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Calcium and titanium isotope fractionation in refractory inclusions: Tracers of condensation and inheritance in the early solar protoplanetary disk

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ABSTRACT

Measured and modeled Ca and Ti isotopic fractionation effects in a diverse suite of refractory inclusions are used to understand processes of condensation in the solar protoplanetary disk where they and their precursor materials formed. This coordinated approach reveals largely decoupled isotopic signatures and implies that few, if any, of the studied inclusions can be considered primary condensates. All studied inclusions are enriched in light Ca isotopes (∼−0.2 to −2.8‰/amu), but only two show correspondingly light Ti isotopes. Studied inclusions exhibit both heavy and light Ti isotope enrichments (∼0.3 to −0.4‰/amu). These refractory element isotopic signatures, therefore, suggest admixture and reprocessing of earlier formed materials with distinct condensation histories. Along with coordinated measurements of ^{50}Ti isotopic anomalies, which span a range from ∼0 to ∼40 epsilon-unit excesses, the comparison of measured and modeled fractionation of Ca and Ti isotopes provides a powerful approach to understanding primitive nebular processes and environments in the protoplanetary disk. Remarkable evidence for Ca isotopic zoning within a typical Type B1 inclusion exemplifies the potential record of the earliest solar nebula that is likely lost and/or overprinted in the isotopic compositions of more volatile elements (e.g., Mg, Si, and O) by later modification processes.

1. Introduction

Calcium-, aluminum-rich refractory inclusions (CAIs) are among the oldest surviving solids in the Solar System. Their chemical and isotopic compositions provide a record of the conditions present in the protoplanetary disk where they formed and guide our understanding of how solids formed in the solar nebula, an important step in the eventual process of planet building. Thermal events that drove evaporation and condensation in the solar nebula resulted in significant mass-dependent isotopic variations in CAIs (e.g., Clayton and Mayeda, 1977; Wasserburg et al., 1977; Niederer and Papanastassiou, 1984; Niederer et al., 1985; Davis et al., 1990; Nagahara and Ozawa, 2000; Richter et al., 2002; Shahar and Young, 2007; Yamada et al., 2006; Young et al., 1998). The magnitudes of these effects are primarily controlled by chemical volatility. While evaporation/sublimation is well explained by both theory and experimental work to produce enrichments in the heavy isotopes that are often exhibited by the moderately refractory elements Mg and Si (e.g., Young et al., 2002), less is understood about the effects of condensation. Because the isotopic effects of condensation are likely to be complicated (e.g., Niederer and Papanastassiou, 1984 and Uyeda et al., 1991), it is unknown if any CAI is a primary condensate that retains evidence of its primordial formation history.

The approach of this study is to compare the isotopic signatures of the refractory elements Ca and Ti to each other and to moderately refractory elements more generally, and to evaluate the results in the context of a theoretical condensation model. Many existing CAI studies target the isotopic composition of an individual element, which upon comparison to the record of other elements often reveal conflicting interpretations. Along with measured ^{50}Ti anomalies, these divergent signatures may indicate real differences in their formation and/or may reflect artifacts produced by comparing the compositions of early formed solids with unrelated histories. This uncertainty can be critically addressed by our coordinated multi-isotopic approach of a common suite of CAIs, which builds on the pioneering work of Niederer and Papanastassiou (1984), Niederer et al. (1985), and Papanastassiou and Brigham (1989). Additionally, our novel theoretical approach

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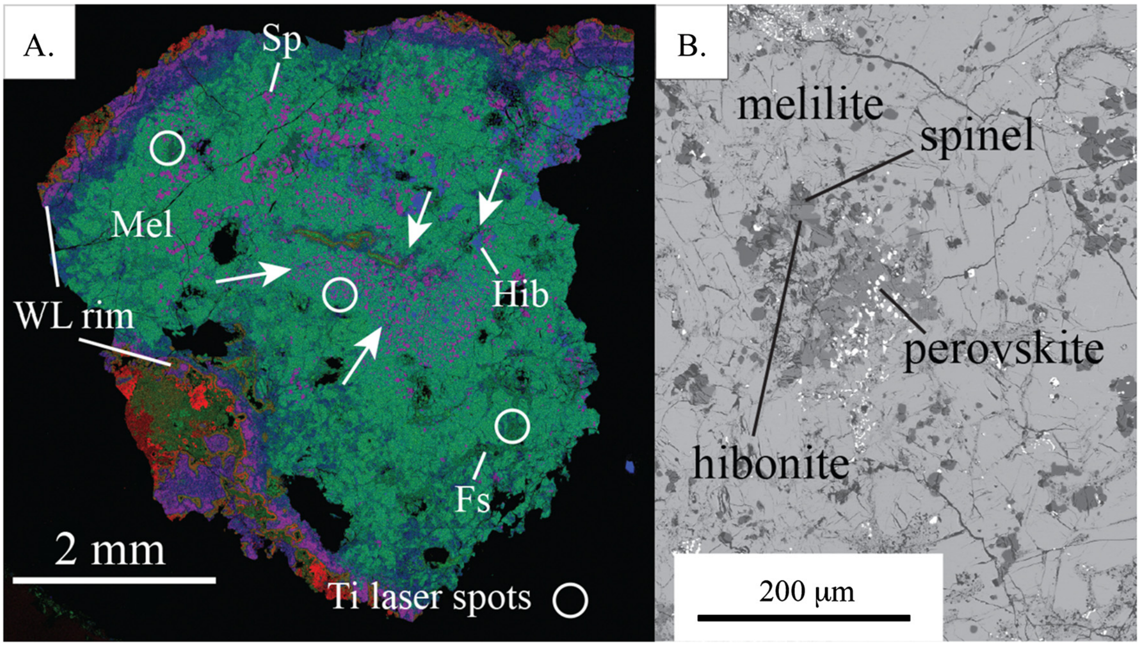

Fig. 1. (A) False color (RGB = Mg–Ca–Al) X-ray scanning electron microscope image of nearly intact coarse-grain Type A inclusion EK5-2-1R. Primary melilite (Mel), fassaite (Fs), Spinel (Sp) ± hibonite (Hib) are shown. Secondary sodalite and nepheline located at the outer margin of the melilite interior. Wark–Lovering (WL) rim surrounds interior. Some olivine-rich host material outside of rim seen. Arrows indicate "mélange" of accessory hibonite, perovskite, and spinel grains concentrated towards the inclusion core. (B) Back-scattered electron (BSE) image showing representative refractory mineral mélange within melilite interior.

to the condensation problem affords a self-consistent model for Ca and Ti (as well as Mg and Si) that allows a direct comparison to the measured isotopic compositions of the studied CAIs. This comparison helps us evaluate the effects of condensation and the overall formation history of these objects. In particular, using Ca and Ti to understand the isotopic effect of condensation will allow us to more accurately assess the initial isotopic ratios of the more volatile Mg and Si potentially overprinted by later evaporation events. Furthermore, these results allow us to assess whether a given CAI is a primary condensate from a homogeneous solar gas or instead represents a mixture of materials from a variety of early reservoirs. Thus, these results can be used to understand key nebular processes and environments in the protoplanetary disk that CAI compositions recorded as they formed.

2. Samples

A diverse group of 6 inclusions from two CV3 meteorites were studied. The suite of samples included: a Type A CAI (EK5-2-1R), a Type B1 CAI (AL4884), two fine-grained inclusions (3B3 and 461 B), and a forsterite-bearing Type B CAI SJ101 from Allende, and a "reworked" Type B CAI (Crucible) from Northwest Africa (NWA 2364). Ca isotope measurements were also performed on a range of planetary materials for reference, including an Allende chondrule, terrestrial basalts and minerals (melilite and augite), and lunar basalts (Apollo samples 12051, 15555, 70035, 70215, 74205, 75015, and 75075). The Smithsonian mineral standards were prepared from rock fragments that were gently crushed, hand-picked, and imaged by SEM, to avoid mixed mineral phases, prior to subsequently being hand powdered and dissolved. The fine-grained 3B3 and 461 B, coarse-grained Type A EK5-2-1R, and chondrule all come from slabs cut from a single sample of Allende.

In general, the studied CAIs exhibit textures and mineralogy that are typical for their sub-type classifications. Exceptions include apparent "mélanges" of accessory refractory hibonite and perovskite (±spinel) within the melilite interior of Type A CAI EK5-2-1R (Fig. 1) and the potentially reworked nature of Type B CAI Crucible (Friedrich et al., 2005). Similar to other coarse-grained Allende CAIs, EK5-2-1R exhibits some secondary sodalite and nepheline at the outer edge of its melilite interior. In Fig. 1, EK5-2-1R appears to be about 3 × 3 mm, but this sample is a non-diametric slice of a previously much larger (∼10 × 10 mm) inclusion (Harper et al., 1990). Crucible, 18 mm in its largest apparent diameter, is cup shaped (hence it has been called "the Crucible") and envelops a portion of the host chondrite (Friedrich et al., 2005). Crucible contains coarsely grained melilite, fassaite, and primary anorthite, with abundant euhedral spinel heterogeneously disturbed throughout. Some anorthite has been altered to secondary melilite (Friedrich et al., 2005). AL4884 is an ∼6 × 10 mm CAI with a heavily microfaulted surface that has been studied extensively by Bullock et al. (2013). The core of AL4884 contains the typical abundant coarse-grained melilite, fassaite, and anorthite of Type B1 inclusions. Its melilite mantle is ∼250–500 μm thick and consists mainly of gehlenitic melilite and minor spinel (Bullock et al., 2013). The microfractures across AL4884 are filled with secondary alteration and there are patchy areas of alteration within the CAI consistent with at least one previous secondary mineralization event. AL4884 was selected for this work in part because of its large size and in part because its pyroxene is particularly Ti-rich (∼5–17 wt.% TiO_2, Bullock et al., 2013). SJ101 is a very large ∼15 × 25 mm sized, forsterite-bearing Type B CAI described in detailed by Petaev and Jacobsen (2009). It consists of coarse-grained grossular, melilite, anorthite, and clinopyroxene crystals separated by sinuous finer-grained forsterite-, clinopyroxene-rich bands. Small spinel grains enclosed in the silicates are distributed homogeneously throughout the inclusion. Minimal amounts of andradite and nepheline are observed in cavities and at the edge of the inclusion. The image shown of the fine-grain inclusion 3B3 in Fig. 2 is a fragment of a large CAI that was originally at least ∼10 × 10 mm in size. It is comprised of ∼5–10 μm sized spinel, hibonite, and alkali-rich melilite. The fine-grained CAIs lack obvious Wark–Lovering rims (Wark and Lovering, 1977). Fine-grained CAI 461 B is relatively small, only about ∼250 × 500 μm in size. Its hibonite 'mantle' is ∼100 μm thick. It contains spinel and hibonite grains within its aggregate interior.