Allendeite and Hexamolybdenum: Two New Ultra-Refractory Minerals in Allende and Two Missing Links

C. Ma*, J.R. Beckett, and G.R. Rossman; Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125, *chi@gps.caltech.edu.

Introduction: During our nano-mineralogy investigation of the Allende meteorite, we discovered two new minerals that occur as micro- to nano-crystals in refractory inclusions: Allendeite, $Sc_4Zr_3O_{12}$, a new Sc- and Zr-rich oxide; and hexamolybdenum, (Mo,Ru,Fe), a Mo-dominant alloy. Allendeite, which may be an important ultra-refractory carrier linking Zr-, Sc- oxides and the more common Sc-, Zr-enriched clinopyroxenes (Cpx) in CAIs, hosts perovskite (Pv), spinel (Sp), Os-Ir-W-Mo alloys, and hexamolybdenum. The observation of two structurally and chemically distinct highly refractory, low-Pt alloy minerals not associated with Fe-Ni alloys provides the first direct physical evidence for at least two separate carriers of the highly refractory metals in CAIs. Hexamolybdenum links Os-rich and Pt-rich meteoritic alloys and may be a precursor of the latter. Both new minerals have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2007-027, 029).

Occurrence, Chemistry and Crystallography: Allendeite and hexamolybdenum occur in a partially altered refractory inclusion ~70 μm x 120 μm in section USNM 7554 (Fig. 1). Fig. 2 shows a single 15x25 μm crystal (revealed by electron backscatter diffraction (EBSD) orientation mapping) of allendeite with included Pv, Os-Ir-Mo-W alloy, and Sc-stabilized tazheranite (Taz; cubic zirconia). There are also linked or isolated 1-5 μm irregular grains, coexisting with Pv, hexamolybdenum (Mo,Ru,Fe), and Os-, Ir-, Mo-, W-rich alloys. The inclusion is largely altered to nepheline (Ne), sodalite and Al-rich, low-Ti augite. Allendeite-Ne contacts are sharp but Pv within alteration, is often rimmed by ilmenite. We observed one grain of Mg-Al Sp in contact with allendeite, hexamolybdenum, and Pv, and rare Fe-Mg-Al Sp in altered regions.

Eight analyses of allendeite by EPMA yield (wt%) ZrO_2 56.58, Sc_2O_3 32.36, TiO_2 5.47, CaO 2.74, HfO_2 1.21, FeO 0.82, Al_2O_3 0.70, Y_2O_3 0.70, V_2O_3 0.35 or $(Sc_{3.01}\ Ti^{4+}_{0.44}\ Ca_{0.31}\ Al_{0.09}\ Fe^{2+}_{0.07}\ Y_{0.04}\ V^{3+}_{0.03})_{\Sigma 3.99}$ $(Zr_{2.95}Hf_{0.04})_{\Sigma 2.99}O_{12}$. No other elements with atomic number > 4 were detected. Ti is proportional to Ca + Fe with a slope of 1.2, suggesting that ~20% of the Ti may be trivalent. [1] observed a chemically similar phase in a grossite-bearing inclusion from the CH chondrite Acfer 182.

EBSD is used for *in-situ* non-destructive crystal structure determination at sub-micron scales. The

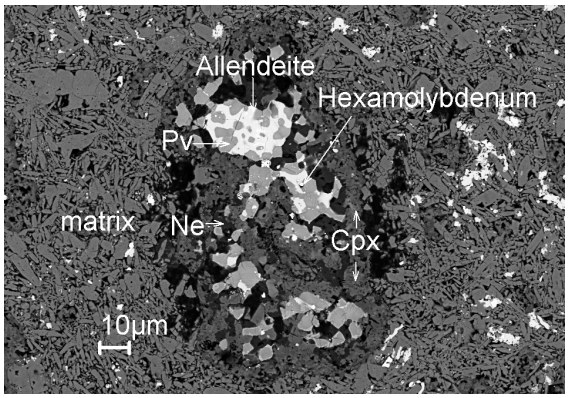

Fig. 1. Backscattered electron (BSE) image of the refractory inclusion containing allendeite and hexamolybdenum.

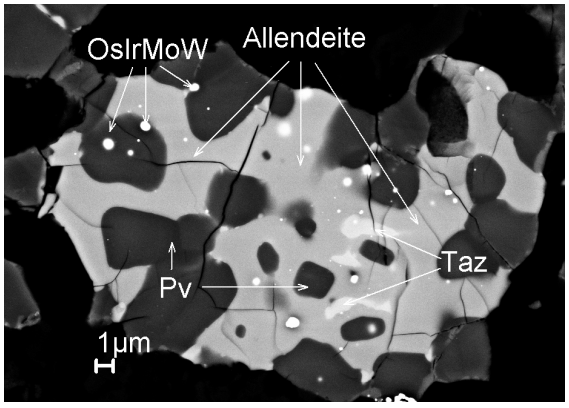

Fig. 2. Enlarged BSE image showing a single crystal of allendeite (cf. Fig. 1) with included Pv, tazheranite and Os-, Ir-, Mo-, W-rich alloys.

EBSD pattern of allendeite is an excellent match to the computed EBSD pattern and the cell parameters of synthetic trigonal, $R\bar{3}$, $Sc_4Zr_3O_{12}$ [2]. Zr and Sc are seven-coordinated to oxygen and randomly distributed on two sets of general sites [2]. Using cell parameters of [2] and our observed chemistry, we obtain a density of 4.84 g/cm^3. Allendeite is named for the locality Pueblito de Allende, Chihuahua, Mexico, where the Allende meteorite fell in 1969.

We observed three hexamolybdenum inclusions in allendeite and a Zr-, Y-rich Pv (Fig. 3) and one 1 μm inclusion in Pv and Cpx in Allende section USNM 3509HC12. The largest (1.2 μm diameter) grain consists of two parts. The upper, larger portion is a Mo-dominant phase and the lower brighter part is Ru-enriched. EPMA shows that the hexamolybdenum

portion of this crystal has an empirical formula $Mo_{0.56}$ $Ru_{0.24}$ $Fe_{0.08}$ $Ir_{0.07}$ $Os_{0.03}$ $W_{0.01}$ $Ni_{0.01}$, and the lower, brighter portion $Ru_{0.41}$ $Mo_{0.39}$ $Ir_{0.10}$ $Fe_{0.05}$ $Os_{0.03}$ $W_{0.01}$ $Ni_{0.01}$. The two smaller grains shown in Fig. 3 are too small for EPMA but the larger grain was confirmed to be hexamolybdenum by EBSD. SEM-EDS analysis yielded $Mo_{0.44}$ $Ir_{0.26}$ $Ru_{0.19}$ $Fe_{0.06}$ $W_{0.04}$ $Os_{0.01}$ (larger grain) and $Mo_{0.82}$ $Ru_{0.08}$ $Fe_{0.04}$ $Os_{0.03}$ $W_{0.02}$ $Ir_{0.01}$ (smaller grain).

The EBSD patterns can be indexed in terms of the *P6$_3$/mmc* structure exhibited by Ru and some intermediate Ru-Mo alloys. The best fit was achieved using cell parameters of synthetic $Mo_{55}Ru_{45}$ [3]. Hexamolybdenum is hexagonal, *P6$_3$/mmc*, a= 2.7506 Å, c = 4.4318 Å, V = 29.04 Å^3 and Z = 2, with a calculated density of 11.90 g/cm^3 via our observed chemistry. The name hexamolybdenum refers to the symmetry (primitive hexagonal) and composition (Mo-rich).

Origin and Significance: Zr-oxides are extremely refractory in nebular environments. ZrO_2 is the highest temperature oxide to appear in condensation calculations for a cooling gas of solar composition [4]. Sc-, Zr-enriched Cpx are observed in CAIs and in some ultra-refractory inclusions [5-6] but previously reported meteoritic Zr oxides are minor grains or tiny inclusions [4,7] that may be exsolution phases rather than primary condensates or evaporative residues. Allendeite, a Zr-rich oxide, and Taz are well posed as sensors of conditions associated with their formation and, by extension, those of other ultra-refractory phases. Allendeite, Pv, and Taz all contain significant amounts of Zr, Sc, Al, Ca, Y, Ti^{4+} and possibly Ti^{3+}, so it is possible to construct exchange reactions with coexisting phases to constrain temperature, oxygen fugacity and/or the partial pressures of vapor species.

Allendeite is probably destroyed through reactions with other phases. For example, the relatively common Zr-, Sc-enriched Cpx in type A CAIs and in the mantles of type B1s [5,8] could reflect a precursor Zr-Sc oxide that dissolved into the melt with some of the Zr and Sc being subsequently incorporated into crystallizing Cpx. The Sc/Zr ratio of such a Cpx depends on Sc/Zr in the dissolving phase assemblage, how much diffusion occurred in the liquid prior to crystallization of the Cpx (Sc^{3+} likely diffuses faster than Zr^{4+}), and the ratio of the Cpx/liquid partition coefficients for Sc and Zr. Taking the effective Cpx-liquid partition coefficients for Zr (1.1) and Sc (2.8) derived by [8] for core Cpx in type B1 inclusions as approximately correct for Sc-, Zr-rich Cpx, leads to Sc_2O_3/ZrO_2 in initially crystallizing Cpx of ~1.5 if no significant diffusion of Sc relative to Zr occurred in the liquid, in reasonable agreement with Sc_2O_3/ZrO_2 (0.8-4.7) in Cpx associated with Zr-, Sc-rich Pv in compact type As [5]. Since allendeite and Pv have low Y_2O_3/Sc_2O_3, we would also expect low Y_2O_3/Sc_2O_3 in the crystallizing Cpx, also as observed.

A wide variety of refractory metal alloys are observed in Fremdlinge or opaque assemblages of CAIs [9] but these probably formed through oxidation/sulfidation at low temperatures of Fe-Ni-rich alloys, possibly leading to exsolution of the observed refractory alloys [9]. Refractory metal nuggets are also observed included in CAIs but these are usually Os-Ir-rich or enriched in Pt, a relatively volatile noble metal, and/or Fe-Ni [10-11], indicative of more evolved alloys. Pt, Fe, and Ni contents of the hexamolybdenum and Os-Ir-W alloys in the Fig. 1 inclusion

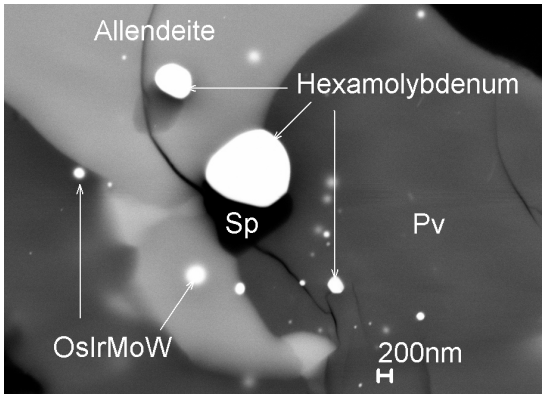

Fig. 3. BSE image showing a portion of Fig. 1 containing hexamolybdenum with allendeite, perovskite, and Os-Ir-Mo-W alloys.

are quite low, leading to the possibility that the alloys are relatively pristine examples of nebular refractory alloys that can yield insight into early nebular processes. [12] inferred that early condensation of refractory elements involved at least three different carriers. We suggest that two of these involved Os-rich alloys and Mo-, Ru-rich hexamolybdenum and its descendents. From a condensation perspective, continued exposure of hexamolybdenum to a cooling gas would likely lead to a reaction to form Pt-rich alloys with the destruction of hexamolybdenum.

References: [1] Weber D. and Bischoff A. (1994) *GCA* 58, 3855. [2] Rossell H.J. (1976) *J. Solid State Chem.* 19, 103. [3] Anderson E. and Hume-Rothery W. (1960) *J. Less-Common Metals* 2, 443. [4] Grossman L. (1973) GCA 37, 1119. [5] El Goresy A. et al. (2002) GCA 66, 1459. [6] Simon S.B. et al. GCA 63, 1233 (1999). [7] Hinton R.W. et al. (1988) GCA 52, 2573. [8] Simon S.B. et al. (1991) GCA 55, 2635. [9] Blum J.D. et al. (1989) GCA 53, 543. [10] Lin Y. et al. (1999) Chinese Sci. Bull. 44, 725. [11] Wark D.A. (1986) EPSL 77, 139. [12] Sylvester P.J. et al. (1993) GCA 57, 3763.