

## Core differentiation of the IVA asteroid

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The group of IVA iron meteorites are regarded as magmatic cumulates that, together, have recorded most of the crystallization sequence of the core of a small planet (e.g. [1]). The main argument for a crystallization process rests on the chemical trends defined by the siderophile elements [2]. Using mathematical parameterization of element partition coefficients [3], we tested the hypothesis of fractional crystallization between a solid and a liquid by calculating the amount of sulfur in the liquid. Because the resulting sulfur concentrations did not follow a simple fractional crystallization law, we instead considered fractional crystallization between a solid and a mush. We calculated two key parameters from the trace element concentrations of the IVA irons [2]: the amount of sulfur in the liquid and the fraction of solid in the mush. The computed fraction of solid in the mush is very near unity during most of the differentiation history, implying that the underlying assumption of crystallization between a solid and a liquid suspension is invalid.

We therefore examined whether the chemical trends observed for siderophile elements in the IVA iron meteorites may record a compaction process rather than crystallization. Elements such as Au and Ni were progressively removed in the process, whereas compatible elements such as Ir and Pt became more concentrated in the residue. The correlation between cooling rates and Ni content in the IVA irons therefore signals a trend opposite to what is commonly admitted in the literature [4] and supports centrifugal solidification and cooling rates increasing as compaction proceeds. In addition, the calculated composition points to sulfur-saturated liquids. Upon compaction, these liquids rose in the solid metal where they were partially trapped as troilite inclusions, such as is observed in a number of IVA irons. The low Th/U ratio of these troilite inclusions [5] may reflect fractionation upon unmixing of minute amounts of silicate melts [6]. Although most of the silicates were subsequently lost, some occasionally survived as silicate inclusions [7].

[1] Chabot and Haack (2006) *Univ. of Arizona Press*, 741-771. [2] Wasson and Richardson (2001) *GCA* **65**, 951-970. [3] Chabot and Jones (2003) *MAPS* **38**, 1425-1436. [4] Rasmussen et al. (1995) *GCA* **59**, 3049-3059. [5] Blichert-Toft et al. (2010) *EPSL* **296**, 469-480. [6] Murrell and Burnett (1986) *JGR* **91**, 8126-8136. [7] Scott and Wasson (1975) *Rev. Geophys. Space Phys.* **13**, 527-546.

## Modeling stable isotope ratios of metals in the weathering zone: mass-balance controls

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During the last decade, the stable isotope composition of metals and metalloids (e.g. Li, B, Mg, Ca, Fe, Cu, Zn, Sr, Mo) in the weathering zone were mapped out. The overarching aim is to improve our understanding of the processes fractionating isotopes and generating elemental transfers between the main compartments (e.g. bedrock, soil, surface water and plants). However, a conceptual framework is still lacking for interpreting isotope data in terms of isotope fractionation factors, or in terms of elemental fluxes. Such a framework represents a prerequisite to identify biogeochemical processes from isotope ratios measured in river material or in the sedimentary record.

To this end, we design a simple steady-state model based on elemental mass-balance equations, and simulate, at first-order, a weathering system from the scale of a soil column to that of continents. The model links (1) isotope compositions of the main compartments of the weathering zone (expressed in the  $\delta$ -unit) (2) isotope fractionation factors  $\Delta_{\text{prec}}$  and  $\Delta_{\text{up}}$  (associated with precipitation of secondary weathering products, and with plant uptake, respectively) (3) elemental fluxes to, within and out of the weathering zone. The fluxes are expressed relative to the supply rate of the considered element into the weathering zone which is, at steady-state, denudation rate times bedrock chemical composition.

Using this model, we show how soil water or river water isotope composition  $\delta_{\text{water}}$  will be offset from the bedrock composition  $\delta_{\text{rock}}$  by an amount that is not only (1) depending on the flux weighted-average of  $\Delta_{\text{prec}}$  and  $\Delta_{\text{up}}$ , but also (2) increasing with increasing elemental flux of combined net precipitation of secondary weathering products and net litter formation, and (3) increasing with decreasing elemental flux resulting from the dissolution of primary minerals. (2) and (3) represent strong mass balance effects that likely depend on the considered element (and on its biogeochemical properties such as solubility, affinity for clay minerals, or importance as a nutrient) and the geomorphic regime of the considered setting (e.g. supply versus kinetically limited weathering). These mass-balance effects have to be taken into account when linking isotope ratios with isotope fractionation factors and biogeochemical processes in the weathering zone.

Furthermore, the model shows that  $\delta_{\text{water}}$  will depend strongly on the intensity of biological uptake only if a significant proportion of the considered element is exported as plant litter, establishing a prerequisite to the use of metal stable isotope ratios in the sedimentary record as a tracer of terrestrial biological activity.

The model also has important implications in terms of sampling strategy: it can be shown in particular that the effects of  $\Delta_{\text{prec}}$  and of  $\Delta_{\text{up}}$  cannot be disentangled using isotope composition of river water or of bulk sediment alone. For this purpose, separates of organic and secondary phases from river particulate load or from topsoil, are needed.