Fe, Co AND NI IN UREILITE METAL AND SILICATES – CONSTRAINTS FOR THE ORIGIN OF UREILITE METAL.

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Introduction: Ureilites are ultramafic, igneous achondrites, which contain olivine (ol), pyroxene (px), metal and carbon. About ~10 vol% dark interstitial, fine-grained matter is usually referred as vein material [1]. Ureilites have lost ~25% basalt [2] and a metal component. Presently, many authors assume that the majority of ureilites formed as asteroidal melting residues [3, 4]. Although heterogeneous in oxygen isotopes [5], ureilites are suggested to originate from a single parent body. Variations in fayalite content are related to simultaneous smelting and melting at various depths [6].

Here, we present Fe, Co and Ni analyses of ol and metal from various monomict ureilites with very different *fa* contents. The goal is to trace the relation between ol and metal in ureilites.

Sampling: We have analyzed Fe, Co and Ni by EPMA and LA-ICPMS in metal and silicates of 7 different ureilites, namely ALH84136 (fa_2), EET87517 (fa_8), LEW85440 (fa_9), ALHA77257 (fa_{13}), EET96042 (fa_{16}), GRA95205 (fa_{18}) and Kenna (fa_{18}).

Petrography: Three different metal occurrences were distinguished: a) metal in "dusty" ol reduction rims, b) round metal inclusions in otherwise clear ol and px grains, and c) vein metal in association with C-rich matter.

Results: a) Fine-grained metal inclusions in the reduced ol rims are generally poor in Ni (<3 wt.%) and Co (<0.25 wt.%) [see also data in 7]. b) Metal inclusions in ol and px contain 3 – 8 wt.% Ni and 0.2 – 0.7 wt.% Co. These inclusions often consist of Fe,Ni metal, sulfides (high-Cr troilite, daubreelithe) and carbides (cohenite). c) Vein metal shows little variation between 3.3 and 5.5 wt.% Ni and 0.33 and 0.54 wt.% Co. It is apparent from the data presented in Fig. 1 that vein metal is largely uniform in composition with respect to Fe, Ni and Co; independent of the *fa*-content of the respective ureilite hosts. Large variations are observed in the Si concentrations, however, which range between <0.1 and 4.9 wt.%.

The concentrations of Ni and Co are low in ol. Ni varies between 16 and 70 μ g/g. The concentration of Co shows a variation between 6 and 43 μ g/g. Both, elements covary with the concentration of FeO in the respective ol.

Thermodynamic modeling: In order to shed light on the relation between ureilite of and vein metal, we calculate temperatures for the equilibration of Fe, Co and Ni between of and metal (Fig 2). In this approach, we use two different metal compositions: a) the measured composition of vein metal and b) the composition of a modeled core metal for each individual ureilite.

The activity coefficients for Fe₂SiO₄, Ni₂SiO₄ and Co₂SiO₄ were taken from [8, 9], those for Ni in metal from [10] and for Co in metal from [11]. The activity coefficient of Fe in metal was assumed to be 1. In our fist set of data, we calculate the equilibration temperatures for the Fe/Ni- and Fe/Co-exchange reactions by using measured ol and vein-metal compositions. The calculations give very different temperatures for Fe/Ni and Fe/Co (Fig. 2). The temperatures for Fe/Ni vary between 1400 and 2000°C. The corresponding temperatures for Fe/Co are much lower and range between 600 and 1000°C, respectively. For the second set of data, we have calculated ol metal equilibration temperatures for a modeled core metal and measured ol compositions. The core metal composition was calculated on base of the Fe, Ni and Co concentrations in the silicate fraction of the UPB (mantle + basalt) and the UBP bulk composition. The calculations consider loss of ~25% basaltic component [2]. The influence of basalt extraction on the Fe, Co and Ni budget was estimated on base of concentrations data of the Earth upper mantle and MOR basalt [12]. We have adopted three different bulk compositions, namely CI1, H and LL [bulk chemical concentration data from 13]. It is apparent from mass balance considerations that Ni in the core metal is a function of FeO in the mantle. High-FeO ureilites give a smaller core with higher Co and Ni concentrations, whereas highly reduced ureilites give larger cores with lower Co and Ni concentrations. This model, however, assumes that each ureilite sources from a different parent body. The calculated equilibration temperatures are now very similar for Fe/Ni and Fe/Co and range between 1000 and 1150°c (Fig 2). An exception is LEW85440 (fa_8), which gives unusual high temperatures for Fe/Ni, whereas the corresponding Fe/Co temperature of 1050°C is in the same range as the other ureilites. EET96331 shows lower equilibration temperatures of about 750°C for both, Fe/Ni and Fe/Co.

Discussion: Our LA-ICPMS trace element data of ureilites ol along with vein metal analyses suggest that ol cores are not in thermodynamic equilibrium with vein metal because calculated equilibration temperatures show large differences for Fe/Ni and Fe/Co. Moreover, Si concentrations of up to 4.9 wt.% in EET96042 require highly reducing conditions that are

incompatible with FeO-concentrations of 16 wt.% in ol. Notably, no correlation exists between the Si and Fe concentration in vein metal. Assuming that Si has been introduced by partial silicate reduction through C, all Fe, Co and Ni should be mixed with metal resulting in high Fe/Co- and Fe/Ni-ratios.

Depending on the FeO content of the UPB and its bulk composition, between 7 and 14 wt.% Ni is expected in the UBP core metal. The vein metal is systematically lower in Ni. One feasible mechanism of decreasing the Ni content of the vein metal is dilution with low-Ni metal from ol reduction. This process, however, is unlikely, as most of the metal from ol reduction is still present in the reduced rims.

Another possibility would be formation and extraction of a sulfide-rich melt as proposed by [7] and formation of residual Fe,Ni metal. Fe,Ni metal that coexists with a S-rich melt (≥13 wt.% S), however, would have a higher Ni/Fe-ratio, i.e. would have more than the calculated 7 – 14 wt.% Ni. Partial melting of S-free Fe,Ni is, in principal, a feasible process for producing Ni-poor residual metal, since $D_{Ni(solid/liquid)} = 0.9$ [14]. Decreasing the Ni content of the residual metal from 7 wt.% down to the observed upper limit of vein metal of 5.4 wt.% Ni, however would require 95% fractional melting and full equilibration of the residual metal. The case is even more unlikely for a metal with a starting composition of 14 wt.% Ni. We therefore exclude that low-Ni vein metal is the product of extraction of S-rich melt or fractional melting of Fe,Ni-metal.

Ureilite vein metal may have been introduced during the impact that led to the break-up of the UPB [15].

The calculated Fe/Ni and Fe/Co temperatures for equilibration of ol with modeled core metal are in the same range, albeit ~100°C lower, as px-px temperatures [16]. The good agreement between Fe/Ni- and Fe/Co-model-temperatures as well as similar temperatures for different ureilites may indicate that ureilite ol has, indeed, equilibrated with UPB core metal. This model, however, requires individual UBPs.

Equilibrating of with a single core with a composition corresponding to a typical ureilite (fa_{18}) gives systematically lower temperatures for low-FeO ureilites. This would be in disagreement to [16], who calculated higher px-px temperatures with decreasing fa.

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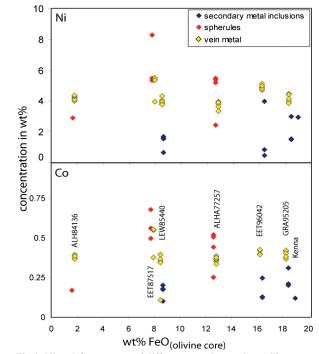


Fig 1: Ni and Co contents of different metal types in ureilites.

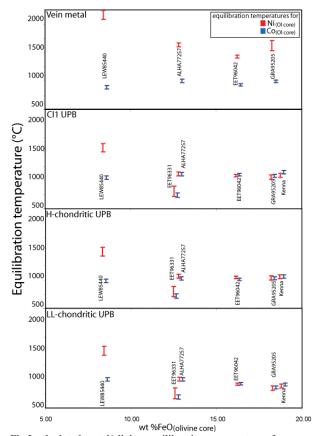


Fig 2 calculated metal/olivine equilibration temperatures for Fe/Ni and Fe/Co for different ureilites, different model UPB compositions and ureilite vein metal.