

METAL-SILICATE PARTITIONING OF Sn: AN UNUSUAL CASE; C. J. Capobianco¹, J. A. De'Aro², M. J. Drake¹, V. J. Hillgren³ ¹Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721; ²Chemistry Dept. University of California, Santa Barbara, CA 93106; ³NASA/JSC, Houston, TX 77058

Metal-silicate partition coefficients for Sn were measured at 1 bar and 1260°C. Highly non-linear behavior on a logD vs. logfO₂ plot was found. A quaternary solution model for the metallic phase, a Ni-Fe-Sn-Ge solid alloy, was formulated yielding activity coefficients for Sn that linearize the data and reveal the participation of Sn⁴⁺ at high fO₂ and Sn²⁺ at low fO₂.

Introduction To correctly interpret the record of core formation left in planetary mantles by siderophile elements we need to understand the important influences on metal-silicate equilibria. Since partitioning between metallic and oxidized phases can usually be shown to be governed by a redox reaction, one of the most important variables is oxygen fugacity, fO₂. A metal-silicate partition coefficient, D, is customarily parameterized on a logD vs. logfO₂ plot because the valence change accompanying the partitioning is available from the slope on such a plot. Eqn. 1 gives the functional dependence of the redox partitioning reaction on fO₂:

$$\log D_M^{met/sil} = -\frac{n}{4} \log fO_2 - \frac{\Delta G^0}{2.303RT} + \log \frac{\gamma_M^{sil}}{\gamma_M^{met}} \quad (1)$$

It is usually assumed that the last two terms, the standard free energy change of the redox reaction and the activity coefficient ratio of siderophile element, M, in metal and silicate are constants. The rationale is that the trace elements are very dilute so Henry's Law can be expected to hold, and alloys of interest, Ni-Fe, exhibit only slightly non-ideal solution thermodynamics so that the metallic phase should provide a relatively constant host. In general, the above assumptions work well, but not always, as we illustrate below for the case of Sn partitioning.

Methods We examined metal-silicate partitioning behavior of Sn in experiments conducted in one atmosphere MoSi₂-element furnaces at 1260°C. Experiments were similar in design to those of [1] and [2]. Metal-silicate charges were contained in alumina crucibles and held in evacuated silica glass tubes during runs of 3 to 10 days. Because of the volatility of Sn compounds we modified the usual assembly to include a solid silica glass rod ring-sealed into the evacuated silica tube such that it reduced the available free volume and confined all chemical species to the isothermal zone of the sample.

In most runs, oxygen fugacity was set by redox equilibria of the isolated metal-silicate assemblage. Ni contents of charges were adjusted to produce various Fe-Ni alloys in our run products allowing different fO₂'s to be set. Experimental fO₂'s were calculated from thermodynamic data of [3] for iron-wüstite (IW) and Fe contents of coexisting metal and silicate glass as outlined in [1]. Several runs used metal-oxide buffers contained in separate crucibles to reach lower fO₂'s.

Starting materials were: 1. oxide mixtures containing 11 wt% CaO, 7 wt% MgO, 13 wt% Al₂O₃, 50 wt% SiO₂, 19 wt% FeO (added as Fe₂O₃) which approximated a basaltic liquid, 2. granular NiS, 3. Fe and Ni metal powders, and 4. SnO₂ and usually GeO₂ (results for Ge not reported here) dopants added in the low wt% level.

Solid metal/liquid silicate partition coefficients were measured by electron microprobe (Cameca SX50) analysis of coexisting phases. We operated at 15kV and 20 nA for major elements. For low level analysis of Sn in the silicate, high beam currents (200 nA) and long count times (300 s) were used on the Lα peak of Sn. This allowed us to detect 50 ppm Sn at the three sigma counting statistical level.

Results and Discussion Elemental weight ratio solid metal/liquid silicate partition coefficients for Sn are plotted in Fig. 1A against fO₂ on a log-log plot. Unfilled circles represent our experimentally determined partition coefficients. Unusual non-linear behavior is exhibited. The slopes are too shallow for common oxidized species of Sn, and, in one region of logfO₂, the slope even changes sign.

Insight into these peculiar results can be found in the binary phase diagrams of Fe-Sn and Ni-Sn, Figs. 2A and 2B. Note that they are extremely different. Fe-Sn contains a miscibility gap, whereas Ni-Sn contains high temperature intermetallic compounds. Although our experiments pertain to the fcc γ phase on the Sn-poor sides of each diagram, we can expect that the chemical interactions leading to the vastly different topologies shown in the centers of the diagrams are also relevant in solid solutions of γ phase.

To account for these disparate interactions we formulated a simple solution model for alloys in our experiments in which only binary interaction coefficients were considered,

$$\frac{\Delta G^{ex}}{RT} = \sum_{i \neq j} X_i X_j (A_{ij} X_j + A_{ji} X_i) \quad (2)$$

where the sum is over distinct combinations of X_iX_j. Coefficients A_{ij} were obtained from the metallurgical literature and values for 1260°C are in Table 1. Activity coefficients for Sn in experimental alloys were calculated using this model.

Fig. 1A plots these activity coefficients as filled symbols. Note the nearly 4 order of magnitude change in activity coefficient of Sn for Fe alloys ranging from

METAL-SILICATE PARTITIONING OF Sn: Capobianco, C. J. *et al.*

Ni-absent to high-Ni. It is indeed a bad assumption that Ni-Fe alloys provide an energetically constant metallic host.

Calculated Sn activity coefficients are combined with measured partition coefficients in Fig. 1B where the metal-silicate chemistry of Sn becomes obvious. The linearized partition coefficients in Fig. 1B show two distinct trends with differing slopes. Although the low f_{O_2} trend is, so far, only two points, the slope is -0.49 and for the better constrained high f_{O_2} trend the slope is -1.0. These results indicate that both Sn^{2+} and Sn^{4+} are participating species. The dashed line in Fig. 1B was fitted to a two-parameter equation, Eqn. 3, where fitted parameters are related to equilibrium constants for the reduction of SnO and SnO_2 (see [4]).

$$\frac{1}{\gamma D_{Sn}^{met/sil}} = \frac{\sqrt{f_{O_2}}}{K_{SnO}^{eq}} + \frac{f_{O_2}}{K_{SnO_2}^{eq}} \quad (3)$$

Examination of binary phase diagrams Ni-M and Fe-M reveals important topological differences for M=Cu, C, and Pb. In these cases we can also expect trace element activity coefficients to vary significantly across Fe-Ni.

Table 1. Interaction coefficients for 1260°C Sn, Fe, Ni, Ge alloys, where only one A_{ij} is given $A_{ij}=A_{ji}$.

A_{SnFe}	2.07	A_{NiFe}	-0.4
A_{SnNi}	-7.87	A_{SnGe}	0.21
A_{NiSn}	-1.59	A_{NiGe}	-7.32
A_{FeNi}	-1.22	A_{FeGe}	-7.32

refs. [5,6,7]

References [1] Drake *et al.* (1989) G.C.A. 53, 2101-2111. [2] Hillgren (1991) G.R.L. 18, 2077-2080. [3] O'Neill (1988) Am. Min. 73, 470-486. [4] Capobianco *et al.* (1993) J.G.R. 98, 5433-5443. [5] *Phase Diagrams of Binary Nickel Alloys* (1991) P. Nash, ed. ASM Internat., Materials Park, OH. [6] *Phase Diagrams of Binary Iron Alloys* (1993) H. Okamoto, ed. ASM Internat., Materials Park, OH. [7] Olesinski *et al.* (1984) Bull. Alloy Phase Diagrams 5, 265-271.

Acknowledgement NASA grant NAGW 3348.

