

COMPOSITIONS OF THE GROUP IVB IRON METEORITES. A. J. Campbell and M. Humayun, Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637 (a-campbell@uchicago.edu).

Introduction: The IVB group is the most refractory-rich and volatile-poor of the iron meteorites, and it is therefore important to understand its origin as a limiting case of core formation processes in protoplanetary bodies. Various fractionation processes have been proposed to explain the compositional range of IVB irons. Scott [1] and Kelly and Larimer [2] favored nebular condensation as the principal mechanism for enriching IVB irons in refractories and depleting them in volatile elements. Grossman and Olsen [3] maintained that some aspects of the IVB metal compositions were not satisfactorily explained by such a mechanism. Rasmussen et al. [4] promoted parent body outgassing, rather than nebular processes, as the means of volatile loss. Both Scott [1] and Rasmussen et al. [4] mentioned oxidation during equilibration with a silicate as possible contributors to the IVB metal formation process.

To better resolve the contributions of each of these possible chemical processes, we have undertaken a systematic study of the trace siderophile element compositions of IVB iron meteorites using laser ablation ICP-MS. The wide range of elements that are measurable using this technique affords an unparalleled evaluation of the origins of IVB metal.

Experimental: Seven of the group IVB iron meteorites were studied: Cape of Good Hope, Hoba, Klondike, Santa Clara, Tawallah Valley, Tlacotepec, and Warburton Range. Each sample was polished and examined by SEM prior to laser ablation ICP-MS analysis. Laser ablation was performed in the line scan mode [5,6]; ablated tracks were 50-100 μm wide, 1.2 mm long, and $\sim 15\text{-}25$ μm deep. Five such scans were made on each sample, and the reported data are the means and standard errors calculated from them. The isotopes ^{53}Cr , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{69}Ga , ^{74}Ge , ^{75}As , ^{95}Mo , ^{101}Ru , ^{105}Pd , ^{182}W , ^{185}Re , ^{192}Os , ^{193}Ir , ^{195}Pt , and ^{197}Au were included in all analyses. Typical errors (1σ) were 0.5-2% for refractory elements, and 2-5% for volatile (less abundant) elements except Ge, which had 5-20% errors. The standards used were Filomena, Hoba, and NIST SRM 1263a [6].

Results and Discussion: The measured compositions of IVB iron meteorites, normalized to Ni and to CI chondrite abundances, are presented in Figure 1. As previously noted [1,2,4], the refractory siderophiles are enriched, and volatile siderophiles

strongly depleted, relative to chondritic abundances. The new data agree very well with the neutron activation data for Cr, Co, Ni, Ga, Ge, As, W, Re, Ir, and Au reported by Rasmussen et al. [4]. The highly refractory siderophiles (Re, Os, W, Ir, Ru, Mo, and Pt) are all enriched relative to Ni and Co. The Pd/Fe ratio is consistently superchondritic, with CI-normalized ratios of 2.4 to 4.4. As volatility increases beyond that of Fe, the elemental abundances drop off by orders of magnitude; the Ge abundances of Cape of Good Hope and Tlacotepec were below detection limits and are not shown in Figure 1.

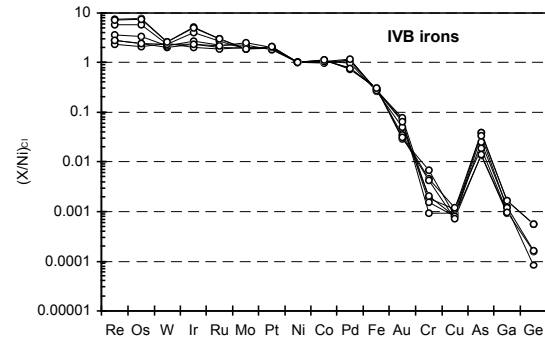


Figure 1. LA-ICP-MS data from group IVB irons.

Table 1. Parameters from fractional crystallization modelling of group IVB irons.

	Initial (X/Ni) _{CI}	D _{metal/melt}		Initial (X/Ni) _{CI}	D _{metal/melt}
Re	7.8	1.71	Co	1.1	0.98
Os	8.5	1.84	Pd	0.86	0.60
W	2.5	1.07	Au	0.052	0.30
Ir	5.0	1.54	Cr	0.0066	1.92
Ru	2.9	1.22	Cu	0.0009	0.83
Mo	2.0	0.81	As	0.033	0.21
Pt	2.0	0.96	Ga	0.0011	0.61
Ni	1.0	0.90	Ge	0.0003	0.66

Modelling of fractional crystallization. The interelement variations in the group IVB irons appear to describe a fractional crystallization process from a metallic melt [1,4]. A multivariate fit to the LA-ICP-MS data was used to calculate the initial composition of the melt and the metal/melt partitioning coefficients (D) for each element, which were assumed to be constant during crystallization. The

least-squares result produced the D values and CI-normalized abundances listed in Table 1.

Comparison of the calculated D values with fits to the experimental partitioning data in the metal-sulfide melt system [7] indicates that the crystallization occurred from a melt of negligible S content, as had been noted by Rasmussen et al. [4]. Melting in the Fe-Ni system at 16 wt% Ni occurs at 1750 K; at this temperature the silicate portion of the IVB parent body must have also undergone significant melting.

Initial composition of the IVB metal melt. The observed refractory element enrichments and volatile element depletions strongly implicate volatility as an important characteristic controlling the composition of the IVB parent body. However, based on the calculated equilibrium compositions of metal during condensation from a solar nebula [e.g., 2,3,8], there is no single temperature at which the calculated metal condensate composition matches the model initial composition of the IVB melt. For example, condensation calculations predict that fractionations between the highly refractory PGEs occur only at temperatures far above the condensation of Fe-Ni, and at the modest levels of refractory element enrichment observed (Fig. 1), the highly refractory PGEs should have chondritic relative abundances. The model IVB initial composition has an abundance pattern that slopes across the refractory PGEs, with $(\text{Os/Pt})_{\text{CI}} \sim 4$ (Table 1). The condensation calculations likewise predict that at the observed levels of refractory element enrichment, the abundances of volatile elements should be lower than observed, in some cases by orders of magnitude. At a nebular pressure of 10^{-3} bar, condensation calculations imply $T=1660$ K for the observed Os/Ir but only $T=1490$ K for the observed Au/Ni. Therefore the volatility pattern apparent in the IVB siderophile element abundances is not the result of a single condensation step. It is possible that such a volatility-based trend could have been produced by mixing of metals with different condensation-volatilization histories, similar to the process apparently recorded in some CAI metal [8]. This multi-stage condensation model obviates the need for extensive outgassing from the parent body [4].

Oxidation in the IVB parent body. Overprinting the volatility-based trend in the compositions of the IVB iron meteorites are depletions in several elements that are sensitive to oxidation conditions. For example, despite the similarity in condensation temperatures of W and Os, of Fe and Pd, and of Cr and Au, the modelled initial IVB ratios are $(\text{W/Os})_{\text{CI}} = 0.30$, $(\text{Fe/Pd})_{\text{CI}} = 0.35$, and $(\text{Cr/Au})_{\text{CI}} = 0.13$. There is also a more modest Mo depletion of $(\text{Mo/Ru})_{\text{CI}} =$

0.67. These ratios suggest that the IVB metal was heavily oxidized prior to the fractional crystallization process. We infer that redox-sensitive siderophiles were partially lost to the silicate portion of the IVB parent body during metal/silicate equilibration and differentiation.

The $f\text{O}_2$ conditions during metal-silicate equilibration can be estimated from the Fe/Pd ratio of the metal, because volatilization has only a small effect on this ratio. For these purposes we make the approximation that the IVB metal equilibrated with a single-phase silicate having CaO, MgO, Al_2O_3 , and SiO_2 in chondritic proportions, plus a complement of FeO balancing the Fe depletion in the metal. (Sodium is assumed to have volatilized, and other lithophiles have negligible solar abundances.) The silicate would then have $X_{\text{FeO}} = 0.21$, whereas the metal has X_{Fe} of 0.84. Assuming ideality, this places the $f\text{O}_2$ at 1.2 log units below the IW buffer, presumably at the IVB melt liquidus temperature of ~ 1750 K.

This is not sufficiently oxidizing to draw a significant fraction of Ni into the silicate, as had been proposed [4], because even at 1750 K the NNO buffer is 4.1 log units above the IW buffer. Conversely, if the fractionation between refractory PGEs and Ni were the result of severe oxidation [4], then Pd/Ni would be superchondritic, Fe would be far more depleted in the metal (to $(\text{Fe/Ni})_{\text{CI}} \sim 0.02$) than is observed, and $(\text{Co/Ni})_{\text{CI}}$ would likewise be well below chondritic in IVB metal, which it is not.

Silicate portion of IVB parent body. No silicate achondrites have been associated with the IVB irons yet, but these results allow some predictions to be made regarding the compositions of such meteorites. They should record significant refractory enrichment and strong volatile depletion similar to those seen in the metal. They should also be FeO-rich ($\text{Mg}\# \sim 0.65$), according to the depletion of Fe in IVB irons, and should likewise contain the other moderately siderophile elements W, Mo, and Cr at levels corresponding to their volatilities and degrees of oxidation apparent in the IVB iron meteorites.

References: [1] Scott E. R. D. (1972) *GCA*, 36, 1205-1236. [2] Kelly W. R. and Larimer J. W. (1977) *GCA*, 41, 93-111. [3] Grossman L. and Olsen E. (1974) *GCA*, 38, 173-187. [4] Rasmussen K. L. et al. (1984) *GCA*, 48, 805-813. [5] Campbell A. J. and Humayun M. (1999) *Anal. Chem.*, 71, 939-946. [6] Campbell A. J. et al. (2002) *GCA*, 66, 647-660. [7] Jones J. H. and Malvin D. J. (1990) *Metall. Trans. B*, 21B, 697-706. [8] Campbell A. J. et al. (2003) *GCA*, 67, 3119-3134.