

The role of sulfides on high field-strength element budget during enstatite chondrite melting

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Introduction

High field-strength elements (HFSE) are usually considered to be incompatible lithophile elements during planetary magmatic processes. However, troilite analyses in enstatite chondrites and achondrites (aubrites) show high Ti concentrations, which are not found in ordinary chondrites [1]. In order to quantify this behavior and to check whether it applies to the other HFSE, we have conducted melting experiments relevant to enstatite chondrites under controlled (and low, down to IW-5) oxygen fugacity. Experiments were performed at 1 atmosphere using evacuated silica tubes, and 5 GPa, using multianvil apparatus. Starting material was doped and experimental products were analyzed using microbeam techniques (electron probe, laser ablation ICP-MS).

Results

For oxygen fugacity (fO_2) about IW-2, sulfide / silicate melt partition coefficients for all HFSE are below 1. As fO_2 is lowered below IW-4, Ti is preferentially incorporated in Fe-rich sulfide. The same applies to V, Nb, and Ta. V and Nb have about the same D (sulfide / silicate melt), while Ta is about one order of magnitude lower. These observations are similar to previous observations on metal / silicate partitioning [2]. However, in the case where metal is present we find that V and Ta have about the same D (metal / silicate melt), about one order of magnitude lower than that of Nb. This result differs from [2]. For the cited elements, pressure does not seem to affect partitioning in the investigated range. In the case of Zr and Hf we find that low fO_2 favors their incorporation into the sulfide phase, while no notable change is found for the metal. Moreover, our results suggest that Zr may be compatible in the sulfide phase at low fO_2 ($D_{\text{sulfide / silicate melt}} > 1$), while D for Hf approaches unity. Pressure appears to increase Zr and Hf solubility in the sulfide phase.

Discussion

The chalcophile character of Zr (and maybe for Hf at more reduced conditions) is a new feature, which may be related to observed Ti behavior in enstatite chondrites and achondrites [1]. If we consider that the Earth's differentiation started at reducing conditions (close to those of enstatite chondrites), Zr and Hf may have been trapped by sulfide melts and stored in a sulfur dominated reservoir. This reservoir may then have been assimilated into the core or, alternatively, it may have remained a separate reservoir in the silicate mantle.

[1] K Keil (1969) Earth Planet. Sci.Lett. 7, 243-248.

[2] J Wade, BJ Wood (2001) Nature 409, 75-78.

CALCIUM ISOTOPE FRACTIONATION IN A TYPICAL KARST FOREST ECOSYSTEM, SOUTHWEST CHINA

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Recent studies have used Ca isotope fractionation to directly trace Ca transport along different biogeochemical pathway in various terrestrial ecosystems [1-3]. In an extension of these studies we present Ca isotope and Mg/Ca compositions of rain water, groundwater, bedrock (carbonates), soil and plant samples measured by TIMS using a ⁴³Ca-⁴⁸Ca double spike to gain information about the biogeochemical processes in a typical karst forest (Guizhou province, Southwest China).

The $\delta^{44/40}\text{Ca}$ of rainwater and groundwater are very similar, both of them are enriched in the ⁴⁴Ca when compared to bedrock, indicating that groundwater is supplied mainly by rain and that there is no significant Ca isotopic fractionation during the dissolution of Ca originating from the carbonate bedrock. Our results confirm previous findings that Ca isotopes will be fractionated down the line from bedrock (0.36 ‰) to forest soil (0.04 ‰) and to leaves (-0.26‰). Organic rich soils are enriched in ⁴⁰Ca relative to organic depleted soils, following the sequence farm land > burnt grass land > forest land > shrub land > grass land. In contrast, Mg/Ca ratios increase from in the same sequence indicating a distinct loss of Ca due to metabolism in plants. The recycling of plant material and soils as well as the variation in $\delta^{44/40}\text{Ca}$ and Mg/Ca in plant-soil ecosystem can be well described by an open-system Rayleigh fractionation model, indicating the preferential enrichment of ⁴⁰Ca and Ca in plants.

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[1] Cobert et al. (2011) GCA 75, 5467-548. [2] Hindshaw et al. (2011) GCA 75, 106-118. [3] Farkas et al. (2011) GCA 75, 7031-7046.