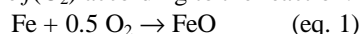


ACTIVITY COEFFICIENTS OF SILICON IN IRON-NICKEL ALLOYS: EXPERIMENTAL DETERMINATION AND RELEVANCE FOR PLANETARY DIFFERENTIATION. I. A. Vogel¹ and H. Palme², ¹Institut für Mineralogie und Geochemie, Universität zu Köln, Zùlpicher Str. 49 b, 50674 Köln, e-mail: ingo.vogel@uni-koeln.de, ²Institut für Mineralogie und Geochemie, Universität zu Köln, Zùlpicher Str. 49 b, 50674 Köln, e-mail: palme@gwp-min.min.uni-koeln.de

Introduction: Metal segregation und subsequent formation of an FeNi core is the major differentiation process in large planets such as the earth, but metal separation and aggregation will also occur in smaller planetsimals such as asteroids. Core formation implies partial or full equilibration of core forming FeNi with liquid silicates, implying partial or complete redistribution of siderophile elements between metal and silicates. This also occurs for the major components of molten silicates such as SiO₂ which will be partly reduced and partition into core forming metal. Most groups of iron meteorites are thought to be derived from metal cores or metal aggregations that formed during melting of planetesimals. The Si content of iron meteorites should thus record the conditions that prevailed during metal-silicate equilibration. The quantification of this process requires a better understanding of the partitioning of Si between metal and silicate which depends on temperature, oxygen fugacity, silicate composition and nickel content of the alloy. One additional parameter that is not well known is the activity coefficient of Si in FeNi-alloys. Literature data [1] only exist for very high Si concentrations, much larger than expected for iron meteorites [2]. We therefore performed experiments at lower Si-concentrations and at various temperatures and alloy compositions to determine the activity coefficients of silicon in iron-nickel alloys.

Experimental: Silicates consisting of an eutectic, quartz saturated anorthite-diopside-quartz-mixture were equilibrated with FeNi-loops in one atmosphere furnaces with controlled oxygen fugacity. The alloy composition was varied from pure iron to pure nickel. Temperature ranged from 1300 to 1400°C. After equilibration times of 2 to 3 days, samples were quenched to glass by quick removal from the furnace, polished sections were prepared and metal and silicates were analyzed with the EMP. The oxygen fugacity was controlled with CO/CO₂ gas mixing and measured with an yttrium-oxide-stabilized zirconium-oxide sensor. The $f(\text{O}_2)$ was also determined by measuring the FeO-content in the silicate glass and calculating the $f(\text{O}_2)$ according to the reaction:



In the calculation activity of FeO in silicate melts an activity coefficient of 1.7 was used according to [3]. Both methods for the determinations of $f(\text{O}_2)$ agreed to

within 0.1 log units at 1400°C and 1350°C, and to within 0.4 log units at 1300°C.

Due to the low silicon content in metal, high probe currents of approximately 1.5 µA, voltages from 10 to 15 kV and beam diameters from 10 to 20 µm were used. Silicon concentrations in metal varied from 140 ppm to 7600 ppm. In all cases Si profiles through the metal loop (0.1 mm metal foil thickness) were measured. Only experiments without zoning of Si in metal were considered.

Results: From the mass fraction of silicon in the alloy measured by EMP $\gamma_{\text{Si}}^{\text{FeNi}}$ was calculated by the following equation:

$$\gamma_{\text{Si}}^{\text{FeNi}} = \frac{M_{\text{Si}}}{M_{\text{FeNi}}} \cdot \frac{\exp\left(-\frac{\Delta_r G}{RT}\right) \cdot p^\circ}{f(\text{O}_2) \cdot w_{\text{Si}}^{\text{FeNi}}} \quad (\text{eq. 2})$$

(M_{Si} and M_{FeNi} are molar masses of Si and the FeNi-alloy, respectively; $f(\text{O}_2)$ is the oxygen fugacity; p° standard ambient pressure (1 bar); $w_{\text{Si}}^{\text{FeNi}}$ mass fraction of Si in FeNi (wt %); $\Delta_r G$ free enthalpy of the reaction $\text{SiO}_2 \rightarrow \text{Si} + \text{O}_2$; R molar gas constant; T temperature in K).

The results for the activity coefficients are given in Table 1 and displayed in Fig.1. In calculating the errors given in Fig. 1, statistical counting errors, errors from oxygen fugacity and temperature were considered.

The results at three different temperatures show a strong dependence of $\gamma_{\text{Si}}^{\text{FeNi}}$ on the Ni content of the alloy. The $\gamma_{\text{Si}}^{\text{FeNi}}$ of the 1400°C data decreases by more than an order of magnitude from pure Fe to pure Ni. The shape of the 1350 and 1300°C data deviates somewhat from the 1400°C data. At low Ni contents the $\gamma_{\text{Si}}^{\text{FeNi}}$ increases with increasing Ni content up to 10 wt% Ni and with further increase in Ni decreases parallel to the 1400°C data. The low Ni experiments at 1350°C were repeated, and the same results were obtained within error limits.

In addition to the decrease of $\gamma_{\text{Si}}^{\text{FeNi}}$ with increasing Ni contents there is also an increase of $\gamma_{\text{Si}}^{\text{FeNi}}$ with increasing temperature. The increase is stronger in low Ni alloys, where a temperature increase from

1300 to 1400°C leads to an increase in $\gamma_{\text{Si}}^{\text{FeNi}}$ by a factor of ten.

The activity coefficients determined here differ by a factor of about 2 compared to those obtained by Bowles et al. [1]. These authors determined with a completely different experimental setup a $\gamma_{\text{Si}}^{\text{FeNi}}$ of $2.1 \cdot 10^{-3}$ at a silicon content of 1.35 %, a nickel content in the alloy of 0.75 % and a temperature of 1560°C compared to a $\gamma_{\text{Si}}^{\text{FeNi}}$ of $1.11 \cdot 10^{-3}$ in pure iron at 1400°C and 450 ppm Si. For an alloy with 32 % Ni at 1560°C, Bowles et al measured a $\gamma_{\text{Si}}^{\text{FeNi}}$ of $1.32 \cdot 10^{-3}$ at a Si content of 2.15 %. This corresponds to a $\gamma_{\text{Si}}^{\text{FeNi}}$ of $4.73 \cdot 10^{-4}$ at 1400°C, 36 % Ni and 860 ppm Si in the alloy, as determined in the present study. Our lower activity coefficient probably reflects the effect of the lower temperatures.

Discussion: The results were applied to the formation of metal cores in small planet such as Vesta. In a “Gedankenexperiment” an Fe₉₀Ni₁₀-alloy was equilibrated with a silicate melt of eutritic composition. From the FeO content of 18.6 % the oxygen fugacity that had prevailed during metal separation was calculated. First, partial silicate melting of the planetary interior was considered. Solidus temperatures are about 1170°C [4]. Equilibration of metal and silicates at 1200°C leads to a Si content in metal of 0.25 ppm Si, using the data obtained in this study. An alternative model to the formation of eucrites by partial melting is fractional crystallization [5]. More or less complete melting of the planet leads to precipitation of metal at high temperatures. The Si content of metal equilibrating with a melt of 18.6 % FeO at 1600°C is calculated as 6.4 ppm. It should thus be possible to distinguish metal formed as residues of partial melting and metals formed by segregation in a completely molten silicate liquid. This would considerably enhance our understanding of the formation of iron meteorites.

Unfortunately Si concentrations of iron meteorites are not well known; they are below 25 ppm [2].

References: [1] Bowles P. J. et al. (1964) *J. Iron steel inst.*, 202 (2), 113–121. [2] Wai C. M. and Wasson J. T. (1969) *Geoch. Cosmoch. Acta*, 33, 1465–1471. [3] Holzheid A. et al. (1997) *Chem. Geol.*, 139, 21–38. [4] Stolper E. (1977) *Geochim. Cosmochim. Acta*, 41, 587–611. [5] Hewins R. H. and Newsom H. E. in *Meteorites and the Early Solar System*, The University of Arizona Press, Tucson, 1988, 73–101.

Table 1. Activity coefficients of Si in NiFe-alloys

wt % Ni	$\gamma_{\text{Si}}^{\text{FeNi}}$
1300°C	
0	$1.29 \cdot 10^{-4}$
10	$2.29 \cdot 10^{-4}$
36	$1.82 \cdot 10^{-4}$
45	$1.35 \cdot 10^{-4}$
100	$1.80 \cdot 10^{-5}$
1350°C	
0	$3.11 \cdot 10^{-4}$
10	$3.76 \cdot 10^{-4}$
36	$2.06 \cdot 10^{-4}$
45	$1.44 \cdot 10^{-4}$
100	$2.37 \cdot 10^{-5}$
1400°C	
0	$1.11 \cdot 10^{-3}$
10	$7.38 \cdot 10^{-4}$
36	$4.73 \cdot 10^{-4}$
45	$3.42 \cdot 10^{-4}$
100	$5.27 \cdot 10^{-5}$

Figure 1.

