

SIDEROPHILE TRACE ELEMENTS IN SILICATE MELTS: SIGNIFICANCE AND STATUS OF UNUSUAL OXIDATION STATES C. J. Capobianco, J. A. DeAro, M. J. Drake and V. J. Hillgren, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

Current status of zero-valent and other unusual oxidation states for siderophile elements in silicate melts is discussed. New data on melt speciation of Ag and Sn are presented. Data consistent with unusual effective valences for Sn of 1+ and 0 in Fe-bearing melts are given. Preliminary data for Ag in Fe-free melts can be fitted to the expected 1+ state but we cannot yet entirely rule out significant zero-valent speciation at low oxygen fugacity.

Experimental evidence consistent with unusually low oxidation states for a variety of siderophile elements dissolved in silicate melts has been reported in several recent studies: Ir⁰ by Amossé et al. (1987); Ni⁰ by Colson, (1990), Steele et al. (1991), Colson, (1992), Ehlers and Grove, (1990), Ehlers et al. (1992) and Schmitt et al. (1989); Pd¹⁺ and Rh^{1.5+} by Capobianco et al., (1992); Ir²⁺ by O'Neill (1993); Pd¹⁺ by Borisov et al., (in press). The geochemical significance of such unusual speciation, particularly the zero-valent oxidation state, is discussed by Colson, (1992) and Capobianco et al. (1993). The presence of significant amounts of zero-valent species in silicate melts, a contentious issue, would produce greater than otherwise expected lithophilicity and incompatibility for the element during igneous processes. Such enhancements would be pronounced at high temperature or low oxygen fugacity and have been used to explain, for examples, Ni abundance in the mantle (Colson, 1992), Ni systematics from igneous systems on Earth (Morse et al., 1991) and the moon (Steele et al. 1992).

Zero-valent Ir in silicate melts has been implicated in the geochemistry of the association of chromite bodies and platinum group elements (PGEs) by Amossé et al. (1990 and 1992). Another hypothesis which does not necessarily involve zero-valent species, but which does recognize the importance of unusually low valence states for PGEs dissolved in silicate melt, has recently been suggested as an alternative explanation for the PGE-chromite association (Capobianco et al. in press).

However there has been some skepticism about the amounts of these unusual species in melts, particularly with regard to the zero-valent species proposed for Ni and Ir. Independent studies by Capobianco and Amelin (1992 and in press), Holzheid et al. (1993 and in press) and Dingwell et al. (1993) have failed to confirm the presence of significant amounts of zero-valent Ni or Co in simple Fe-free silicate melts. Neither were O'Neill et al. (1993) convinced by their Ir solubility experiments in Fe-free silicate melts that zero-valent Ir played a significant role.

On the other hand, for an Fe-bearing system in which a significant fraction of dissolved Ni⁰ was inferred from an olivine-melt partitioning study by Ehlers et al. (1990, 1992) some corroboration is provided by a single datum in Steele et al. (1991).

Zero-valent species must be present in any silicate melt having a finite activity of the element of interest; thermodynamics of partial molar entropies of mixing

mandate it. But whether the zero-valent concentration is ever an appreciable fraction of the total concentration of an element in a melt is a matter of chemistry over which opinions are unequally divided in the glass science and metallurgical literature, with those not believing in significant zero-valent speciation holding sway.

Among the early proponents of significant zero-valent solubility is Weyl (1953) who likens the physiochemical mechanism to a "frozen metallic vapor." To set a bound on the concentration of such a dissolved vapor we can use the metallic vapor pressure of an element, say for example, Ni, to calculate the density of Ni vapor at 1550° C and 1 bar. If we then assume that this vapor is completely contained in a silicate melt, a concentration for the metallic vapor near 10 ppb is calculated. This amount of dissolved Ni⁰ would amount to 10% of the total Ni concentration when the oxygen fugacity is approximately IW-8. Evidence for greater zero-valent concentrations than the above would imply that the zero-valent species is actually concentrated by the melt relative to the vapor and hence that there is some chemical stabilization of these species by the melt.

Along these lines Montana et al. (1993) argued against noble gases, such as Xe and Ar, being dissolved as species merely occupying voids in the melt structure, instead they suggest that specific melt sites control the solubility. One might ask, if noble gases chemically interact with a silicate melt then why not neutral metals?

Some indirect support for the presence of melt sites capable of housing zero-valent species comes from recent high P, T metal-silicate partitioning experiments of Walker et al. (1993) and Hillgren et al. (in press). They report decreasing metal-silicate partition coefficients for a variety of trace elements with increasing temperature. Although there may be other ways to explain this phenomenon, which was not anticipated from previous lower temperature metal-silicate experiments, enhanced solubility of zero-valent species at high temperature is one mechanism, as outlined in Capobianco et al. (1993).

Moreover, Walker et al. (1993) interpret their data in terms of the "closing of the solvus" between metallic liquid and liquid silicate. If this was not simply an uncontrolled oxidation-reduction process during their experiment, then closing the solvus implies that the silicate liquid can accept metallic components in

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abundance, carrying the implication that such sites are plentiful at high enough temperature. And unless there is some qualitative transformation of a melt as temperature is increased then lower temperature melts should also contain sites capable of housing zero-valent species.

Because of the potential significance to geochemistry of zero-valent species in silicate melts a series of experiments is underway to try to reproduce the results of one of the better documented cases from the metallurgical literature (Richardson and Billington, 1956) of zero-valent speciation of Ag in silicate melts. Fig. 1 plots our new solubility data for Ag versus oxygen fugacity. These data were measured using the electron microprobe from glasses equilibrated (at 1293° C for at least 16 hrs.) in AgPd alloy crucibles in a gas mixing furnace (using CO-CO₂-N₂-O₂ gas mixtures).

Although these data are consistent with Ag dissolved as a 1+ species (see Schmitt et al. 1989 for explanation) the two most reduced runs are only marginally represented by the fitted univalent curve. Further experiments are underway to better quantify and extend the trend into more reducing conditions.

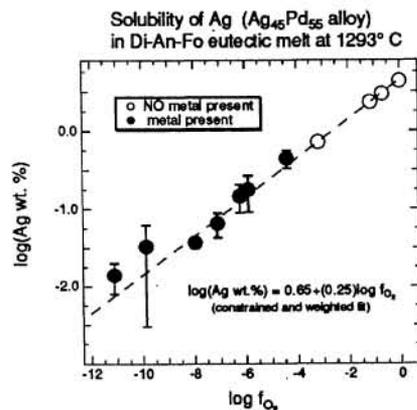


Figure 1. Fitted curve was constrained to a slope of 0.25 and was weighted by the reciprocals of the $\pm 2\sigma$ error bars. Filled symbols represent glasses which contained finely dispersed metallic particles. Although analytical errors in such runs are larger the univalent trend seems to be generally followed despite the presence of these particles, except perhaps for the two lowest oxygen fugacity points. This suggests that the metallic particles may be quench features.

We also present intriguing new data on Sn metal-silicate partitioning. Experiments which produced these data are part of a larger study to examine the metal-silicate partitioning of several chalcophile elements. However the results for Sn illustrate some novel melt chemistry attributable to a variable valence state for Sn in silicate melts.

Metal-silicate partition coefficients for Sn are plotted in Fig. 2 versus oxygen fugacity. Experimental techniques which produced these data are identical to those in Hillgren (1991) and are evacuated silica tube

experiments in which the oxygen fugacity is set by the Fe/Ni ratio of the metallic phase and its equilibration with the silicate.

The effective valence of Sn clearly changes with oxygen fugacity in these series of runs. However, apparent, but not necessarily real, valence changes for trace elements can be produced if the oxidation of the element is controlled by other than the reduction of molecular oxygen, which is the formalism usually adopted. For example, if metallic Sn were oxidized by Fe³⁺ in a system in which metallic Fe constrained the Fe³⁺/Fe²⁺ ratio (see Johnston 1964) then the Sn content of the melt, provided it was small, would also become buffered and independent of oxygen fugacity. Some process akin to this may explain the unusual flattening trend to the data in Fig. 2.

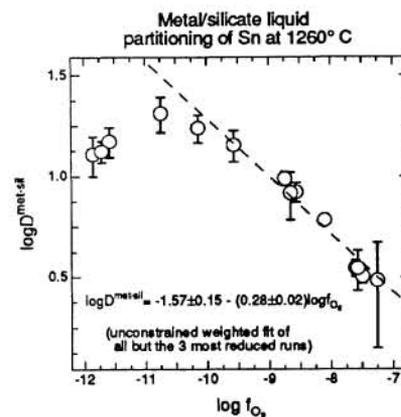


Figure 2. Linear curve was fitted only to data above an oxygen fugacity of 10^{-11} bars and was weighted by the reciprocals of the $\pm 2\sigma$ error bars. A slope of -0.28 ± 0.02 is consistent with predominantly Sn¹⁺.

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