



(LA,Q)-ICPMS trace-element analyses of Durango and McClure Mountain apatite and implications for making natural LA-ICPMS mineral standards

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ABSTRACT

Apatite, the most abundant phosphate mineral in the Earth's crust and uppermost mantle, is able to accept a wide variety of trace elements into its crystal structure. Many of these trace element substitutions are below the detection limit of Electron Microprobe Analysis, but can be determined by laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS). LA-ICPMS elemental abundance determinations typically employ sample-standard bracketing using either standard glasses or an appropriate matrix-matched reference material. In this study we have undertaken laser ablation (>3000 analyses) and low-blank solution Q (quadrupole)-ICPMS trace-element analyses on crushed 150–300 µm aliquots of Durango and McClure Mountain apatite to assess the accuracy of apatite elemental abundance determinations when using NIST 612 standard glass as the primary LA-ICPMS trace element standard. An accuracy (relative to the solution data) and precision of <5% can be obtained for most trace elements (Y, the REE, Sr, Mn, V, Th and U) in LA-ICPMS analyses of crushed Durango separates; the McClure Mountain data are similarly accurate for most trace elements but yield larger intra-crystal variability. Durango raster and image mapping experiments demonstrate some Durango crystals are more homogenous than others; the raster experiments also show that Durango typically exhibits less zoning parallel to the C-axis compared to perpendicular to the C-axis. A protocol for developing a homogenous Durango apatite trace-element reference material is suggested, and involves slicing the interior portions of several Durango crystals parallel to the C-axis, undertaking rapid LA-ICPMS raster experiments to characterize trace-element zoning, crushing the most homogenous crystal to 150–300 µm and determining its trace-element contents by low-blank solution ICPMS. This generic approach can easily be modified and applied to characterize other natural LA-ICPMS mineral standards.

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1. Introduction

Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$, is a very common accessory mineral in igneous rocks, as apatite typically has a low solubility in silicate melts and phosphorous is not easily incorporated in the crystal lattices of the major rock-forming minerals (Piccoli and Candela, 2002). Apatite also occurs in metamorphic rocks of pelitic, carbonate, basaltic, and ultramafic composition at all metamorphic grades, and is virtually ubiquitous in clastic sedimentary rocks. Apatite can incorporate more than half of the periodic table into its crystal structure due to the variety of cation sites – a regular tetrahedron and two distinct M (M1 and M2) polyhedra (Hughes and Rakovan, 2015 and references therein). Divalent cations such as Sr, Ba, Pb, Cd, Mg, Fe, Mn, Co, Ni, Cu, and Zn typically substitute into the M1 and M2 sites, while trivalent cations such as the REE are envisaged to undergo more complex charge-coupled substitutions

within the disparate M polyhedra, such as $\text{Na}^+ + \text{REE}^{3+} \leftrightarrow 2\text{Ca}^{2+}$ and $\text{Si}^{4+} + \text{REE}^{3+} \leftrightarrow \text{P}^{5+} + \text{Ca}^{2+}$ (Hughes et al., 1991). The variable chemical composition of apatite has resulted in a variety of applications in a large variety of fields including mineralogy and crystal chemistry, petrology, biomineralization, geochronology, biomedical applications and materials science (Kohn et al., 2002).

While apatite has been routinely characterized for decades (e.g. Roeder et al., 1987) by Electron Microprobe Analysis (EPMA), many of the trace element substitutions in apatite are below the detection limit of EPMA (~100 µg/g). The high sensitivity of laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is ideally suited for measuring trace-element contents in geological materials, and in particular the very low counting mode background noise for all REE elements ensures detection at the sub-µg/g level. Elemental abundance determinations by LA-ICPMS in minerals (such as apatite) typically employ sample-standard bracketing using standard glasses, as natural mineral standards are often insufficiently homogeneous, especially in terms of their trace-element abundances. LA-ICPMS is typically a

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forgiving analytical method for matrix differences between samples and standards when internal standardization is used (e.g. [Sylvester, 2008](#)). However matrix effects (at the percent range) between standard glasses with different major element compositions have been documented using 193 nm (solid state) laser-ablation systems for some elements (e.g., Rb, Y, Pb; [Jochum et al., 2007](#)). Approaches to avoiding fractionation effects due to matrix differences include employing a femto-second laser which does not show significant matrix-dependency ([Jochum et al., 2014](#)), or the generation of matrix-matched powder-pellet standards (e.g. [Garbe-Schönberg and Muller, 2014](#)). There now exist several pressed-powder pellet carbonate standards (such as USGS MACS-1 or MACS-3), which enable carbonate trace-element abundance data standardized against NIST to be compared against. Using this approach, NIST glasses have been demonstrated to be suitable standards for carbonates for refractory lithophile elements, although accurate analysis of volatile chalcophile/siderophile elements still requires matrix-matching using 193 nm (solid state) laser-ablation systems ([Jochum et al., 2012](#)).

Although phosphate glasses doped in a variety of trace elements have been developed for in-situ micro-beam techniques ([Klemme et al., 2008](#)), apatite LA-ICPMS trace element analyses typically employ NIST standard glass standards as the primary elemental abundance standard. In this study we employ gem quality crystals and crushed aliquots of the widely-used Durango apatite reference material, and apatite separates from a hornblende–biotite syenite (McClure Mountain apatite). The crushed separates have been characterized by a comprehensive LA-ICPMS study using NIST 612 as the primary elemental abundance standard, while low-blank solution ICPMS analyses have been undertaken on aliquots of these same mineral separates. The goal is to compare the LA-ICPMS analyses with the solution data for a suite of trace elements to: i) assess the accuracy of apatite elemental abundance determinations when using NIST 612 as the primary LA-ICPMS trace-element standard, ii) characterize the variability in the LA-ICPMS data and iii) ultimately use these findings to suggest a protocol for developing precise and accurate in-house apatite trace-element reference materials. Apatite trace-element data have many applications in igneous petrogenesis (e.g. [Chu et al., 2009](#)) and sedimentary provenance studies (e.g. [Morton and Yaxley, 2007](#)) and can be combined with U–Pb and/or fission track data ([Chew and Donelick, 2012](#)). Additionally the approach (LA-ICPMS mapping of large crystals to determine the degree (and scale) of trace-element heterogeneity, followed by crushing and solution-ICPMS characterization of aliquots) is generic and can easily be modified and applied to characterize other natural LA-ICPMS mineral standards such as zircon, rutile or titanite.

2. Materials

2.1. Petrogenesis of Durango apatite

Durango apatite is a distinctive yellow-green fluorapatite that is found as exceptional coarse crystals within the open-pit iron mine at Cerro de Mercado, on the northern outskirts of Durango City, Mexico. The iron deposit resulted from the eruption of an iron-rich magma with elevated contents of fluorine, chlorine, carbon dioxide and water at the southern margin of the Chupaderos caldera complex ([Lyons, 1988](#)). Sheeted flows and flow breccias formed a volcanic dome above an intrusive feeder system. Iron oxides crystallized as magnetite, with abundant, clear, yellow-green apatite crystals forming concurrently in gas cavities and open breccias ([Lyons, 1988](#)). Massive iron oxide ores associated with silicic igneous rocks such as Cerro de Mercado represent a poorly understood class of deposit, with debate centring on whether they formed by crystallization of immiscible iron-oxide magmas or precipitation from iron-bearing hydrothermal fluids. Well-documented examples such as Cerro de Mercado are typically hosted by subaerial rhyolite calderas, and the iron ores are found at specific stratigraphic

horizons in the volcanic sequence at which there were significant changes in the chemistry of the extrusive rocks ([Kesler, 1997](#)).

The iron deposit formed between the eruptions of two major ignimbrites from the Chupaderos caldera ([Lyons, 1988](#)). ^{40}Ar – ^{39}Ar single-crystal sanidine–anorthoclase ages from these ignimbrites have yielded an age of 31.51 ± 0.10 Ma for the underlying units (mean of three analyses) and 31.34 ± 0.08 Ma for the overlying ignimbrite, yielding a reference age of 31.44 ± 0.18 Ma (2σ) for the formation of the iron deposit and hence Durango apatite itself ([McDowell et al., 2005](#)). Twenty-four (U–Th)/He analyses of Durango yield a mean age of 31.02 ± 1.01 (1 σ), with a mean U/Th (wt/wt) ratio of 0.054 calculated from 30 analyses ([McDowell et al., 2005](#)).

2.2. Durango apatite as a reference material

Durango apatite has been characterized by a wide range of analytical techniques for a variety of geological applications. The vast majority of these are low-temperature thermochronology studies, where it is widely used as an age standard in apatite fission track and (U–Th)/He dating. More recently, it has been investigated by a wide spectrum of in situ micro-beam analytical techniques. Given its popularity amongst mineral collectors and in museum displays, it can be easily purchased at major mineral exhibitions.

Durango apatite has been widely used as an apatite fission-track age standard since the 1970s (e.g. [Mark et al., 1971](#); [Naeser and Fleischer, 1975](#)) and subsequently in studies of apatite fission track lengths and annealing (e.g. [Laslett et al., 1984](#); [Green et al., 1986](#)). It is widely used in helium diffusion studies in bulk crystal (U–Th)/He apatite dating (e.g. [Wolf et al., 1996](#); [House et al., 1999](#); [Farley, 2000](#)) and in situ (U–Th)/He apatite dating ([Boyce and Hodges, 2005](#)). It has also been used as a reference material in (U–Th)/Ne chronometry ([Gautheron et al., 2006](#)).

Durango apatite has been investigated for its hydroxyl content by infrared spectroscopy ([Baumer et al., 1985](#)) and in elemental diffusion studies in apatite including rare earth elements ([Cherniak, 2000](#)) and uranium and manganese diffusion ([Cherniak, 2005](#)). It has been employed as an apatite material in high-temperature experimental petrology studies (e.g. [Harlov and Foerster, 2003](#); [Antignano and Manning, 2008](#)) and its oxygen and hydrogen isotope composition has been investigated by secondary ion mass spectrometry (SIMS) ([Zhou et al., 2012](#); [Hallis et al., 2012](#)). The volatile inventory (F, Cl, Br, S, C) of Durango apatite has been investigated in a comprehensive study by [Marks et al. \(2012\)](#) by a variety of analytical methods, including EPMA, LA-ICPMS, SIMS, pyrohydrolysis combined with ion chromatography, Fourier Transformed Infrared Spectroscopy (FTIR), Instrumental Neutron Activation Analysis (INAA) and Total Reflection X-ray Fluorescence Analysis (TXRF), while high precision Cl, Br and I measurements on Durango apatite have been undertaken using the noble gas method ([Kendrick, 2012](#)). The time-dependent intensity variation of halogen analyses in Durango apatite by EPMA has also been investigated by [Stormer et al. \(1993\)](#), [Goldoff et al. \(2012\)](#) and [Stock et al. \(2015\)](#). Durango apatite is close to end-member fluorapatite in composition (e.g. 3.53 wt.% F, [Young et al., 1969](#)), with EPMA Cl determinations varying between 0.37 and 0.46 wt.% ([Carlson et al., 1999](#); [Marks et al., 2012](#); [Chew et al., 2014a](#); [Yang et al., 2014](#)).

Durango apatite has also recently been employed as a secondary standard in U–Pb apatite dating studies by single collector LA-ICPMS ([Chew et al., 2011](#); [Chew et al., 2014b](#)), LA-multi-collector (MC)-ICPMS ([Thomson et al., 2012](#); [Cochrane et al., 2014](#)) and SIMS ([Li et al., 2012](#)). Other recent LA-ICPMS applications include characterization as a reference material for Sm–Nd and Sr isotope studies ([Foster and Vance, 2006](#); [Fisher et al., 2011](#); [Yang et al., 2014](#)) and for fission-track dating ([Hasebe et al., 2004](#); [Chew and Donelick, 2012](#); [Soares et al., 2015](#)). The study of [Yang et al. \(2014\)](#) also published major element (EPMA) and trace element (LA-ICPMS) from four separate Durango crystals and an aliquot of McClure Mountain apatite. However,

despite a large body of EPMA major element data demonstrating Durango apatite is homogenous (1 to 5% RSD) at the 10- μ m level (Frei et al., 2005), its potential as an apatite standard for trace-element microanalysis by LA-ICPMS (e.g. an assessment of the internal reproducibility and a comparison with low-blank solution ICPMS data) has yet to be investigated in detail.

2.3. McClure mountain apatite: petrogenesis and applications as a reference material

The McClure Mountain complex comprises a series of ultramafic to low-Si alkali igneous intrusions in the Wet Mountains region of Colorado, USA. The complex is composed of early mafic–ultramafic layered intrusions such as olivine gabbro, pyroxenite, anorthosite and dunite, which are intruded by massive hornblende–biotite syenite and then by nepheline syenite (Parker and Hildebrand, 1963; Shawe and Parker, 1967). A series of carbonatites, lamprophyres, and quartz–barite–thorite dikes and veins crosscuts these older units (Olson et al., 1977). Hornblende from the hornblende–biotite syenite intrusives suite has been widely used as a ^{40}Ar – ^{39}Ar age standard (MMhb; Alexander et al., 1978; Samson and Alexander, 1987). MMhb has been dated at 520.4 ± 3.4 Ma (K–Ar, Samson and Alexander, 1987), 523.1 ± 5.2 Ma and 523.3 ± 1.8 Ma (total-fusion ^{40}Ar – ^{39}Ar , Renne et al., 1998; Spell and McDougall, 2003). Schoene and Bowring (2006) obtained a weighted mean $^{207}\text{Pb}/^{235}\text{U}$ thermal ionization mass spectrometry (TIMS) date from ten chemical-abraded zircon fractions of $523.98 \pm 0.12/0.18/0.74$ Ma (MSWD = 1.4; internal errors/with tracer calibration errors/with tracer calibration and decay constant errors) from the same quarry as yielded the MMhb hornblende standard. Apatite from the same sample has yielded $^{207}\text{Pb}/^{235}\text{U}$ -cooling ages of $523.51 \pm 1.47/1.53/2.09$ Ma (MSWD = 2.1) with a common Pb correction undertaken using a 3D total Pb–U isochron approach (Schoene and Bowring, 2006). McClure Mountain apatite has been used subsequently as a standard in U–Pb apatite dating studies by LA-ICPMS by Thomson et al. (2012) and Chew et al. (2014b). The Sm–Nd and Sr isotope systematics of McClure Mountain apatite have been investigated by LA-MC-ICPMS (Yang et al., 2014), who suggest it has good potential as an apatite standard for in situ Sr isotopic analyses. Yang et al. (2014) also presented halogen EPMA data for McClure Mountain apatite, which yielded a F content of 3.37 wt.% and a Cl content of 0.02 wt.%.

2.4. Durango and McClure Mountain apatite samples used in this study

The main Durango crystal examined in this study (Dur-DonG) is a $2 \times 1 \times 1$ cm transparent, light-yellow prism supplied by Ray Donelick and originally obtained from the E.M. Barron Collection at the University of Texas at Austin. This crystal was crushed to yield a 150–300 μ m grain separate which was mounted in epoxy resin pucks. The second Durango crystal examined in this study (Dur-DCa) is a large ($4.5 \times 3 \times 2.8$ cm) hexagonal prism with one euhedral termination while the other termination is incomplete. The crystal was sliced to yield a c-axis perpendicular section for LA-ICPMS imaging (Section 3.2, Fig. 1A). Approximately 75% of the crystal was then crushed and sieved to yield a 150–300 μ m grain separate which was mounted in epoxy resin pucks, similar to the Dur-DonG crystal. Several other smaller Durango crystals (typically between $1 \times 0.5 \times 0.5$ cm and $2 \times 1.25 \times 1.25$ cm) were also mounted in a series of epoxy resin pucks (both c-axis parallel and c-axis perpendicular mounts) and ground and polished to expose the central portions of the crystal interiors for LA-ICPMS elemental profiles (Fig. 2), but no mineral separates were made from these samples. One of these c-axis perpendicular crystals (Dur-11) was chosen for LA-ICPMS imaging (Section 3.2, Fig. 1H).

The McClure Mountain apatite sample was supplied by Ray Donelick and is the same hornblende–biotite syenite sampled for the MMhb ^{40}Ar – ^{39}Ar hornblende age standard and by the U–Pb TIMS accessory mineral dating study of Schoene and Bowring (2006). Apatite occurs

as euhedral crystals 50–200 μ m in diameter. Schoene and Bowring (2006) documented the presence of apatite inclusions in every major phase in the rock (K-feldspar, plagioclase, hornblende, biotite and clinopyroxene), indicating it was an early liquidus phase.

3. Methods

3.1. LA-ICPMS trace element spot analyses

Apatite trace element data were acquired using a Photon Machines Analyte Exite 193 nm ArF Excimer laser-ablation system with a Helex 2-volume ablation cell coupled to a Thermo Scientific iCAP Qc at the Department of Geology, Trinity College Dublin. Mineral separates of Durango (from the Dur-DonG crystal) and McClure Mountain apatite are routinely analysed in the laboratory as age standards in U–Pb apatite dating applications, often with simultaneous acquisition of trace-element data. Durango and McClure Mountain apatite trace-element abundance measurements are also undertaken in the laboratory in LA-ICPMS apatite fission-track dating sessions and are also part of this dataset (protocol described in Cogné et al., 2014; Chew et al., 2014b). In both fission track and U–Pb dating applications, crystals of McClure Mountain apatite are randomly selected from the grain separate mount. Randomly selected crystal shards of Durango apatite are used in U–Pb dating applications, but fission-track dating sessions typically analyse a subset of c. 20 Durango crystal shards (out of a total pool of 80 Durango c-axis parallel grains that were etched and counted to determine their spontaneous fission track densities which is directly related to the uranium content). By analysing the U/Ca ratio of apatite unknowns and a subset of these Durango crystals in each session (Ca in our Durango apatite is assumed stoichiometric as EPMA analyses demonstrate a variation of ± 0.2 wt.% Ca, and hence it is used as an internal standard) the fission-track ages of apatite unknowns can be determined. This method is the LA-ICPMS equivalent of the fission track “zeta” calibration approach of Hurford and Green (1983).

Typically twenty-eight isotopes (^{31}P , ^{35}Cl , ^{43}Ca , ^{55}Mn , ^{86}Sr , ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{200}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U and mass 248 ($^{232}\text{Th}^{16}\text{O}$) were acquired using a 5 Hz laser repetition rate and a fluence of c. 3.9 J/cm² (Table 1). ^{51}V and ^{75}As were also analysed in some sessions. The pulse energy is comfortably above the ablation threshold for NIST612 glass and apatite on our LA-ICPMS system, yet not set too high so as to reduce the effects of melting on the crater walls which can cause fractional evaporation of volatile elements (e.g. Garcia et al., 2009). The laser repetition rate was chosen as to yield relatively shallow pit diameter/depth ratios, which minimizes fractionation of trace elements such as Pb, As and Zn (Mank and Mason, 1999) and downhole-fractionation of U–Pb (Woodhead et al., 2004). Each analysis comprised a 25 s baseline measurement followed by a 45 s ablation. The laser spot size was determined by the grain size of apatite unknowns, was kept constant for a given session, and typically ranged from 30 to 60 μ m, with the majority of sessions employing spot sizes of 30 or 47 μ m. Analyses were conducted over a 24 month period. During the first 15 months both He and Ar were fed into the two-volume cell as the carrier gas (c. 0.8 l/min He and c. 0.7 l/min Ar), while during the last 9 months of analysis 0.65 l/min He carrier gas was fed into the cell and was subsequently mixed with 0.7 l/min Ar make-up gas. An in-house developed variable-volume signal-smoothing device was used to mix in the Ar along with a small volume of N_2 (ca. 6 mL/min) to enhance signal sensitivity and reduce oxide formation. The ICPMS was tuned using NIST 612 standard glass to yield Th/U ratios of unity and low oxide production rates (ThO^+/Th^+ typically <0.2%).

Analytical sessions typically comprised blocks of six standard analyses (two each of Durango, McClure Mountain and Madagascar apatite), two NIST612 standard glass analyses followed by 20 unknown samples. Madagascar apatite is a c. 473 Ma U–Pb apatite age standard (Thomson et al., 2012) that was used as the primary age reference material in U–Pb

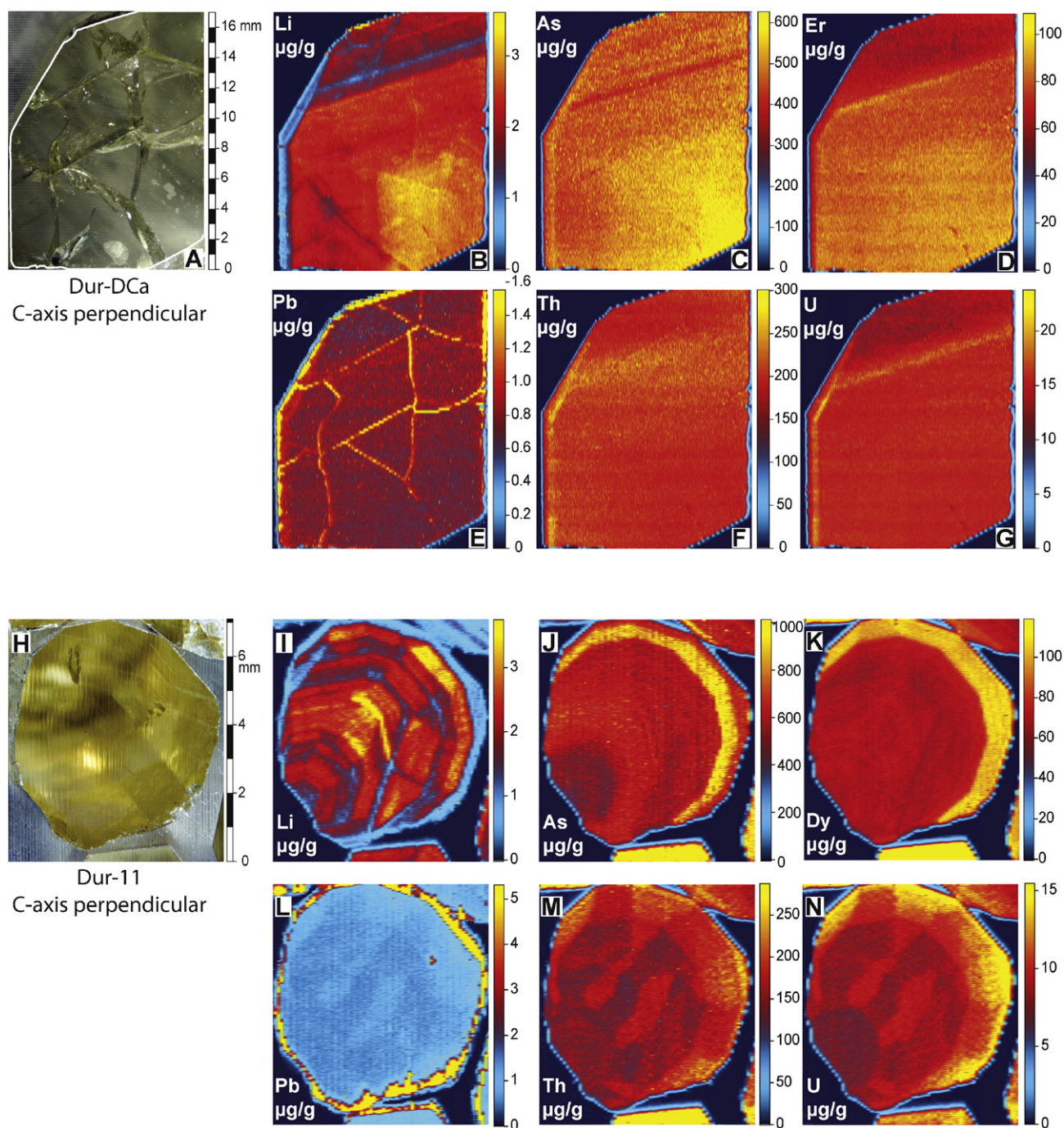


Fig. 1. A) Transmitted light image of a quarter section (perpendicular to the c-axis) of the Dur-DCa crystal. B–G) LA-ICPMS element maps for Li, As, Er, Pb, Th and U. H) Transmitted light image of a section (perpendicular to the c-axis) of the Durango Dur-11 crystal. I–N) LA-ICPMS element maps for Li, As, Dy, Pb, Th and U.

apatite dating sessions, but as no solution ICPMS data are available for this crystal fragment no Madagascar apatite LA-ICPMS trace-element data are presented in this study. The raw isotope data were reduced using the “Trace Elements” data reduction scheme within the Iolite package of Paton et al. (2011), using NIST612 glass as the primary trace-element abundance standard. User-defined time intervals are established for the baseline correction procedure to calculate session-wide baseline-corrected values for each isotope. ^{43}Ca was used as an internal standard to account for variations in ablation yield, with an assumed apatite Ca content of 40 wt.% (equivalent to 56 wt.% CaO). Sample-standard bracketing was then applied to ^{43}Ca -normalized elemental ratios (using a user-specified spline fit within Iolite such as a

weighted mean, a linear fit or a smoothed cubic spline) to account for session drift in isotopic or elemental ratios.

3.2. LA-ICPMS trace-element image mapping

LA-ICPMS trace element image mapping was undertaken using the same analytical setup as for the spot analyses. The procedure is similar to that adopted by Ubide et al. (2015) and is outlined briefly below. Image maps were made by “rastering” the sample under the ablation site. To produce the full map, adjacent lines (or “rasters”) were ablated in a successive manner. The final ablated area was rectangle-shaped to facilitate production of trace element maps

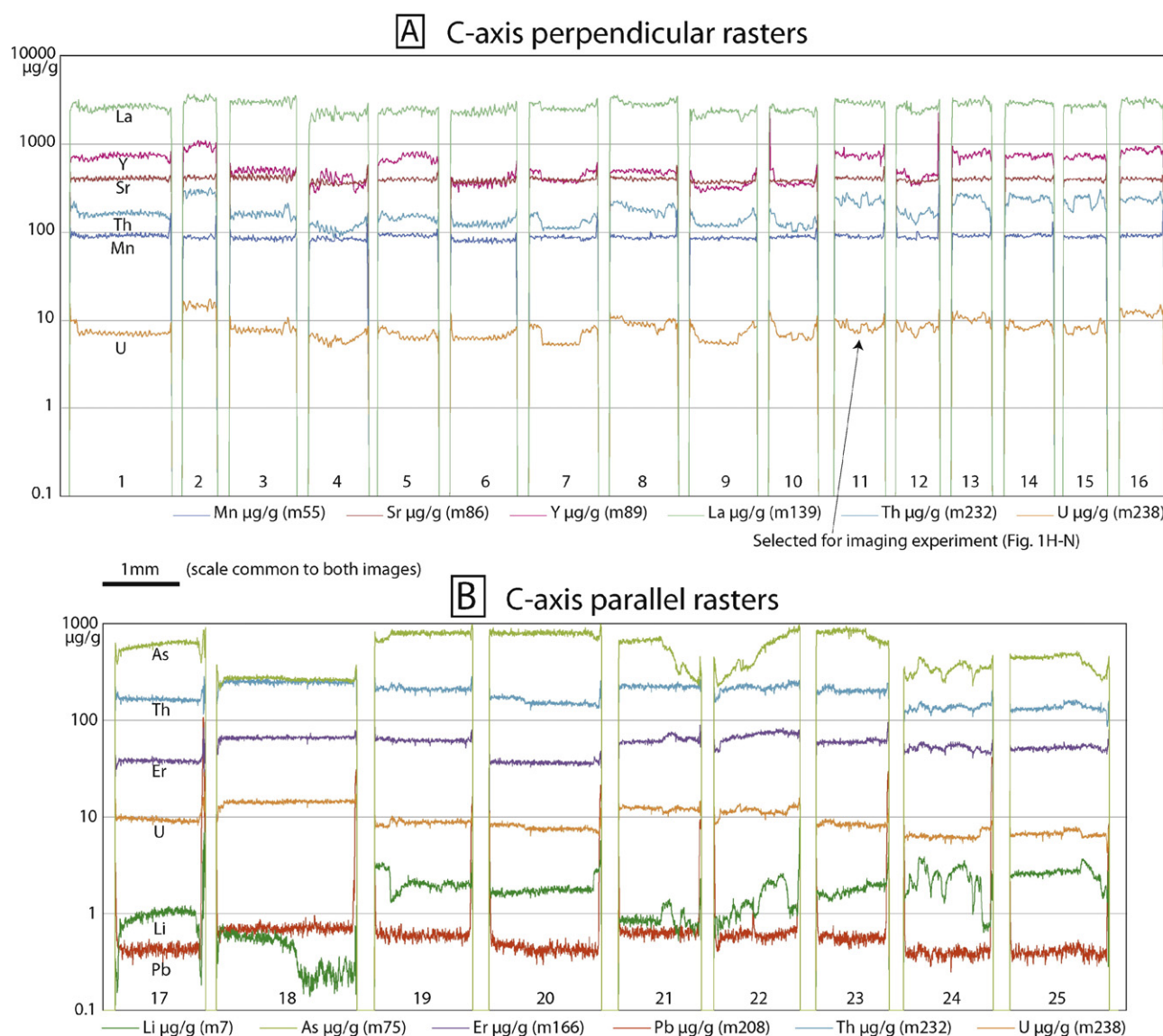


Fig. 2. A) c-Axis perpendicular LA-ICPMS elemental profiles across 16 separate Durango crystals. B) c-Axis parallel LA-ICPMS elemental profiles across nine separate Durango crystals.

using the “Image from Integrations” module in Iolite. Both image maps (Fig. 1) employed a laser fluence of 6 J/cm², a repetition rate of 8 Hz and a total dwell cycle of 125 ms. Although the system has

Table 1
Analytical parameters for different sessions.

Laser parameters	
Instrument	Photon Machines Analyte Exite ArF Excimer 193 nm
Washout	25 s
Background	15 s
Analysis duration	45 s
Laser repetition rate	5.0 Hz
Spot size ^a	30 to 60 μm diameter
Energy	3.9 J/cm ²
Carrier gas 1 ^a	0.6–0.8 L/min He
Mass spectrometer parameters	
Instrument	Thermo Scientific iCAP Qc
Plasma RF power	1450 W
Plasma carrier gas flow	0.7 L/min
Isotopic and sample information	
Number of isotopes measured ^a	28–33
Total analysis time per cycle ^a	Typically c. 500 ms

^a Parameters that were changed between analytical sessions.

a fast washout (90% signal reduction in less than 1.5 s), 25 s was allowed for washout between lines to avoid any carry-over from standards to samples and vice versa. NIST612 glass reference material was used as the calibration standard and ablated with the same parameters as the samples. Two NIST612 lines were analysed at the beginning and end of each experiment and systematically every 10 sample lines. For the experiment in Fig. 1A–G, seven isotopes were analysed: ⁷Li (25 ms), ³⁵Cl (25 ms), ⁴³Ca (10 ms), ⁷⁵As (5 ms), ¹⁶³Dy (5 ms), ²⁰⁸Pb (10 ms), ²³²Th (5 ms) and ²³⁸U (15 ms). A 180 μm spot size and a scan speed of 100 μm/s were employed. The experiment in Fig. 1H–N employed the same dwell cycle with the exception that ¹⁶⁰Er (5 ms) replaced ¹⁶³Dy. A 95 μm spot size and a scan speed of 60 μm/s were used. Data reduction and production of trace element distribution maps was undertaken with the Iolite software (Paton et al., 2011) using the “Trace Elements” data reduction scheme in “Semi-Quantitative” mode (which in Iolite corresponds to not employing an internal standard isotope). Following data reduction, trace element distribution maps were built with the Iolite module “Images From Integrations”. The scales on both image maps in Fig. 1 were then normalized to a Ca content of 40 wt.% using the measured Ca values of 41.76 wt.% (Dur-DCa, Fig. 1B–G) and 45.6 wt.% (Dur-11, Fig. 1I–N).

Table 2
SQ-ICPMS trace element concentrations (all in ng/g) of Durango (DCa & DonG) and McClure Mountain apatites.

		Dur-DCa									
Digest		1		2		3		4			
shards		10 mg		20 mg		10 mg		20 mg			
		avg	%RSD	avg	%RSD	avg	%RSD	avg	%RSD	avg	%RSD
W-2 Calibration value											
Li	9158	1215	3.6	1220	6.6	1308	1.2	1239	9.2	1240	6.0
Mg	38414000	84790	1.1	81190	5.3	84060	4.4	82830	7.2	83190	4.9
V	261597	31490	2.6	32050	4.5	31760	2.7	32100	3.1	31870	3.2
Mn	1293000	96000	4.9	95630	6.3	95140	6.1	93950	5.8	95150	5.5
As	1260	921100	2.7	945800	3.0	934300	2.3	948300	2.1	939000	1.9
Sr	194828	506500	0.8	500000	1.0	504500	0.7	502800	0.8	501900	0.9
Y	20113	1015000	0.5	1015000	1.0	1019000	1.0	1017000	0.9	1017000	1.1
La	10521	4317000	3.5	4141000	0.6	4255000	2.5	4198000	1.0	4239000	2.6
Ce	23216	5921000	3.6	5664000	0.4	5738000	1.5	5715000	1.4	5777000	2.8
Pr	3025	533100	2.4	530400	2.2	528900	0.6	527900	0.7	530100	2.4
Nd	12911	1713000	0.9	1704000	0.9	1727000	1.1	1719000	0.1	1728000	2.7
Sm	3266	255400	2.8	249200	1.1	253500	1.0	253200	1.0	251100	0.9
Eu	1094	20570	1.6	20270	2.2	20610	1.1	20470	1.2	20500	1.2
Gd	3708	228800	4.3	223300	1.0	225800	1.6	225700	0.7	225900	1.8
Tb	615	30550	2.9	29890	1.5	30270	4.0	30230	3.1	30270	3.0
Dy	3808	169900	2.5	166100	0.6	169100	1.0	168400	0.9	167000	0.5
Ho	803	35040	1.7	34360	1.7	34850	1.0	34880	0.5	34780	1.4
Er	2222	92360	2.2	92010	3.4	92280	0.2	91820	1.2	91940	2.1
Tm	327	11940	1.9	11700	1.6	11850	0.8	11880	0.6	11840	1.4
Yb	2058	60520	1.9	59280	1.5	60660	2.0	60230	1.3	60210	1.8
Lu	301	6637	0.9	6518	0.5	6617	0.6	6641	0.6	6600	1.0
W	240										
Pb	7528	690	2.6	695	3.5	696	1.6	685	1.1	689	2.2
Th	2104	359800	1.2	356600	1.8	360400	0.6	360100	0.7	358900	1.2
U	505	18820	2.1	18570	2.7	18790	1.8	18660	2.4	18660	2.2
Th/U		18.65	1.2	18.60	0.7	18.65	1.5	18.78	0.7	18.67	1.0
U/Pb		27.21	2.9	27.04	3.9	27.12	1.4	27.06	1.6	26.94	2.2
Sm/Nd		0.1472	0.1	0.1472	0.5	0.1468	0.1	0.1473	0.9	0.1471	0.4
Y/Ho		28.82	1.6	28.95	1.8	28.97	1.3	28.71	1.3	28.81	1.3

Notes: All concentrations normalized to 40 wt.% Ca.

3.3. LA-ICPMS backgrounds and potential interferences

When considering the LA-ICPMS spot analysis data from the low mass end of the periodic table, polyatomic interferences and interference from doubly-charged REE need to be considered. For a representative session on Dur-DonG apatite (60 μm spot at 5 Hz), the baselines and baseline-corrected intensities (in parentheses) for key isotopes are: ^{35}Cl : 40 kcps (5 kcps); ^{51}V : 400 cps (20 kcps) ^{55}Mn : 120 kcps (100 kcps); ^{75}As : 400 cps (220 kcps). The high background on ^{55}Mn is cyclical (frequency 30 min^{-1} and an amplitude of 30% of the total Mn background) which may introduce some scatter to the Mn data in sessions when baselines are not defined for every analysis. Peak scanning on the mass 56 background shows that it is not related to low-mass tailing of the $^{40}\text{Ar}^{16}\text{O}^+$ peak; stopping the flow of the N_2 signal optimisation gas reduces the mass 55 background from 120 kcps to 5 kcps which strongly suggests it is a $^{40}\text{Ar}^{14}\text{N}^+\text{H}^+$ or $^{40}\text{Ar}^{15}\text{N}^+$ background. The effect of adding N_2 into the central channel gas substantially increasing the backgrounds on masses 29, 31, 42, 51, 52 and 55 due to the nitrogen-based polyatomic interferences is well-documented in the literature (e.g. Hu et al., 2008).

Polyatomic interferences involving ^{35}Cl could potentially affect ^{51}V ($^{35}\text{Cl}^{16}\text{O}^+$) and ^{75}As ($^{35}\text{Cl}^{40}\text{Ar}^+$) on Durango apatite only, as McClure Mountain is essentially chlorine-free (0.02 wt.% Cl from EPMA, Section 2.3) and the ^{35}Cl intensity barely registers above background. The mass 35 background of ~40 kcps is not a polyatomic interference (Chew et al., 2014a) implying it is ^{35}Cl . Assuming all the mass 55 background (400 cps) is $^{35}\text{Cl}^{16}\text{O}^+$ and all the mass 75 background (400 cps) is $^{35}\text{Cl}^{40}\text{Ar}^+$, gives $^{35}\text{Cl}^{16}\text{O}^+$ and $^{35}\text{Cl}^{40}\text{Ar}^+$ production rates of 1% which

are both maximum estimates. For Dur-DonG apatite, the baseline-corrected $^{51}\text{V}/^{35}\text{Cl}$ ratio = 9.5 (mean of >1700 analyses) and the baseline-corrected $^{75}\text{As}/^{35}\text{Cl}$ count ratio = 36.5 (mean of >600 analyses). With $^{35}\text{Cl}^{16}\text{O}^+$ and $^{35}\text{Cl}^{40}\text{Ar}^+$ production rates both of 1% and 0.11% of the ^{51}V signal and 0.03% of the ^{75}As signal in Dur-DonG apatite are a result of Cl interference.

Doubly-charged REE could have an effect on ^{75}As ($^{150}\text{Nd}^{++}$, $^{150}\text{Sm}^{++}$), particularly given the high LREE + MREE abundances in Durango apatite. The REE^{2+} production rate was determined in one Durango experiment by measuring $^{143}\text{Nd}^+$ and $^{143}\text{Nd}^{2+}$ (mass 71.5) and $^{141}\text{Pr}^+$ and $^{141}\text{Pr}^{2+}$ (mass 70.5), yielding dimer production rates of 0.36% and 0.48% respectively for Nd and Pr. Assuming a Sm and Nd REE^{2+} production rate of 0.4%, these dimers account for less than 0.5% the apparent ^{75}As signal in Durango apatite. Additionally ^{75}As is not coupled to the REE behaviour in the Durango raster experiments (Fig. 1). However the effect of doubly-charged REE on ^{75}As in McClure Mountain apatite is more significant; although it is more depleted in LREE + MREE than Durango by a factor of two, it is significantly more depleted in As and hence REE dimers account for ~20% of the apparent ^{75}As signal in laser ablation analyses of McClure Mountain apatite and were corrected for.

LA-ICPMS spot analyses (60 μm spot at 5 Hz) were undertaken on a subset of ~60 crystals of each of Dur-DonG, Dur-DCa and McClure Mountain apatite using the collision cell of iCAP Qc in Kinetic Energy Discrimination (KED) Mode, with a He flow rate of 3.8 mL/min into the collision/reaction cell. For Dur-DCa apatite, the baselines and baseline-corrected intensities (in parentheses) for key isotopes are: ^{35}Cl : 27 cps (37 cps); ^{51}V : 1.5 cps (3.2 kcps); ^{55}Mn : 43 cps

Dur-DonG						McClure Mountain							
1		2				1		2		3			
10 mg		10 mg				10 mg		10 mg		20 mg			
avg	%RSD	avg	%RSD	avg	%RSD	avg	%RSD	avg	%RSD	avg	%RSD	avg	%RSD
2891	2.4	2909	0.9	2897	1.9	6408	5.3	5822	3.7	5663	4.2	5964	6.9
128900	3.5	130000	6.4	129400	4.9	53340	3.7	49670	3.3	45800	3.7	49220	7.4
28440	2.7	29080	3.2	28800	3.1	18440	5.0	18480	5.0	18640	5.9	18530	5.0
99280	2.9	101300	1.3	100300	2.4	100200	5.7	99250	5.6	98740	6.4	99400	5.4
605700	2.1	607300	4.7	606500	3.4	20900	2.0	20790	1.9	20480	2.9	20720	2.3
494800	0.6	498700	2.0	497200	1.6	3919000	2.4	3891000	1.9	3897000	2.4	3902000	2.1
784100	0.6	785000	0.8	785000	0.8	216800	2.2	216100	1.5	213900	2.0	215600	1.8
3772000	1.2	3797000	1.3	3786000	1.3	1786000	1.2	1748000	1.3	1760000	1.8	1764000	1.5
5319000	1.4	5294000	1.6	5306000	1.4	2894000	1.7	2833000	1.3	2850000	2.0	2859000	1.6
473700	1.9	471300	1.8	472500	1.3	278500	0.5	273200	0.3	274000	1.0	275200	1.1
1538000	1.8	1530000	1.9	1534000	1.7	904700	0.2	883100	0.6	892100	0.4	894400	1.0
214800	0.4	215500	1.5	215200	1.1	107700	1.1	105900	1.4	106500	2.2	106700	1.5
18820	0.5	18960	1.9	18900	1.4	41670	1.5	40850	1.5	41060	2.3	41190	1.7
186500	0.4	187200	1.7	186900	1.2	74800	1.1	73750	1.5	74410	1.7	74320	1.3
24240	0.5	24250	1.7	24250	1.2	8701	0.8	8545	1.2	8531	1.2	8593	1.3
129700	0.3	130000	1.3	129900	0.9	41880	2.3	41510	2.6	41460	3.2	41620	2.2
26330	0.6	26360	1.8	26350	1.3	8028	1.8	7907	1.4	7914	1.8	7950	1.5
68510	0.1	68830	1.5	68690	1.1	20450	1.4	20360	1.1	20080	2.5	20300	1.6
8712	0.5	8771	1.8	8745	1.4	2739	0.6	2717	1.0	2693	2.4	2717	1.4
44840	0.9	45290	2.0	45100	1.6	15920	1.2	15910	0.9	15680	1.5	15840	1.2
5148	0.9	5194	2.0	5174	1.6	2258	0.4	2249	0.7	2225	1.7	2244	1.1
1856	4.0	1912	3.3	1884	3.8	195700	5.1	156700	3	144400	4.6	165600	14
3359	0.9	2931	2.7	3115	7.6	4597	3.2	4383	2.4	4221	0.9	4430	5.4
235100	0.5	234700	0.6	235000	0.5	64380	-	64450	2.1	62750	4.1	63710	3.0
12980	1.7	13020	1.8	13000	1.6	18960	2.8	17960	2.1	17800	2.6	18420	5.2
17.78	0.0	17.81	0.2	17.80	0.2	3.51	-	3.54	0.6	3.47	1.8	3.51	1.4
3.85	2.5	4.40	2.3	4.11	7.8	4.12	0.4	4.09	1.8	4.17	0.3	4.12	1.3
0.1410	0.3	0.1405	0.3	0.1408	0.3	0.1178	0.6	0.1179	0.6	0.1179	0.8	0.1178	0.4
29.75	0.2	29.81	1.0	29.78	0.7	27.42	0.8	27.47	0.2	27.23	0.4	27.37	0.6

(7 kcps); ^{75}As : 75 cps (32 kcps). The low Cl intensities (three orders of magnitude lower than the ^{75}As signal) and low backgrounds on ^{55}Mn and ^{75}As enable these data to be compared with the solution data and the main laser-ablation spot dataset without the effect of potential polyatomic interferences. However the suppression of signal intensities at the low mass end of the periodic table in KED mode and higher REE dimer production rates (1.06%) increases the effect of the doubly-charged REE on ^{75}As in laser-ablation analyses of McClure Mountain apatite, such that they account for nearly 50% of the mass 75 signal.

3.4. Solution ICPMS trace element analyses

Aliquots of 10.0 or 20.0 (± 0.2) mg of Dur-DCa (4 samples), Dur-DonG (2 samples) and McClure Mountain apatite (3 samples) (Section 2.4) were transferred to pre-cleaned (acid-leached) 30 mL polypropylene (PP) bottles. Typically, a 20 mg aliquot of each mineral separate would comprise ca. 250 grains. A 20,000 (± 0.0050) g mass of 5% (v/v) HNO_3 was added to each PP bottle and the acid was left to react until all apatite crystals were dissolved. From these bottles, separate 20,000 $\times$, 100,000 $\times$, or 200,000 $\times$ dilutions of the sample in 2% HNO_3 loaded with an enriched isotope and elemental internal standard mixture (^6Li , Rh, Re, Bi, ^{235}U) were prepared gravimetrically in test tubes for solution quadrupole (SQ)-ICPMS analysis. All acids were prepared from a stock of in-house triply (sub-boiling) distilled concentrated HNO_3 and diluted with ultra-pure Milli-Q water. Analyses were performed at Trinity College Dublin using the same Thermo iCap-Qc as the laser ablation ICPMS method (Section 3.1). All solutions were

introduced to the ICPMS with an ESI SC-2 DX autosampler coupled with an ESI μFast system. Using this setup, solutions were taken into a 1 mL Teflon loop and injected into a Peltier-cooled double-pass spray chamber at a rate of 140 $\mu\text{L min}^{-1}$ with the aid of a micro-peristaltic pump. All sample introduction tubing was cleaned between samples with pure HNO_3 (2–4% v/v) using an on-board autosampler rinse sequence.

Samples were analysed in several experimental sessions that were each preceded with: instrument tuning to maximize sensitivity across the full analyte range; tests of oxide and dimer production rates on elements with isobaric interferences; and natural isotope ratio measurements of $^6\text{Li}/^7\text{Li}$ and $^{235}\text{U}/^{238}\text{U}$. The solution ICP-MS experiment analyte list typically included: ^7Li , ^9Be , ^{25}Mg , ^{31}P , $^{43,44}\text{Ca}$, ^{51}V , ^{55}Mn , ^{71}Ga , ^{75}As , $^{84,86}\text{Sr}$, ^{89}Y , ^{133}Cs , ^{135}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{149}Sm , ^{151}Eu , ^{159}Tb , ^{160}Gd , ^{161}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{184}W , $^{204,206,207,208}\text{Pb}$, ^{232}Th , and ^{238}U . Experiment batches followed a design modified from Eggins et al. (1997) with a sample run sequence of: carrier acid blank, laboratory standard and sample unknown procedural blanks, calibration standards (USGS rock standard W-2a), quality control standards (USGS rock standards BHVO-2, AGV-2, BIR-1), sample unknowns, calibration standards (W-2a) and final acid washout. Silicate rock standards were digested following previously described methods (e.g., Babechuk et al., 2010). Monitor samples (typically an additional USGS rock standard) bracketed all standards and unknowns at intervals of every 5–7 samples. Following the analysis of apatite samples, an additional acid rinse was performed to ensure washout of Th to near-background levels prior to introducing the next sample and permit bracketed blank subtraction; background levels of Th never exceeded

Table 3

Summary of LA-ICP-MS data for Durango (Don-G, DCa) and McClure Mountain apatites and comparison with solution ICP-MS data.

Element	Solution ppm	RSD %	Laser spots ppm	RSD%	Max	Min	n	Laser vs soln. (%)	Laser spots ppm	RSD%	Max	Min	n	KED vs soln. (%)	KED vs all laser (%)
Dur-DonG all laser data									Dur-DonG KED 60 µm spot data						
V	28.80	3.1	30.74	8.7	41.37	23.91	612	6.7	29.80	5.3	33.74	27.40	57	3.5	−3.0
Mn	100.30	2.4	104.60	24	445	33.08	1758	4.3	106.85	1.9	111.15	101.40	57	6.5	2.1
As	606.5	3.4	512.6	9.1	729	415.7	612	−15.5	495.6	5.5	563.6	443.6	57	−18.3	−3.3
Sr	497.2	1.6	516.9	4.1	618	439.6	1758	4.0	472.0	2.1	493.4	452.4	57	−5.1	−8.7
La	3786	1.3	3720	7.6	5190	3020	1758	−1.7	3943	2.8	4212	3677	57	4.1	6.0
Ce	5306	1.4	5184	7.4	6760	4250	1758	−2.3	5207	2.6	5451	4804	57	−1.9	0.4
Pr	472.5	1.3	451.6	5.2	583.3	234.6	1758	−4.4	456.3	2.7	480.7	416.3	57	−3.4	1.0
Nd	1534	1.7	1567	7.5	2174	1053	1758	2.1	1597	3.2	1683	1427	57	4.1	1.9
Sm	215.2	1.1	223.6	5.6	293.7	172.9	1758	3.9	225.78	3.1	237.9	201.1	57	4.9	1.0
Eu	18.90	1.4	18.88	4.6	22.84	15.35	1758	−0.1	20.12	3.1	21.37	18.87	57	6.4	6.6
Gd	186.9	1.2	189.2	6.4	264.7	150	1758	1.2	194.1	3.0	208.2	173.5	57	3.9	2.6
Tb	24.25	1.2	23.03	4.7	27.71	18.99	1758	−5.1	24.16	2.7	26.00	22.12	57	−0.4	4.9
Dy	129.9	0.9	135.9	5.1	163.7	110.9	1758	4.6	133.2	2.7	140.4	123.6	57	2.6	−2.0
Y	785.0	0.8	824	5.4	1001	624	1758	4.9	834.1	2.2	875	793	57	6.3	1.3
Ho	26.35	1.3	26.63	4.9	36.08	22.98	1758	1.1	26.58	2.8	28.30	24.74	57	0.9	−0.2
Er	68.69	1.1	71.89	5.4	90.9	55	1758	4.7	67.94	3.0	73.32	63.77	57	−1.1	−5.5
Tm	8.75	1.4	8.98	5.1	11.26	7.27	1758	2.7	8.39	3.2	8.97	7.74	57	−4.1	−6.6
Yb	45.10	1.6	47.83	5.7	62.6	37.22	1758	6.1	45.84	3.3	49.82	43.00	57	1.6	−4.2
Lu	5.17	1.6	5.43	5.9	6.8	4.5	1758	5.0	5.29	3.8	5.84	4.89	57	2.3	−2.6
Pb	3.12	7.6	0.71	30	4.4	0.416	1758	−77.3	0.71	17.6	1.29	0.54	57	−77.1	1.0
Th	235.0	0.5	252.5	7.6	379.3	195.2	1758	7.4	244.1	4.6	269.2	220.0	57	3.9	−3.3
U	13.00	1.6	13.11	8.0	18.98	9.24	1758	0.9	13.09	4.4	15.07	11.90	57	0.7	−0.1
McClure Mountain all laser data									McClure Mountain KED 60 µm spot data						
V	18.53	5.0	16.63	42	36.91	1.87	498	−10.3	16.98	38.8	33.79	4.68	64	−8.4	2.1
Mn	99.40	5.4	103.2	34	378	1.5	1533	3.8	103.41	17.8	170.63	72.77	64	4.0	0.2
As	20.72	2.3	9.19	77	64.4	2.54	498	−55.6	17.35	24.5	57.5	20.3	64	−16.2	88.8
Sr	3902	2.1	3841	11	6330	2461	1533	−1.6	3504	6.7	4042	3063	64	−10.2	−8.8
La	1764	1.5	1681	21	5090	706	1533	−4.7	1642	15.7	2536	1208	64	−6.9	−2.4
Ce	2859	1.6	2751	24	6930	1222	1533	−3.8	2744	15.4	3540	1552	64	−4.0	−0.3
Pr	275.2	1.1	254.9	24	678	87.5	1533	−7.4	249.47	16.2	323.2	127.7	64	−9.3	−2.1
Nd	894.4	1.0	893	28	2900	112.6	1533	−0.2	870.29	17.2	1112	388	64	−2.7	−2.5
Sm	106.7	1.5	106.5	32	376.3	23.08	1533	−0.2	102.5	20.3	148.0	36.3	64	−4.0	−3.8
Eu	41.19	1.7	38.92	25	86.6	15.17	1533	−5.5	40.37	21.7	62.15	25.29	64	−2.0	3.7
Gd	74.32	1.3	73.7	33	255.8	19.18	1533	−0.8	72.54	20.7	110.9	25.0	64	−2.4	−1.6
Tb	8.59	1.3	7.79	35	27.71	1.609	1533	−9.4	7.89	22.3	11.99	2.21	64	−8.2	1.4
Dy	41.62	2.2	41.6	37	181	7.88	1533	−0.1	39.39	23.1	59.6	10.4	64	−5.4	−5.3
Y	215.6	1.8	220	43	1937	53.1	1533	2.0	216.2	25.7	457	65	64	0.3	−1.7
Ho	7.95	1.5	7.64	38	42.87	1.556	1533	−3.9	7.44	23.6	13.16	2.18	64	−6.4	−2.6
Er	20.30	1.6	20.05	41	154.9	4.29	1533	−1.2	18.58	26.2	39.36	5.29	64	−8.5	−7.3
Tm	2.72	1.4	2.58	48	25.97	0.587	1533	−5.1	2.38	30.8	6.14	0.71	64	−12.5	−7.8
Yb	15.84	1.2	15.50	53	175.8	2.14	1533	−2.1	14.75	33.8	41.47	5.14	64	−6.9	−4.9
Lu	2.24	1.1	2.16	52	23.52	0.492	1533	−3.6	2.10	31.3	5.47	0.88	64	−6.4	−2.9
Pb	4.43	5.4	3.08	57	32.9	1.015	1533	−30.5	2.83	32.1	5.16	1.50	64	−36.0	−7.9
Th	63.71	3.0	53.4	79	876	13.45	1533	−16.2	45.77	39.7	87.7	20.2	64	−28.2	−14.3
U	18.42	5.2	16.27	42	82.1	4.682	1533	−11.6	15.72	31.4	26.80	8.17	64	−14.7	−3.4
Element	Solution ppm	RSD %	Laser spots ppm	RSD%	Max	Min	n	KED vs soln. (%)	Spots ppm Dur-Marks ^a	Spots ppm Dur-DCa ^b	Spots ppm Dur-Fish ^b	Spots ppm Dur-Griff ^b	Spots ppm Dur-Hou ^b	Spots ppm McClure ^b	
Dur-DCa KED 60 µm spot data									Data from other sources						
V	31.87	3.2	33.81	28	51.5	17.79	58	6.1	36	-	-	-	-	-	
Mn	95.15	5.5	110.70	2.7	118.6	105.2	58	16.3	114	-	-	-	-	-	
As	939.0	1.9	886.7	28	1261	473	58	−5.6	825	-	-	-	-	-	
Sr	501.9	0.9	475.4	3.0	516	439	58	−5.3	500	482	456	491	476	3422	
La	4239	2.6	4404	8.7	4941	3492	58	3.9	3310	4285	3176	3819	3334	1609	
Ce	5777	2.8	5659	7.0	6415	4793	58	−2.0	4430	5405	3635	5178	4561	2362	
Pr	530.1	2.4	494.8	7.1	561	424	58	−6.7	320	488	307	496	436	126	
Nd	1728	2.7	1751	7.5	2018	1489	58	1.4	870	1677	1009	1745	1514	843	
Sm	251.1	0.9	261.6	9.3	315.7	214.9	58	4.2	120	237	127	244	207	102	
Eu	20.50	1.2	21.31	6.6	25.03	18.45	58	4.0	16.9	21	15	22	20	37	
Gd	225.9	1.8	237.2	11	291.1	188.4	58	5.0	103	204	105	206	174	77	
Tb	30.27	3.0	30.88	12	38.46	23.48	58	2.0	13.5	28	13	27	23	8.3	
Dy	167.0	0.5	173.7	12	218.8	128.3	58	4.0	68	154	68	146	123	40	
Y	1017	1.1	1069	11	1233	811	58	5.1	410	911	427	886	762	206	
Ho	34.78	1.4	35.12	12	44.2	26.03	58	1.0	15	32	14	30	25	7.4	
Er	91.94	2.1	90.91	13	113.9	65.4	58	−1.1	35	83	34	77	64	18	
Tm	11.84	1.4	11.25	13	14.19	8	58	−5.0	5	10	4	10	8	2.3	
Yb	60.21	1.8	60.87	12	76.6	43.4	58	1.1	27	59	27	56	47	14	
Lu	6.60	1.0	6.75	11	8.4	4.99	58	2.3	3.8	6	4	7	6	1.9	
Pb	0.69	2.2	0.95	13	1.261	0.667	58	38.4	0.7	0.9	0.4	0.7	0.6	3.7	
Th	358.9	0.8	350.1	13	456.8	254.8	58	−2.4	175	320	151	270	231	38	
U	18.66	2.2	17.71	14	23	12.85	58	−5.1	12.4	20	7	11	11	12	

1% of the signal intensity in sample unknowns throughout an experiment sequence.

Three channels per peak were measured with dwell times ranging from 10 to 30 ms with 20–40 sweeps over 4 runs to produce an average analyte intensity. For signals over 1000 cps, the (internal) precision of the average intensity was typically lower than 1% (1 σ RSD) and ranged from 1 to 5% for signals between 50 and 1000 cps. The average intensities were corrected for blank, drift (using the internal standard and monitors), and isobaric interferences offline. Calibration of the corrected intensities used the average intensity calculated from multiple analyses of the W-2a standard and applying either the laboratories' (trace elements) or the USGS' (major elements) recommended abundances (Table 2). Final element abundances in the digested apatite were calculated by normalizing all values to a Ca content of 40 wt.%. This strategy was used to provide consistency with the laser data and to minimize compounding error associated with the high dilution factors of the digested crystals. Nevertheless, dilution factors calculated from Ca-normalization and the mass/mass procedural weigh-in did not deviate by more than 5%. Analysis at multiple dilution factors was necessary to optimize the measurement of some analytes in ideal detector configurations and more closely match standard and unknown intensities to acquire precise data for all of the reported elements. Trace-element contents from each digest (average or single measurement) are reported in Table 2 in addition to an average value for each of the specific apatites (Dur-DCa, Dur-DonG and McClure Mountain). The ratios (wt/wt) of Th/U, U/Pb, Sm/Nd, and Y/Ho are also reported for each apatite. The quality control standards analysed throughout the experimental sessions were accurate, within the measurement uncertainty, relative to previously reported values of long-term means (e.g., Kamber, 2009; Babechuk and Kamber, 2011; Babechuk et al., 2015). The latter studies demonstrate that most trace-element abundances determined with the applied external calibration technique are externally reproducible to better than 5% and typically close to 1% (1 σ RSD).

3.5. Solution ICPMS interferences and backgrounds

Background-equivalent concentrations (BEC) for most analytes during the solution analyses were in the pg g⁻¹ to fg g⁻¹ range (e.g., all REE BECs were less than 100 fg g⁻¹). Manganese backgrounds in 2% HNO₃ (used as a sample carrier) were always lower than 2000 cps (BEC of less than 15 pg g⁻¹) and insignificant relative to the sample Mn intensities. Thus Mn determination was not influenced by the same high baseline corrections of the LA-ICP-MS analyses generated by ⁴⁰Ar¹⁴N¹H⁺ or ⁴⁰Ar¹⁵N⁺ interferences.

To correct for common oxide, hydroxide, and dimer isobaric interferences, three solutions (a mixture of Ba + Nd, pure Dy, and pure Ce) were analysed routinely prior to unknowns. All other oxide production rates (e.g., SmO⁺ on Ho) were scaled from their initially measured rates on the instrument using the relative change in the NdO⁺ on Gd ratio (measured as ¹⁶⁰Gd/¹⁴⁶Nd; Ulrich et al., 2010; Aries et al., 2000). Most important for the analysis of apatite is correcting for isobars of the LREE oxides on the masses measured for the MREE to HREE as well as LREE dimers interfering on masses ⁷¹Ga and ⁷⁵As. Similar to the LA-ICPMS experiments, the low Ga/REE ratio of the apatite and ¹⁴²Ce⁺⁺ and ¹⁴²Nd⁺⁺ dimer production accounted for >90% of the intensity on ⁷¹Ga⁺ and inhibited its accurate measurement. Correction of the LREE dimers ¹⁵⁰Sm⁺⁺ and ¹⁵⁰Nd⁺⁺ on ⁷⁵As⁺ (production rates of 0.14 to 0.28% and 0.03 to 0.15%, respectively) was insignificant for the Durango samples (ranging from 1 to 3% of the signal intensity). The lower As/LREE ratio of the McClure Mountain apatite made the correction from these dimers more significant (ranging from 20 to 35% of the signal

intensity). Additional oxides and dimers of the REE appear to have influenced the measured intensities on other masses, although attempts to accurately resolve the interferences were not made in this study. Specifically, (1) the signal on mass 85 (Rb) appears to be highly influenced by HREE dimers (Yb and Er) and possibly also Sr hydrides, (2) the accurate measurement of the high-field-strength-elements Hf, Ta, W in Dur-DCa and Dur-DonG apatite was hindered by isobaric interferences from oxides of the MREE–HREE (TbO⁺, GdO⁺, DyO⁺, HoO⁺, ErO⁺), and (3) Nb determinations were influenced by ¹⁸⁶W⁺⁺ in high-W samples. Therefore abundances for the elements Rb, Nb, Hf, and Ta are not reported.

A matrix containing Cl can produce interferences from ArCl⁺ and ClO⁺. However, both fluorapatites analysed in this study have low Cl contents and, as discussed in the LA-ICPMS Section 3.3, Cl-based interferences appear to be minor to negligible for the analysis of the Durango and McClure apatites. To confirm this, masses 35 (Cl) and 77 (assuming contribution from only ⁴⁰Ar³⁷Cl⁺) were monitored in one solution experiment and a matrix test with varying HCl concentrations was performed. These tests showed a contribution of not more than 0.3% on mass 51 (V) from ³⁵Cl¹⁶O⁺ and not more than 0.06% on mass 75 (As) from ⁴⁰Ar³⁵Cl⁺. The contribution to mass 55 (Mn) from ³⁷Cl¹⁸O⁺ was not detectable at the ³⁵Cl levels of the diluted apatite samples. It is noted, however, that other analysis strategies (e.g., Cl matrix removal, analysis with a mass spectrometer with greater mass resolution or analysis with collision/reaction cell) may be required for determination of these elements in chlorapatites.

4. Results

4.1. LA,Q-ICPMS trace-element data for Dur-DonG apatite

For solution-ICPMS data from Dur-DonG apatite, excellent reproducibility (<3% RSD) is obtained between the two digests for all elements (Table 2) except V (3.1%), As (3.4%), W (3.8%), Mg (4.9%) and Pb (7.6%). The trace element ratios Y/Ho, Sm/Nd, and Th/U, reproduce better than 1%, whereas U/Pb has a poorer reproducibility of 7.8%.

LA-ICPMS spot analyses were undertaken on 1758 crystals of Dur-DonG apatite, although there is only V and As data for 612 analyses (Table 3). There is good agreement between the spot and solution data with Mn, Sr, Y, all REE except Tb and Yb, and U all within 5% of the solution value (Table 3, Fig. 3A), and Tb, Yb and Th within 10% of the solution value. Two elements in the spot data deviate by more than 10% from the solution value: As (−15.5%) and Pb (−77.3%), and are outside analytical uncertainty (1 SD) of the solution value.

LA-ICPMS spot analyses were undertaken on a set of 57 crystals of Dur-DonG apatite using the collision cell of iCAP Qc in Kinetic Energy Discrimination (KED) Mode (Section 3.3) to remove the effect of potential polyatomic interferences, and compared with the solution data and the spot data from the main Dur-DonG dataset (Fig. 3B, Table 3). There is a good correspondence between the two laser datasets (Fig. 3B), with only Sr (−8.7%), La (6.0%), Eu (6.6%), Er (−5.5%) and Tm (−6.6%) deviating by more than 5% of the corresponding elemental abundance in the main laser dataset, and all elements within 10% of the main laser dataset.

4.2. LA,Q-ICPMS trace-element data for Dur-DCa apatite

For solution-ICPMS data from Dur-DCa apatite, many elements exhibit excellent reproducibility (<3% RSD) between the four separate digests: As, Sr, Y, the REE Pr to Lu, Pb, Th, and U. Good reproducibility (3–5% RSD) is obtained for V, Mg, La and Ce and moderate

Notes to Table 3:

Notes: McClure Mountain laser-ablation As contents corrected for ¹⁵⁰Sm²⁺ and ¹⁵⁰Nd²⁺ dimers.

^a Marks et al. (2012).

^b Yang et al. (2014).

reproducibility is obtained for Mn and Li (5–10%). The selected trace element ratios (Y/Ho, Sm/Nd, Th/U, U/Pb) all reproduce better than 3%.

LA-ICPMS spot analyses were undertaken on 58 crystals of Dur-DCa apatite using the collision cell of iCAP Qc in Kinetic Energy

Discrimination (KED) Mode. There is good consistency between the KED laser ablation and solution data with La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th all within 5% of the solution value and V, As, Sr, Ce, Pr, Gd and Tb within 10% of the solution value (Fig. 3E, Table 3).

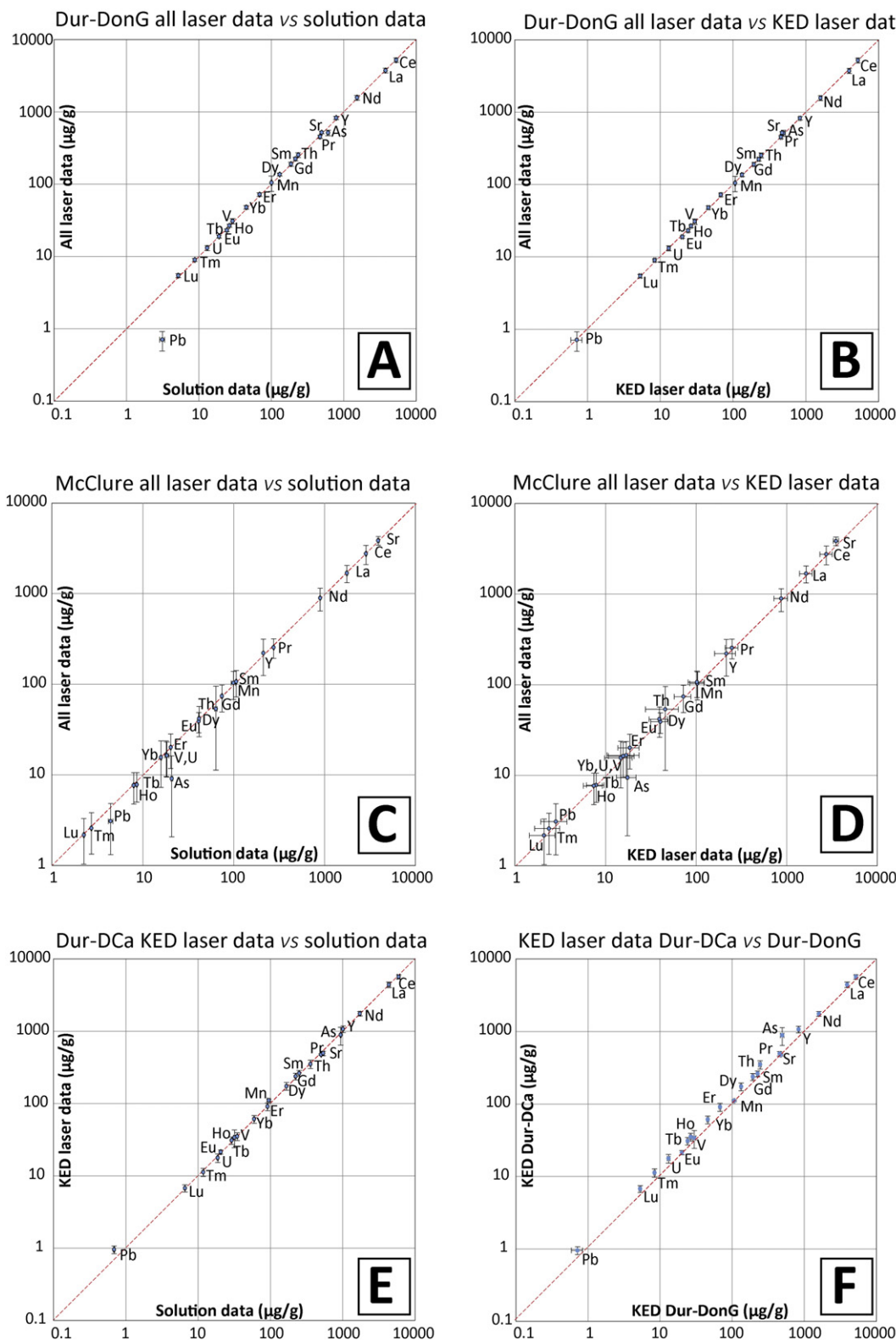


Fig. 3. A) All LA-ICPMS Dur-DonG spot data ($n = 1758$) plotted against solution data. B) All LA-ICPMS Dur-DonG spot data plotted against the LA-ICPMS KED spot data ($n = 57$). C) All LA-ICPMS McClure Mountain spot data ($n = 1533$) plotted against solution data. D) All LA-ICPMS McClure Mountain spot data plotted against the LA-ICPMS KED spot data ($n = 64$). E) LA-ICPMS Dur-DCa KED spot data ($n = 58$) plotted against solution data. F) Dur-DCa LA-ICPMS KED spot data plotted against Dur-DonG LA-ICPMS KED data.

Two elements in the KED spot data deviate by more than 10% from the solution value: Mn (16.3%) and Pb (38.4%).

4.3. LA-Q-ICPMS trace-element data for McClure Mountain apatite

For solution-ICPMS data from McClure Mountain apatite, several elements exhibit excellent reproducibility (<3% RSD) between the three separate digests: As, Sr, Y, the REE La to Lu, and Th. Good reproducibility (3–5% RSD) is obtained for V, and moderate reproducibility (5–10% RSD) is obtained for Li, Mg, Mn, Pb and U, and poor reproducibility (>10%) is obtained for W (14%). The selected trace element ratios of the McClure Mountain apatite are very reproducible (<2% RSD), but different (e.g., Th/U, Sm/Nd) from that of Durango, reflecting the separate environment of its formation (Sections 2.1, 2.3). W is present in the McClure apatite at significantly higher abundance than in the Durango apatite (166.6 µg/g). It is thought that the high abundance and poor reproducibility of W reflect severe and heterogeneous contamination of the apatite during sample preparation (tungsten carbide contamination from a jaw crusher, and/or sodium polytungstate during heavy mineral separation). W was not routinely analysed during the laser spot analyses, but one McClure Mountain LA-ICPMS session which did employ W as an analyte has yielded a mean W content of ~25,000 ng/g. However, most analyses were <1000 ng/g with occasional outliers with significantly elevated W. This behaviour was not observed in either of the Durango aliquots (Dur-DCa and Dur-DonG) which were crushed using an agate and steel pestle respectively and not passed through heavy liquids, nor in unpublished data of several hundred detrital apatites from modern river sands derived from granitic basement in the Massif Central, France. These apatites did not pass through a jaw crusher and were not separated using sodium polytungstate, and exhibited mean W contents of <1000 ng/g W.

LA-ICPMS spot analyses were undertaken on 1533 crystals of McClure Mountain apatite, although there is only V, Ga and As data for 498 analyses (Table 3). There is good agreement between the spot and solution data with Mn, Sr, La, Ce, Nd, Sm, Gd, Dy, Y, Ho, Er, Yb and Lu all within 5% of the solution value (Fig. 3C, Table 3), and V, Pr, Eu, Tb, and Tm within 10% of the solution value. Four elements in the spot dataset deviate by more than 10% from the solution value: As (–55.5%), Pb (–30.5%), Th (–16.2%) and U (–11.6%) although all but As overlap within their analytical uncertainty (1 SD).

LA-ICPMS spot analyses were undertaken on a subset of 64 crystals of McClure Mountain apatite using the collision cell of iCAP Qc in Kinetic Energy Discrimination (KED) Mode, and compared with the solution data and the spot data from the main McClure Mountain dataset (Fig. 3D, Table 3). There is a good correspondence between the two datasets, with only As (88.8%) and Th (–14.3%) falling outside of 10% of the corresponding elemental abundances in the main dataset (Fig. 3D, Table 3).

4.4. Comparison between the Dur-DonG and Dur-DCa apatite LA-Q-ICPMS data

In a comparison of the solution-ICPMS datasets, Dur-DonG has a near-identical Sr abundance relative to Dur-DCa (differing by 1.4%). The relative abundances for most other trace elements differ more significantly, however. Vanadium, Mn, and Eu differ between 5 and 10%, the REE La to Tb (minus Eu) differ between 10 and 20%, Mg, Y, the REE Dy to Lu, Th, and U differ between 20 and 50%, and Li and Pb exhibit the most extreme differences of 80 and 128%, respectively. By contrast to Dur-DCa where W intensities were too close to the detection limit to produce reliable data, Dur-DonG had a significantly higher W content (mean of 1884 ng/g). Most trace element ratios are similar between Dur-DCa and Dur-DonG, with a percent difference as follows: Y/Ho (3.0%), Th/U (4.8%), and Sm/Nd (4.4%). In addition, CI-chondrite normalized pattern topographies are very similar between the two

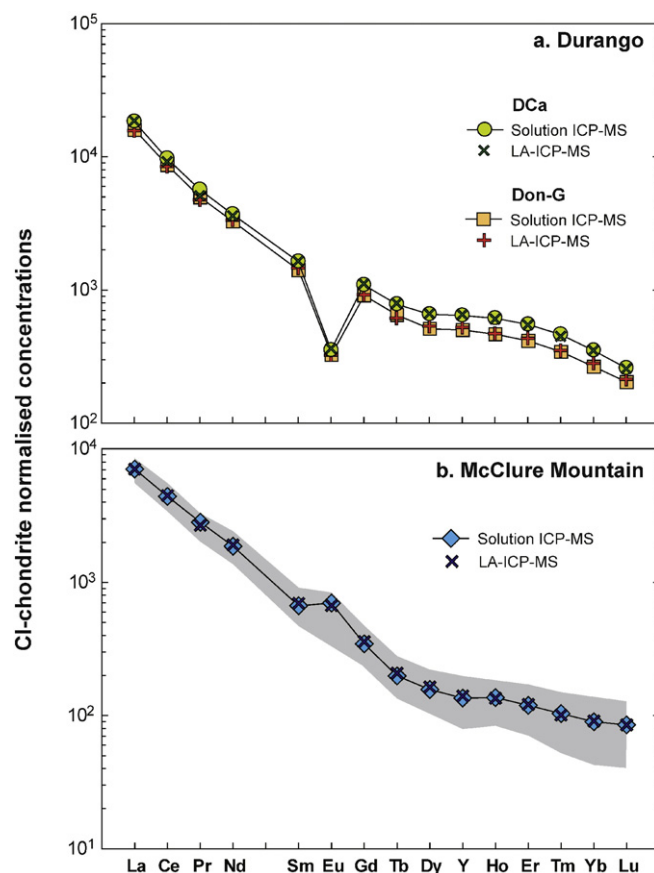


Fig. 4. CI-chondrite normalized REE + Y data for (a) Durango (Dur-DCa and Dur-DonG) and (b) McClure Mountain apatites. Solution ICPMS contents are taken from the mean values reported in Table 2 and LA-ICPMS contents are taken from the overall means reported in Table 3. 1σ RSD errors (reproducibility) of the solution values for both apatites are smaller than the symbols, whereas the errors on the LA-ICPMS values are close to the symbol size for only the Durango apatites. The grey shaded area represents the 1σ RSD errors for the LA-ICPMS mean values of McClure Mountain. CI-chondrite values from Sun and McDonough (1989).

Durango apatite aliquots despite the difference in REE abundance (Fig. 4a). The significantly higher Pb content of Dur-DonG compared to Dur-DCa (3.12 vs 0.69 µg/g), however, results in a much lower U/Pb ratio (4.11 vs. 26.94, differing by 147%). The higher W and Pb in Dur-DonG relative to Dur-DCa is thought to be the result of surface contamination of the grain shards, either along original fractures inside the large Durango crystal (Fig. 1E, Section 5) or produced during the preparation of the crushed Dur-DonG apatite crystals using a steel pestle (Section 4.3).

Fig. 3F illustrates the elemental abundances of Dur-DCa apatite plotted against Dur-DonG apatite using the KED laser ablation datasets, as both were acquired in the same session under the same analytical conditions. The larger relative standard deviations of Dur-DCa is evident (cf. Table 3), demonstrating that the Dur-DCa is significantly more heterogeneous than Dur-DonG. Dur-DCa is enriched between 10 and 30% in most elements, with the exception of Mn, Sr and Eu which are nearly identical in both datasets. The similarity in Eu between both datasets is due to the larger negative Eu anomaly in Dur-DCa (Fig. 4a). Arsenic (+78.5%) is significantly more enriched in Dur-DCa.

Other data for Durango apatite and McClure Mountain apatite are listed in Table 3, including a Durango apatite from Marks et al. (2012), and four separate Durango crystals (including Dur-DCa) and McClure Mountain apatite from Yang et al. (2014). The Dur-DCa and McClure Mountain apatite data from Yang et al. (2014) yield elemental abundances which are on average 10% lower than the solution-ICPMS and

LA-ICPMS data from this study. The five Durango apatites analysed by Yang et al. (2014) and Marks et al. (2012) are relatively homogenous in terms of their Sr contents, show moderate variation in LREE abundances (La ranging from 3176 to 4285 $\mu\text{g/g}$) and larger variation in the HREE (Yb ranging from 27 to 59 $\mu\text{g/g}$), consistent with the larger variation exhibited by the HREE between Dur-DCa and Dur-DonG in this study (Fig. 4a). Th and U range between 151 to 320 $\mu\text{g/g}$ and 7 to 20 $\mu\text{g/g}$ respectively (Table 3), and are moderately correlated with increasing REE content.

4.5. Durango c-axis parallel and c-axis perpendicular LA-ICPMS raster data

Sixteen c-axis perpendicular and 9 c-axis parallel elemental profiles were undertaken on a suite of separate euhedral Durango crystals, ranging in size from $1 \times 0.5 \times 0.5$ cm to $2 \times 1.25 \times 1.25$ cm (Fig. 2). The profiles were undertaken as close as possible through the centre of the crystals. Mn, Sr, Y, La, Th and U were measured in the c-axis perpendicular profiles (Fig. 2A). The Sr and Mn profiles in the c-axis perpendicular sections are essentially flat, which is consistent with the low standard deviations for Sr and Mn in the Durango spot datasets and show little variation from grain to grain (c. 450 $\mu\text{g/g}$ and 90 $\mu\text{g/g}$ respectively). La and Y are moderately zoned in the c-axis perpendicular profiles, and exhibit moderately coupled behaviour. U and Th exhibit significant zoning in several profiles and strongly coupled behaviour (Fig. 2A), which is moderately coupled to the REE behaviour. Li, As, Er, Pb, Th and U were measured in the c-axis parallel profiles. Th, U and the REE (Er) are significantly less zoned compared to the c-axis perpendicular profiles (Fig. 2B). The Pb profiles are essentially flat, but Li and As (not measured on c-axis perpendicular sections) exhibit significant zoning.

4.6. Durango c-axis perpendicular LA-ICPMS image maps

C-axis perpendicular sections for LA-ICPMS image mapping were made from two Durango crystals. One crystal which exhibited significant zoning was selected from the c-axis perpendicular profile dataset (Dur-11, highlighted on Fig. 2A), along with a c-axis perpendicular section from the Dur-DCa crystal (Fig. 1A). Only a quarter c-axis perpendicular section was mapped of the Dur-DCa crystal as the entire c-axis perpendicular slice would not fit in a 25 mm diameter epoxy resin puck. Li in both maps (Fig. 1B, I) exhibits significant oscillatory zoning. The REE (Er in Dur-DCa, Fig. 1D; Dy in Dur-11, Fig. 1K) also exhibit oscillatory zoning, with Dy in Dur-11 exhibiting very subtle zoning in the core mimicking the Li zoning pattern. Arsenic also exhibits oscillatory zoning in both maps. In Dur-DCa, the As pattern is similar to that of Er and U (Fig. 1C), with the exception of a thin internal band near and parallel to the upper face of the crystal which is depleted in As but enriched in Er and U. Th and U behaviour is strongly coupled in both maps, but in addition to oscillatory zoning in Dur-11, Th (Fig. 1M) and U (Fig. 1N) also exhibit a complicated sector zoning pattern. The distribution of Pb (mass ^{208}Pb) closely reflects the Th pattern in Dur-11 (Fig. 1L), likely reflecting variation in radiogenic ^{208}Pb . Both crystals exhibit substantial enrichment of Pb on the crystal edges. While some of this may reflect contamination by common Pb-bearing material on the crystal surfaces (e.g. the fractures in Dur-DCa also exhibit elevated Pb, Fig. 1E), the Pb-rich outer zone in Dur-11 is up to 0.5 mm wide and is likely a primary feature reflecting late stage incorporation of Pb into the crystal rim.

5. Discussion — summary of the laser-ablation versus solution-ICPMS data

The laser ablation and solution Q-ICPMS trace-element analyses on crushed 150–300 μm aliquots of Durango and McClure Mountain apatite demonstrate that Y, the REE, Sr, Mn, V and U are highly reproducible in both datasets, and that using NIST 612 standard glass as a primary elemental abundance standard using our analytical setup exhibits no significant elemental fractionation between the laser ablation and solution

data. Discrepancies between the solution and laser ablation data were found for three elements: As, Pb and Th. The Th data for both Durango aliquots are within 10% of the solution value, but the McClure Mountain apatite data differ from the solution value by -16.2% (main LA-ICPMS dataset) and -28.2% (64 crystal LA-ICPMS KED dataset). Raster experiments across 13 crystals of McClure Mountain apatite show that Th is significantly zoned in McClure Mountain apatite, with the rims on average 10% enriched in Th relative to the cores, and hence the laser ablation Th data (which are typically sited in the cores) may underestimate the true Th content. Raster experiments (not illustrated) also show that As is often significantly zoned in McClure Mountain and moderately zoned in Durango (Dur-DonG) apatite and intra-crystal variability explains the large standard deviations in the As laser ablation spot data. REE dimers were demonstrated to account for $<1\%$ of the apparent ^{75}As signal in laser ablation analyses of Durango apatite, but the significantly lower As contents in McClure Mountain apatite result in $^{150}\text{Nd}^{++}$ and $^{150}\text{Sm}^{++}$ forming $\sim 20\%$ of the apparent ^{75}As signal. The laser-ablation Pb data are within or close to analytical uncertainty of the solution values for McClure Mountain (-30.5%) and Dur-DCa ($+38.4\%$), but Dur-DonG deviates significantly from the solution value (-77.3%). Preliminary solution experiments on individual crystals or small (5 or 10 crystal) aliquots typically yielded values close to the laser ablation Pb content with occasional outliers of high Pb (10–20 $\mu\text{g/g}$) grains or small aliquots. It is speculated that these represent grains with elevated Pb on the crystal surface and probably related to either the sample preparation or Pb incorporation along fractures in the original crystal (similar to Fig. 1E), that would not be detected during laser ablation, which is supported by occasional significant spikes in Pb on the grain boundaries in raster experiments (not illustrated) on aliquots of the Dur-DonG crystal.

6. Conclusions and implications for making natural apatite standards

NIST 612 standard glass can be used as a primary standard for apatite measurements for Y, the REE, Sr, Mn, V, Th and U. Crushed aliquots of Durango apatite analysed by solution ICPMS make an excellent secondary standard for quality control of the apatite trace-element data. In particular, Sr appears to be highly reproducible with low standard deviations in both the Durango solution and LA-ICPMS spot and raster data and also LA-ICPMS data from the literature, and clearly has potential as an alternative to Ca as an internal elemental standard. Natural mineral separates from granitic rocks such as apatite from the McClure Mountain syenite also yield LA-ICPMS data in close agreement with the solution ICPMS data (e.g. Fig. 3C). However the McClure Mountain syenite natural mineral separates have significantly larger intra-crystal variations in most trace elements (typically 20–40% RSD on the McClure Mountain 64 crystal LA-ICPMS KED data, Table 3) than the crushed single crystal Durango separates ($<5\%$ RSD for most elements on the 57 crystal Dur-DonG LA-ICPMS KED dataset, Table 3). Problematic elements in apatite laser-ablation trace-element analyses include As which exhibits substantial intra-crystal variability even in crushed 150–300 μm aliquots of Durango apatite and requires correction for REE dimers in apatites with low As concentrations, while Pb contamination on grain surfaces can cause discrepancies between solution-based and laser-ablation apatite trace-element analyses.

The ability to accurately and rapidly measure trace element abundances in apatite by LA-ICPMS has several potential petrogenetic applications. Although apatite is typically a minor constituent in magmatic rocks, it is a powerful monitor of magmatic processes as it incorporates a large range of trace and minor elements into its crystal structure. Although much of this research has focussed on its volatile and halogen content as a petrogenetic indicator and a fingerprint for metasomatic processes, magmatic apatite can also exert a dominant control on the geochemical behaviour of trace components like the REEs, Sr, U, and Th in melts and magmatic fluids (Webster and Piccoli, 2015). These trace elements partition in favour of silicate melts relative to apatite (Prowatke and Klemme,

2006), with apatite preferentially incorporating the middle REEs relative to the lighter and heavier REEs. Jennings et al. (2011) demonstrate that the Sr content of magmatic apatite correlates with whole-rock Sr content (which is a function of plagioclase fractionation during magmatic differentiation), while Y contents in apatite correlate positively with whole-rock silica contents. Mg, Cl, Mn, Fe, Y, and Ce in apatite have been applied to tephra correlation problems in the eastern U.S. and between North America and Europe (Sell and Samson, 2011) while apatite REE geochemistry which has been demonstrated to have significant potential in geochemical exploration (Belousova et al., 2002) and sandstone provenance studies (Dill, 1994; Morton and Yaxley, 2007).

6.1. A protocol for making natural apatite trace element standards

The low relative standard deviations for many elements on the Dur-DonG crushed mineral separate demonstrates the potential application of Durango apatite as a laser-ablation trace-element primary or secondary reference material. An accuracy and precision of <5% was obtained for most trace elements in 57 crystal Dur-DonG LA-ICPMS KED dataset (Table 3). The trace element homogeneity of this crystal was not determined prior to crushing, and it is likely the precision and accuracy could be improved with an even more homogenous mineral separate. Some Durango crystals are clearly more homogenous than others, as evidenced by the larger standard deviations in the Dur-DCa aliquot (Table 3) and the Durango raster (Fig. 2) and image mapping experiments (Fig. 1). The raster experiments demonstrate that Durango apatite typically exhibits less zoning parallel to the C-axis compared to perpendicular to the C-axis. A suggested protocol for generating aliquots of Durango apatite that are sufficiently homogenous to act as a trace-element reference material is to characterize several Durango crystals. The crystal terminations should be removed, and the crystals should then be cut into three slices parallel to the C-axis. The central slice should then be polished on both sides suitable for laser ablation analyses, and one quick C-axis parallel and one C-axis perpendicular raster should be undertaken on both sides of each crystal. The most homogenous crystal in terms of the trace elements of interest is then crushed to 150–300 µm (with care taken to minimize contamination) and solution ICPMS analyses are undertaken on a series of 20 mg aliquots (ca. 250 grains) to give precise reference trace-element abundances that averages out remaining heterogeneities from crystal zonation. Additionally the approach (LA-ICPMS mapping of large crystals to determine the degree (and scale) of trace-element heterogeneity, followed by crushing and solution-ICPMS characterization of aliquots) is generic and can easily be modified and applied to characterize large, gem-quality crystals of other mineral phases (e.g. zircon, rutile and titanite) to act as natural LA-ICPMS mineral standards.

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Appendix A. Supplementary data

Supplementary data to this article (all laser spot data for McClure Mountain, Dur-DCa and Dur-DonG, Table SD1) can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2016.03.028>.

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