



(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 (1σ), 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,

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