

EXPERIMENTAL STUDIES OF THE VOLATILITY OF V AND MN. E.E. Shaffer\*, A.J.G. Jurewicz\*\*, and J.H. Jones\*\*\*. \*Division of Geological and Planetary Sciences, 170-25, Caltech, Pasadena, CA 91125. \*\*Lockheed ESC, C23, 2400 NASA Rd. 1, Houston, TX 77058. \*\*\*SN2, NASA/JSC, Houston, TX 77058

**INTRODUCTION** The depletion patterns of V, Cr, and Mn in the Earth and Moon are strikingly similar to one another and distinct from those of the other Terrestrial planets [1]. The process by which these two bodies developed such similar depletion patterns (V>Cr>Mn relative to chondrites) is still uncertain. One hypothesis, favored by Ringwood and others, is that these depletion patterns represent a genetic relationship between the Earth and Moon. They postulate that the Earth formed from the solar nebula with approximately chondritic abundances of V, Cr, and Mn and that V, Cr (and perhaps Mn) were then fractionated into the metallic core, thus depleting the mantle. Later, impact or fission freed some of this depleted mantle material, which then accreted to form the Moon [2,3,4]. This hypothesis requires the depletion of V, Cr, and Mn by siderophile fractionation, which is thought to occur only under very reducing conditions or very high pressure [5]. Recent work by Drake et. al. has found that low pressure fractionation in a reducing environment yields a depletion pattern in which Mn> Cr> V, the reverse of that found in the Earth and Moon [1]. Whether metal-silicate fractionation at very high pressure can produce the correct V-Cr-Mn pattern is still not known; however, preliminary studies indicate that this process also gives rise to depletion patterns opposite to those of the Earth and Moon [6]. However, high pressure does appear to increase the siderophile tendencies of both V and Cr [6].

An alternative hypothesis postulates that the Earth and Moon share similar abundances of V, Cr, and Mn because of a pre-existing depletion of these elements in that part of the solar nebula where the Earth and Moon formed. One possible mechanism for nebular depletion is volatilization; however, the volatility of V has been thought to be too low for this theory to be plausible. To evaluate the validity of this objection, experiments were performed to investigate the volatilities of V and Mn.

**METHODS** An oxide mix with a Sc-doped eucrite composition was prepared and fused into a glass at 1350°C. The quenched glass was ground under ethanol to a particle size of 88 microns. Aliquots of this base composition were then doped to 1.0 +/- 0.1 wt% levels of V<sub>2</sub>O<sub>5</sub> and MnO using high-purity (99.99%) V<sub>2</sub>O<sub>5</sub> and MnO<sub>2</sub>, respectively. Samples of the base glass, V-doped mix, and Mn-doped mix were suspended on Pt wires and run in a Deltech gas-mixing furnace at a temperature of 1400°C under an fO<sub>2</sub> of IW+2 for 30 min. The resulting charges were analyzed using an electron microprobe to confirm homogeneity of the starting material and to verify the starting compositions.

A series of experimental charges were then run. Two 100 mg pellets, one of V- and one of Mn-doped mix, were fused to Pt60-Rh40 wire loops. These loops were connected to hangwires by small-diameter Pt-Rh "zap" wires. By melting this wire using an electrical current, the samples could be rapidly quenched in water at the end of the run. Samples were placed in the furnace and run at 1400°C under an fO<sub>2</sub> of IW-1 for 4 hours. After that time, a continuous roughing pump vacuum of ~10<sup>-2</sup> to 10<sup>-3</sup> bars was maintained on the furnace to remove any gaseous V or Mn species, thus reducing their partial pressures and facilitating volatilization. This was done because previous experiments run without evacuation did not show significant loss of either V or Mn. Also, these low pressures more closely approximate the pressure conditions postulated for the solar nebula. Runs of 24, 36, and 47 hours under vacuum were made. The 24 and 47 hour runs experienced some air leakage after evacuation. Consequently, these charges are very oxidized, and qualitative Mossbauer analysis indicates that they represent an fO<sub>2</sub> between QFM and air. The 36 hour run was successfully maintained under vacuum without measurable air leakage and these charges remained reduced. The quality of the vacuum for this run was, presumably, also greatly improved.

**RESULTS** The volatilization experiments show significant V loss in all runs. A 35% +/- 5% depletion of V from original levels is seen in the 24 hour, oxidized sample and a 70% +/- 5% depletion is present in the 47 hour, oxidized charge. Because V loss from the silicate charges might be caused by solid-solution within the Pt-Rh loops as well as by volatilization, microprobe analysis was done on the sample loops. No V was found. More significantly, an initially V-free Mn charge run alongside the 24 hour V charge showed an increase in V content to about 0.15 wt%, indicating definite vapor transport. Mn, thought to be more volatile than V, showed no significant depletion after 24 hours under vacuum (the 47 hour, oxidized Mn charge was not recovered). In contrast, the reduced (initially IW-1), 36 hour charges showed almost total depletion of V and nearly 50% depletion of Mn. Again, no V or Mn was found in the Pt-Rh loops.

**CONCLUSIONS** Our preliminary results indicate that V can indeed be volatile. In fact, of the eight elements in our experimental charges (Si, Al, Fe, Mg, Ca, Sc, Mn, V), V is the most volatile under these experimental conditions. Normalized to Sc, concentrations of Si, Al, Mg, and Ca remained constant. Our experiments seem to indicate that V loss correlates best with time at temperature and quality of vacuum. The difference in V loss between the 24 hour and 47 hour oxidized experiments indicates a correlation with time at temperature. The greater loss of V in the 36 hour experiment, compared to the 47 hour experiment, suggests either a dependence on the quality of vacuum or the  $fO_2$ . Since V oxides are thought to be most volatile under oxidizing conditions [7], we favor the former explanation.

Application of these experiments to the conditions of the solar nebula is not straightforward. The oxygen fugacities of the 24 and 47 hour experiments are clearly higher than that of the solar nebula. However, meteoritic evidence suggests that V can indeed be somewhat volatile. For example, CV chondrites are depleted in V relative to Sc and Al [8] and some CAI's are also depleted in V [7].

In the case of our 36 hour experiment, the initial  $fO_2$  of IW-1 was probably approximately maintained. Little FeO (~5 wt.%) remained in the silicate charge, and substantial Fe was present in the Pt-Rh loop, implying an  $fO_2$  below IW. Oxygen fugacities significantly lower than IW-1 would have led to the reduction of Si and the formation of Pt-Si alloys, which were not observed. Thus, it appears that the kinetics of vaporization allow the wholesale volatilization of V from a silicate liquid at 1400°C and ~IW-1 on a 24 hour timescale. IW-1 is lower than the intrinsic  $fO_2$  of some Allende CAI melilites [9]. Consequently, we believe that nebular volatilization of V, Cr, and Mn may be a viable alternative for the establishment of the V-Cr-Mn signatures of the Earth and Moon.

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