

ZINC LOSSES FROM AND ZINC ISOTOPIC ABUNDANCES IN RESIDUES FORMED BY HEATING OF Zn, ZnO, ZnS, AND Zn-DOPED SILICATE GLASS. S. Xue¹, Y. Yu², Roger H. Hewins², G.S. Hall¹, and G.F. Herzog¹ 1) Department of Chemistry and 2) Department of Geological Sciences, Rutgers University, New Brunswick, NJ 08903.

Background - Open-system evaporation of a volatile element from a well-mixed liquid leaves behind a residue enriched in the heavy isotopes of that element. Lunar soils [1,2], deep-sea spheres [3], and a few meteorites [4] provide examples of such enrichments for several elements. In the case of the moderately volatile element Zn, a 50% loss due to evaporation of the atom translates into an expected mass-dependent fractionation of approximately +0.5%/AMU. To find out whether 1) losses of Zn might occur and 2) leave an isotopic imprint under conditions relevant to the formation of chondrules, we carried out a set of controlled heating experiments. The siting and the chemical form of Zn in chondrules are not well understood [5] although recent work [6] points toward an association with S in chondrule rims. To examine a variety of possibilities we took Zn as the metal, the oxide, and the sulfide (sphalerite).

Experimental Methods - The sources of zinc were Zn powder, Zn wire, and ZnO (all reagent grade) and powdered sphalerite (ZnS) containing 64% Zn supplied by G. Harlow (American Museum of Natural History). To make experimental charges analogous to chondrules, we used a ground silicate glass with a composition similar to that of type IIAB chondrules [7] spiked with either Zn, ZnS, or ZnO powder. The mixtures of silicate with either Zn or ZnS were pressed into 55-mg pellets. To try to optimize sample homogeneity, the mixture of silicate with ZnO was heated, quenched, and ground prior to making pellets.

Silicate samples were prepared in duplicate, one set for electron microprobe and one for chemical analyses. All samples were heated in a Deltech vertical muffle tube furnace. Pure Zn and ZnS powders, (~100 mg each) were evaporated from quartz crucibles; all other experimental charges were supported by platinum wires. Furnace temperatures ranged from 650°C for Zn metal to 1310-1510°C for silicates. Isothermal heating times lasted from 2 to 30 min. Flash heating and controlled cooling experiments were performed on some of the silicate samples following procedures described elsewhere [8]. Different furnace gases were used: H₂/CO₂ or CO/CO₂ with fO₂ of IW-0.5 for the silicate mixtures; and He/H₂ for Zn metal. Melting of the silicate mixtures produced beads of glass and crystals up to 3 mm in diameter. All materials were quenched in air. Polished sections were examined with a Jeol 8600 electron microprobe set for rastering at an accelerating voltage of 15 kV.

For Zn analyses, samples were weighed and dissolved in HF, HNO₃ and HCl. Zn was isolated by ion exchange [2] with yields of 90-95%. Isotopic ratios were measured by ICP-MS [2]. The data were reduced to δ values after corrections for procedural blanks (~ 0.5 ppb) and instrumental mass fractionation (~ 2.5%/AMU). In all but the few cases where the concentrations of Zn in solution fell below 20 ppb, the uncertainties in $\delta^{66}\text{Zn}$, and $\delta^{68}\text{Zn}$ were $\pm 2\%$ and $\pm 3\%$ (1- σ), respectively. From the measured δ values, we calculated the degree of mass fractionation, Φ , for each sample from the slope of a plot of $\delta^{64}\text{Zn} = 0$, $\delta^{66}\text{Zn}$, and $\delta^{68}\text{Zn}$ vs. the relevant atomic mass. To a first approximation, the quantity Φ can be regarded as the average of $\delta^{66}\text{Zn}/2$ and $\delta^{68}\text{Zn}/4$. We estimate the 1- σ uncertainty in Φ to be $\pm 0.08\%$ /AMU.

Results - The results of seven sets of heating experiments are summarized in Figure 1. With one exception, all heated samples lost more than 25% of the zinc originally present. The one exception was a sample of pure ZnO (melting point = 1975°C), which was heated to 1600°C for 12 minutes. Silicate mixtures held at temperatures above 1500°C for more than 10 minutes retained less than 1% of the Zn initially present. All three silicate+Zn mixtures were subjected to flash heating followed by cooling at initial rates from 8 to 100 °/min. With other conditions fixed, the loss of Zn was greater for slower cooling, as observed previously for Na and S [8]. The nature of the furnace gas affected loss rates. Silicate + ZnS samples lost Zn in H₂/CO₂ gas at comparable or higher rates than in CO/CO₂. Higher loss rates also obtained for silicate + Zn samples in H₂/CO₂ than in He. The furnace gas affected the character of the product, too. In silicate + ZnS samples, Zn partitioned between ZnS and a glassy phase and some

FeO converted to FeS, presumably by reaction with ZnS. In the presence of H₂, some FeO was reduced to Fe and some reacted to produce FeS while a portion of the Zn migrated to glass; remaining ZnS was below detection limits in the energy dispersive mode of the electron microprobe.

When added as metal or oxide, zinc underwent mass-dependent fractionation to a modest degree in all heated samples. The maximum degree of fractionation observed, was $\Phi = 0.5\%/AMU$ (i.e., $\delta^{66}Zn \sim 10\%$ and $\delta^{68}Zn \sim 20\%$). For a given type of sample material, Φ tends to increase with the fraction of Zn lost. However, all values of Φ for losses greater than about 20% depart significantly from the theoretical Rayleigh curve. Such departures may indicate that the evaporating species diffuses more slowly to than it escapes from the surface of the molten sample. In contrast to the results for Zn and ZnO, no isotopic fractionation was observed when Zn was introduced as sphalerite, even for Zn losses as high as 85%.

Discussion - The experimental conditions that we chose differ from those pertinent to chondrule formation in known ways (higher ambient pressure, larger sample size, and higher zinc concentration) and unknown ways (initial chemical form of Zn, detailed time-temperature profiles, influence of dust). Nonetheless, a substantial body of laboratory experience indicates that the heating protocols and silicate composition adopted reproduce many important features of chondrules. From the experimental results we therefore conclude that the loss of Zn from true chondrule melts seems a likely outcome, whether Zn is initially present in sulfide or an oxidized phase. To the extent that Zn occurs as the oxide, some degree of mass-dependent fractionation also seems likely, although the relevance of the particular trends shown in Figure 1 remains to be established. To the extent that Zn in chondrules derives from sulfides, our data give no reason to expect a significant degree of mass-dependent isotopic fractionation and indeed, we have observed none in a limited number of chondrule samples [2]. On the other hand, we do not yet wish to rule out the possibility of isotopic fractionation from sulfide for two reasons: 1) Zn is mass fractionated in lunar soils [2] where it is strongly associated with sulfur [9]; and 2) as Humayun and Clayton [10] stress, the likelihood of isotopic fractionation could increase appreciably with smaller sample size.

Conclusions - Under heating conditions thought to produce reasonable facsimiles of chondrules, silicate mixtures doped with zinc, whether as metal, oxide, or sulfide, lose appreciable quantities of that element -- from 25 to more than 90%. When introduced as metal or as oxide, but not as sulfide, the Zn also undergoes mass-dependent fractionations up to about 0.5%/AMU. These observations are thought to be more relevant to the interiors of chondrules than to their rims, as the rims are enriched in Zn [6].

References - [1] Humayun M. & Clayton R.N. (1995) *Geochim. Cosmochim. Acta* 59, 2115-2130. [2] Xue S. et al. (1995) *Meteoritics* 30, 603. [3] Xue S. et al. (1995) *Geochim. Cosmochim. Acta* 59, 4975-4981; Nyquist L.E. et al. (1995) *Meteoritics* 30, 558-559; Davis A.M. & Brownlee D.E. (1993) *Lunar Planet. Sci. XXIV*, 373-374. [4] Koga A. et al. (1994) *Lunar Planet. Sci. XXV*, 723-724; Rosman K.J.R. et al. (1980) *Earth Planet. Sci. Lett.* 48, 166-170. [5] Grossman J.N. & Wasson J.T. (1987) *Geochim. Cosmochim. Acta* 51, 3003-3011. [6] Brearley A.J. et al. (1995) *Geochim. Cosmochim. Acta* 59, 4307-4316. [7] Radomsky P.M. & Hewins R.H. (1990) *Geochim. Cosmochim. Acta* 55, 935-942. [8] Yu Y. et al. (1995), *Meteoritics* 30, 604-605. [9] Haskin L. & Warren P. (1991) In: *Lunar Sourcebook, A User's Guide to the Moon*, 357-474 [10] Humayun M. & Clayton R.N. (1995) *Geochim. Cosmochim. Acta* 59, 2131-2148.

