

OXIDATION OF REFRACTORY METAL-RICH ASSEMBLAGES AT HIGH TEMPERATURES; A. Bischoff<sup>1</sup> and H. Palme<sup>2</sup>. <sup>1</sup>Institut für Mineralogie, Corrensstr. 24, 44 Münster, F.R. of Germany; <sup>2</sup>Max-Planck-Institut für Chemie, Saarstr. 23, 65 Mainz, F.R. of Germany.

Refractory metal-rich phases in Ca,Al-rich inclusions from Allende and other carbonaceous chondrites are among the first solid phases formed in the solar nebula (1). These alloys or aggregates of alloys associated with more volatile components (fremdlinge) must have formed at high temperatures, despite occasionally contrary claims. Alloys of Os, Ir, and Ru also contain, in contrast to terrestrial occurrences, significant amounts of the low vapor pressure metals W and Mo. These two elements are, however, the first to be oxidised under increasing oxygen fugacity. Refractory element patterns of bulk Ca,Al-rich inclusions and of single metal grains often show depletions of W and Mo, that can be ascribed to form under more oxidising conditions than those conventionally assumed in the solar nebula (2). Recent reports of Ca-tungstate and molybdate in one of these inclusions demonstrate the variability in oxygen fugacities that is required to explain the observed mineral assemblages (3). In order to better understand the formation of these complex phases we have separated large fremdlinge (>50 µm) from a Ca,Al-rich inclusion (Allende A37), using the Ir-tracer method (4). Three refractory siderophile element-rich aliquots were separated from the inclusion A37, and their bulk compositions were obtained by INAA. These three samples show very similar patterns (Fig. 1): the refractory elements W, Re, and Os are strongly enriched compared with the more volatile elements Mo, Ru, and Pt. After the determination of the bulk chemistry the aliquots were embedded and stepwise mounted and polished to get the fremdlinge at the surface. The fremdlinge were studied petrographically with a Hitachi Scanning electron microscope. All fremdlinge are primary composed of a Ni-Fe metal concentrated within the center and a fine-grained intergrowth of oxides and sulfides at the edges. The Ni-Fe metal poikilitically encloses three different components: a) tiny Os-particles, b) small domains of a W- and Mo-containing oxide, and c) a V<sub>2</sub>O<sub>5</sub>-rich Fe-oxide (Fig. 2). Typical analyses are listed in Tab. 1. The W- and Mo-bearing phase appears to be Ca(W,Mo)O<sub>4</sub> (Fig. 3). The fine-grained intergrowth of oxides and sulfides at the edges also contains small Os-particles; however, their sizes reach only half the size of those within the Ni-Fe metal. We suggest that these Os-particles were also affected by secondary alteration. We further suggest that the described fremdlinge exist as isolated bodies within the CAI A37. They were incorporated under high velocity after their formation, as suggested by their shape and their elongated texture. Chemical and textural information can be synthesized into a model for the formation of these aggregates.

1) Condensation: the contents of refractory metals in the bulk particle are consistent with a condensation origin (Fig. 1). The volatility-controlled pattern is typical for a number of refractory metal nuggets and fremdlinge (e.g. 4). The slight Mo and W depletion may indicate higher than normal solar nebula oxygen fugacity (2). Calculated conditions for formation from condensation are:  $H_2O/H_2=5 \cdot 10^{-3}$ ,  $T=1672$  K,  $p=10^{-3}$  atm.

2) Oxidation of the refractory metal alloy: W and Mo are the first refractory metals to form oxides under increasing oxygen fugacity. The composition of the W and Mo-rich phases suggests scheelite (CaWO<sub>4</sub>) and powellite (CaMoO<sub>4</sub>) (or a solid solution) as relevant phases. Fig. 4 shows how scheelite and powellite could form by reaction of the gas with solid W (assumed activity 0.1) or Mo (assumed activity 1). If condensation of melilite is considered, the partial pressure of Ca would be reduced and thus restrict the formation of scheelite and powellite to high temperatures requiring oxygen fugacities corresponding to  $H_2O/H_2$  ratios of 1-10 (Fig. 4). Formation of Ca(W,Mo)O<sub>4</sub> from a refractory metal alloy at high temperatures is the only plausible way to produce these phases: a) the bulk Mo and W contents fit into the patterns of the other refractory metals. b) besides W and Mo only Ca was detected in the oxide phases (no Si or Al). Formation of Ca(W,Mo)O<sub>4</sub> by reaction with solid oxide or silicate would require other elements to be present c) Ca(W,Mo)O<sub>4</sub> cannot be a product of direct condensation. The condensation temperature for scheelite at  $H_2O/H_2$  of  $5 \cdot 10^{-4}$  is 1486 K and at a  $H_2O/H_2$  ratio of 5, 1559 K, without considering depletion of Ca-partial pressure by condensation of melilite. Powellite condensation temperatures are more than 100 K lower.

3) Condensation of Ni-rich metal and V-oxides: After formation of Ca(W,Mo)O<sub>4</sub> at high oxygen fugacity a temperature decrease would result in the condensation of the Ni-rich metal enclosing the whole assemblage. Above an oxygen fugacity corresponding to  $H_2O/H_2$  of 1 iron begins to significantly oxidise in the gas phase; therefore the resulting alloy becomes correspondingly Ni-rich. At 1400 K and a  $H_2O/H_2$  ratio of 3 an alloy with 34.4% Fe, 61.8% Ni, 3.4% Co, and 0.4% Cr is in equilibrium with a gas of solar composition. The Ir from the original metal condensate would diffuse into the Ni-rich metal. At higher oxygen fugacities however V would completely condense as oxide, perhaps in solid solution with magnetite, a phase that is actually observed. The nominal condensation temperature for magnetite at an  $H_2O/H_2$  ratio of 3 is 1413 K.

4) At still lower temperatures condensation of sulfur and reaction of sulfur with the existing assemblage occurred, occasionally forming  $\text{MoS}_2$ .

In summary: The particles described by us provide additional evidence for large variations in oxygen fugacities at high temperatures in the early solar system: From a  $\text{H}_2\text{O}/\text{H}_2$  ratio of  $5 \cdot 10^{-4}$ , conventionally assumed in the solar nebula and corresponding to  $p_{\text{O}_2}$  of  $7 \cdot 10^{-17}$  atm. at 1680 K to  $6.7 \cdot 10^{-9}$  atm. for a  $\text{H}_2\text{O}/\text{H}_2$  ratio of 5 at the same temperature. Oxygen fugacities inferred from the color of hibonites cover a similar range (5).

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Tab. 1: Representative analyses of Os-particles (1-3), and Ni-Fe metal (4, 5); n.d. = not detected; data in wt%.

	1	2	3	4	5
Fe	7.7	7.6	6.3	31.0	35.0
Co	0.23	0.62	0.14	1.66	1.95
Ni	2.45	7.9	5.3	55.3	59.0
Ru	6.1	5.9	5.7	n.d.	n.d.
Re	5.4	5.1	6.8	n.d.	n.d.
Os	68.2	63.8	77.0	2.24	2.86
Ir	3.6	5.7	1.57	7.5	3.0
Mo	3.4	n.d.	n.d.	n.d.	n.d.
Tot	97.08	96.62	102.71	97.70	101.81

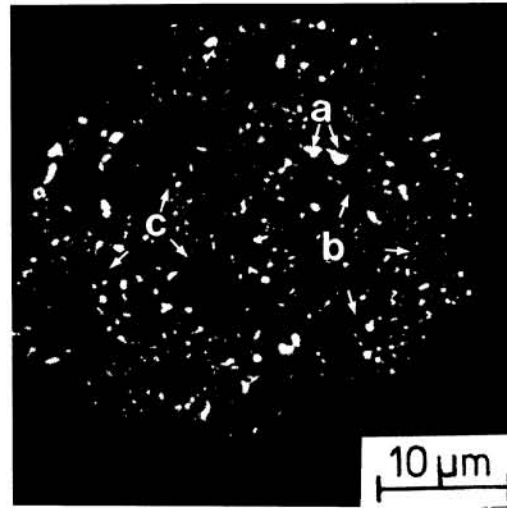


Fig. 2

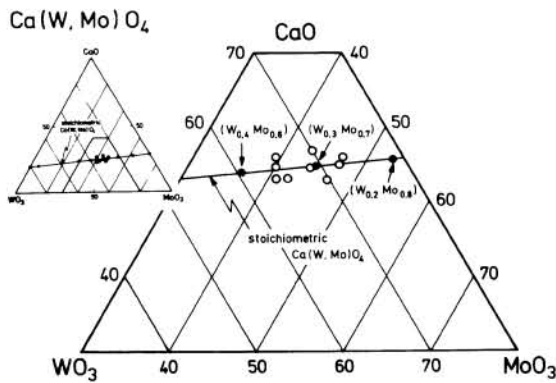


Fig. 3

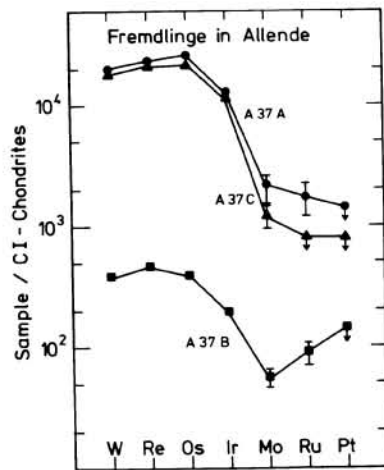


Fig. 1

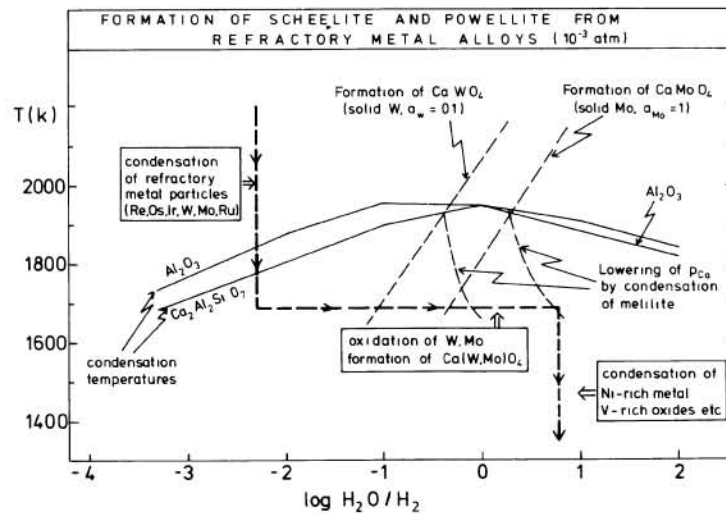


Fig. 4