

THE MULTISTAGE FORMATION HISTORY OF FREMDLING AL-OA1: A TEM/EMPA STUDY OF A COMPLEX OPAQUE ASSEMBLAGE; Don D. Eisenhour and Peter R. Buseck, Departments of Geology and Chemistry, Arizona State University, Tempe, Arizona 85287-1404.

Fremdlinge, optically opaque objects in Ca-, Al-rich inclusions (CAIs), contain complex mixtures of refractory-rich, volatile-rich, highly reduced, and highly oxidized phases. It was originally suggested that Fremdlinge formed either by direct condensation from the solar nebula [1,2] or as the residuum from the evaporation of chondritic material [3]. More recently these hypotheses have been modified to include processes involving immiscible melts [4] and multistage events with varying oxygen fugacities [5-8]. We report on a TEM/EMPA investigation of a complex Fremdling, AL-OA1, and its implications on the *multiple* processes involved in the formation of Fremdlinge.

AL-OA1 is from a typical Allende type-B1 CAI, ~ 1.5 cm in diameter, with a fassaite (10-14 wt% TiO₂) core, a melilite (Åk₀₁ - Åk₇₀) mantle, and a perovskite-rich rim. AL-OA1 is located at the center of the fassaite core and consists of two compositionally distinct zones. Zone #1, which accounts for ~ 90% of the Fremdling by volume, is composed of Ni-Fe-metal, pentlandite, pyrrhotite, V-magnetite, apatite, molybdenite, and Os-, Ru-rich and Pt-, Ir-rich nuggets. Zone #2, a roughly spherical region ~ 200 μm in diameter, consists of pyrrhotite, V-magnetite, scheelite, fassaite, and hedenbergite, but is free of pentlandite, apatite, Ni-Fe-metal, and Pt-group metal nuggets. The boundary between these zones is well defined by the presence of an apatite rim that encloses zone #1 but not zone #2. In a high-contrast, backscattered-electron image (fig. 1), zone #2 appears dark (with the exception of two bright scheelite grains) because of its lack of Ni-Fe-metal and Pt-group metal nuggets.

A change in the V content of V-magnetites occurs across the boundary between these two zones. In zone #1 they have an average composition of Fe(Fe_{0.38}V_{0.38}Cr_{0.25}Ti_{0.03})₂O₄, with V contents from grain to grain varying from 9.5 to 12.5 atom%; in zone #2, V contents are 2 to 4% lower, ranging from 6.5 to 8.5 atom%, with an average composition of Fe(Fe_{0.44}V_{0.26}Cr_{0.25}Ti_{0.05})₂O₄. Cr concentrations in V-magnetites are similar in both zones, with Cr varying greatly from grain to grain and within individual grains, from < 1% to almost pure FeCr₂O₄. Where Cr varies within an individual grain, the grain is zoned with the rim enriched relative to the core.

Three types of Ni-Fe metal were identified: 1) single-crystal γ-Ni-Fe, 2) coarsely polycrystalline Ni-Fe, and 3) finely polycrystalline Ni-Fe. Grains of single-crystal γ-Ni-Fe, the most common type, range in size from 0.5 to 40 μm, and have an average composition (in atom %) of Ni-62, Fe-35, Co-1.8, Pt-0.7, Ir-0.5. Pt and Co concentrations remain fairly constant (1.6-1.7% Co, 0.7-0.8% Pt); however, Ir varies from 0.3 to 2.0%, with each unit of increase in Ir coupled to a unit increase in Fe and a two-unit decrease in Ni. The coarsely polycrystalline Ni-Fe occurs as <1 μm clumps of 10 to 20 nm grains and appears to be enclosed in V-magnetite. This type of metal is predominantly pure Ni-Fe (<2% Pt+Ir), with Ni varying from 45 to 75% between clumps, but constant in any one clump. The finely polycrystalline Ni-Fe also occurs in <1 μm clumps, but individual grains are <3 nm across. Pt + Ir concentrations are higher in this fine phase than the others, varying between clumps from 10 to 16%, but in the constant ratio of Pt/Ir = 2.2 (which is similar to the solar abundance ratio of 2.1). The Ni content also varies (44-50%) between clumps, but is constant in any single clump. A layered Ni-Fe-hydroxide is commonly found associated with this finely polycrystalline Ni-Fe. This phase has a 7 Å spacing and a Ni/Fe ratio similar to that of the associated polycrystalline Ni-Fe.

Os-, Ru-rich nuggets, which are common in pentlandite, pyrrhotite, apatite, and in some Ni-Fe-metal, are spherical single-crystal hcp alloys ranging in size from <50 to 500 nm. These nuggets vary greatly in composition, both from nugget to nugget and within individual nuggets, having an average composition (in atom %) of Os-48, Ru-29, Fe-18, and Ni-5, but ranging from 18 to 67% Os, 8 to 44% Ru, 12 to 24% Fe, and 3 to 8% Ni. In this phase there is a 3:1 Ru to Fe substitution for Os. This is reflected in the compositional ranges of Os, Ru, and Fe (36% for Ru, 12% for Fe and ~48% for Os). Within individual nuggets, compositional variations occur as irregular lamellae, with Os enriched toward rims.

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Discussion: Chemical and textural evidence suggests that the two distinct zones in AL-OA1 formed separately under markedly different conditions and subsequently coalesced to form a single object. While variations in the compositions of Pt-group metal nuggets in zone #1 *may* be attributed to low temperature phase separation rather than lack of equilibration, it is difficult to reconcile the variations in Ni-Fe-metal compositions in the same way. It also seems unlikely that secondary processes would produce the observed range of Ni-Fe compositions. This suggests that not only did zones #1 and #2 not equilibrate, but that zone #1, itself, never reached equilibrium. One possible explanation, consistent with observation, is that the fine-grained Ni-Fe phases escaped equilibration because they were trapped inside preexisting spinels. The different V contents in magnetites in zones #1 and #2 suggest that V is a primary chemical component of Fremdlinge, while strong Cr concentration gradients and similar Cr distributions in both zones suggest a late-stage introduction of Cr. This is also supported by the lack of V and abundance of Cr in magnetites located in veins surrounding AL-OA1. Further evidence for secondary processes is exhibited by the presence of Ni-Fe-hydroxide, which suggests an aqueous alteration event. It seems highly improbable that the composition of AL-OA1 can be explained solely by the solidification of immiscible melts and subsequent alteration event(s), or by any series of processes whereby a single object is progressively altered.

References: [1] Palme, H. and f. Wlotzka (1976), *Earth Planet. Sci. Lett.*, 33, 45-60; [2] El Goresy, A., et al. (1978), *Proc. Lunar Planet. Sci. Conf.*, IX, 1279-1303; [3] Palme, H., et al. (1982), *Earth Planet. Sci. Lett.*, 61, 1-12; [4] Blum, J. D., et al. (1989), *Geochim. Cosmochim. Acta*, 53, 542-556; [5] Armstrong, J. T., et al. (1985), *Geochim. Cosmochim. Acta*, 49, 1001-1022; [6] El Goresy, A., et al. (1984), *Lunar Planet. Sci.*, XV, 242-243; [7] Bischoff, A. and H. Palme (1986), *Lunar Planet. Sci.*, XVII, 54-55; [8] Blum, J. D., et al. (1989), *Geochim. Cosmochim. Acta*, 53, 483-489.

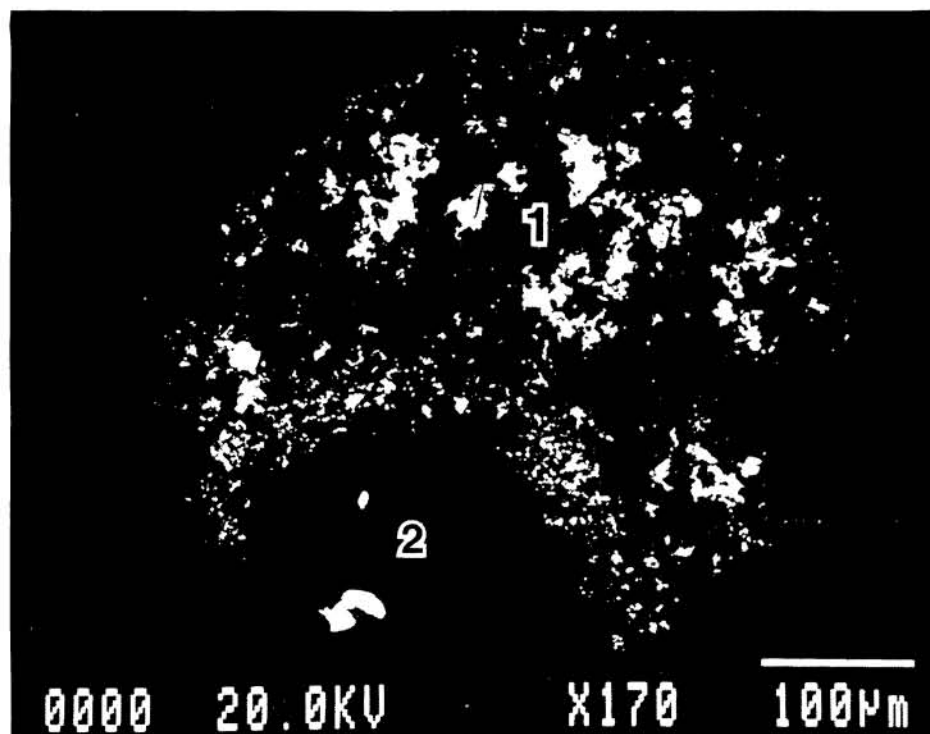


Fig. 1. High-contrast, backscattered-electron image of AL-OA1. Only Ni-Fe-metal, Pt-group metals and scheelite are visible in this image. Zone #2 is the roughly spherical, dark region in the lower portion of the image. The two bright grains in zone #2 are both scheelite. The contrast in the rest of the image is created by metals in zone #1.