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## Modeling fractional crystallization of group IVB iron meteorites

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#### Abstract

A  $^{187}$ Re $^{-187}$ Os isochron including data for all twelve IVB irons gives an age of  $4579 \pm 34$  Ma with an initial  $^{187}$ Os/ $^{188}$ Os of  $0.09531 \pm 0.00022$ , consistent with early solar system crystallization. This result, along with the chemical systematics of the highly siderophile elements (HSE) are indicative of closed-system behavior for all of the HSE in the IVB system since crystallization.

Abundances of HSE measured in different chunks of individual bulk samples, and in spot analyses of different portions of individual chunks, are homogeneous at the  $\pm 10\%$  level or better. Modeling of HSE in the IVB system, therefore, is not impacted by sample heterogeneities. Concentrations of some other elements determined by spot analysis, such as P, Cr and Mn, however, vary by as much as two orders of magnitude and reflect the presence of trace phases.

Assuming initial S in the range of 0 to 2 wt.%, the abundances of the HSE Re, Os, Ir, Ru, Pt, Rh, Pd and Au in bulk IVB irons are successfully accounted for via a fractional crystallization model. For these elements, all IVB irons can be interpreted as being representative of equilibrium solids, liquids, or mixtures of equilibrium solids and liquids.

Our model includes changes in bulk D values (ratio of concentration in the solid to liquid) for each element in response to expected increases in S and P in the evolving liquid. For this system, the relative D values are as follow: Os > Re > Ir > - Ru > Pt > Rh > Pd > Au. Osmium, Re, Ir and Ru were compatible elements (favor the solid) throughout the IVB crystallization sequence; Rh, Pd and Au were incompatible (favor the liquid). Extremely limited variation in Pt concentrations throughout the IVB crystallization sequence requires that D(Pt) remained at unity.

In general, D values derived from the slopes of logarithmic plots, compared with those calculated from recent parameterizations of D values for metal systems are similar, but not identical. Application of D values obtained by the parameterization method is problematic for comparisons of the compatible elements with similar partitioning characteristics. The slope-based approach works well for these elements. In contrast, the slope-based approach does not provide viable D values for the incompatible elements Pd and Au, whereas the parameterization method appears to work well. Modeling results suggest that initial S for this system may have been closer to 2% than 0, but the elements modeled do not tightly constrain initial S.

Consistent with previous studies, our calculated initial concentrations of HSE in the IVB parent body indicate assembly from materials that were fractionated via high temperature condensation processes. As with some previous studies, depletions in redox sensitive elements and corresponding high concentrations of Re, Os and Ir present in all IVB irons are interpreted as meaning that the IVB core formed in an oxidized parent body. The projected initial composition of the IVB system was characterized by sub-chondritic Re/Os and Pt/Os ratios. The cause of this fractionation remains a mystery. Because of the refractory nature of these elements, it is difficult to envision fractionation of these elements (especially Re–Os) resulting from the volatility effects that evidently affected other elements.

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#### 1. INTRODUCTION

The IVB iron meteorite group currently consists of 12 meteorites. Most previous studies of IVB irons have concluded that they formed as a result of fractional crystallization of a metallic liquid that likely coalesced as an asteroidal core (Schaudy et al., 1972; Rasmussen et al., 1984; Campbell and Humayun, 2005). Tungsten isotope studies have shown that the parental metallic liquids to these meteorites segregated from silicates within several million years of the formation of the solar system (Horan et al., 1998; Scherstén et al., 2006). Crystallization evidently followed soon afterwards. Smoliar et al. (1996) reported a precise  $^{187}\text{Re}-^{187}\text{Os}$  isochron age of  $4527\pm29~\text{Ma}$  for a suite of 6 IVB irons, indicating early crystallization and subsequent closed-system behavior. Osmium isotopic data presented in Shen et al. (1996) are also consistent with that conclusion.

Compared with other iron meteorite groups, the IVB group is compositionally unusual with high concentrations of Ni (~16-18 wt %) and refractory elements, such as Ir, coupled with low concentrations of volatile elements including Ga and Ge (Fig. 1). Consequently, some previous studies have concluded that the parent body from which the IVB iron meteorites crystallized was distinctly non-chondritic in bulk composition (Kelly and Larimer, 1977; Rasmussen et al., 1984; Campbell and Humayun, 2005). The unusual chemical characteristics of the IVB irons could be the result of nebular fractionation processes (Kelly and Larimer, 1977), processes that may have taken place within the parent body, such as volatile outgassing and/or oxidation (Rasmussen et al., 1984), or a combination of nebular and parent body processes. Most recently, Campbell and Humayun (2005) concluded that no single condensation or heating process could generate the observed volatility

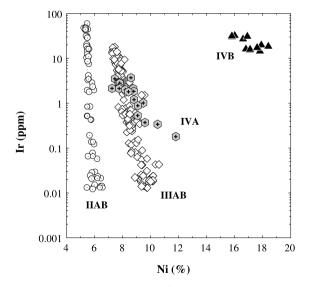


Fig. 1. Nickel (wt.%) versus Ir ( $\mu$ g/g) for magmatic iron groups. Iridum data for IVB irons are from this study and Ni and other Ir data for the IIAB, IIIAB, IVA, IVB irons are from Wasson (1999), Wasson and Richardson (2001), Campbell and Humayun (2005) and Wasson et al. (2007).

relation between the elements present in the projected parental melt to the IVB irons. They proposed a three stage sequence of events to form the IVB parent body that included high temperature nebular condensation, preferential accretion of some refractory-rich components to the parent body, and thermal homogenization and oxidation in the parent body.

Despite the requirement for complex processing to generate the parental melt, the chemical evolution of the IVB system resulting from crystallization of the metallic liquid may be the simplest of the major iron meteorite systems to study. This is, in part, due to low presumed initial concentrations of volatile elements such as S and P, whose presence can lead to complex partitioning behavior of trace elements in metallic systems (Jones and Drake, 1983; Jones and Malvin, 1990; Chabot, 2004). Further, the IVB irons are structurally classified as "ataxites", lacking macroscopic intergrowth of taenite and kamacite. As a consequence of their uniform structure at the macroscopic scale, individual IVB irons are generally chemically homogeneous, and the small pieces that are analyzed for chemical concentrations are unlikely to be substantially biased due to sampling inhomogeneity. The chemical simplicity of the IVB irons, therefore, makes them an appealing target for testing crystal-liquid fractionation models in iron systems.

Here we examine the <sup>187</sup>Re-<sup>187</sup>Os isotopic systematics of the IVB irons and precisely measure highly siderophile element abundances (HSE: Re, Os, Ir, Ru, Pt, Rh, Pd and Au) in bulk samples of each IVB iron. In addition, we re-measure the abundances of these elements and measure 13 additional elements by spot analysis using laser ablation ICP-MS as a means of assessing sample homogeneity and for attempting to further constrain the chemical characteristics of the parental liquid to the IVB irons.

The chief objective of this study is to assess whether a simple fractional crystallization model can account for the variations in the concentrations of each of the HSE among IVB irons. To do this we first examine the <sup>187</sup>Re-<sup>187</sup>Os isotopic systematics of all IVB irons in order to assess whether or not closed-system behavior prevailed following crystallization of each meteorite. Our assumption is that IVB meteorites that plot within uncertainties of a precise, primordial isochron are likely to have had little to no open-system behavior of other HSE subsequent to crystallization. Thus, variations in the concentrations of the HSE among meteorites that are co-isochronous can be attributed solely to primary magmatic processes.

Fractional crystallization of the IVB system is modeled using new HSE data generated for bulk samples of IVB irons. To do this, bulk distribution coefficients or *D* values (the concentration ratio of the element in the solid metal to liquid metal) were estimated by two methods. One is to use the parameterization method of Chabot and Jones (2003) to calculate *D* values appropriate for most of the HSE as functions of estimated changes in S and P content. The parameterization provides mathematical expressions for changes in the *D* values for some HSE as functions of changes in S, P and C (C is not considered here) concentrations, that are consistent with experimental observations. Details of the parameterization used for each element are

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