CHEMICAL COMPOSITIONS OF REFRACTORY INCLUSIONS FROM LEOVILLE, EFREMOVKA AND VIGARANO; P.J. Sylvester[1] and L. Grossman[1,2], [1]Department of the Geophysical Sciences, [2]The Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA

A high proportion of Ca-, Al-rich inclusions from Leoville and Vigarano, members of the reduced subgroup of C3V chondrites, have refractory element fractionations that are rare or absent in those from Allende, a member of the oxidized subgroup [1,2]. Discovery of refractory inclusions with such compositions is important because they may record information about processes that occurred in parts of the solar nebula not sampled by Allende inclusions. We have thus continued the search for them in Leoville and Vigarano, and extended it to Efremovka, a third member of the reduced subgroup of C3V chondrites. The chemical compositions of ten, 221-1492 µg inclusions were determined by INAA: four compact type A's, one from Leoville (L1) and three from Efremovka (Ef1, 2, 3); three type B2's, one from Vigarano (Vig1) and two from Leoville (L2, 5); a type B1 from Vigarano (Vig2); a fluffy Type A from Leoville (L4); and a fine-grained Leoville inclusion (L3). Their detailed petrography is described in [3].

Mean compositions of both type A and B inclusions have super-chondritic CaO/Al_2O_3 ratios, but that for type A's ($1.37 \pm 0.08 \times C1$) is greater than that for type B's ($1.09 \pm 0.09 \times C1$). These ratios are greater than those of mean compositions of type A ($0.92 \pm 0.11 \times C1$) and B ($0.81 \pm 0.05 \times C1$) Allende inclusions determined by bulk analysis [4], but similar to those of mean compositions derived from point counts of thin sections of type A ($1.38 \pm 0.08 \times C1$) and B ($1.13 \pm 0.08 \times C1$) Allende inclusions [5] and corrected for secondary alteration. Beckett [5] and Wark [6] suggested that bulk analyses of Allende inclusions reflect loss of Ca relative to Al during secondary alteration and that corrected analyses are more likely to give their pre-alteration CaO/Al_2O_3 ratios. This seems to be confirmed by the similarity of CaO/Al_2O_3 ratios in the corrected analyses of Allende inclusions [5] to those in bulk analyses of inclusions in this work, in which the modal proportion of secondary alteration products is much less than in Allende inclusions [3]. Super-chondritic CaO/Al_2O_3 ratios in refractory inclusions may reflect condensation of their precursors after removal of a previously condensed, Al-rich phase such as corundum [5]. Since type A inclusions have greater CaO/Al_2O_3 ratios than type B's, more corundum may have been removed before type A's condensed than before type B's condensed. As in both bulk [4] and corrected [5] analyses of Allende inclusions, the mean composition of type B's has a greater MgO/Al_2O_3 ratio than that of type A's (0.31 ± 0.04 vs. 0.18 ± 0.03) in this work. Since Mg is more volatile than Al in a solar gas, the greater MgO/Al_2O_3 ratios of type B's suggest that they were removed from chemical communication with the gas at lower temperatures than were type A's.

L2, L4, Ef1, Ef2, Ef3 and Vig1 have Group I (unfractionated) REE patterns and REE concentrations of ~23, ~19, ~18, ~13, ~16 and ~20 × C1 chondrites, respectively. They are thus similar to most Allende coarse-grained inclusions, which have Group I patterns and are enriched to ~18 × C1 [7]. The precursors of such inclusions probably separated from the nebular gas at a low enough temperature that each REE had fully condensed into them. The type A inclusions, L4, Ef1, Ef2 and Ef3, have positive Eu anomalies (Eu/Sm = 1.2 to 2.1 × C1), suggesting that their precursors preferentially sampled melilite in the nebula. Only four of eight Allende type A's have Eu/Sm > 1.2 × C1 [4,8]. L1, L5 and Vig2 have modified Group I patterns in that light REE are fractionated from heavy REE (La/Lu ~0.8 × C1 in L1 and L5, ~1.3 × C1 in Vig2), as in several Allende [4,8] and Vigarano [1,2] inclusions. The Leoville fine-grained inclusion (L3) has a Group II REE pattern (La, Ce, Sm ~110 × C1, Dy ~60 × C1, Lu ~0.2 × C1), like that of fine-grained inclusions from Allende [9], Leoville [1] and Vigarano [2]. Group II inclusions condensed from the nebular gas after removal of high temperature, ultra-refractory condensates.

Six of nine coarse-grained inclusions have unusual or unique refractory siderophile compositions compared to those of most Allende coarse-grained inclusions. In nine of the latter, mean C1 chondrite-normalized concentrations of each of Re, Os, Ir and Ru are 16.2 ± 0.4 and, in each of the nine inclusions, these siderophiles are fractionated from one another by <20% [7]. Re, Os, Ir and Ru are similarly unfractionated in L4, L5 and Ef3, mean concentrations being $24.6 \pm 1.1 \times C1$ in L4, $14.8 \pm 1.2 \times C1$ in L5 and $14.7 \pm 0.7 \times C1$ in Ef3. In L1, however, Ru has an enrichment factor (16.6 ± 0.3 relative to C1 chondrites) that is less than those of Re, Os and Ir by >20%. Re/Ru, Os/Ru and Ir/Ru ratios are 1.39 ± 0.06, 1.40 ± 0.03 and $1.27 \pm 0.02 \times C1$, respectively. In Vig2, the enrichment factor of Os (22.6 ± 0.2) is greater than those of Re, Ir and Ru by >20%, with Os/Ir and Os/Ru ratios of $1.26 \pm 0.01 \times C1$ and a Re/Os ratio of $0.73 \pm 0.04 \times C1$. This enrichment pattern is similar to that of Vig 1623-3, a Vigarano inclusion analyzed by Mao et al. [1], in which Re, Ir and Ru concentrations are ~11 × C1 and that of Os is ~27 × C1. In Vig1, enrichment factors relative to C1 chondrites decrease from Re and Os (~57), which are most refractory, to those for Ir (~44) and Ru (~25), which are progressively less refractory. In L2, Re, Os and Ir are uniformly enriched to 105-110 × C1, whereas Ru is 66 × C1. In Ef2, Re and Os are ~145 × C1, Ir is 114 × C1 and Ru is 81 × C1. In Ef1, Re and Os are ~115 × C1 and Ir and Ru are 22 and 17 × C1, respectively. In Allende coarse-grained inclusions, C1 chondrite-normalized concentrations of W and Mo are equal to or less than those of Re, Os, Ir and Ru [7,10]. Five coarse-grained inclusions studied here have Mo/Ir ratios within 20% of the C1 ratio. Of these, L5 has a chondritic W/Ir ratio, Vig1 has chondritic W/Re and W/Os ratios, but a super-chondritic W/Ir ratio ($1.30 \pm 0.03 \times C1$), and L4, Vig2 and Ef3 have sub-chondritic W/Ir ratios (~0.7 × C1). Both Mo and W show negative anomalies in all other coarse-grained inclusions, with C1 chondrite-normalized Mo/Os always < W/Os.

Refractory siderophiles are carried into refractory inclusions by metal alloy condensate phases. Sylvester et al.

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[11] proposed that W and Mo condensed into a bcc alloy; Re, Os and Ru into an hcp alloy; and Ir, Pt and Rh into an fcc alloy. If an alloy is removed from the nebular gas at a temperature above that at which its constituent refractory siderophiles have fully condensed, depletions of the more volatile siderophiles relative to the less volatile ones will result, relative to C1 chondrites. Sylvester *et al.* [11] inferred that such fractionated alloys accreted into precursors of Allende inclusions because, in one such inclusion, metal alloy assemblages have large fractionations of siderophiles from one another. Thus, in inclusions with chondritic ratios of Re, Os, Ru and Ir, such as L4, L5, Ef3 and most Allende coarse-grained inclusions, large numbers of hcp and fcc alloy grains must have been sampled so that fractionations between refractory siderophiles of the two different alloys, and those between siderophiles of the same alloy, were averaged out. This apparently was not the case for most of the inclusions studied here. In Ef1, Ef2 and Vig1, enrichment factors for Ir are less than those for Re and Os. Either Ir was incompletely condensed into the fcc alloy grains or, relative to their nebular proportions, those fcc grains were under-sampled compared to hcp grains. L1, L2, Vig1, Ef1 and Ef2 seem to have preferentially sampled hcp grains with chondritic Re/Os and super-chondritic Os/Ru ratios. In a solar gas, Os is slightly more volatile than Re, and significantly more refractory than Ru. Thus, at a pressure of 10^{-3} atm, hcp alloys removed from such a gas below ~1750 K, where Re and Os are fully condensed, and above ~1490 K, where Ru is fully condensed, will have chondritic Re/Os and super-chondritic Os/Ru ratios. Removal temperatures for the mean compositions of model hcp alloys in L1, L2, Vig1, Ef1 and Ef2 range from ~1655 K for Ef1, whose Os/Ru ratio is $6.85 \pm 0.04 \times$ C1, to ~1590 K for L1, whose Os/Ru ratio is $1.40 \pm 0.03 \times$ C1. The large enrichment factors for Re and Os in L2, Vig1, Ef1 and Ef2 relative to those in typical Allende coarse-grained inclusions imply that the total amount of hcp alloy accreted by the former inclusions is 3.5-9.1 times that accreted by the latter ones. It may seem curious that Re, Os and Ru are averaged out to their chondritic proportions in Allende inclusions even though they sampled less hcp alloy than L2, Vig1, Ef1 and Ef2. The latter inclusions, however, sampled hcp alloys which, on average, were removed from the nebular gas at temperatures above which Ru fully condenses, whereas Allende inclusions sampled hcp alloys with lower mean equilibration temperatures. Vig2 appears to have preferentially sampled hcp alloy grains with sub-chondritic Re/Os and super-chondritic Os/Ru ratios. Since Re is more refractory than Os, hcp alloy grains with sub-chondritic Re/Os ratios can condense from a cooling solar gas only if high temperature hcp alloy grains with super-chondritic Re/Os ratios were removed from that gas previously. Such removal at 1840 K yields a subsequently condensing hcp alloy at 1630 K with a Re/Os ratio of ~0.75 × C1 and an Os/Ru ratio of ~1.5 × C1, as in Vig2. Negative W and Mo anomalies in L1, L2, Ef1 and Ef2 probably reflect under-sampling of bcc relative to hcp and fcc alloy grains in the nebula. Negative W anomalies without accompanying Mo anomalies in L4, Vig2 and Ef3 may be the result of preferential sampling of bcc alloy grains with sub-chondritic W/Mo ratios. These can condense after removal of early, high temperature bcc alloys which, because W is more refractory than Mo in a solar gas, have super-chondritic W/Mo ratios. An alternative model which also explains W and Mo depletions in bulk inclusions is condensation from an oxidizing gas [10]. Since Mo is more volatile than W in an oxidizing gas, Mo depletions are larger than W depletions in condensates from such a gas, which is the case for L1, L2, Ef1 and Ef2, but not for L4, Vig2 and Ef3.

Like other coarse-grained refractory inclusions of the reduced subgroup of C3V chondrites, the nine analyzed here have lower Au (<1.1-5.0 ppb) contents than those of the oxidized subgroup (6-800 ppb Au) [1,12]. Na contents in the former (170-860 ppm), except for Vig1 (2020 ppm) and Vig2 (1540 ppm), are lower than those of 29 of 37 of the latter [1,12]. This is consistent with the paucity of secondary alteration products in all coarse-grained inclusions of this work, except Vig1, [3] and supports the notion that most coarse-grained inclusions of the reduced subgroup were altered in the nebular gas at a higher temperature or for a shorter time than those of the oxidized subgroup [1,2]. The fine-grained Leoville inclusion (L3), like another (Leo 3536-1) analyzed by [1], has lower Na (640 ppm) and Au (<1.1 ppb) contents than Allende fine-grained inclusions (1.1-5.1 % Na, 3-42 ppb Au) [9,13]. Two Vigarano fine-grained inclusions, however, have Na and Au contents comparable to those in their counterparts in Allende [2]. An Efremovka fine-grained inclusion (E14) has a low Na content [14] like those in the two Leoville fine-grained inclusions and a high Au content like those in Vigarano and Allende. Thus, while Leoville fine-grained inclusions seem to have been altered at higher temperatures or for a shorter time than those in Allende, this does not appear to be so for those in Vigarano. The Efremovka fine-grained inclusion may have been altered at a temperature above which Na is significantly condensed but below which Au is significantly condensed.

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