

METAL AND SIDEROPHILE ELEMENTS IN UREILITES: RECONCILIATION WITH SMELTING?

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Introduction: Bulk ureilites have near-chondritic abundances of trace siderophile elements (Fig. 1), which is difficult to reconcile with any igneous model for their silicates [1]. It is particularly problematic [2-4] for the smelting model in which silicate *mg* (molar Mg/[Mg+Fe]) is controlled by pressure-dependent carbon redox reactions [5-7]. The smelting reaction ($\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$) predicts a correlation of *mg* with metal content, or (if the metal is removed) depletion of trace siderophile elements. In contrast, ureilites have uniformly low metal contents, and their siderophile element abundances are not correlated with *mg* [8]. We address this problem using petrologic modeling, combined with petrographic [9] and trace element [10] characterization of metal in ureilites.

Modeling: A number of workers [8,11-13] have noted that ureilite siderophile element abundances are correlated with solid metal/liquid metal distribution coefficients ($D_{\text{sm/lm}}$) in the Fe-S system, suggesting removal of an FeS-rich liquid. However, no melting models have reproduced ureilite patterns in detail, or explained the role of C in their genesis.

Our approach to modeling metal and siderophile elements in ureilites follows the model of [5,14] for heating, melting, smelting, and silicate melt extraction on the ureilite parent body (UPB). However, in that work we did not consider low-T melting in the Fe-S system. Here we assume that ureilite precursors had Fe+FeS contents in the range of known CC.

We consider a system that initially consists of Fe, FeS and graphite. In the Fe-C-S system the eutectic composition is similar to that in the Fe-S system, including very little C [15]. Therefore it is reasonable to consider melting below the Fe-C eutectic (1153°C) in terms of the pure Fe-S system. By the time the Fe-C eutectic is reached, it is likely that much of the S has been lost by extraction of S-rich liquid. Thus, we consider melting of metal to occur in two stages: (1) a low-T stage in the Fe-S system and (2) a high-T stage in the Fe-C system. Our modeling is similar to that of [8] in this regard, but differs in that we use phase relations to more accurately constrain the low-T stage.

Low-T Melting in the Fe-S System: If Fe and FeS are present melting of a metallic phase begins at 988°C, below the temperature (~1050°C) at which silicate melting (or smelting) begins on the UPB [5]. Because the percolation threshold for Fe-S liquids in solid

silicate matrices is not clear [16,17], we consider a range of behaviors from pure fractional to batch.

Pure fractional melting in the Fe-S system is a highly constrained process in which a single parameter, the initial Fe-S bulk composition, completely determines the degree of melting and siderophile element fractionation. When melts are continuously removed, all melting happens at the eutectic, and proceeds until either FeS or Fe is exhausted. For bulk compositions on the Fe side of the eutectic, only solid Fe remains. At this point melting ceases and does not resume until the Fe-C eutectic is reached. The degree of melting at the eutectic thus depends only on the initial bulk composition. Because all melting happens at the eutectic the partition coefficients are fixed. Hence, for a given initial composition, there is a unique siderophile pattern in the residue after melting.

Figure 1a shows calculated siderophile element patterns in residual Fe after fractional melting, for different starting compositions (mass fraction $x_{\text{FeS}} = \text{FeS}/[\text{Fe} + \text{FeS}]$). Strongly fractionated ureilite patterns are reasonably modeled by fractional melting with x_{FeS} of ~0.78-0.8. Weakly fractionated ureilite patterns can only be modeled well when x_{FeS} is less than ~0.6. The ($D_{\text{sm/lm}}$) used are based on [18].

Batch melting is not as constrained as fractional melting because degree of melting must be specified. For a given temperature, degree of melting is determined by x_{FeS} . The liquid composition used to calculate $D_{\text{sm/lm}}$ [18] is the liquidus at the extraction temperature. Ureilite patterns are reasonably well modeled at values of x_{FeS} similar to those in fractional melting (Fig. 1b). Thus, a solid residue of either batch or fractional melting in the Fe-S system can, to first order, explain the siderophile patterns of ureilites. However, neither process provides a perfect fit. Furthermore, a major problem is to explain the diversity of patterns. Highly fractionated siderophile patterns arise only for a narrow range of high x_{FeS} in the starting material. Slightly fractionated patterns can be produced either at small x_{FeS} , where the degree of melting is low, or by retaining some Fe-S melt. Extreme heterogeneity of the starting material seems implausible, thus we favor the latter.

Smelting and Melting at Higher T: Smelting on the UPB is expected to begin at temperatures between 1050 and 1200°C, depending on depth [5]. The metal

produced by smelting should to first order be pure Fe, and thus would simply dilute siderophile abundances in the metal that remains after melting in the Fe-S system. The metal produced by smelting may be solid or liquid, depending on whether temperature is below or above the Fe-C eutectic and whether any S-rich liquid remains. However, when the temperature reaches 1153°C there will be a second stage of metal melting. It has been argued [8] that the lack of any signature of solid metal/liquid metal fractionation in the Fe-C system, such as Re/Os or As/Au fractionation [19], fails to support the smelting model. However, no such fractionation should be expected. Ureilites contain an excess of graphite—the bulk composition is on the C-rich side of the Fe-C eutectic. Thus, at the eutectic any solid metal that remains must completely melt, and the melt would contain the entire complement of siderophile elements. Fractionation at the Fe-C eutectic between liquid metal and graphite should not be significant.

Physical modeling [5,14] indicates that low metal contents in ureilites are not a problem for smelting, since the majority of metal produced by smelting will separate from the silicates. However, dilution of low-T residual metal by smelting should still lead to a correlation of mg with siderophile abundance. We suggest that several processes could have blurred such a correlation: (1) retention of random amounts of low-T melt; (2) movement of metal both up at the onset of smelting [5] and ultimately down [14], leading to complex mixing; and (3) late-stage shock redistribution, as seen in Hughes 009 [9,10].

The Fe-C-S-P spherules: Some ureilites contain 5-150 μm spherules consisting of carbide, metal, sulfide and phosphide, present mainly in pigeonite [9,20]. Textures and minor element compositions of these spherules indicate that they were liquids. Their predominance in pigeonite supports the smelting model, in which pigeonite crystallizes (at the expense of residual olivine) from silicate liquid and is thus the mineral most likely to trap metallic liquids. The S and P contents of the spherules are a clear indication that not all metallic melts formed at low-T were lost. However, a puzzling feature of these spherules is that their trace element patterns and abundances are essentially identical to those of grain boundary metal [10]. Thus they are not simple samples of the low-T liquid. One possibility is that during cooling the metal in the spherules and grain boundaries re-equilibrated, due to relatively rapid diffusion through pigeonite along dislocations and/or other extended defects [21]. Other clues to this puzzle may be that they are

volumetrically minor and seem to occur only in the more ferroan (deeper) ureilites.

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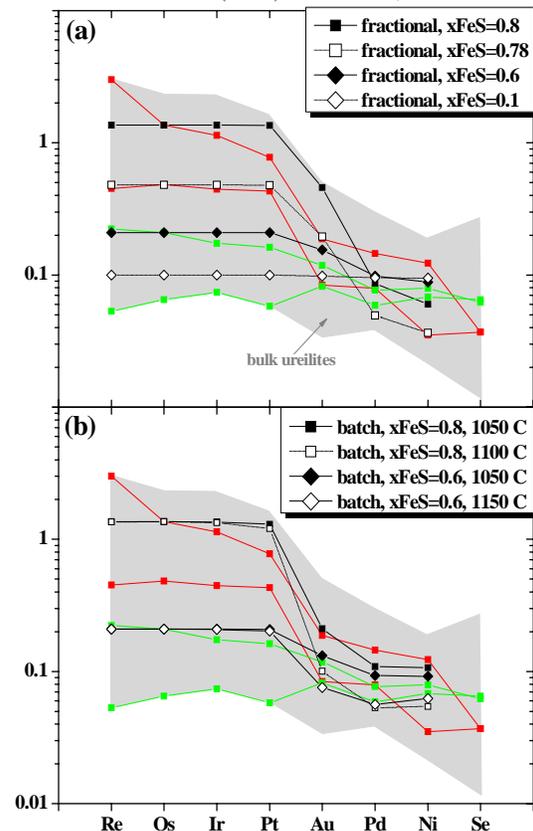


Fig. 1. Results of fractional and batch melt extraction compared to the most (red) and least (green) fractionated ureilites. Calculated patterns are for residual metal (levels adjusted to bulk rocks). This comparison is justified by trace element data [10] which show that grain boundary metal is the main host of siderophiles. Sources of data given in [10].