

CHEMICAL STUDIES OF VOLATILIZATION RESIDUES OF CHONDRITES. V. Ekambaram¹, L. Grossman^{1,2} and E. A. King³. ¹Dept. of the Geophysical Sciences, University of Chicago, Chicago, IL 60637; ²Enrico Fermi Institute, University of Chicago; ³Dept. of Geosciences, University of Houston, Houston, TX 77004.

Grossman *et al.* (1) studied trace element contents of volatilization residues of the Murchison and Allende meteorites produced in air using a solar furnace (2,3). A remarkable result of those experiments is that Ir and Os, two of the most refractory elements in a gas of solar composition, were strongly depleted relative to refractory lithophiles compared to the starting materials. For example, the top of a bead produced by volatilization of Allende was enriched in refractory lithophiles by ~15% compared to the starting material, indicating only ~15% volatilization loss, but >99.7% of the Ir and >94% of the Os were lost. Wondering if this is a general result of rapid volatilization of chondrites, we conducted the present experiments to see if this effect could be reproduced in an H₂ atmosphere and to check if these siderophile elements were being lost by alloying with the water-cooled Al base of the crucible that contains the sample during heating.

To test the latter possibility, an Allende sample was volatilized in air upon a thin Al disc placed on the floor of the crucible. Al scrapings sampled from the region of this false base which had been discolored during heating of Allende contain higher concentrations of most elements than a piece of the same Al which had not been so used. Because Ir and Os contents of the Al increased by <0.9ppb and <8.7ppb, respectively, however, and because the Al plate weighed only five times more than the sample of Allende, loss of these siderophiles to the Al base can only account for <1% depletion of Ir and <6% depletion of Os from Allende, ~2 orders of magnitude less than what is observed.

Many samples produced in these experiments possess a hemispherical shape, having curved tops and flat bottoms. Because the beam was focussed on the tops of these beads, the tops experienced the highest temperatures and the bottoms the lowest.

ALL-191 is an Allende residue produced in H₂. A sample from its top, consisting of olivine, diopside and rare metal beads, is uniformly enriched in refractory lithophiles by a factor of ~4.5 compared to the starting material, indicating volatilization of ~78% of the original sample. Instead of having enrichment factors similar to those of the refractory lithophiles, however, Ir and Os are depleted to levels which are <1.6x10⁻³ and <.09 of their initial concentrations. A sample of Ni-Fe was removed from the metallic basal layer of this residue. Although it has a higher concentration of Ir than the top of the residue, it is still depleted in Ir and Os by factors of >30 and >3.6, respectively, compared to the starting material. Depletion of Ir and Os from the top of ALL-191 cannot be accounted for by scavenging of siderophiles by metallic Ni-Fe and settling of this material to the bottom. Furthermore, recall that Ir and Os were lost from both the top and bottom of an Allende residue in our earlier experiments in air (1), in which no metallic basal layer formed. We conclude that Ir and Os are preferentially lost relative to refractory lithophiles when Allende is volatilized rapidly and that this phenomenon is independent of the oxidation state of the gas in which the meteorite is immersed. Although the exact loss mechanism is unclear, it may be related to formation of volatile Ir and Os halides by reaction of these metals with halogens in the volatilizing material. Formation of IrF₆ was proposed to account for enormous enrichment of Ir relative to Al in particulates from Kilauea volcanic emissions compared to Hawaiian basalt (4).

CM2-15 is a Murchison residue produced in H₂. Relative to the starting

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material, Sc and most REE are enriched in the top layer, consisting of olivine and diopside, by a factor of ~ 9.5 and Ca, Al and Ti are enriched only by a factor of 6.5, indicating volatilization loss of 85-90% of the original material. When normalized to the starting material, the REE pattern of this sample has large negative Eu and Yb anomalies, enrichment factors for these elements being only 5.2 and < 0.6 , respectively. Although negative Yb anomalies were produced previously in volatilization residues of synthetic samples prepared in vacuum and in H_2 (5), the one found here is much larger than in (5). Furthermore, this is the first time a volatilization residue has been produced whose Yb anomaly is much greater than its Eu anomaly, despite the failure of thermodynamic calculations to predict such a feature during vapor-solid equilibrium processes (6). It is thus conceivable that volatilization was involved in the origin of REE patterns in those refractory inclusions in Murchison which have large negative Yb anomalies unaccompanied by similarly large negative Eu anomalies (7). This sample is depleted in Ir and Os by factors of > 500 and > 4 , respectively, relative to the original material. Ir and Os are depleted in an Ni-Fe-Si bead removed from the top of CM2-15 to levels which are .09 and $< .25$, respectively, of their concentrations in the starting material but are enriched by factors of 3.4 and 48, respectively, in an Ni-Fe sample from the metallic basal layer. Although it is conceivable that Ir and Os were lost from the top of CM2-15 by alloying with Ni-Fe which sank into the basal layer, this did not occur in ALL-191. Furthermore, Murchison residues produced in air (1) suffered Ir and Os loss despite the absence of a basal metal or magnetite layer.

CM2-13 is a Murchison residue produced in vacuum. It is flat and contains an upper layer of spinel, diopside and forsterite and a lower layer of Ni-Fe and iron sulfide. Most refractory lithophiles are enriched in the top layer by a factor of ~ 6 relative to the starting material, indicating that $\sim 84\%$ of the original sample was volatilized. Ce and V are depleted by factors of > 5 and > 6 , respectively, indicating relatively oxidizing conditions. Ir and Os are depleted from the top by factors of > 40 and > 14 , but are enriched in the bottom layer by factors of 66 and 5, respectively, relative to the starting material. Again, although Ir and Os could have been removed from the top during settling of the metal and sulfide layer, we doubt this for the reasons cited for CM2-15.

When powders are heated in our apparatus (2), a molten bead forms and both silicate and metallic material spatters from it which falls to the crucible floor around the bead. In some experiments, heating was interrupted, spattered material was gathered around the main bead and heating was resumed. We note that this procedure was followed in those experiments in which Ir and Os were found in the basal layer but that spattered material was never recombined with the main bead in those cases in which Ir and Os were completely lost. It is conceivable that some material was spattered prior to Ir and Os loss from it. This material would have remained cool while the main bead was heated intensely and may have served as condensation sites for Ir and Os being volatilized from the main bead. When such spattered material is reunited with the main bead, it may not suffer much further Ir and Os volatilization, as its position around and near the base of the main bead is relatively cool compared to the top of the bead where the beam is focussed. Further analyses are planned to test this hypothesis.

REFERENCES: 1. Grossman, L. *et al.* (1982) *Meteoritics* 17, 226. 2. King, E.A. (1982) *JGR* 87, A429-A434. 3. MacPherson, G.J. *et al.* (1982) *LPS XIII*, 459-460. 4. Zoller, W.H. *et al.* (1983) *Science* 222, 1118-1121. 5. Nagasawa, H. & Onuma, N. (1979) *LPS X*, 884-886. 6. Davis, A.M. & Grossman, L. (1979) *GCA* 43, 1611-1632. 7. Ekambaram, V. *et al.* (1983) Submitted to *GCA*.