REFRACTORY METAL NUGGETS AS AN INDICATOR OF ALTERATION PROCESSES IN A V-RICH Ca-Al-RICH INCLUSION.

J. M. Paque, J. R. Beckett, and D. S. Burnett. California Institute of Technology, Division of Geological and Planetary Sciences, M. S. 100-23, Pasadena, CA 91125, julie@paque.com.

Introduction: CAIs are studied for the insight they may yield into the primitive solar nebula but, because multiple processes may have affected these objects, it is important to understand how a given process influenced pre-existing phases and/or produced new ones. There are many studies on refractory metal nugget (RMN) chemistry, but few on RMN petrography and none on the consequences of RMN alteration. In this work, we consider how the alteration of melilite in Allende CAI A-WP1 influenced the compositions of RMN that were originally included in the melilite. Systematic variations in compositions of the RMN between those occurring in altered regions of the inclusion and those fully enclosed in melilite [1] reflect differences in the exposure of metal grains to the altering medium; these variations can potentially be used to constrain the nature of the altering medium and the conditions under which alteration took place.

Petrography and Alteration: A-WP1 is a broken fragment of a Type A CAI from Allende, initially described by [1-2]. Melilites (200 to 500 µm; Åk 8-23 mole %) poikilitically enclose spinel, hibonite, perovskite, rare UNK [3] and RMN. UNK occurs frequently as V-, Sc-bearing crystals hosting RMN in melilite (Fig. 1). Rare fassaite occurs as micron thick rims on some spinels (Fig. 2), usually coexisting with perovskite. The fassaite is Sc_2O_3-poor (0.4-0.8 wt. %) relative to Sc-UNK (1.1 to 5.0 wt. %). Zoning in melilite is highly irregular but the grains are single crystals based on electron backscatter diffraction. The melilite is altered to fine grained grossular and anorthite along fractures but, in more heavily altered areas, sodalite and nepheline are common. This is similar to the two-stage alteration described by [4]. In addition, there is a fine-grained (submicron), highly aluminous (Al>>Si) alteration material.

RMN are micron to submicron sized and occur in three different petrographic settings, totally enclosed within melilite, along grain boundaries between spinel and melilite, and in altered areas. RMN often occur in grossular + anorthite assemblages along fractures in or grain boundaries between melilites. They are uncommon in areas of nepheline + sodalite alteration, and were not encountered in the highly aluminous alteration. High resolution imaging of the RMN indicate that those in the altered areas of the inclusion can be multiphase clusters consisting of several loosely aggregated particles <0.5 µm in size. RMN within melilite appear to be uniform grains up to 1 µm in diameter.

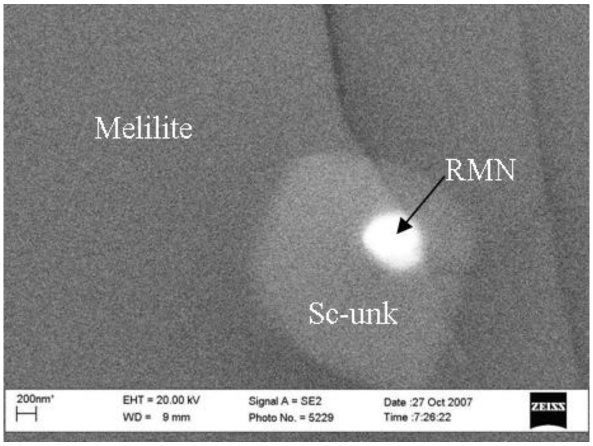

Figure 1. RMN in melilite are commonly surrounded by Sc, V-rich UNK. The scale bar in the lower left of the secondary electron image is 200 nm.

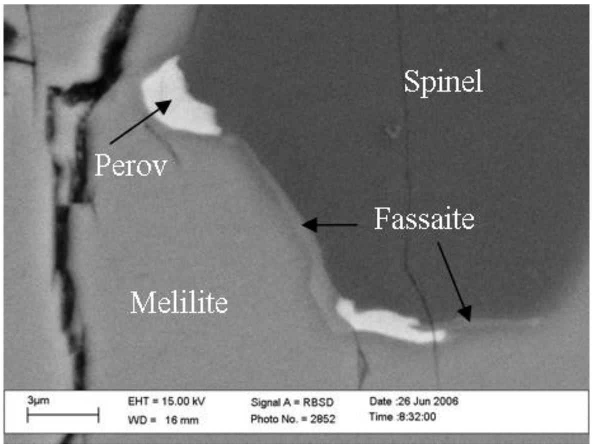

Figure 2. Perovskite and fassaite on spinel enclosed within melilite.

RMN Chemistry: We separate the alloys into V-rich (X_V > 0.06) RMN, which includes all grains hosted by melilite, and V-poor RMN (X_V < 0.06), all of which are in altered regions of the inclusion. RMN in melilite have roughly chondritic proportions of the refractory metal (Re, W, Mo) and platinum group (Os, Ir, Ru, Pt, Rh) elements (Fig. 3), consistent with a survey conducted by [7] of Allende Type A inclusions. V, Ni, and Fe are in subchondritic proportions but the siderophile character of V is clearly revealed. This is generally assumed in discussions of the origin of Fremdlinge [e.g., 8], but without direct evidence.

For RMN included in melilite, most elements are in approximately constant ratios but V (X_V = 0.06-0.50) and Ni (X_{Ni} = 0.001-0.15), which are anti-correlated, are quite variable. Some RMN in the altered regions are indistinguishable from grains wholly included in melilite but others display very low V ($X_V < 0.06$) and enhanced Fe and Ni (e.g., Fig. 4). Concentrations of the refractory metals in these V-depleted alloys are also sharply lower than expectations based on trends established by the melilite hosted grains. These depletions are not caused solely by dilution of the refractory metals by Fe+Ni because grain sizes of RMN occurring in melilite and alteration are broadly similar while dilution would require order of magnitude increases in grain volume. This suggests that the refractory metals were mobile during the alteration process and lost to the RMN. For V-poor RMN, X_{Ni} ranges over an order of magnitude (Fig. 4), extending to compositions similar to those in alloy-oxide-sulfide complexes in Allende chondrules [9]. Ni was excluded from the aluminous spinel as in magnetite but it is present in minor, but measurable, amounts in the altered regions (perhaps residing in Ni-bearing phases along grain boundaries). We observed no coexisting magnetite, perhaps, in contrast to the chondrules, because the Ni-rich alloy compositions were approached from relatively, refractory-rich, Fe-poor compositions.

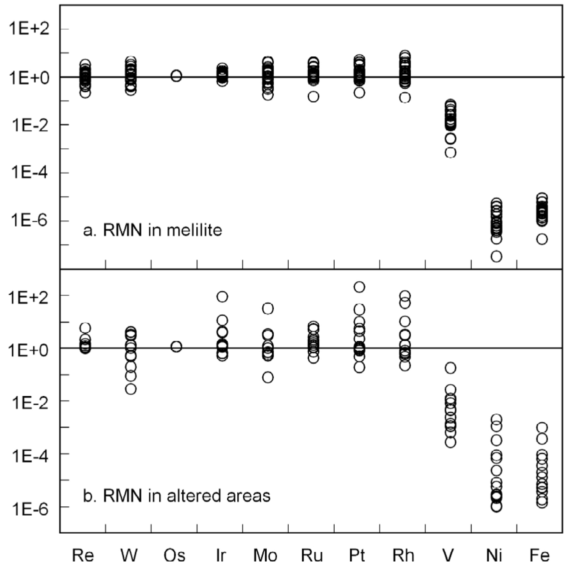

Figure 3. Compositions of RMN relative to C1 chondrite values and normalized to Os=1.0. Elements on the horizontal axis are ordered in terms of increasing volatility (decreasing condensation temperature) normalized to C1 chondritic values [6] and Os=1.0. RMN in melilite (a) are more restricted in composition than RMN from altered areas (b).

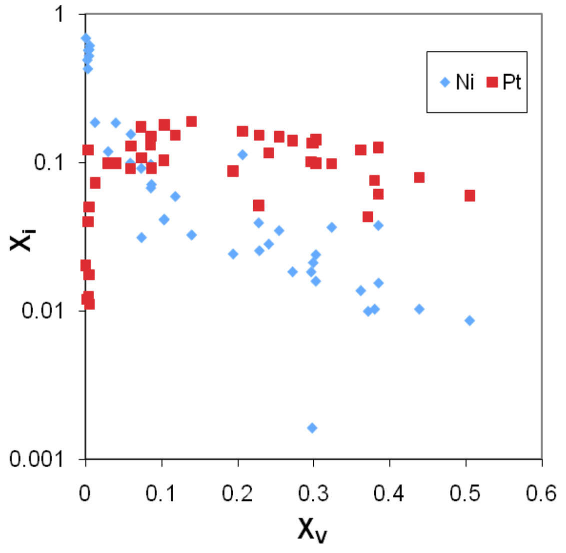

Figure 4. Mole fractions of Ni and Pt plotted versus V for RMN in A-WP1.

Discussion: A basic issue for the RMN is whether or not the nuggets, while included in melilite, interact with an altering medium and, if so, which elements were mobile. The presence of Fe and V in spinels included in melilite is consistent with at least some interaction, perhaps through cracks. If the high V alloys were affected by the same process, then V was lost and Ni gained, but most elements including Fe do not appear to have been strongly affected. In contrast, the low-V alloys are characterized by a trend generated by mobile elements towards very high Ni, low V, and low refractory elements (Fig. 4), that was presumably driven by oxidizing redox conditions and possibly chlorination (sodalite + nepheline in the alteration assemblage implies a significant partial pressure of NaCl and many of the elements in the RMN may be volatile as gaseous chlorides and complexed with gaseous alkali chlorides). V and the refractory metals were lost to the RMN during this process and Ni was gained. The lack of magnetite coexisting with the low-V alloys may reflect the absence, in contrast to alloys in chondrules and Fremdlinge, of large amounts of Fe in the initial alloys. Details of RMN chemistry in the altered areas of A-WP1 may provide additional insight into conditions during the alteration process, the relative volatilities of the refractory elements, and the origin of Fremdlinge and opaque inclusions.

References: [1] Paque J. M. (1989) *LPS XX*, 822-823. [2] Paque J. M. (1985) *LPS XVI*, 651-652. [3] Paque J. M. et al. (1994) *Met. 29*, 673-682. [4] Fagan T. J. et al. (2007) *MPS 42*, 1221-1240. [6] Anders E. and Grevesse N. (1989) *GCA 53*, 197-214 [7] Wark D. A. (1983) *Ph.D. Diss*. [8] Paque J. M et al. (2007) *MPS 42*, 899-912. [9] Haggerty S.E. and McMahon (1979) *PLPSC 10*, 851-870.