gradually transforms to more thermodynamically stable phases, such as goethite and hematite.^{47,49} It was Bohm (1925)⁵⁰ who first demonstrated that an “amorphous $\text{Fe}(\text{III})$ hydroxide” rapidly transformed to pure goethite when maintained under 2 M KOH at 150 °C for 2 hours, whereas hematite was the main end product if the material was subjected to hydrothermal conditions.⁴⁸ This demonstrated that this ferrihydrite–goethite transformation is highly temperature- and pH-dependent. The rate of transformation of ferrihydrite is relatively slow at ambient temperature. For example, Schwertmann & Murad⁴⁸ recorded 19% of the initial concentration of ferrihydrite remained after 970 days at $\text{pH} \leq 6$. However, at a temperature of 92 °C, crystallization occurs faster, with hematite formation beginning within 10 minutes and a complete transformation occurring after 116 hours. Our experiments did not reveal the presence of ferrihydrite in the XRD patterns. However, we cannot fully disregard the possibility of its formation. Due to the rapidity of its transformation in the temperature and pH parameters of our experiments, we cannot discard the possibility that it may have been present as a transient phase during the very early stages of the reaction, quickly crystallising to the more thermodynamically stable goethite and hematite.

In our experiments, temperature significantly influenced the oxidation processes of siderite, affecting the kinetics, polymorph selection, and formation of chemical textures during the replacement reactions due to increased dissolution rates and differences in solubilities. At the lowest temperature of 50 °C, we recorded the initial dissolution of siderite and the crystallization of a thin layer of goethite that covered the entire surface of the siderite grain (Fig. 4). However, the transformation did not progress further once the siderite surface had been covered by goethite. Our PHREEQC calculations revealed that even during the earliest stages of dissolution of siderite ($\text{SI}_{\text{siderite}} = -15$), the aqueous solution can become supersaturated in goethite ($\text{SI}_{\text{goethite}} = +2.78$), showing that the dissolution of just a few monolayers of the siderite surface would result in a fluid boundary layer that would allow the crystallisation of this iron oxide. We propose that this coating of goethite on the siderite grains isolated the host from the aqueous solution, halting any further dissolution of siderite, and promoting a state of partial equilibrium^{36,51,52} which inhibited further recrystallisation and formation of REE carbonates. A similar result was observed by Yu *et al.*, 2023, 2024 who investigated the effects of dissolved oxygen (DO) concentrations on As(v) adsorption onto siderite. They found that while As(v) adsorption capacities increased with an increase in DO concentration, excess DO caused fast oxidation of siderite, constraining As(v) adsorption. This was due to the production of a coating of $\text{Fe}(\text{III})$ oxides on the surface of the pristine siderite that prevented any further oxidation of the host.^{53,54}

At 165 °C we observed an increase in the amount of goethite precipitation as well as its subsequent transformation to hematite (Table 1). Parallel to the Fe^{2+} oxidation processes we also observed the crystallisation of REE carbonates. The transformation of goethite to hematite is strongly influenced by

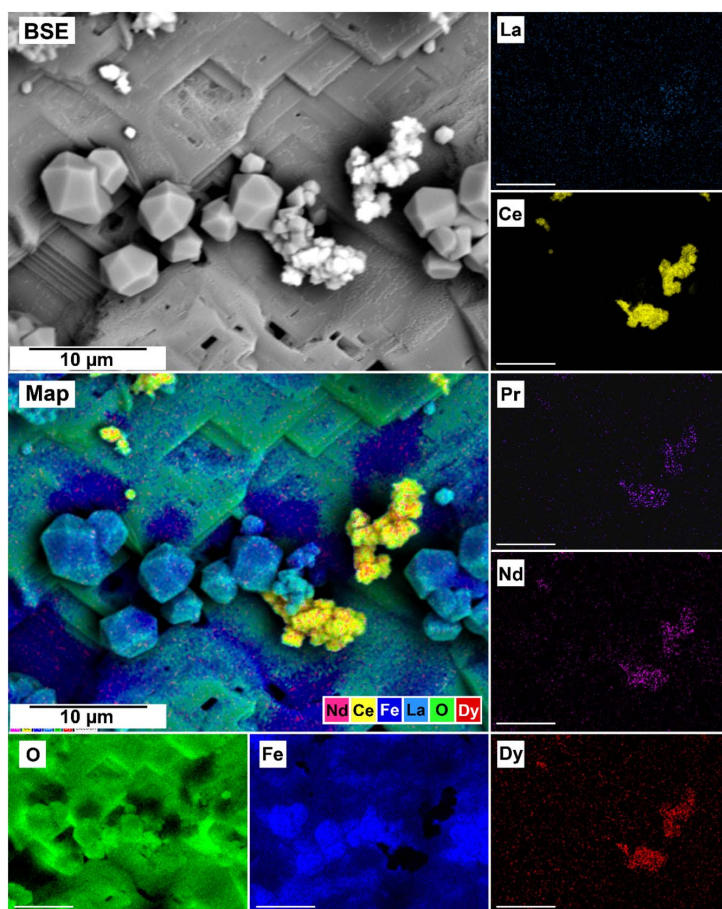


Fig. 7 Breakdown of siderite and subsequent detachment of the newly formed hematite and cerianite crystals in equal concentration experiments at 205 °C after 24 hours.

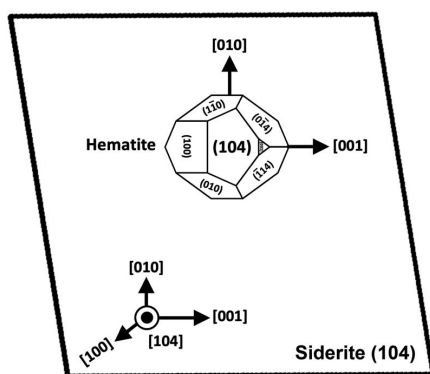


Fig. 8 Schematic diagram showing the epitaxial relationship between hematite and siderite crystals.

temperature and pH.^{55–58} It is known that the transformation from goethite to hematite can occur at temperatures ranging from 160–300 °C.^{48,57,59} There is also a relationship between temperature and pH, with faster transformation rates at higher temperatures coinciding with higher pH. For example, Das *et al.* (2010)⁴⁷ reported the formation of goethite and hematite at 50 °C and pH 2 after 7 days, while similar peak intensities were evident on after 5 days at pH 7 and after only after 21 hours at pH 10. Concomitantly, the transformation of goethite to hematite was also observed with extended reaction time. Hematite formation was also promoted at near neutral pH conditions, while goethite formation was favour acidic (~4) or highly alkaline (~12) conditions.^{47,48} This is consistent with the evolution of our experiments: Our REE solution had an initial pH of ~5.5, promoting the formation of goethite. As the siderite dissolved and REE carbonates formed, the pH gradually became more basic, moving towards a pH of ~8.2, promoting the transformation from goethite to hematite.

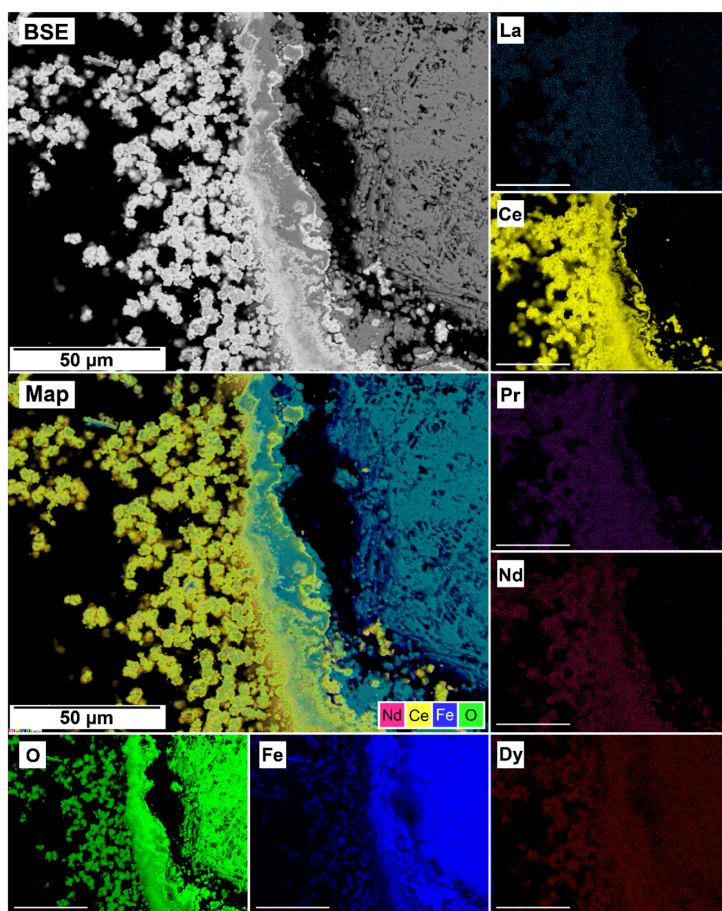


Fig. 9 SEM-BSE image of siderite fully replaced by hematite and cerianite at 205 °C after 1 week in equal concentration experiments and EDS maps of La, Ce, Pr, Nd, Dy, O, and Fe showing the homogenous distribution.

The solubility of siderite and the rate of its dissolution are highly dependent on temperature and pH. Bénézeth *et al.*, 2009 (ref. 60) investigated the solubility of natural siderite from 25 to 250 °C. Their experimental work showed that the values for $\log_{10} K_{\text{sp-siderite}}$ decrease with increasing temperature. For example, at 50 °C $\log_{10} K_{\text{sp-siderite}} = -10.19$ compared to $\log_{10} K_{\text{sp-siderite}} = -12.19$ at 200 °C. Concomitantly, and similar to other divalent cation carbonates, the dissolution rate of siderite decreases with an increase in pH. Golubev *et al.* (2009)³⁸ experimentally demonstrated that this decrease follows a linear trend, spanning approximately 1.5 orders of magnitude between pH 1 and 5. Furthermore, the dissolution rate is strongly temperature-dependent, exhibiting a variation of approximately 2 orders of magnitude between 25 and 100 °C. Taking the initial pH of the REE-bearing aqueous solution (5.1) into consideration, at 50 °C the solubility of siderite would be $\sim 10^{-10.0}$ – $10^{-11.1}$ mol cm⁻² s⁻¹ and at 100 °C the value would be $\sim 10^{-10.0}$ – $10^{-9.9}$ mol cm⁻² s⁻¹. Although no dissolution rates have been reported for temperatures above 100 °C, the observed

trend suggests that the dissolution rate would increase ~ 1.5 – 2.0 orders of magnitude at 200 °C.

At low pH values, particularly in acidic conditions (pH < 5), the dissolution of siderite is promoted due to the increased activity of hydrogen ions in the solution. The adsorption of H⁺ onto the mineral surface enhances the dissolution process, leading to higher concentrations of dissolved Fe²⁺ in the aqueous phase.⁶¹ Studies have shown that siderite dissolution rates increase significantly at pH levels around 2 to 5, where the mineral becomes more reactive.⁶¹ This increased dissolution can facilitate the release of Fe ions, which can subsequently precipitate as iron oxides such as magnetite or hematite, depending on the redox conditions present.⁶²

Conversely, at neutral to alkaline pH levels (pH ≥ 7), the solubility of siderite decreases, resulting in slower dissolution rates. In circumneutral conditions, the stability of siderite is enhanced, making it more resistant to dissolution.⁶³ In environments with circumneutral pH, siderite can persist due to the buffering capacity of the surrounding media, which limits the

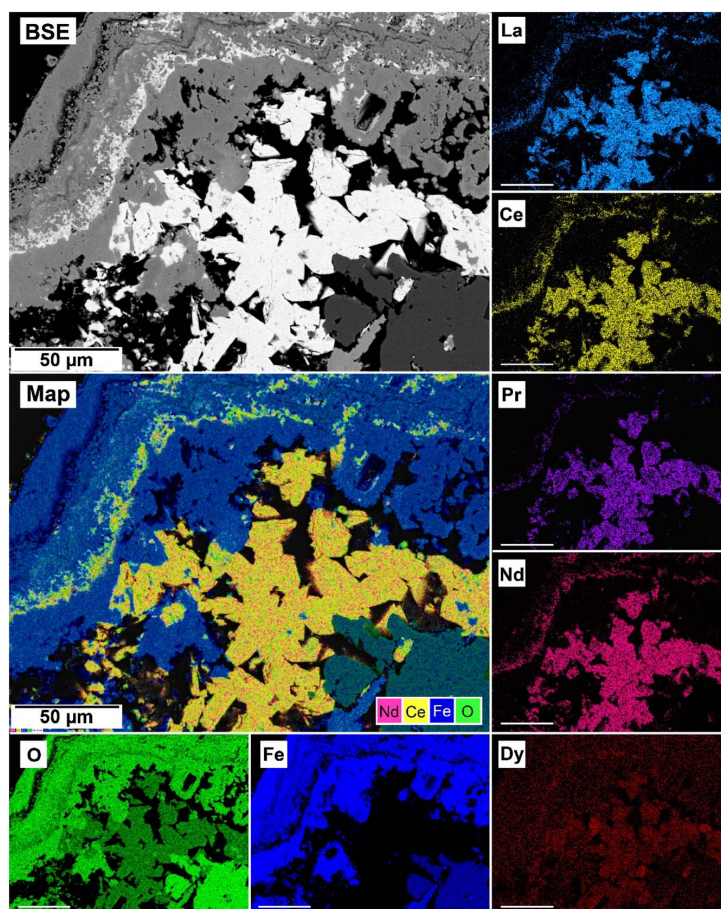


Fig. 10 Partial replacement of the siderite host with kozoite in equal concentration experiments at 165 °C after 24 hours.

availability of H^+ ions necessary for dissolution.⁶³ This resistance to dissolution can hinder the formation of iron oxides and REE-bearing minerals, as the necessary precursor ions may not be sufficiently available in the solution.

Furthermore, carbonate species HCO_3^- and CO_3^{2-} can also influence the dissolution kinetics of siderite. These species can act as inhibitors of dissolution at higher pH levels, as they compete with H^+ ions for adsorption sites on the mineral surface.⁶⁴ This competition can further reduce the rate of siderite dissolution and, consequently, the availability of iron for subsequent mineral formation.

The formation of REE-bearing minerals is also pH-dependent. In acidic conditions, the increased solubility of siderite can lead to higher concentrations of Fe^{2+} in solution. For example, the presence of dissolved REE in acidic brines can facilitate their incorporation into iron oxides precipitating from the dissolved siderite.⁶⁵ However, in neutral to alkaline conditions, the reduced dissolution of siderite limits the availability of Fe^{2+} , thereby slowing the formation of the iron oxide minerals.

Siderite–hematite epitaxial overgrowth

An interesting feature observed in the 165 °C experiments was the presence of oriented overgrowths of the newly formed hematite on the surface of siderite (Fig. 6). This epitaxial overgrowth is not unexpected, given that hematite and siderite share the same crystal system (trigonal) and space group ($R\bar{3}c$). Siderite has lattice parameters of $a = b = 4.6916 \text{ \AA}$, and $c = 15.3796 \text{ \AA}$,⁶⁶ while hematite lattice parameters are $a = 5.038 \text{ \AA}$ and $c = 13.772 \text{ \AA}$.⁶⁷ These structural similarities suggest a favourable fit for epitaxial growth (Fig. 15). The misfit values have been calculated using the expression:⁶⁸

$$mf(\%) = \frac{t_{[uvw]sub} - t_{[uvw]over}}{t_{[uvw]over}} \times 100$$

These can be used to quantify the degree of lattice mismatch between the epitaxial overgrowth and the substrate. In this expression, $t_{[uvw]sub}$ and $t_{[uvw]over}$ correspond to the repeating periods along the matching directions $[uvw]$ of the substrate (siderite) and the overgrowth (hematite), respectively (van der Merwe, 1978).⁶⁹

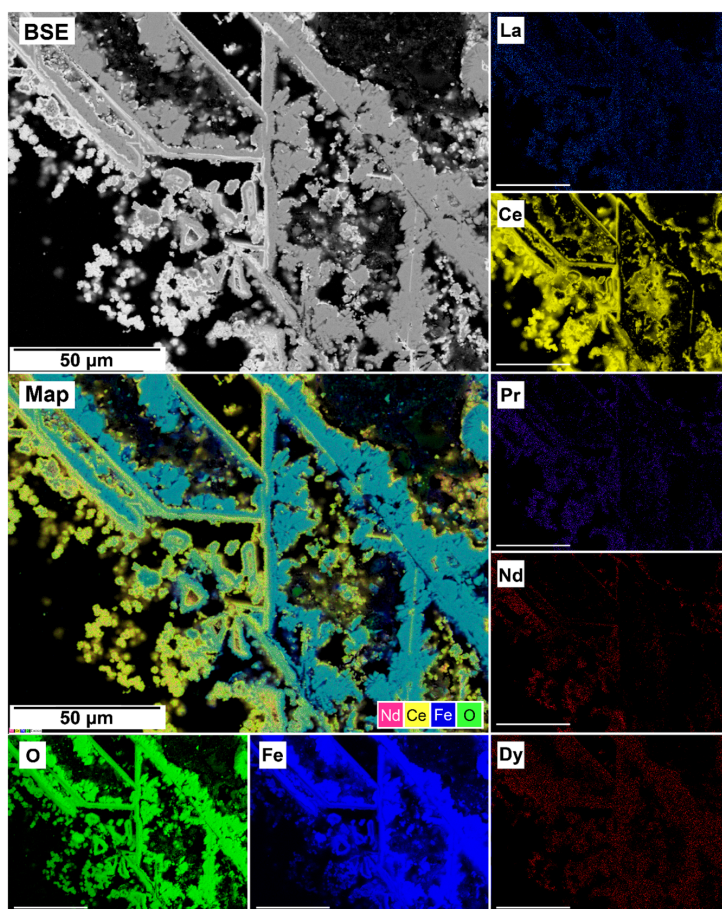


Fig. 11 SEM-BSE image of siderite grain fully replaced by hematite and cerianite at 205 °C after 24 hours in the PAAS experiments and EDS maps of La, Ce, Pr, Nd, Dy, O, and Fe showing the heterogenous distribution.

The calculated misfit values for the $(104)_{\text{sid}}[010]_{\text{sid}}\parallel(104)_{\text{hem}}[010]_{\text{hem}}$ and the $(104)_{\text{sid}}[001]_{\text{sid}}\parallel(104)_{\text{hem}}[001]_{\text{hem}}$ alignments are -6.93 and $+0.59\%$ respectively, falling well below the generally accepted limits (15–20%) required for epitaxial overgrowth to occur.⁷⁰ The negative value indicates that the unit cell of hematite is very slightly contracted along the $[010]$ direction of epitaxy of siderite, while the small positive value shows an almost perfect match (with a slight expansion) of the unit cell of goethite with respect to the siderite in the $[001]$ direction.

As hematite forms as a consequence of the hydrothermal alteration and Fe^{2+} to Fe^{3+} oxidation process, there are two factors that need to be taken into account: first is the slightly larger molar volume of hematite ($30.39 \text{ cm}^3 \text{ mol}^{-1}$)⁷¹ compared to siderite ($29.33 \text{ cm}^3 \text{ mol}^{-1}$)⁷¹ which is likely contributing to the loss of orientation once the hematite crystals grow and coalesce. Second is the dissolution and breakdown of siderite due to the hydrothermal replacement by REE carbonates and the Fe^{2+} to Fe^{3+} oxidation process, contributing to the

subsequent detachment of the newly formed hematite crystals from the host (Fig. 7). However, it is important to consider that although the ideal composition of pure siderite is FeCO_3 , this mineral is an end member of a complex solid solution (CaCO_3 – MgCO_3 – FeCO_3) and therefore can contain other divalent ions such as Ca^{2+} , Mg^{2+} or Mn^{2+} , alongside impurities such as Zn^{2+} , Co^{2+} , or Cd^{2+} .⁷² These chemical variations have the potential to influence the matching unit cells and subsequently impact the kinetics of siderite replacement processes, as well as the final solid morphology of hematite.

Formation of rare earth carbonates and their secondary replacement by cerianite

Our 165 °C experiments resulted in the partial replacement of the siderite host with the rare earth carbonates kozoite and hydroxylbastnasite (Fig. 10 and 13). The reaction sequence for REE carbonates was found to be time- and temperature-dependent,³⁷ with the initial formation of kozoite between 50 and

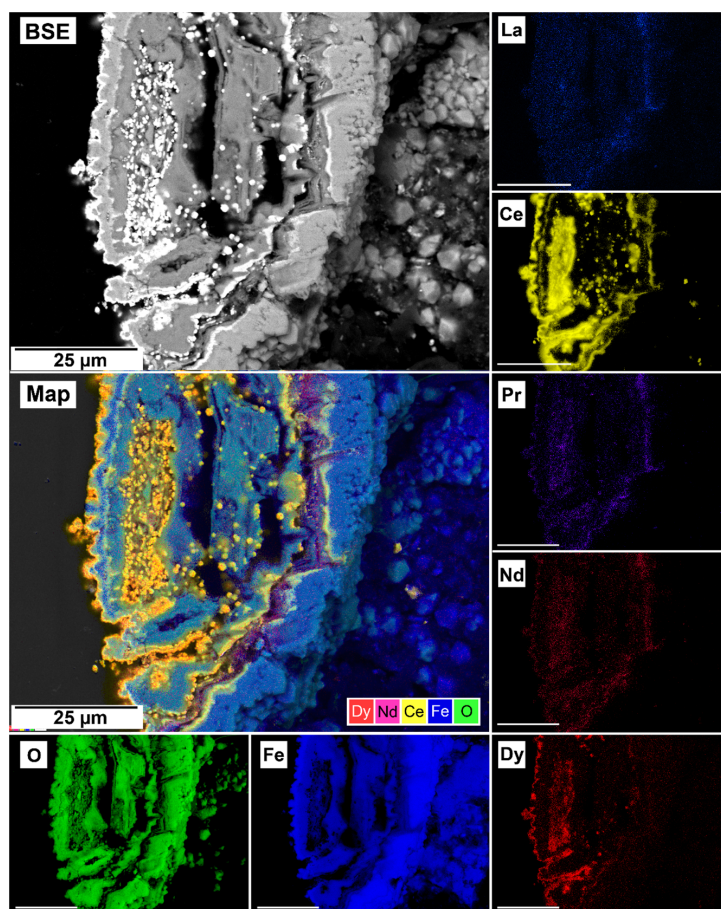
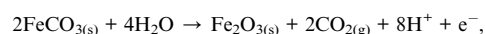


Fig. 12 Selected grain of siderite from an equal concentration experiments at 205 °C after 24 hours incorporation of Dy in cerianite as impurities.

165 °C and its subsequent transformation to the more stable hydroxylbastnasite at temperatures ≥ 165 °C. The rate of crystallization and composition of the REE-bearing phases is known to be controlled by the solubilities and dissolution rates of the host grain, the REE ratio in solution, as well as the evolving fluid composition during the replacement process.³⁷ The dissolution of siderite and its subsequent replacement from the periphery inwards was a consequence of the lower solubilities of REE carbonates compared to the siderite host. The solubility products for pure Nd-hydroxylbastnasite and Nd-kozoite have been calculated to be $\log(K_{sp}) = -23.8 \pm 0.1$ and $\log(K_{sp}) = -22.3 \pm 0.2$, respectively,³⁴ while the solubility product of siderite, $\log(K_{sp}) = -10.94 \pm 0.4$ (ref. 56) is much higher. Our PHREEQC calculations show that high supersaturation levels for kozoite and bastnasite ($SI > 1-3$) as well as cerianite ($SI > 11$) are reached when the REE-bearing solutions (equal concentration or PAAS) are equilibrated with siderite at 165–205 °C, also even if the solution has not fully reached saturation for the host. Siderite dissolution rates have also been shown to increase with

temperature.³⁸ Besides, the siderite transformation to hematite due to the Fe^{2+} to Fe^{3+} oxidation,



was translated into the release of CO_2 and therefore in the gradual acidification of the aqueous solution, which promoted the subsequent dissolution of all carbonates after 1 week in equal concentration experiments and 24 hours in PAAS experiments (Table 1).

Point analysis of the EDS maps showed that the uptake and incorporation of the REE in the newly formed carbonates was dependent on the initial concentration in solution. In the equal concentration experiments, the uptake of REE by the crystallising carbonate occurs in the same ratio as their composition in the aqueous solution, indicating that the crystallising carbonate mirrors the REE composition of the surrounding solution ($SI-4^\dagger$). Conversely, in the PAAS solution experiments, the REE ratio is different compared to the equal concentration,

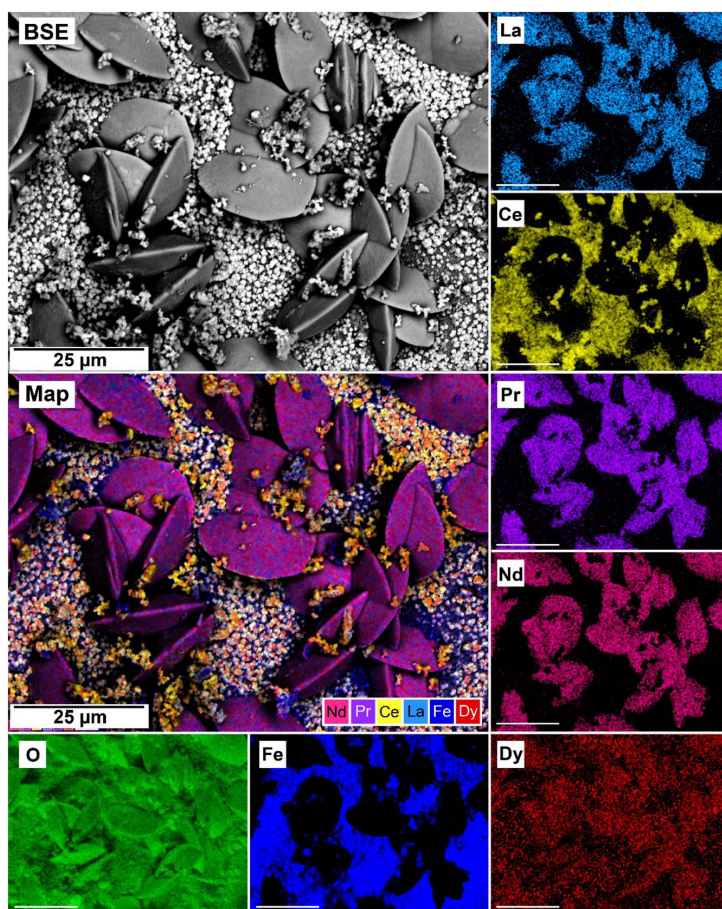
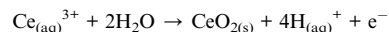


Fig. 13 SEM-BSE image of siderite grain being replaced with bastnasite in the equal concentration experiments at 205 °C after 24 hours and EDS maps showing the almost homogenous distribution of REE.

but still reflects the higher concentration of La, Ce, and Nd in the original solution (SI-4†). On one hand, this aligns with the typical composition of the REE carbonates bastnasite and kozoite. Bastnasite has a hexagonal structure that tends to uptake the light REE (La to Nd) which are in a 9-fold coordination with oxygen,^{17,73} with the heavier Dy only entering as impurities. Heavier REE could potentially be incorporated into the bastnasite structure, however, this would require higher pressure conditions that are outside of our experimental range. In contrast, the intermediate phase kozoite is orthorhombic and it can include both lighter and heavier REE,¹⁷ perfectly accommodating Dy. On the other side, the mirroring of the REE ratios of the initial aqueous solution (equal concentration and PAAS experiments) could be explained by assuming that kozoite and bastnasite are both primary phases forming in their respective reactions and have not formed *via* metastable intermediate precursors (*e.g.*, lanthanite and tengerite; Vallina *et al.*, 2015;¹⁷ Szucs *et al.*, 2021;³⁵ Szucs *et al.*, 2022).³⁶ This would also

explain why we did not observe any zoning in the REE carbonates as reported in Maddin *et al.*, (2024).³⁷ At 205 °C siderite was fully replaced by hematite and the rare earth carbonates by cerianite. The solution-mediated oxidation of Ce^{3+} to Ce^{4+} initiates cerianite, as described by this reaction:



The oxidation of Ce^{3+} to Ce^{4+} is triggered by several factors. First, Ce^{4+} has the electron structure of a noble gas, making it more stable than Ce^{3+} , and the higher temperatures provide the energy needed to facilitate the loss of an electron. Second, as stated earlier, as our system progressed towards equilibrium, the pH would increase from ~ 5 towards ~ 8.2 . The higher concentration of OH^{-} ions allow the formation of Ce-hydroxo-complexes which facilitate the Ce^{3+} to Ce^{4+} oxidation process,⁷⁴ especially at the surface–solution interface of the REE minerals.⁷⁵ As Ce^{4+} is incompatible within the carbonate

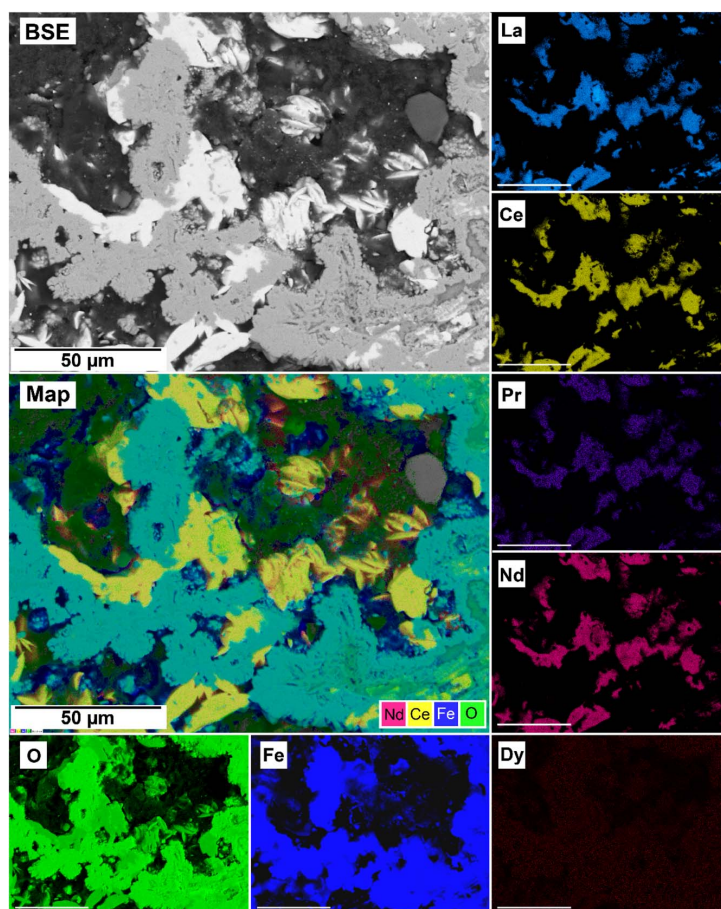


Fig. 14 SEM-BSE image of siderite grain being replaced with kozoite in PAAS solution at 165 °C after 24 hours and EDS maps showing the almost heterogenous distribution of REE.

structure, it combines with oxygen, forming the cerianite (CeO_2) oxide.

Our experimental data shows that the Fe^{2+} to Fe^{3+} oxidation initiated prior to the Ce^{3+} to Ce^{4+} oxidation process, revealing a lower energy barrier required for the former compared to the later under our experimental conditions. However, both processes happened simultaneously during most of the duration of the experiment. As both oxidation processes progressed, the pH lowered, dissolving the host and the REE carbonates. At the end of the reaction, the only REE remaining in solid-state was Ce in the cerianite, as well as a small amount of Dy present as impurities in the structure of cerianite. Our experimental design (sealed hydrothermal reactors containing a limited atmosphere, under conditions of autogenous pressure) created an oxidizing environment that favoured the oxidation of Ce^{3+} to Ce^{4+} reaction. Had our experiments been conducted using anoxic water and a pure N_2 atmosphere, the presence of carbonates such as siderite would have also

buffered the pH of the aqueous solution, increasing the stability of the HCO_3^- ions relative to CO_2 . However, these changes would not have a significant influence on the redox state and the formation of Fe and Ce oxides (goethite, hematite and cerianite) would most likely not have occurred. Consequently, Ce would have been incorporated into the newly formed kozoite and bastnasite as Ce^{3+} along with the other REEs in the system. However, in the studied conditions, Ce had a significant impact of the kinetics of the replacement reactions, showing that the rate of decarbonation is dependent on the ratio of Ce relative to other REE in solution. In the PAAS solution, where Ce is dominant compared to the other REE, the higher concentration of Ce leads to a faster release of CO_2 , resulting in quicker decarbonation and dissolution of all the carbonates. Consequently, the full decarbonation process can occur in less than 24 hours. In contrast, in the equal concentration experiments (where REE are present in equal concentrations) all carbonates dissolved after 24 hours.

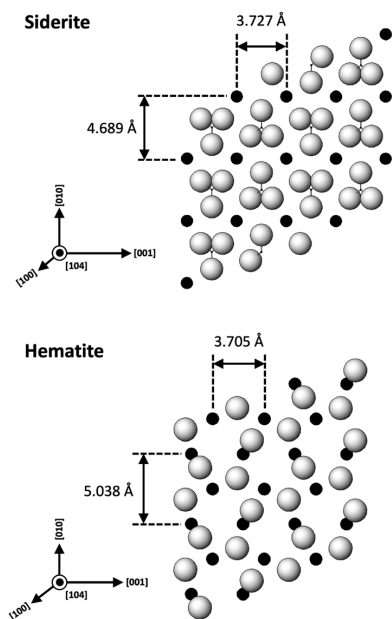


Fig. 15 Projection of the atomic structures of a (104) slices of hematite and siderite showing the main directions of epitaxy and repeating periods.

The replacement of kozoite and bastnasite is also enhanced by the smaller molar volume of cerianite ($23.86 \text{ cm}^3 \text{ mol}^{-1}$) compared to kozoite ($45.59 \text{ cm}^3 \text{ mol}^{-1}$) or bastnasite ($44.91 \text{ cm}^3 \text{ mol}^{-1}$) which increased the porosity of the parent phase.⁷¹ This porosity helps maintain supersaturation levels at the carbonate–solution interface, allowing the replacement reaction to continue and releasing REE back into the solution. Some REE, such as Dy^{3+} and Nd^{3+} , have ionic radii similar to Ce^{4+} and can be incorporated into cerianite as impurities. Depending on the Ce concentration in the fluid, the crystallization of cerianite could trigger the formation of symplectic textures, as described by Maddin *et al.* (2024).³⁷ In these textures, cerianite grows into the nanometer-sized pores created by the dissolution of the REE carbonate.⁷⁶ Fig. 9 and 14 may indicate the early development of these symplectic textures at the nanoscale.

In natural systems, REE-bearing-carbonatites form through the immiscibility of carbonate–silicate magma and through the fractional crystallization of carbonate minerals from carbonate magma. The REE form complexes and the magmatic hydrothermal system enables their migration. REE circulation is further promoted by fractures in the deposit, which also provide the space necessary for REE-mineral precipitation. Our hydrothermal replacement experiments in REE-aqueous solutions offers insight into the potential mechanisms and conditions needed for the possible formation of REE-minerals. The differences in molar volumes observed in our experiments, along with the increasing porosity they created, can be correlated to the fractures found in natural ore

deposits. As many of the world's carbonatites also host hematite-bearing ores, the use of siderite as our reactant was ideal. The REE uptake by the iron oxides formed was negligible in our experiments; however, further investigation into the use of oxidation processes to separate Fe from REE-bearing ores could have significant potential for improving ore processing techniques and enhancing the economic viability of mining operations.

Conclusion

The interaction between siderite and multi-component rare earth element (La, Ce, Pr, Nd and Dy) – bearing aqueous solutions resulted in the formation of iron oxides, goethite ($\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$) and hematite (Fe_2O_3), metastable REE-bearing minerals kozoite ($\text{REE}(\text{CO}_3)(\text{OH})$) and bastnasite ($\text{REE}(\text{CO}_3)(\text{OH}, \text{F})$), and the rare earth oxide cerianite (CeO_2). The newly formed phases were the consequence of two oxidation processes, Fe^{2+} to Fe^{3+} , promoting goethite and hematite crystallisation, and Ce^{3+} to Ce^{4+} , resulting in cerianite formation. Both processes were found to be highly dependent on temperature. At low temperatures, the formation of REE carbonates was inhibited due to a coating of goethite layer that isolated the siderite and created a situation of partial equilibrium. At higher temperatures, the dissolution of siderite was promoted and differences in solubility allowed for the formation of kozoite and bastnasite. However, the continuing oxidation processes acidified the solution, initiating the dissolution of all carbonates and resulted in hematite and cerianite being the final phases in our system.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest.

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Nanophase REE phosphate crystallization induced by vivianite oxidation: mechanistic insights and mineralogical implications†

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Our study investigates the interaction between multi-component rare earth element (REE; La, Ce, Pr, Nd, Dy)-bearing aqueous solutions and vivianite ($\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) grains under hydrothermal conditions (50–165 °C). The results revealed the solution-mediated, progressive oxidation and dissolution of vivianite. This resulted in the formation of iron phosphates, metavivianite [$\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$], and giniite [$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{PO}_4)_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$], iron oxide hematite [Fe_2O_3], and rare earth phosphates, rhabdophane [$\text{REE}(\text{PO}_4) \cdot \text{H}_2\text{O}$] and monazite [(LREE) PO_4]. The extent of the reactions was found to be dependent on temperature, pH, and the concentration and ionic radii of the rare earths in solution. The rate of vivianite oxidation and dissolution increased with increased temperature, with 50% of vivianite transformed after 32 days at 50 °C, and 100% transformed after 28 days and 4 hours at 90 and 165 °C respectively. The pH of the solutions at all three temperatures maintained the stability of rhabdophane, and only at the highest temperature of 165 °C it began to transform to monazite. Understanding the stability of iron phosphates, their transformation products, and their capacity to incorporate REEs is crucial for resource recovery, especially in the extraction of REEs from waste materials.

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Introduction

Phosphate rocks are considered to be an essential resource as they provide the raw material for phosphoric acid and fertilizers utilized in agriculture, thereby contributing to the sustainability of the world's food supply. They are also gaining increased interest as a potential rare earth element (REE) source.¹ With their unique optical, magnetic, and catalytic properties, REEs are becoming more and more essential in modern technologies and are considered critical metals.^{2,3} However, as minable concentrations of REEs are limited, there is a substantial risk to their supply and availability.⁴ REE deposits that contain iron phosphates are of significant interest due to their potential economic value and strategic importance. One example is the Mount Weld carbonatite deposit in western Australia, which has been identified as a secondary rare earth phosphate deposit where phosphates, such as monazite, are enclosed within iron oxide minerals.^{5,6} The deposit, which is enclosed within a weathering cap of an intrusive plug⁷ and contains an average REE grade of 9.8 wt% $\sum \text{REE}_2\text{O}_3$ and REE concentrations up to

45 wt% $\sum \text{REE}_2\text{O}_3$, is now considered one of the richest deposits in the world.⁸ Phosphorite-type rare earth deposits, such as the early Cambrian Zhijin phosphorite, China, are also known for their high concentrations of REEs including yttrium (REEY),⁹ as well as heavy REE enrichment.¹⁰ During its formation, which was initiated by the breakup of supercontinent Rodinia, the local reducing environment promoted the release of REEY from hydroxides which dramatically increased the concentration of REEY in the seawater. As the supercontinent continued to break apart, there was an upwelling of hydrothermal fluids which carried phosphorous-rich materials. The upwelling processes contributed to the reducing environment and concomitantly to the dissolution of REEs. The upwelling currents carried the P- and REE-rich complexes to the upper oxidising surface waters, where they were able to mix and form REEY-rich apatite.⁹ Studies have also shown a correlation between REE distribution and phosphorous in sedimentary phosphate deposits,¹¹ with particular interest in the microdistribution of REEs in specific mineral phases and their locations. Further analysis of the Zhijin deposit by Xiong *et al.* (2024) revealed that the REE distribution was highly correlated with that of phosphorous and that they occur as lattice defects in apatite *via* isomorphic substitution. Lastly, an association of Fe with P and REEs has been observed in high-P ooidal iron ores, with some of the largest resources located in Morocco.¹ Current research indicates that their formation is linked to large igneous provinces, upwelling, marine hypoxia, and rifting.^{12,13} The recent discovery

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by the state-owned Swedish mining company LKAB of a significant REE deposit in the Kiruna iron ore mine in north Sweden has the potential to provide a substantial REE source for Europe. LKAB has reported mineral resources of rare earth metals exceeding one million tonnes of oxides, making it the largest known deposit of its kind in Europe. The rare earths at Kiruna occur together with phosphorous in apatite in an iron ore deposit.

In order to better understand the relationship and mineralization pathways between iron phosphates and REEs we chose to react the mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) with multi component REE-bearing aqueous solutions at hydrothermal conditions. Vivianite is a common Fe(II)-phosphate mineral found globally in marine, freshwater, and terrestrial systems.¹⁴ Its formation in natural deposits is a complex process influenced by redox conditions, sedimentary deposits, porewater interactions, and the presence of key elements such as Fe, P and S. The aim of this study is to investigate whether the interaction of vivianite with rare earth-bearing aqueous solutions would lead to the various processes and/or transformations such as dissolution–recrystallization and oxidation. With REEs present in the aqueous solution, their interaction with vivianite has the potential to result in the formation of rare earth phosphate compounds or solid-solutions. These reactions could involve the precipitation of rare earth phosphates or the incorporation of REEs into the crystal structure of vivianite. It is well known that vivianite has the capability to uptake elements from aqueous solution.¹⁵ Therefore, the interaction between vivianite and REEs in aqueous solution could potentially lead to the adsorption or complexation of the REEs onto the vivianite surface.³ The formation of such compounds could impact the speciation and mobility of the REEs in the aqueous solution. Further research into the specific mechanisms and outcome of these interactions could provide valuable insights into the behaviour of REEs and iron phosphates in natural aquatic and hydrothermal environments. The replacement of iron phosphates by REE-phosphates like rhabdophane, monazite or xenotime would have important implications for resource recovery, particularly in the context of REE from waste materials. Transforming iron phosphates into stable rare earth phosphates can significantly enhance the recovery of economically valuable REEs from sources such as industrial waste and contaminated soils, supporting their critical role in high-tech and green energy industries.

Methods

The interaction of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) grains with multi-component REE (La, Ce, Pr, Nd, Dy) aqueous solutions was investigated at hydrothermal conditions (50–165 °C). Vivianite crystals were crushed in a ceramic mortar and sieved to extract 0.5–1.0 mm clasts. Five single REE bearing solutions were prepared, La, Ce, Pr, Nd and Dy, with a total concentration of 50 mM. These solutions were produced *via* the dissolution of single REE nitrate salts, $\text{REE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.9% purity), in de-ionized water (18.18 MΩ cm). These five specific REE were chosen as they are representative of both light (La, Ce, Pr, and Nd) and heavy (Dy) REE. This group of REE from

La to Dy also represent 72% of the ionic radii of the lanthanides as well as being some of the most abundant REE in the Earth's crust.¹⁶ To better understand the effect of ionic radii of the five REEs and to what extent these ions are taken up by the vivianite host, two different sets of experiments were conducted, one with equal concentrations of the five REEs and one with the concentrations of the five REEs normalized to the commonly used Post Archean Australian Shale standard (PAAS),¹⁷ to mimic the REE concentrations found in continental crust and in natural geological fluids. For the equal concentration experiments, 4 mL of each of the five REEs were used to give a total solution volume of 20 mL for each experiment. For the PAAS experiments, a 1 L bulk solution was made and 20 mL of this was used for each experiment.

For each experiment, 0.1 g of vivianite grains were added to 20 mL of each of the 50 mM REE-bearing solutions and placed in 25 mL Teflon-lined and capped stainless-steel autoclaves. The reactors were then placed in a pre-heated oven at 50, 90, and 165 °C. Solid samples were then extracted using a sterilized metal spatula at increasing time intervals from 4.5 hours to 7 weeks. The samples were then placed in plastic Eppendorf tubes and dried in a 30 °C oven for at least one hour.

In order to identify and quantify the formation of crystalline solids present in our samples, several grains were selected from each experiment ensuring that each time and temperature variable was represented. The selected grains were ground to a consistently fine powder using an agate pestle and mortar. The minerals were identified and quantified with powder X-ray diffraction (XRD). Conventional powder XRD patterns were collected using a Siemens/Bruker D5000 powder X-ray diffractometer (Cu K α radiation, 0.01° per step from 5 to 60° 2 θ at 0.2° min^{−1}; 4.5 hours scans per sample). Identification of crystalline phases was carried out with the DiffraSuite EVA software from Bruker in combination with the Powder Data File (PDF-4, the International Centre for Diffraction Data).¹⁸ Pattern-matching refinement and quantification of crystalline phases were carried out with the Rietveld refinement software TOPAS.¹⁹ Finally, scanning electron microscopy (SEM) was used to obtain high resolution images to characterize changes in the morphology of the vivianite host grains and identify newly formed phases. Analyses were conducted in the iCrag Lab at Trinity College Dublin using a TIGER S8000 FEG-SEM operating under high vacuum conditions and equipped with two Oxford X-Max 170 mm² EDS detectors and an X4 pulse processor running the Oxford Aztec analysis software.

Saturation indexes of solid phases during the equilibration of the REE-bearing aqueous solutions with respect to vivianite were calculated with the hydrogeochemical code PHREEQC²⁰ using the LLNL database and the solubility products of REE-bearing phosphates and Fe oxides determined by.²¹

Results

Analysis of all solid samples obtained from the replacement reactions showed the formation of surface precipitates that either partially or totally replaced the vivianite host grain. The combination of powder X-ray diffraction (XRD), scanning

electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) allowed us to identify and quantify the newly formed phases and interpret the mechanisms responsible for the alteration and decomposition of vivianite and the precipitation of the newly formed phases.

Powder X-ray diffraction (XRD)

The interaction between vivianite and multi-component rare earth element (La, Ce, Pr, Nd and Dy)-bearing aqueous solutions resulted in the formation of iron phosphates, metavivianite ($\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$; PDF 00-030-062) and giniite ($\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{PO}_4)_4(\text{OH})_2 \cdot 2\text{H}_2\text{O}$; PDF 00-033-0669), iron oxide, hematite (Fe_2O_3 ; PDF 00-013-0534), and rare earth phosphates, rhabdophane ($\text{REE}(\text{PO}_4) \cdot \text{H}_2\text{O}$; PDF 00-035-0614) and monazite ($(\text{LREE})\text{PO}_4$; PDF 00-029-0403) (Fig. 1). Full quantitative data is available in Table 1.

The extent of the replacement reaction was found to be time and temperature dependent. At 50 and 90 °C we observed the gradual transformation of vivianite to metavivianite and the subsequent precipitation of rhabdophane (Table 1). At 90 °C the

formation of giniite was recorded after 28 days. At 165 °C, the vivianite to metavivianite transformation was not observed due to the extremely fast transformation rate, and all of the host vivianite recrystallizing in less than 4 hours.

The observed mineralogy was also found to be temperature- and REE ratio-dependent. At 50 °C, transformation of vivianite to metavivianite proceeded at a faster rate in the equal concentration solutions compared to the PAAS solution. For example, 28% of the vivianite was consumed after one day in the equal concentration compared to 12% in the PAAS solution. At the end of the experiment (32 days), 60% of the vivianite had been consumed in the equal concentration solution compared to 45% in the PAAS solution.

At 90 °C, transformation of vivianite to metavivianite was slower compared to 50 °C, with less than 1% of vivianite consumed in the first 2 days. However, in contrast to the 50 °C experiments, it was observed that the PAAS solution experiments progressed at a slightly increased rate with 9% of vivianite consumed after 5 days compared to less than 1% in the equal concentration solution. There were also minor amounts of rhabdophane (1–4%) precipitation in the early stages (1–5 days) of the PAAS solution experiments compared to no rhabdophane detected in the equal concentration experiments after the same time.

At 165 °C, the initial solution concentrations played a less critical role. Similar consumption rates (<4 hours) of vivianite were recorded in both equal concentration and PAAS solutions. The subsequent transformation of vivianite to metavivianite, giniite and hematite as well as the precipitation of rhabdophane and its transformation to monazite occurred almost in parallel when comparing the equal concentration and PAAS solution experiments.

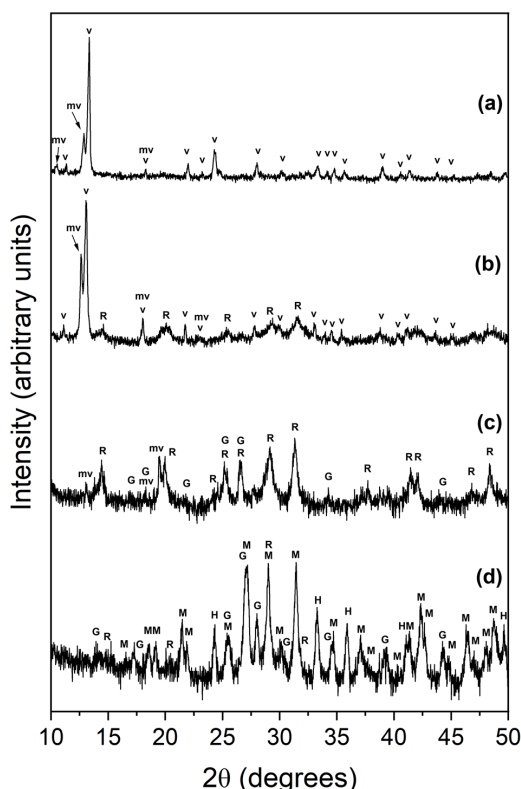


Fig. 1 Powder XRD diagrams from samples obtained at (a) 50 °C equal concentration experiments, 24 hours; (b) 50 °C, equal concentration experiments, 32 days; (c) 90 °C, PAAS experiments, 28 days; (d) 165 °C PAAS experiments, 1 week. Bragg peaks have been assigned to the following phases: vivianite (v), metavivianite (mv), rhabdophane (R), giniite (G), monazite (M), hematite (H).

Scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS)

SEM imaging revealed the formation of crystalline phases on the surface of the vivianite grains. These newly formed phases were observed as surface precipitates that partially or fully covered the vivianite host grains. In some experiments, vivianite was fully replaced from the periphery inwards (Fig. 2). SEM photomicrographs showed that metavivianite initially formed in the dissolution pits of vivianite (Fig. 4a and b) and consisted of acicular aggregates with individual needles not exceeding lengths larger than 1 μm and thicknesses of ~50 nm. At 50 °C the crystals looked acicular (Fig. 3a–c), at higher temperatures their morphology during the early stages of crystallization consisted mainly of clusters of irregular flakes with random orientation. At 50 °C we also observed the growth of nanometric flakes and acicular crystals of rhabdophane on the surface of metavivianite (Fig. 3d–f). The rhabdophane crystals were needle-like and sometimes formed a radiating pattern around a central point. However, these showed a less than perfect symmetrical orientation resulting in a slightly irregular, but still overall radiating appearance (Fig. 3e and f). Each individual crystal from the radiating structure had a length < 1 μm and a thickness of no more than 100 nm. At 90 °C we observed the growth of giniite crystals along with metavivianite on the

Table 1 Experimental conditions, identities and morphologies of the solid iron phosphates and iron oxides formed during the interaction of vivianite with multi-component (La, Ce, Pr, Nd, and Dy) REE-bearing aqueous solutions (equal concentration and PAAS experiments) at 50, 90, and 165 °C^a

Equal concentration					PAAS			
T (°C)	Time (days)	% phase consumed	Phase formed	Morphology	Time (days)	% phase consumed	Phase formed	Morphology
50	1	28	Metavivianite	Bladed flaky crystals	1	12	Metavivianite	Bladed flaky crystals
	3	30	Metavivianite		3	21	Metavivianite	
	9	16	9% metaviv., 7% rhab.	Metaviv: bladed flaky crystals rhab: flakes & needle-like	9	44	32 metaviv., 12 rhab.	Metaviv: bladed crystals, rhab.: flakes & needle-like
	18	47	13% metaviv., 34% rhab.		18	21	<1% metaviv., 21% rhab.	
	25	57	31% metaviv., 27% rhab.		25	33	<1% metaviv., 33% rhab.	
	32	60	24% metaviv., 36% rhab.		32	45	3% metaviv., 42% rhab.	
90	1	<1%	Metavivianite	Bladed flaky crystals	1	1	<1% metaviv., <1% rhab.	Metaviv: bladed flaky crystals, rhab.: flakes & needle-like
	2	<1%	Metavivianite		2	1	<1% metaviv., <1% rhab.	
	5	<1%	Metavivianite		5	9	5% metaviv., 4% rhab.	Metaviv: bladed flaky crystals, rhab.: flakes, needle-like & nano-spherulites
	28	100	64% rhab., 32% giniite, 4% monz.	Rhab: flakes & nano spherulites gin.: polygonal prisms, monz.: polygonal composite prisms	28	100	5% metaviv., 57% rhab., 38% giniite	Metaviv: bladed flaky crystals, rhab.: flakes, needle-like & nano-spherulites
	0.2	99	94% giniite, 4% rhab., 2% hema.	Gin.: polygonal prisms; rhab. flakes & nano spherulites hema. nm polygonal prism aggregates	0.2	100	81% giniite, 16% rhab., 3% hema.	Gin.: polygonal prisms; rhab: flakes & nano spherulites, hema.: nm polygonal prism aggregates
	2	100	85% giniite, 10% rhab., 3% hema., 2% monz.	Gin.: polygonal prisms flakes & nano spherulites hema.: nm polygonal prism aggregates monz.: polygonal composite prisms	2	100	74% giniite, 5% rhab., 7% hema., 13% monz.	Gin.: polygonal prisms flakes & nano spherulites, hema.: nm polygonal prism aggregates, monz.: polygonal composite prisms
165	7	100	50% giniite, 11% rhab., 19% hema., 20% monz.	Gin.: polygonal prisms flakes & nano spherulites hema.: nm polygonal prism aggregates monz.: polygonal composite prisms	7	100	40% giniite, 8% rhab., 19% hema., 33% monz.	Gin.: polygonal prisms flakes & nano spherulites hema.: nm polygonal prism aggregates monz.: polygonal composite prisms

^a Metavivianite (metaviv.), rhabdophane (rhab.), giniite (gin.), monazite (monz.), hematite (hema.).

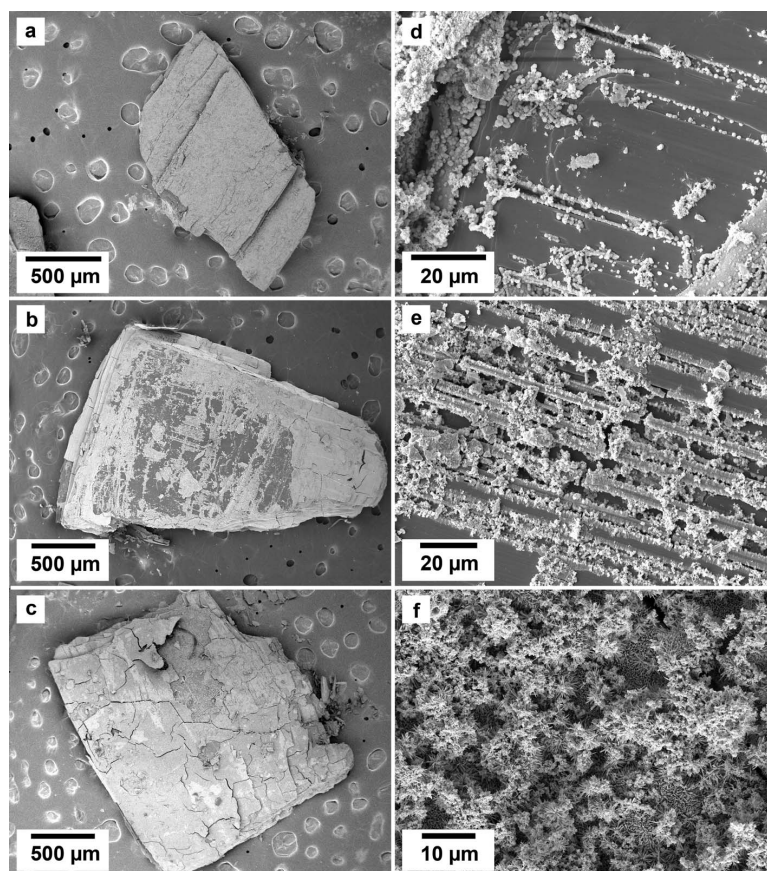


Fig. 2 SEM micrographs of the surface of vivianite grains exposed to equal concentration REE-bearing solutions at 50 °C showing (a–c) the surface appearance due to the replacement of the vivianite by newly formed crystals; images (d–f) show details of the micro- and nanocrystalline materials gradually covering the host grain.

surface of vivianite (Fig. 4c and d). The giniite crystals consisted of individual equant polygonal prisms with sizes between 600 nm and 2 μm. At 165 °C nanorods of rhabdophane began to cover the surface of giniite (Fig. 5a), sometimes forming spherulitic-type structures (Fig. 5b and c). Nanocrystals of hematite were also observed on the surface of rhabdophane. These consisted of nm polygonal prism aggregates with sizes < 200 nm (Fig. 5d). Finally, monazite presented as elongated composite prisms with polygonal consisting of acicular or flaky subunits. These subunits were aligned parallel or subparallel to the prism's elongation, giving the overall crystal a textured or layered appearance. The subunits had lengths between 500 nm and 2 μm and created a fibrous or platy surface on the prism's faces, reflecting their acicular or flaky nature (Fig. 5e and f).

SEM-EDS maps showed relatively homogenous uptake of the five REEs in the equal concentration solution experiments (ESI – Image 1†). In contrast, in the PAAS solution experiments the uptake of REE reflect their original concentration in the aqueous solution, with higher concentrations of La, Ce, and Nd (ESI – Image 2†).

Discussion

The dissolution of vivianite and the subsequent formation of iron phosphates metavivianite and giniite, iron oxide hematite and REE-phosphates rhabdophane and monazite were the result of three simultaneous processes: (i) the solution-mediated oxidation of vivianite during its dissolution, coupled with the formation of secondary iron phosphates, (ii) the replacement of the iron phosphates by REE phosphates, and (iii) REE phosphate mineral transformation reactions. In fact, all three processes were mediated by the aqueous solution, with pH, temperature, and the ionic radius of the rare earths present in solution, playing key roles in the extent and rate of the replacement reactions.

The progressive and concurrent oxidation and dissolution of vivianite

Under oxic conditions, vivianite is unstable, and structural Fe^{2+} oxidizes rapidly to Fe^{3+} . While the vivianite crystal structure

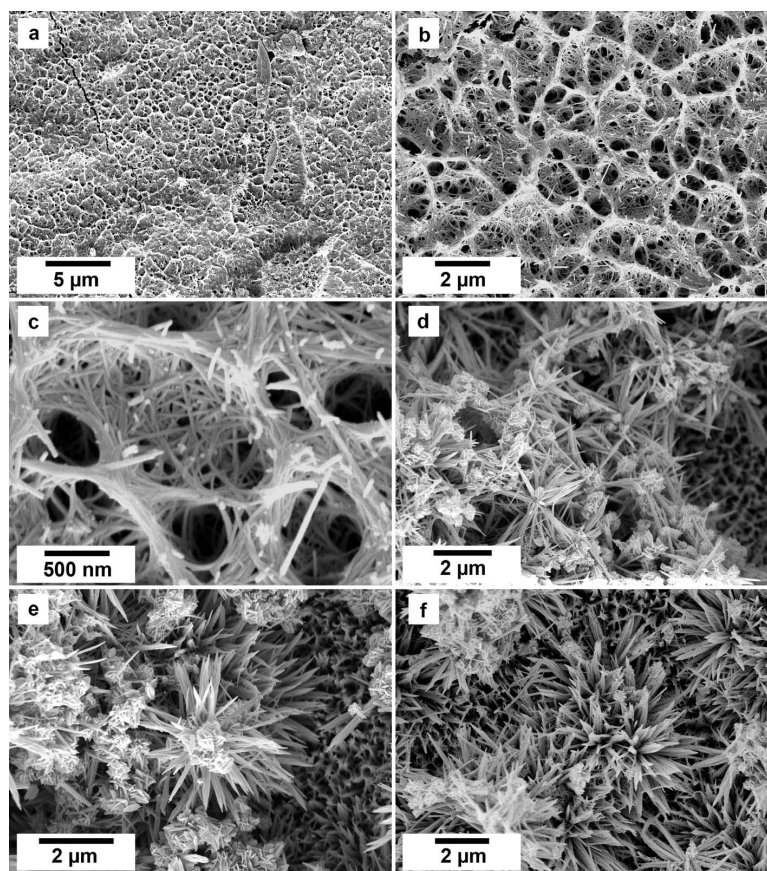


Fig. 3 SEM photomicrographs showing the nanophases obtained in the experiments using equal concentration of REEs at 50 °C. (a–c) Surface of vivianite covered by metavivianite nanoaggregates; (d–f) growth of rhabdophane needle aggregates on the surface of the metavivianite.

seems to maintain stability until an oxidation degree of $\sim 50\%$,²² the additional positive charge of the Fe^{3+} needs to be balanced by the conversion of a H_2O ligand into an OH^- group and the release of a H^+ . Therefore, upon further oxidation of Fe^{2+} above the 50% threshold, the crystal structure is impacted, leading to significant surface modification, structural distortion, and phase changes.^{23–25} In our experiments, the progressive oxidation of vivianite resulted in the formation of metavivianite and giniite, where 66% and 80% of the Fe is Fe^{3+} respectively, and hematite (100% Fe^{3+}). Crystallisation of these phases was the result of the solution-mediated coupled oxidation and dissolution of vivianite. This is a complex process that involves the interplay between oxidation reactions and the solubility of vivianite in aqueous environments and is strongly influenced by the aqueous solution chemistry, pH, and temperature.

The oxidation of vivianite crystals occurs more rapidly in solution compared to exposure to air due to enhanced availability of reactants, favourable environmental conditions, and different kinetic mechanisms that facilitate faster oxidation rates. In aqueous environments, the presence of dissolved

oxygen (DO) significantly enhances the oxidation kinetics of Fe^{2+} ions in vivianite. Several studies indicate that the oxidation of Fe^{2+} to Fe^{3+} is also facilitated in solution due to the higher concentration of reactive species, which can lead to faster reaction rates compared to the limited diffusion of oxygen in air.^{26,27} Additionally, the kinetics of oxidation in solution are governed by different mechanisms than those occurring in air. In air, the oxidation process is primarily limited by the diffusion of oxygen in the mineral structure, which can create a slower reaction environment. In contrast, in solution, the oxidation can occur through direct contact with dissolved oxygen, leading to a more rapid dissolution and transformation of vivianite.^{28,29} Furthermore, the layered structure of vivianite, which is stabilized by hydrogen bonds, can be disrupted more easily in solution, allowing for easier access of oxidizing agents to the Fe^{2+} sites.^{29,30} The interaction of vivianite with water creates a dynamic environment where the solubility of oxygen is higher, allowing for more efficient oxidation processes. The aqueous medium also allows for better thermal management, as

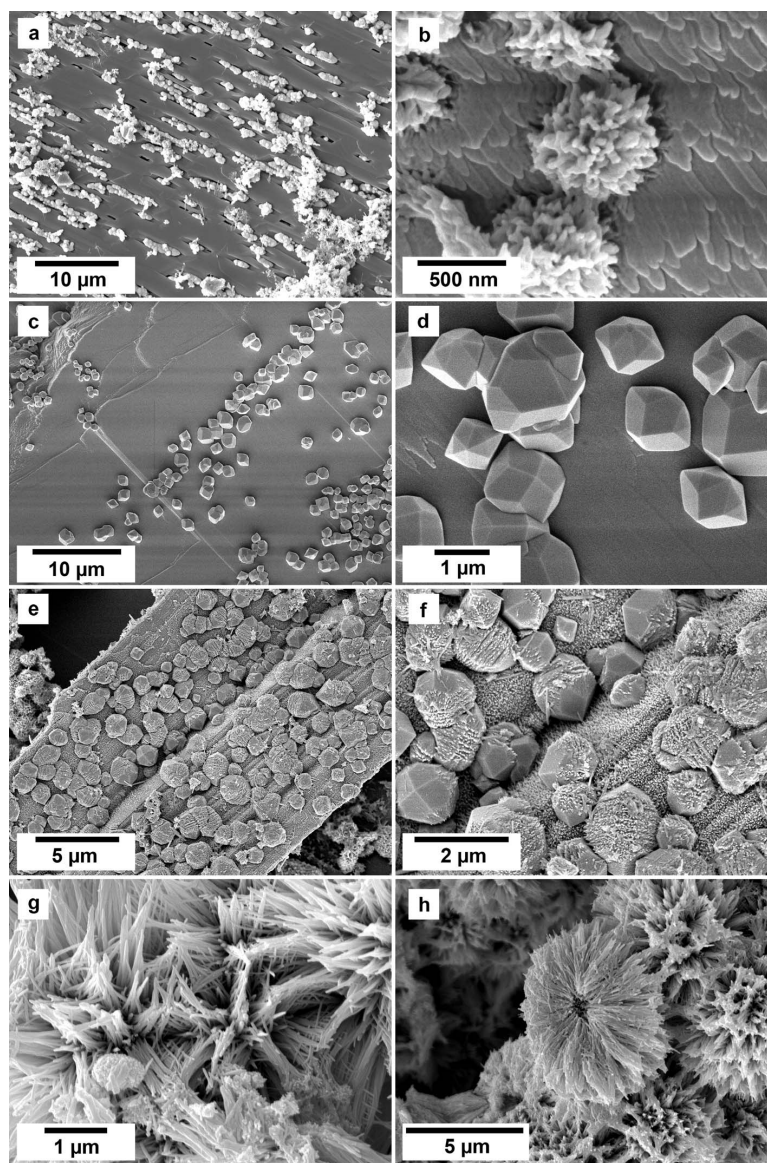


Fig. 4 SEM photomicrographs showing the nanocrystalline solids obtained in the experiments at 90 °C using equal REE concentration solutions. (a and b) Surface of vivianite becoming covered by metavivianite nanoaggregates; (c and d) growth of giniite crystals on the surface of the vivianite; (e and f) early stages of growth of rhabdophane on the surface of giniite. (g and h) Rhabdophane nanoaggregates and spherulites covering the surface of the host crystals.

temperature fluctuations can be more easily controlled, thereby influencing the rate of oxidation reactions.¹⁴

The kinetics of oxidation were found to be temperature-dependent with metavivianite more abundant at 50 °C. At 90 °C, small amounts of metavivianite were recorded, however, after 28 days all metavivianite had transformed to giniite, a phase that was not seen at 50 °C. At the highest temperature of 165 °C, no metavivianite was detected, giniite was the main phase with

around 20% transformed to hematite. Increased temperature significantly affects the oxidation of vivianite in aqueous environments by accelerating the reaction kinetics and altering the mineral's stability. As temperature rises, the solubility of gases, including oxygen, decreases, but the diffusion rate of oxygen in water increases, which enhances the oxidation rate. This can lead to enhanced oxidation rates of Fe^{2+} ions present in vivianite. At elevated temperatures (155–185 °C), such as those

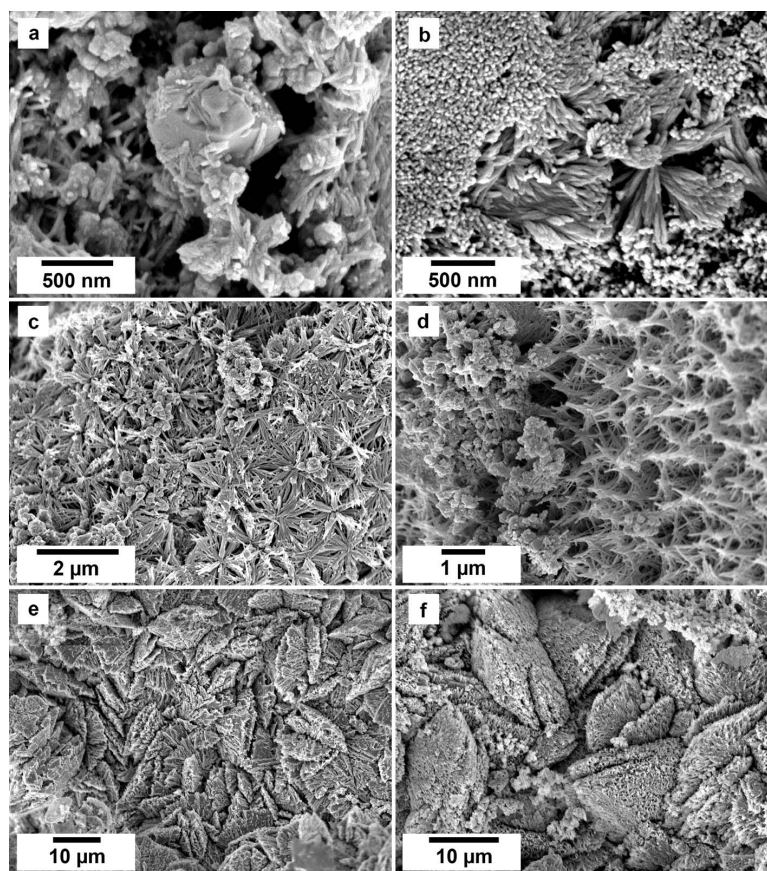


Fig. 5 SEM photomicrographs showing the nanocrystals obtained in the experiments at 165 °C in the PAAS solution experiments. (a) Surface of giniite becoming covered by rhabdophane nanorods; (b and c) growth of rhabdophane nanocrystals on the surface of the host, sometimes forming spherulitic-type aggregates (c); (d) nanocrystals of hematite on rhabdophane. (e and f) Monazite and rhabdophane aggregates.

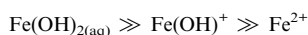
observed by Wang *et al.*, vivianite will undergo partial transformation into various iron phosphate phases such as strengite and giniite. This auto-oxidation is facilitated by the decomposition of water at higher temperatures.³¹ The increased thermal energy not only enhances the mobility of ions but also promotes the breaking of chemical bonds within the vivianite structure, thereby accelerating the oxidation process.³² Studies have shown that even moderate increases in temperature can compromise the structural integrity of vivianite leading to significant alterations in the crystal structure, subsequently enhancing its susceptibility to oxidation.¹⁴ For example, the presence of bound water in the vivianite crystal plays a crucial role in stabilizing the structure, however, as temperature rises, the hydration layer can be disrupted, making the Fe^{2+} ions more accessible to oxidizing agents.³³ In our experiments, vivianite partially dissolved at 50 °C, however at higher temperatures, vivianite was fully replaced by giniite and rhabdophane (90 °C) and giniite, hematite, rhabdophane, and monazite (165 °C). This is in agreement with Metz, *et al.*, 2024 who experimentally

demonstrated that the maximum temperature at which vivianite is stable under oxic conditions is between 65 and 75 °C.

The slower transformation kinetics at 50 °C could also be explained by a partial equilibrium situation in which a crust of nano-sized metavivianite covering the vivianite host hinders further oxidation and dissolution.^{34–36} Similar results were recorded by Yu *et al.*, 2023 in their investigation of the effects of dissolved oxygen (DO) concentrations on As(v) adsorption onto the iron carbonate siderite. They found that excess DO caused fast oxidation of siderite which in turn constrained As(v) adsorption. This was due to the production of a coating of Fe(III) oxides on the surface of the siderite that prevented any further oxidation of the host.^{37,38}

The oxidation of vivianite in water is also significantly influenced by pH, which affects both the stability of the mineral as well as the kinetics of oxidation reactions through the alteration of iron and phosphate speciation. When vivianite is oxidised, the Fe^{2+} and phosphate ions present in its structure can be released into the aqueous phase, leading to the

dissolution of vivianite. The oxidation of Fe^{2+} to Fe^{3+} results in the release of protons (H^+) into the solution, which will initially lower the pH. At low pH, extensive protonation at the vivianite surface results in the weakening of structural $\text{Fe}-(\text{PO}_4)$ bonds due to polarization of water molecules promoting Fe detachment.³⁹ The Fe can then undergo hydrolysis and lead to the formation of various hydrolysed ferrous species, such as $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})_2^+$. This has been experimentally shown to be dependent on the pH of the solution. Morgan and Lahav described the fundamental equilibrium and thermodynamic principles governing the kinetics of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). They propose a pH dependent range of $\sim 5 < \text{pH} < \sim 8$ and a pH independent range of $\sim 5 > \text{pH} > \sim 8$. In other words, the overall oxidation rate depends on the distribution of these three species in the aqueous phase, which is pH dependent. At pH below ~ 4 , Fe^{2+} concentration dominates, and the rate is independent of pH. At pH above ~ 5 , $[\text{Fe}(\text{OH})_2]$ determines the rate because it is far more readily oxidised than both Fe^{2+} and FeOH^+ . Between pH 5 and 8, the $\text{Fe}(\text{OH})_2$ concentration rises steeply with pH and the overall oxidation rate increases accordingly. Finally, at $\text{pH} > \sim 8$ $[\text{Fe}(\text{OH})_2]$ no longer varies with pH and the oxidation is again independent of pH.⁴⁰ This is in agreement with Luther, 1995 who used molecular orbital theory to show that hydrolysed ferrous iron species are more readily oxidised than non-hydrolysed ferrous species:



However, as the oxidation progresses and ferric iron precipitates, the overall effect can lead to an increase in pH due to the consumption of protons during the formation of insoluble iron oxides.⁴¹

Integration of PHREEQC modelling with the experimental results

PHREEQC calculations provided valuable insights into the stability and transformation of Fe- and REE-bearing phases during the interaction of vivianite with REE aqueous solutions. The calculated saturation indices confirmed the thermodynamic favourability of iron oxyhydroxide precipitation, with $\text{Fe}(\text{OH})_3$, goethite, and hematite exhibiting high SI values across all conditions. Notably, the high SI of hematite (+24.82 at 50 °C) aligns with our experimental observations of progressive oxidation from vivianite to giniite and ultimately to hematite at higher temperatures. Similarly, REE-phosphates such as rhabdophane and monazite displayed variable SI values depending on the specific REE present, with Ce-monazite reaching an SI of 9.91 at 50 °C, suggesting preferential formation under equilibrium conditions.

The PHREEQC-derived pH trends further support our experimental findings regarding phase stability and transformation. The initial solution pH (~ 5.1) increased to ~ 6.93 at 50 °C, promoting Fe hydrolysis and the subsequent oxidation of $\text{Fe}(\text{OH})_2$. At this temperature, vivianite remained relatively stable, preventing its complete dissolution and full transformation into metavivianite and rhabdophane. As the

temperature increased to 90 °C, the pH remained stable (~ 6.90), but here, the conditions exceeded the previously reported vivianite stability zone (65–75 °C). Consequently, after 28 days, all vivianite had fully oxidised and dissolved, leading to the crystallisation of giniite and rhabdophane. At 165 °C, the pH slightly decreased (~ 6.50) but remained within the favourable range for Fe hydrolysis and oxidation. Under these conditions, vivianite dissolution was rapid and complete, with any unincorporated Fe^{3+} precipitating as hematite. This transition from vivianite to giniite and hematite, along with the precipitation of REE-phosphates, is well supported by both experimental observations and PHREEQC predictions.

The stability of rhabdophane under all temperature conditions aligns well with the PHREEQC-calculated saturation indices, reinforcing its role as a key intermediate phase in REE-phosphate formation. However, at 165 °C, a transformation from rhabdophane to monazite was experimentally observed. This transformation is driven by thermal dehydration, structural rearrangement, and increasing thermodynamic stability of monazite at elevated temperatures. While rhabdophane is more soluble at lower temperatures, monazite exhibits significantly lower solubility and greater density, making it the thermodynamically favoured phase at 165 °C. This transformation is also influenced by the ionic radius of REEs, where larger REEs such as La, Ce, and Nd promote earlier dehydration and structural collapse of rhabdophane.

Despite cerianite (CeO_2) consistently exhibiting positive SI values in PHREEQC calculations, its formation was not observed in our experiments. This is because the oxidation of Ce^{3+} to Ce^{4+} is not strongly favoured at near-neutral pH compared to alkaline or highly basic conditions.^{42–44} Under the experimental conditions used in this study, Ce remained in the trivalent state, leading to the preferential precipitation of Ce-bearing monazite rather than cerianite. If the pH were to evolve into the basic range, the oxidation of Ce^{3+} to Ce^{4+} would become thermodynamically favourable, promoting the dissolution of Ce-bearing phosphates. Under such conditions, Ce^{4+} could lead to the destabilisation and subsequent dissolution of rhabdophane and monazite in contact with the solution. This behaviour is analogous to the destabilisation of Ce-bearing carbonates under alkaline conditions.^{42–45}

The strong agreement between PHREEQC modelling and experimental results validates the oxidation-driven pathway from vivianite to giniite and hematite while confirming the stability and transformation mechanisms of REE-phosphates under varying conditions.

Replacement of iron phosphates by rare earth element phosphates

The replacement of iron phosphates by rhabdophane, a hydrated rare earth phosphate, can occur through several mechanisms, including dissolution–precipitation reactions. When iron phosphates, like vivianite, metavivianite and giniite dissolve in the presence of rare earth-bearing solutions, the released phosphate ions can react with dissolved REE ions to form rhabdophane. The presence of REEs has been shown to

stabilize the formation of rhabdophane through ionic interactions. The effect of the REE³⁺ ionic radius on the formation and stability of rhabdophane is a significant factor in understanding its crystallization behaviour and thermodynamic properties. One key observation is that the ionic radius of the rare earth ion directly affects the stability of rhabdophane. Larger lanthanide ions, such as La³⁺–Gd³⁺ with ionic radii ranging from 1.250–1.105 Å,⁴⁶ are more favourable for the formation of rhabdophane due to their ability to stabilize the crystal lattice.⁴⁷ Smaller lanthanide ions, such as Gd³⁺–Lu³⁺ with ionic radii ranging from 1.105–0.995 Å,⁴⁶ tend to destabilize the rhabdophane structure. The incorporation of smaller ions can lead to an increased lattice strain and reduced stability, making the rhabdophane more susceptible to transformation into other phosphate structures, such as monazite or xenotime.⁴⁸

With time, we recorded the replacement of the iron phosphates, metavivianite and giniite, with REE-phosphates rhabdophane and monazite. As the vivianite dissolution progressed, releasing phosphate ions into the solution, it created conditions favourable to REE-phosphate precipitation. Normally these conditions would be governed by the solubility products of the initial vivianite and the subsequent newly formed rhabdophane and monazite. However, the solubility products for vivianite are $\lg K_{sp} = -35.76 \pm 0.076$ (ref. 49) and range for rhabdophane from $\lg K_{sp} = -25.6 \pm 0.8$ (Pr) to -24.9 ± 1.7 (Eu).⁵⁰ As rhabdophane is more soluble than vivianite, it should not be forming in these conditions. We, therefore, propose that the crystallization processes happening in our experiments are driven by the oxidation of vivianite and secondary Fe²⁺-bearing phosphates. Equilibrium with respect to vivianite is never reached as the majority of Fe²⁺ in solution is constantly oxidising to Fe³⁺. The process is enhanced by the higher temperatures, which promotes further dissolution of the host, enriching the fluid with PO₄ and more Fe²⁺, which, again, will oxidise to Fe³⁺. As the oxidation process is progressive and not instantaneous, some of the Fe²⁺ will incorporate in the metastable phases metavivianite and giniite. As the system progresses, the fluid becomes highly enriched in PO₄ because vivianite is unable to reach equilibrium with the aqueous solution, increasing the supersaturation levels for the REE phosphates. The PO₄ will therefore combine with the REE in solution to form rhabdophane which at some point will transform to monazite as temperatures increased from 90 to 165 °C, contributing to the depletion of phosphate in the aqueous solution and the crystallisation of iron oxides. The observed behaviour is in agreement with Gausse *et al.*, 2016, who noted that the solubility of rhabdophanes is influenced by thermodynamic equilibria, which can shift in favour of rhabdophane precipitation when iron phosphates are dissolved. They demonstrated that in aqueous environments at temperatures below 90 °C, rhabdophane is more stable than the corresponding monazite-type phase.

Supersaturation levels at the host-mineral-solution interface would also contribute to the rapid crystal nucleation of secondary REE-phosphates. The dissolution of only a few monolayers of the surface host is sufficient enough to initiate the formation of a fluid boundary layer near the surface of the

host seed, resulting in the development of a surface precipitate.⁵¹ The high concentration of PO₄ ions at the fluid boundary layer of the vivianite, metavivianite and giniite compared to the bulk solution promoted the high supersaturation levels required for the spherulitic crystals of rhabdophane that we observed in our 165 °C experiments.

It has also been shown that the presence of iron oxyhydroxides play a role in the adsorption and desorption processes that govern the availability of REE and phosphates in solution. Beyond the formation of specific iron and REE phosphate minerals, the surface properties of the iron-bearing phases formed during vivianite oxidation also play a crucial role in phosphate and REE mobility and availability. Fe²⁺ minerals, like vivianite, generally exhibit a lower surface charge density and a different surface affinity for phosphate compared to Fe³⁺ minerals, such as hematite or the iron oxyhydroxides that form during vivianite oxidation. As vivianite (Fe²⁺) oxidizes and transforms into metavivianite, giniite (mixed Fe²⁺/Fe³⁺), and ultimately hematite (Fe³⁺) and iron oxyhydroxides, the dominant surface chemistry shifts, promoting the formation of rhabdophane and monazite, therefore contributing to depletion of phosphate in the aqueous solution and the crystallization of iron oxides. Belogub *et al.*, 2021 discussed how the interaction between iron oxyhydroxides and phosphate ions can influence the formation of rhabdophane, as these interactions can affect the mobility and concentration of REE in the environment. It is the sorption of REE on iron oxyhydroxides that cause early REE scavenging from solutions, with a pH > 5.⁵² Sorption and desorption of REEs on iron oxyhydroxides depend on particle size and morphology, crystallographic defects, composition, and purity of the sorbent surface.⁵³ Concomitantly, adsorption capacity also strongly depends on the pH and the ionic strength of the solution. The combination of these properties determines whether adsorption takes place *via* the formation of outer-sphere or inner-sphere complexes.^{54,55} REE adsorption on iron oxyhydroxides, occurring before rhabdophane formation, can involve both inner-sphere and outer-sphere complexation mechanisms. The specific type of complexation plays a key role in determining the thermodynamic stability and crystal properties of rhabdophane. Inner-sphere complexes are characterized by direct coordination between the rare earth ions and the surface hydroxyl groups of iron oxyhydroxides. This type of complexation typically results in stronger chemical bonds, leading to enhanced stability of the adsorbed species. Studies have shown that the inner-sphere complexes are less sensitive to changes in ionic strength of the aqueous solution, making them more stable under varying environmental conditions.⁵⁶ For example,⁵⁷ indicated that inner-sphere adsorption sites are strong and stable, which is crucial for the retention of REEs in solid phases such as rhabdophane. The formation of inner-sphere complexes on iron oxyhydroxides can also contribute to the overall stability of rhabdophane by reducing the mobility of REEs, thereby limiting their release back into solution.⁵⁸ In contrast, outer-sphere complexes involve weaker electrostatic interactions where REE ions are held at the surface of the iron oxyhydroxides *via* water molecules without forming strong chemical bonds. This type of complexation is more sensitive to

ionic strength. As ionic strength increases, the stability of the outer-sphere complexes can decrease due to competition with other ions in solution.⁵⁹ The lower stability of outer-sphere complexes can lead to higher desorption rates and reduced retention of REEs in the environment.⁵⁶ The presence of both types of complexes in the formation of rhabdophane suggests that the stability of the mineral can be influenced by the conditions in which it forms. For example, at lower pH values (~ 4 – 7), the competition between REEs and protons can lead to increased outer-sphere complexation, while higher pH levels (~ 7 – 9) promote inner-sphere complexation due to the availability of hydroxyl groups for coordination.⁶⁰ For each of our temperature parameters, 50, 90, and 165 °C, the pH of the aqueous solution evolved from an initial value of 5.1 (before vivianite was added to the aqueous solution) to ~ 6.93 , 6.90, and 6.50 respectively. These pH values would allow for the more stable inner-sphere complexation, and this would be consistent with the formation of rhabdophane at all temperatures. Also, the slightly lower value of the pH 6.50 at 165 °C (compared to 6.90 at 90 °C) could also promote for the initiation of rhabdophane transformation to monazite.⁶¹

Transformation of rhabdophane to monazite

Rhabdophane, a hydrated rare earth phosphate, can transform to monazite, an anhydrous rare earth phosphate. The transformation of rhabdophane to monazite is influenced by several factors, including temperature, pH, REE speciation and ionic radii, hydration state, and differences in solubility (Pan *et al.*, 2024). At higher temperatures hydrous rhabdophane will undergo dehydration, and the structural changes will facilitate its conversion to the more thermodynamically stable anhydrous monazite.⁶² Full dehydration towards anhydrous rhabdophane takes place between 190 and 240 °C, with the irreversible transformation into monazite in aqueous solution occurring at temperatures above 500 °C.⁶³ The rhabdophane crystal structure presents as hexagonal symmetry and consists of alternating PO₄ tetrahedra and LnO₈ polyhedral linked together in chains along the [100] direction creating large one-dimensional channels, which accommodate the water molecules. Monazite presents as monoclinic symmetry with a crystal structure comprised of PO₄ tetrahedra and LnO₉ polyhedral also linked together in chains along the *c*-axis, but in a much more compact way.⁶⁴ The transformation process involves the progressive loss of water from larger channels along the *c*-axis of the rhabdophane structure, leading to the conversion to monazite.^{65,66} This loss of water molecules is crucial for stabilizing the monazite structure and can commence within the temperature range of 110–400 °C. This leads to the formation of anhydrous hexagonal CePO₄, before transitioning to the monoclinic form of CePO₄, monazite.⁶⁷ The thermal stability of monazite at high temperatures is well documented, with full transformation from rhabdophane completed at temperatures > 900 °C when heated in air.⁶⁸ However, it has been reported that the process can be initiated at significantly lower temperatures, particularly in the presence of water⁶⁸ and can also occur in samples that have been heat-treated during synthesis.⁶⁵ While solubility values vary in the literature for

monazite at our experimental conditions, all are in agreement that monazite is less soluble than rhabdophane at temperatures of 165 °C.^{48,69–71} Results from Van Hoozan *et al.*, also demonstrate that the solubility of monazite end members, LaPO₄, PrPO₄, NdPO₄, and EuPO₄, decrease sharply with increasing temperatures between 100 and 250 °C.

The transformation kinetics from rhabdophane to monazite can also be influenced by the ionic radius of the rare earth elements involved. Shelyug *et al.* demonstrated that the transformation temperature decreases with an increase in the ionic radius of the lanthanides. For example, when heated in air, the temperature required to transform the larger La-bearing rhabdophane to monazite is ~ 750 °C, compared to 900 °C to fully transform the smaller Gd-bearing rhabdophane.⁴⁸ This is in agreement with⁷² who demonstrated that the smaller, heavier REEs tend to form inner-sphere complexes. The formation of inner-sphere complexes typically results in a more stable adsorption site, requiring higher heat for transformation.

In our experiments at 165 °C, we recorded the initiation of the transformation of rhabdophane to monazite. However, as the temperature is well below the reported temperature range of 700–900 °C for complete transformation in air and 500 °C in aqueous solution, we observed only a 20 and 30% transformation in the equal concentration and PAAS solutions respectively. We propose that while the transformation was initiated by the dehydration of rhabdophane, it is the solution chemistry containing mainly larger REE ions La, Ce, Pr, Nd, with ionic radii of 1.250, 1.220, 1.200, and 1.175 Å respectively, that helped to facilitate the transformation at relatively lower temperatures. As stated above, larger, lighter REEs tend to form outer-sphere complexes, and can begin to transform at lower than expected temperatures. SEM-EDS maps showed a relatively homogenous uptake of the REEs in the equal concentration experiments. However, in the PAAS solution experiments there was a preferential uptake of the larger, lighter REE which also correlated to their original concentration in the aqueous solution, with higher concentrations of La, Ce, and Nd. In contrast, point analysis revealed no Dy incorporation into the rhabdophane. This could be the result of its low concentration in the PAAS solution as well as its incompatible smaller ionic radii of 1.075 Å⁴⁶ (ESI Images 1 and 2†).

Conclusion

The interaction of vivianite grains with multi-component REE-aqueous solution resulted in the progressive oxidation and dissolution of vivianite and its transformation to iron phosphates, metavivianite and giniite and iron oxide hematite. The rate of vivianite dissolution increased with increasing temperature, with metavivianite and giniite being replaced by the rare earth phosphate rhabdophane. The pH range of ~ 6.5 – 6.93 maintained the stability of rhabdophane for all three experimental temperatures (50, 90, and 165 °C). At the highest temperature of 165 °C we observed the partial transformation of rhabdophane to monazite. The transformation initiated below the documented temperature of 500 °C for complete transformation. Therefore, we propose that it is the incorporation of

larger REE and their tendency to form more weakly bound outer-sphere complexes. The transformation of iron phosphate, such as vivianite, into more stable and less soluble REE-phosphates has potential applications in REE recovery, particularly in waste materials, contaminated soils, and mine waste waters.

Data availability

The data that support the findings in this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest.

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