CHEMICAL COMPOSITIONS OF FREMDLINGE FROM A TYPE A ALLENDE INCLUSION;

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Calcium-aluminum-rich inclusions (CAI's) from CV3 chondrites contain aggregates, referred to as Fremdlinge and composed of FeNi-metal, Pt-metal alloys, V-rich magnetite, whitlockite, pentlandite, pyrrhotite and molybdenite. Fremdlinge are thought to have formed by high-temperature condensation of submicron-sized W, Re, Os, Ir, Mo, Ru, Pt and Rh metal alloys from the nebular gas; addition of Fe, Ni, Co and P to those alloys by reaction with the gas at lower temperatures; incorporation of the alloys together with oxide and silicate precursor condensate minerals into CAI's; partial melting of bulk CAI's to form silicate melts containing immiscible liquid droplets of Fe, Ni, Co, P and refractory siderophiles; coalescence, cooling and crystallization of those droplets to form metal-phosphide aggregates; and, finally, subsolidus exsolution, oxidation and sulfidation of those aggregates. SYLVESTER et al. [1] determined bulk chemical compositions of ten Fremdlinge from Egg-6, a Type B Allende inclusion, and found, in each, large fractionations of refractory siderophiles from one another relative to C1 chondrites. To explain those fractionations, they proposed a model for refractory siderophile element condensation in which Re, Os and Ru, whose high-temperature crystal structures are hcp, form one alloy; Ir, Pt and Rh, which are fcc, form another; and W and Mo, which are bcc, form a third. No attempt was made by [1] to explain fractionations involving W and Mo, because of possible loss of these elements relative to other refractory siderophiles during late-stage oxidation [2, 3], but virtually all fractionations between Re, Os, Ir, Ru, Pt and Rh were matched by their model. There is some question, however, whether bulk compositions of the Fremdlinge of [1] are representative of those of all Fremdlinge in CV3 chondrites and, thus, whether the three-phase model is generally applicable. There are only a few other bulk chemical compositions of Fremdlinge reported in the literature and a large majority of those are also from Egg-6 [3]. Using an optical microscope, we discovered numerous, sulfide-rich objects in TS68, a large compact Type A inclusion. Eleven of these objects were extracted by breaking the CAI into pieces with stainless steel dental tools and crushing the pieces between sapphire discs, freeing sulfides from silicates. Six of the objects were large enough for a split of each to be made into a polished thin section. SEM study of the sections revealed the presence of FeNi-metal, pentlandite, Fe-sulfide, V-rich magnetite, Ca-phosphate and Pt-metal nuggets. All eleven Fremdlinge were weighed with a microbalance, and analyzed by INAA.

Five Fremdlinge were heavy enough (27.5 μg in F20 and 1.2-2.4 μg in F21, F25, F26, F29) to be weighed with small errors (<10%). Concentrations of refractory siderophile elements in those samples are $\leq 800 \times$ C1 chondrites, compared to larger enrichment factors of 10^3-$10^5 \times$ C1 for most of the refractory siderophile elements in all but one (F5) of the ten Fremdlinge of [1]. Ratios of volatile siderophiles such as Fe, Ni and Co, and chalcophiles such as Se, to refractory siderophiles tend to be larger in the Fremdlinge of this study than in those of [1]. Ni/Os and Se/Os ratios, for instance, are low, $<0.004 \times$ C1 and $<0.002 \times$ C1, respectively, in each of the Fremdlinge of [1], except F5. In this study, chondrite-normalized Ni/Os ratios range from 0.006-0.04, except in F26 and F30, where they are 0.72 ± 0.04 and 0.15 ± 0.02, respectively. Se/Os ratios range from 0.004-$0.009 \times$ C1, except in F26, where this ratio is higher ($0.29 \pm 0.02 \times$ C1), and F27 and F28, where it is lower ($<0.002 \times$ C1). In the Fremdlinge of [1], chondrite-normalized enrichment factors for Au are anomalously large compared to those for other volatile siderophiles and, thus, Au/Ni ratios, for example, range from 3.8-$391 \times$ C1. Here, Au/Ni ratios range from 4.6-$44.5 \times$ C1, except in F22, F23 and F26, where they are <1.0, <1.9 and $<0.11 \times$ C1, respectively. When C1 chondrite-normalized ratios of refractory siderophiles to Os are plotted in order of decreasing condensation temperature in a solar gas (W>Re>Os>Ir>Mo>Ru>Pt) for each of the Fremdlinge of this study, all but three (F21, F25, F29) have patterns that are similar in shape to those of the Fremdlinge of [1]. Magnitudes of fractionations between Re and Os, Ru and Os, or Ir and Os, however, are larger in every one of the samples of this study, except F20 and F21, than in the Fremdlinge of [1]. Subchondritic Re/Os fractionations in F24 and F28, and superchondritic Ru/Os fractionations in F26 and F30 are so large, in fact, that they reach the limit of the sizes of those fractionations which can be produced in the three-phase condensation model.

F20, F24, F27 and F28 of this study, like F6 and F11 of [1], exhibit a pattern of progressively rising enrichment factors with increasing siderophile element volatility from W to Pt, with the exceptions of Mo and Ru, which have anomalously low enrichment factors. According to the three-phase condensation model, F20, F24, F27 and F28 formed from precursor hcp and fcc alloy grains that condensed from a cooling solar gas after removal of high-temperature hcp and fcc grains. Since Re is slightly more refractory than Os, and Ir is more refractory than Pt, high-temperature hcp and fcc condensate alloy grains have, respectively, superchondritic Re/Os and Ir/Pt ratios. Removal of high-temperature hcp and fcc grains from the nebular gas leaves that gas, and low-temperature hcp and fcc grains which subsequently condense from it, with subchondritic Re/Os and Ir/Pt ratios. By mixing these low-temperature grains in a ratio of fcc to hcp that is greater than the nebular ratio, a Fremdling precursor with enrichment factors that rise from Re to Os to Ir to Pt is produced. In F24 and F28, Re is depleted relative to Os by ~25% compared to C1 chondrites, whereas in the Fremdlinge of [1], this depletion does not exceed 20%. High-temperature hcp precursors of F24 and F28, therefore, must have been removed from the gas at an unusually low temperature (1840K at 10^{-3} atm). In fact, because their condensation temperatures are so similar, Re cannot be depleted relative to Os by much more than 25% compared to C1 chondrites, if, as is assumed in the three-phase model, both elements condense into a common alloy phase. Negative Ru anomalies in F20, F24, F27 and F28 result from removing low-temperature hcp alloy grains from the nebular gas at a temperature above that at which Ru, the most volatile of the refractory siderophiles in that alloy, fully condenses. In F27 and F28, which have unusually small C1 chondrite-normalized Ru/Os ratios of 0.096 ± 0.003 and 0.193 ± 0.005, respectively, removal temperatures of hcp grains must have been unusually high (1655-1670 K at 10^{-3} atm).

In F22, F23, F26, F29 and F30 of this study, enrichment factors for Ir are much lower than those for Re and Os. Chondrite-normalized Ir/Os ratios range from ~0.1-0.2 in F22 and F23 to ~0.4-0.5 in F26, F29 and F30. According to the three-phase model, precursors of these Fremdlinge accreted fcc and hcp alloy grains in a ratio of fcc to hcp that is much smaller than the nebular ratio. None of the Fremdlinge of [1] have Ir/Os ratios as low as F22 and F23, however, so fcc precursor grains of those two Fremdlinge must have been particularly undersampled relative to hcp grains. F23, F26 and F30 are like F5 of [1] in that, in addition to Ir depletions, they have larger enrichment factors for Ru than for Re and Os. Chondrite-normalized Ru/Os ratios range from 1.68 ± 0.04 in F23 to 14.8 ± 0.9 in F26. After high-temperature hcp grains containing much of the Os were removed from the nebular gas, hcp precursor grains of these Fremdlinge formed at relatively low temperatures, and Ru fully condensed into those grains. None of the Fremdlinge of [1] have Ru/Os ratios as high as F23, F26 and F30. In the latter, therefore, unusually large fractions of Os must have condensed into the high-temperature hcp grains, requiring an unusually low removal temperature for those grains. In F29, there is a progressive decrease in enrichment factors from Re to Os to Ru, which is not seen in any of the Fremdlinge of [1]. Chondrite-normalized Re/Os and Ru/Os ratios are 1.274 ± 0.006 and 0.84 ± 0.01, respectively. Because Re is slightly more refractory than Os, high-temperature hcp grains have superchondritic Re/Os ratios, as does F29. Those grains, however, also have strongly subchondritic Ru/Os ratios, much lower than that in F29, because Os is much more refractory than Ru. Thus, two hcp precursor components are required to form this Fremdling. One condensed at high temperature with superchondritic Re/Os ratios that are greater than, and subchondritic Ru/Os ratios that are smaller than, those in F29. Another condensed at low temperature with Re/Os and Ru/Os ratios that are nearly chondritic.

In F21, unlike any Fremdling of [1], chondrite-normalized enrichment factors for Re and Os are greater (by a factor of ~1.2) than those for Ir and Pt, and the latter are greater (by a factor of ~1.5) than that for Ru. Hcp precursors of F21 must have been removed from the nebular gas above the temperature at which Ru fully condensed to account for the depletion of Ru relative to Re and Os. To explain the depletion of Ir and Pt relative to Re and Os, the proportion of hcp to fcc grains sampled by F21 must have been greater than the nebular proportion of these grains. In F25, also unlike any Fremdling in [1], enrichment factors for Re and Os are smaller than that for Ru, and the latter is smaller than those for Ir and Pt. Chondrite-normalized Ru/Os, Ir/Ru and Re/Os ratios are 1.55 ± 0.03, 1.31 ± 0.02 and 1.14 ± 0.02, respectively. Hcp precursors of F25 are a mixture of two components. The superchondritic Re/Os ratio is inherited from a component removed from the nebular gas at high temperature, whereas the superchondritic Ru/Os ratio reflects that of another component that condensed later, at lower temperature, from the same gas. The latter component is enriched in Ru relative to Os because much of the Os condensed earlier into the high-temperature component. Ir and Pt are enriched relative to Re, Os and Ru in F25 because the ratio of fcc to hcp grains sampled was greater than the nebular ratio.

Fractionations relative to C1 chondrites among Re, Os, Ru, Ir and Pt in the Fremdlinge of TS68, like those in the Fremdlinge of Egg-6, can be explained by the three-phase condensation model. Using the SEM, however, we have found numerous sulfide-rich veins throughout TS68 and Egg-6, and some of those veins intersect Fremdlinge. Wavelength-dispersive, electron probe analyses of spots in two of five veins in TS68, and one of two veins in Egg-6, have measurable concentrations of Ru (0.05-0.17 wt %). Since partitioning experiments [4] indicate that Ru is much more chalcophile than Os, Ir and Pt, it is possible that the large fractionations of Ru relative to Os, Ir and Pt seen in some of the Fremdlinge in Egg-6 and TS68 are due not to condensation, as discussed above, but to late-stage mobilization of Ru in sulfide veins.

REFERENCES: [1] SYLVESTER et al. (1990) *GCA* 54, 3491-3508. [2] KOHLER et al. (1988) *LPSC* XIX, 627-628. [3] PALME et al. (1989) *LPSC* XX, 814-815. [4] FLEET et al. (1991) *JGR* 96, 21949-21958.