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Calcium and neodymium radiogenic isotopes of igneous rocks: Tracing crustal contributions in felsic magmas related to super-eruptions and continental rifting

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ABSTRACT

Radioactive decay of ^{40}K within the continental crust produces a unique Ca isotopic reservoir, with measurable radiogenic ^{40}Ca excesses compared to Earth's mantle (εCa = 0). Thus, igneous rocks with values of $\varepsilon\text{Ca} > 1$ unambiguously indicate a significant old, crustal contribution to their source magma. At our current level of analytical precision, values of $\varepsilon\text{Ca} < 0.5$ are indistinguishable from mantle-like Ca isotope compositions. So, whereas ^{40}Ca excesses clearly define crustal contributions, the source contributions of igneous rocks with mantle-like Ca isotopic composition are less certain. The calcium in these rocks could be derived from partial melting of: young crust, crust with mantle-like K/Ca compositions, or the mantle itself. Here we present Ca isotopic measurements of intermediate to felsic igneous rocks from the western United States, and two crustal xenoliths found within the Fish Canyon Tuff (FCT) of the southern Rocky Mountain volcanic field (SRMVF), USA. Their isotope geochemistry is used to explore their source compositions and to help distinguish new mantle-derived additions to the crust from reworked older crust.

Irrespective of age or tectonic setting a majority of the intermediate to silicic igneous rocks studied exhibit mantle-like Ca isotope compositions. Mantle-like Ca isotopic data for leucogranites associated with the beginning of Rio Grande rifting in Colorado indicate that felsic melts were generated from newly formed lower crust related to earlier calc-alkaline magmatism. These data also indicate that the Nd isotopic signature in early rift magmas is controlled by the lithospheric mantle, even if the major mantle source reservoir is the asthenospheric mantle.

The two crustal xenoliths found within the 28.2 Ma FCT yield εCa values of 3.6 and 7.0, respectively. The ^{40}Ca excesses of these Precambrian source rocks are supported by K–Ca geochronology. However, like several other ignimbrites from the SRMVF and from Yellowstone, USA, the FCT ($\varepsilon\text{Ca} \sim 0.3$) has a Ca isotope composition that is indistinguishable from the mantle. Nd isotopic analyses of the FCT imply that it was generated from 10–75% of an enriched component, and so the Ca isotopic data appear to restrict that component to newly formed lower crust, low K/Ca crust, or enriched mantle. Contrary to these findings, several large ignimbrites and one granitoid from the SRMVF show significant ^{40}Ca excesses. These tuffs (Wall Mountain, Blue Mesa, and Grizzly Peak) and one granitoid (Mt. Princeton) are sourced from near, or within the Colorado Mineral Belt. Collectively, these data indicate that felsic, Precambrian crust likely contributed less than 50% of the material to the petrogenesis of many of the large ignimbrites that have erupted across the western United States. However, the crustal components that contributed to magmas in the Colorado Mineral Belt have ^{40}Ca excesses; consistent with felsic, Precambrian crust.

1. Introduction

Oceanic igneous rocks have compositions and isotopic signatures that indicate they are derived from partially melting mantle sources. The sources of felsic magmas erupted through, or emplaced in continental crust are less clear. Evidence for crustal calcium in some oceanic island arcs has been reported in the early studies of Marshall and DePaolo (1989), but resolved at levels that were near the analytical capabilities available at that time. The petrogenesis of felsic magmas in the continental crust can involve,

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in addition to melting of mantle rocks, partial melting of existing crust, fractional crystallization, magma mixing, and assimilation (bulk and selective). The relative importance of these different processes can vary during magma genesis in part due to differences in the thermal structure of the crust and the mass influx from the underlying mantle (DePaolo, 1981; Jellinek and DePaolo, 2003; Annen et al., 2006). It is important to understand how these different processes operate in order to develop planetary differentiation models that accurately account for the formation of new crust and crust-mantle interactions as continents age. Also, looking at younger systems, which generally have been affected less by metamorphic processes, is useful for establishing guidelines that can be applied to older, less well-preserved rock sequences.

Trace element radiogenic isotopes (namely Nd, Sr, and Pb) have long been used to assess the sources of magmas and the role of assimilation–fractional crystallization (i.e. AFC) processes in magma differentiation. In fact, a Nd crustal index (NDI) that calls upon the strength of thermal and mass influx has been proposed (Perry et al., 1993). Significant isotopic variability may (e.g., Gray et al., 2008) or may not (e.g., Coleman et al., 1992) be present in compositionally diverse magma systems. At a larger scale, regional trends can be strong (Farmer and DePaolo, 1983) and likely tied to large tectonic features and crust of different ages. The addition of Os isotopic data has been useful for working on these problems because it can indicate lower crust involvement in magma genesis (Hart et al., 2003). Hafnium isotopes have also proven to be useful for direct comparison to Nd, and Hf in zircon (Kemp et al., 2007) is useful when whole-rock compositions are disturbed (cf. Stelten et al., 2013; Simon et al., 2014). However, given all these tools, there are still many unresolved issues regarding the petrogenesis of felsic magmas, with a principal one being the ability to distinguish the contributions of mantle sources in magmas that clearly have a large component derived from preexisting continental crust.

Of the major elements in igneous rocks, calcium is unique because its most abundant isotope (^{40}Ca) is one of the two daughter products from the branched decay of ^{40}K, another major element. Thus, measuring the ^{40}Ca enrichment in felsic igneous rocks can help assess the involvement of older, K-rich crustal rocks in the petrogenesis of magmas without relying on knowledge of the trace element behavior (e.g., distribution coefficients for Rb and Sr). In addition, because ^{87}Rb/^{87}Sr (parent/daughter) is approximately 30,000 times ^{40}K/^{40}Ca (parent/daughter), the Rb–Sr system has much more variability, which is useful for analyzing diversity, but creates complexities when distinguishing mantle from crust, and necessitates very accurate age corrections for high Rb/Sr rocks. Combining Nd isotopic ratios with Ca isotopic ratios is useful because whereas non-radiogenic Nd can be indicative that either old continental crust or lithospheric mantle was involved in the petrogenesis, Ca isotopes can potentially distinguish between crustal and lithospheric mantle sources (Fig. 1).

This contribution builds on work from Marshall and DePaolo (1989), which used the K–Ca system to trace crustal recycling in felsic magmas from the western United States. Here we report an expanded data set obtained from felsic volcanic and plutonic rocks from the western United States. In addition, we present documentation of a well-defined offset between the standard reference material for Ca (SRM 915a) and rocks representative of Earth's mantle, as well as new methods for analysis of 6 Ca isotopes by Thermal Ionization Mass Spectrometry (TIMS) with long-term external reproducibility of $<0.5\varepsilon$ (2σ) on the ^{40}Ca/^{44}Ca measurement.

2. Methods

Calcium isotopic measurements reported here are from unspiked samples using TIMS. Approximately one-third of the data collected for this study were obtained at UCB employing the sample handling and mass spectrometry described in Simon et al. (2009). Significant effort has been made to improve upon these methods and to accurately integrate the data from UCB with those obtained at NASA Johnson Space Center (JSC), Fig. 2.

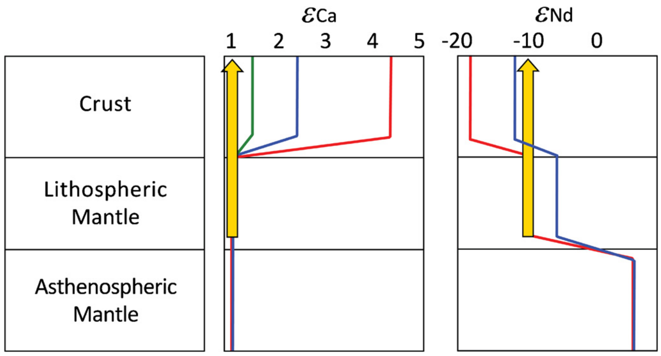

Fig. 1. Schematic diagram illustrating potential Ca and Nd isotopic signatures from the asthenospheric mantle, lithospheric mantle, and crust. Colored lines show hypothetical magma generation paths and the large yellow arrows show that with Nd isotopes it is often difficult to distinguish lithospheric mantle from crust. The combined usage of Ca and Nd isotopes provides greater clarity into the involvement of old felsic crust. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

2.1. *JSC sample digestion and Ca purification methods*

Whole-rock samples ($\sim$50 mg) were powdered with an agate mortar and pestle and dissolved in a combination of concentrated HNO_3 and HF in pressurized dissolution vessels at 180 °C for 48 to 72 h. After pressurized dissolution the acid-sample mixtures were dried and dissolved in HNO_3, if any insoluble material was present the mixture was evaporated to dryness again and dissolved in HNO_3; and this process was continued until all material was in solution. A portion of this solution was then evaporated to dryness and dissolved in dilute HNO_3 and Ca was purified with cation exchange chromatography using a vacuum box following procedures similar to Pourmand and Dauphas (2010). Ca blank introduced during dissolution and column chemistry was approximately 50 ng, approximately 1/20th to 1/30th of this is loaded for an individual run ($\sim$3 μg of sample to $\sim$2 ng of blank per run). Loading blank was less than 1 ng. Thus, the total Ca blank is not affecting the isotope measurements of the unknowns at our level of precision.

Samples were analyzed using Thermo-Finnigan Triton multicollector mass spectrometers at the University of California at Berkeley (Simon et al., 2009) and at the Lyndon B. Johnson Space Center in Houston (see Table S1).

2.2. *JSC mass spectrometer and data reduction methods*

During loading, a parafilm "dam" was used to tightly control the location of the sample on the filament. Phosphoric acid was first applied to the center of Re filaments and dried, then approximately 3 μg of Ca in dilute HCl was applied to the filament and dried, finally another application of phosphoric acid was applied and dried. Filament configuration consisted of two filaments (ionization and evaporation) in face-to-face geometry. Ionization filament temperature was continually monitored and kept as close to 1450 °C as possible (±5 °C). These conditions are critical to ion beam stability, removal of volatile K, and staying below source temperatures where Ti ionizes. Evaporation filament current ranged from 1800 to 2200 mA.

Multidynamic analyses involved measurement of ^{39}K, ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca, and ^{48}Ca, in three different lines (Table S1) using Faraday collectors with 10^{11} Ω resistors. ^{47}Ti was measured