Experimental determination of the metal/silicate partition coefficient of Germanium: Implications for core and mantle differentiation

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ARTICLE INFO

ABSTRACT

Germanium is a moderately siderophile, and volatile element that exhibits a depletion in Earth's mantle and other planetary and asteroidal basalts (relative to chondritic values). Attempts to explain these depletions have not been satisfactory, but there have also been too few experimental studies to constrain the chemical behavior of Ge. Experimental data have been challenging due to difficulties in analyzing the low (1 to 100 ppm) concentrations of Ge in silicate melts. In this study we examine the role of temperature and silicate melt composition in controlling the value of D(Ge) metal/silicate, by carrying out new experiments at high temperature and pressure. The experimental glasses were analyzed using laser-ablation ICP-MS, which can detect levels of Ge much lower than possible with the electron microprobe. Our new results show that D(Ge) metal/silicate decreases with increasing temperature over the range from 1500 to 1900 °C. Additionally, changing silicate melt composition from basalt to peridotite causes a small increase in D(Ge) metal/silicate, compared to the decrease observed in previous studies across a different range of melt composition. These results, combined with previous studies at higher pressures and with S-bearing metallic liquids, show that there are high PT conditions at which the Ge concentration Earth's primitive upper mantle can be explained through metal-silicate equilibrium in a magma ocean stage, where equilibration took place at 40 ($\pm$4) GPa and 3200 ($\pm$200) °C. Additionally, estimated Ge contents of the lunar, Martian and HED parent body mantles can be explained by magma ocean conditions in all of these bodies early in the solar system. These calculations all take into account both the volatile and siderophile nature of Ge.

Published by Elsevier B.V.

1. Introduction

Siderophile elements in planetary mantles and cores can provide information about the conditions of core formation and planetary accretion (Ringwood, 1979; Wänke, 1981). Currently there are several different hypotheses addressing the conditions of the early Earth. Some studies propose conditions allowing a shallow magma ocean (Righter, 2003), others a deep magma ocean (Li and Agee, 2001), while some hypothesize heterogeneous accretion which requires no magma ocean at all (Newsom and Sims, 1991). Many previous experimental and modeling studies have focused on elements such as Ni, Co, Mo, W or P. However many siderophile elements have not been studied in detail, and a quantitative and thorough understanding of their behavior has remained elusive. Specifically, Ge is a moderately siderophile element found in both the mantle and core, and has yet to be studied systematically at high temperatures. Previous models are still unable to account for Ge depletion in Earth's mantle relative to CI

chondrites, such as the model for heterogeneous accretion discussed by Newsom and Sims (1991).

Germanium is the focus of this study for several other reasons. First, there are a large number of Ge analyses of planetary materials (e.g., Wasson and Baedecker, 1970; Warren et al., 1999) making it an element whose partitioning behavior, if determined, can be applied immediately to a wide variety of planetary materials. Second, Germanium is a volatile element as well, making it of interest to accretion processes since some models call for late volatile acquisition (Schönbächler et al., 2010; Yi et al., 2000), whereas other call for early volatile acquisition (King et al., 2010; Righter et al., 2008). Third, Ge has many isotopes, making it of growing interest to the isotope cosmochemistry community (Hirata, 1997; Luais, 2007; Luais et al., 2009; Rouxel et al., 2006). And fourth, among the moderately siderophile elements, Ge has the largest low pressure metal silicate D, with some values approaching 10,000 (e.g., Holzheid et al., 2007; Schmitt et al., 1989), which make it critical to testing a wide range of models.

In this study, experiments were designed and carried out to quantify the partitioning of Ge between core forming metallic liquid and basalt-like to peridotite-like silicate melts. These experiments allow the relative effects of temperature and silicate melt composition

to be evaluated. Because the solubility of Ge in silicate melts can be very low (<100 ppm), the electron microprobe analysis cannot be used and we have therefore used laser ablation ICP-MS techniques. Using this latter approach, melt concentrations as low as 30 ppm have been measured in our experimental glasses. These new experiments provide new data for Ge and allow further testing of models for early Earth differentiation. The data is also used to assess the conditions of metal–silicate equilibrium in other differentiated rocky bodies including Mars, the Moon, or asteroid 4 Vesta, through analyses of meteorites and Apollo samples.

2. Experimental techniques

The sample used for these experiments was a powder containing 70 wt.% Knippa basalt (KB—Table 1), composition described in Lewis et al. (1993), and 30 wt.% Fe_{95}–Ge_5 (wt.%) metal mixture. Two different types of capsules were used: MgO and graphite. All experiments were performed using a ½″ non-end-loaded piston cylinder apparatus (Quickpress, Depths of the Earth Company) at constant pressure using $BaCO_3$ pressure medium. Once the samples were brought to a constant pressure of 1.0 GPa, they were then heated to the target temperature. Samples were brought to temperatures high enough to attain equilibrium (see Section 4) and were heated for durations based on diffusion times across capsule distance (e.g., 15 min at 1900 °C and 180 min at 1500 °C; Table 1). The temperature was measured using Type C thermocouple (W-Re) wires with an accuracy of ±2 °C. Samples were quenched by turning off the power while maintaining oil pressure by vigorous hand pumping until the temperature reached 100 °C.

Three different series were performed—a time series with graphite capsules (Table S1) and two temperature series each with a different capsule (MgO and graphite; Table 1). Sixteen different runs were produced from temperatures between 1500 °C and 1900 °C.

3. Analysis

All samples were analyzed for major element composition using a Cameca SX100 for electron microprobe analysis (EMPA) at NASA-JSC. A 10 μm beam was used at 15 kV and 10 nA. Metal standards were Fe and Ge metals and NBS steel standards. Silicate standards were natural feldspars (Na and K), glasses (Si, Al, Fe, Mg, and Ca), rhodonite (Mn), rutile (Ti), and apatite (P). For carbon analysis in metals, samples and C-bearing steel standards (NBS # 1164, 1176, 1177, and 1178) were coated with Al to avoid C contamination from conventional carbon coating. Copper tape was used to aid conductivity near the edges of samples and sample holders. Spectrometer crystal PC2 was used to give the highest peak:background ratios for the analysis.

For all samples, Ge content of the glasses was lower than the detection limit of the EMPA. Therefore, samples were also analyzed for trace element composition using the Laser Ablation Inductively Coupled Mass Spectrometer (LA–ICP-MS) at Rice University. Analyses of minor and trace elements (P, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, Sn and W) were done by laser ablation inductively coupled plasma mass spectrometry (ICP-MS) at Rice University using ThermoFinnigan Element 2 ICP-MS coupled to a New Wave 213 nm laser ablation system (Agrinier and Lee, 2007). Analyses were performed in medium mass resolution (m/Δm = 3500) in order to resolve all major isobaric molecular interferences. Isotopes analyzed were ^{30}Si, ^{31}P, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{69}Ga, ^{73}Ge, ^{74}Ge, ^{118}Sn, and ^{182}W (Tables 1 and S2). Data from the analysis of isotope ^{74}Ge at MR (medium resolution) was used to calculate Ge in ppm in the silicates. Measurements of several isotopes of the same element, such as for Ge and Mo, were conducted for additional assurance that interferences were not a problem. Drift of mass calibration was corrected for by centering on $^{40}Ar^{40}Ar^+$ dimer in each measurement. Laser was set at 10 Hz pulse frequency and an energy density of 10 J/cm². Measurements consisted of about 10 analyses of gas flow background followed

Table 1
Summary of experimental conditions, and quenched metallic and silicate liquid analyses (gl = glass, qm = quenched crystalline matte; lm = quenched liquid metal); all experiments performed at 1.0 GPa. Durations given in minutes. Ge in silicate portion was analyzed by LA–ICP-MS.

Sample	KB	72109	61509	62409	61909	72309	62509b	72409	72009	62409b	93009
T		1500	1600	1700	1800	1900	1500	1600	1700	1800	1900
Capsule/duration		MgO/180	MgO/90	MgO/45	MgO/15	MgO/10	C/180	C/90	C/45	C/15	C/15
ΔIW		−1.97	−2.22	−2.36	−2.3	−2.24	−1.72	−1.77	−1.73	−1.74	−1.74
Phases		lm, gl	lm, gl	lm, gl	lm, qm	lm, qm	lm, gl	lm, gl	lm, gl	lm, gl	lm, gl
Silicate											
SiO_2	42.49	31.9(3)	31.1(2)	34.2(3.6)	34.2(3.5)	31.1(3.2)	38.8(2)	39.6(2)	38.9(2)	38.5(2)	38.5(2)
TiO_2	3.27	4.27(9)	4.06(14)	2.81(1.45)	2.66(1.35)	2.27(1.25)	3.34(10)	3.32(7)	3.30(8)	3.32(7)	3.31(6)
Al_2O_3	11.76	10.8(2)	12.2(6)	8.7(4.5)	8.2(4.1)	8.0(4.3)	9.9(1)	10.5(1)	10.7(1)	11.5(1)	11.2(1)
FeO	11.00	12.63(25)	9.38(17)	8.04(2.05)	8.51(2.39)	9.91(2.21)	15.64(19)	14.93(14)	15.70(21)	15.15(14)	16.62(14)
MnO	0.22	0.17(3)	0.15(3)	0.12(4)	0.13(4)	–	0.20(3)	0.20(3)	0.21(3)	0.19(3)	0.20(3)
MgO	12.33	16.3(5)	22.9(1.7)	32.5(12.7)	33.1(12.7)	37.0(11.5)	13.7(1)	13.48(10)	13.23(11)	13.46(9)	13.51(8)
CaO	11.59	15.17(30)	14.09(77)	10.08(5.12)	9.52(5.23)	9.61(4.97)	11.37(11)	11.48(10)	11.31(12)	11.37(11)	11.20(11)
Na_2O	3.05	4.18(14)	3.61(45)	2.57(1.75)	2.27(1.75)	2.50(1.52)	2.57(6)	2.65(7)	2.58(6)	2.56(8)	2.54(7)
K_2O	2.03	2.29(7)	2.05(18)	1.49(93)	1.34(92)	1.54(88)	1.40(4)	1.47(4)	1.45(3)	1.41(4)	1.42(3)
P_2O_5	0.83	0.96(6)	0.85(8)	0.40(20)	0.49(22)	0.23(15)	0.68(8)	0.67(7)	0.58(7)	0.56(7)	0.15(5)
Total	99.66	98.69	100.34	100.93	100.52	102.00	97.57	98.24	97.99	97.66	99.07
NBO/T	–	2.06	2.22	2.74	2.8	3.41	1.60	1.62	1.63	1.61	1.60
Ge ppm	–	171(9)	153(8)	101(5)	79(4)	235(12)	120(6)	119(6)	213(11)	270(14)	1017(50)
Metal											
P		0.018(9)	0.104(3)	0.34(18)	0.35(25)	0.40(20)	0.102(21)	0.081(24)	0.16(8)	0.23(11)	0.024(8s)
Fe		94.84(33)	93.88(38)	94.43(50)	93.17(55)	94.20(48)	93.31(49)	92.76(39)	92.85(58)	93.05(98)	93.00(62)
Ge		4.21(13)	4.68(17)	4.33(18)	4.85(25)	4.50(21)	3.95(36)	4.55(40)	4.1(1.0)	4.2(5)	5.54(22)
C		0	0	0	0	0	3.9(2)	3.5(2)	4.13(25)	4.1(2)	3.9(2)
Xc		0	0	0	0	0	0.21	0.209	0.21	0.211	0.211
Total		99.07	98.66	99.10	98.37	100.15	101.26	100.84	101.24	101.58	101.30
D(Ge)		246	306	429	614	191	329	382	192	156	54
D(Ge) T re-calc		246	229	274	420	140	329	361	190	152	53
D(Ge) melt comp. re-calc		246	360	673	1620	849	–	–	–	–	–

by 40–50 measurements of the ablation signal. Gas background was averaged and then subtracted from ablation signal. Background-corrected signals were converted to concentrations using a combination of internal and external standards. ^{57}Fe was used as an internal standard for quenched metallic liquids and ^{25}Mg for glasses and quenched silicate liquids. Hoba (0.059 ppm Ge) and Filomena (177 ppm Ge) iron meteorites were used as external standards for the metals (Campbell and Humayun, 2005; Wasson et al., 1989) while USGS basaltic glass standards (BHVO2g—1.6 ppm Ge, BCR2g—1.5 ppm Ge, and BIR1g—1.2 ppm Ge) were used for the silicate glasses (Jochum et al., 2005). Finally, limit of detection for each analysis was estimated at 3 times the standard deviation of the background divided by the sensitivity of the instrument as monitored by ^{25}Mg (see also Agrinier and Lee, 2007), and uncertainties are typically ~5% of the amount present (1σ). For partition coefficients, this corresponds to a typical uncertainty of 10% on the reported values of the partition coefficient; these are the error bars presented in the figures.

4. Results

Run products consisted of mixtures of glass surrounding metallic spheres (Fig. 1). Most silicate melts quenched to a glass, but in the highest temperature experiments carried out in MgO capsules, the silicate melt became so MgO-rich that quenching to a glass was impossible even given the high quench rates upon termination of an experiment. For these experiments, >50 points were analyzed by EMPA and averaged over a large area (>50 μm^2) so that the representative bulk composition was obtained. The metallic liquids all quenched to spheres of homogeneous bulk composition, but many points were analyzed and averaged in case of μm scale quench phases. Metal from experiment Ge72409, for example, contained 4.55 wt.% Ge, with a 1σ value of 0.22 (Table 1). This narrow range of Ge contents across nearly 500 μm demonstrates that the metals are very homogeneous.

On average, metal spheres from the MgO capsule runs showed a slightly higher Ge content with 4.2–5.2 wt.% Ge vs. 4.0–4.6 wt.% Ge in the samples using graphite capsules. Although these wt.% levels of Ge are much higher than the amount expected in Earth's core, such high levels are necessary so that the Ge content of the co-existing silicate melt is high enough to analyze. For example, if the metals contained 20 ppm Ge, as might be the case for Earth's core, the corresponding silicate melt may contain <0.1 ppm Ge which is close to being unmeasurable. While higher than natural levels, these concentrations of Ge are comparable to previous studies (Capobianco et al., 1999; Jana and Walker, 1997a,b) and still lower than the concentrations of W and Mo in Fe–C metal used in previous metal-silicate experimental studies such as Walter and Thibault (1995) and Cottrell et al. (2009, 2010).
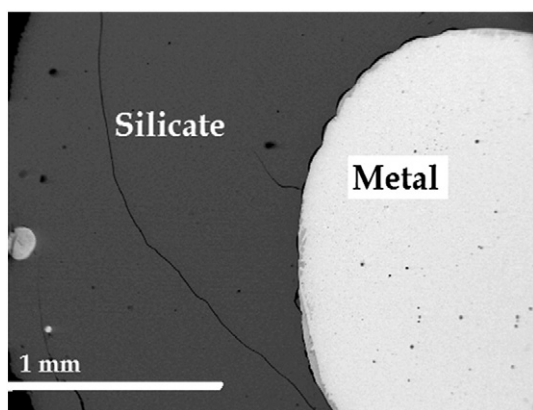

Fig. 1. Back scattered electron (BSE) image of sample Ge62409b, run in a graphite capsule at 1800 °C for 15 min. The large white region is quenched metallic liquid and the surrounding gray area is silicate melt (glass). White bar is 1 mm scale bar.

4.1. Equilibrium

Several lines of evidence can be used to assess whether equilibrium was approached in these experiments. First, if the reaction of metal with silicate did not reach completion or equilibrium, there will be variable silicate compositions according to the equilibrium $2Fe + Mg_2SiO_4 + O_2 = 2MgO + Fe_2SiO_4$ and one might expect to find zoned metal or silicate. However, the metals and silicate melts are not compositionally zoned, indicating that equilibrium has been attained (see Table 1 and Fig. 1). Second, experiments Ge60309, Ge60209b, 72409, and Ge60509b define a time series carried out at 30, 60, 90 and 120 min, respectively, at 1.0 GPa and 1600 °C. After 30 min, the D's do not change (within error of measurements) and the system has equilibrated (Fig. S1, Supplementary information). In the absence of Ge diffusion data in basaltic silicate melts, comparison can be made to other similar cations. Germanium diffusion can be estimated by consideration of its Zr^2 values, where Z is the charge and r is the ionic radius. Ge^{2+} would have a Zr^2 value of 2 0.65 = 1.3 and Ge^{4+} would have a value of 4 0.53 = 3.2 (using ionic radii of Shannon, 1976 and the summary of Richter et al., 2003). Either of these relatively low values indicates a diffusion coefficient for Ge comparable to other siderophile elements such as Fe, Nb and fast diffusers such as Mg and Ca, all of which have been studied under similar conditions to those here. Finally, the experiments reported here are longer than experiments for which time series have been done for slow diffusing elements such as W^{4+} and P^{5+}, as well and Ga^{3+} and Sn^{4+} (Righter and Drake, 1999, 2000; Righter et al., 1997).

4.2. Reaction with capsules

The graphite capsules reacted with the metallic portion of the starting material to form C-bearing metallic liquids. The measured C contents in the quenched metallic liquids were 3.45 to 4.1 wt.%, which corresponds to X_C (mole fraction of C in Fe metal) = 0.21 (+/− 0.01), in agreement with previous studies of Fe–C alloys in this pressure range (Dasgupta and Walker, 2008; Righter et al., 2010). For the Fe–C system, between temperatures of 1300 °C and 1800 °C, the carbon solubility curve is nearly vertical at roughly 5.5 wt.%C in the Fe metal. In the Fe–C–Ge system, the amount of C will be lower than in the Fe–C binary (simply by dilution effects of Ge), but the metallic liquid C content still appears to be constant over this temperature range. Therefore, for the graphite capsules series of experiments, the silicate and metal melt compositions are nearly constant over the span of temperatures in this study.

There were significant differences in silicate melt MgO (wt.%) with increasing temperature for the five experiments that were run in MgO capsules (Table 1). The starting material originally contained ~13% MgO but as the basalt reacted with the capsules, the amount of MgO within the sample increased to between 16 and 37 wt.% (also seen by Righter et al., 2009, 2010). The melt compositions are reproducible from experiment to experiment at any given temperature, and three analyses of different areas in the melts yielded similar results (i.e., they are homogeneous). The range of melt compositions in this series spans relatively polymerized basalt to de-polymerized peridotite. One way of characterizing the degree of silicate melt depolymerization is to calculate the NBO/T value, which is the ratio of non-bridging oxygens to tetrahedrally coordinated cations (as defined by Mysen (1991) and Mills (1993)). NBO/T for the MgO series experimental silicate melts ranged from 2.2 to 3.4, and as compared to the graphite capsule series melts which have a value near 1.6 (Table 1). Also, as mentioned previously, the graphite capsules reacted with the metallic portion of the sample to form C-bearing metallic liquids. The measured C contents in the quenched metallic liquids were 3.45 to 4.1 wt.%.

4.3. Oxygen fugacity

Oxygen fugacity (fO$_2$) is also necessary to take into consideration because partition coefficients can be sensitive to fO$_2$ changes. Oxygen fugacity for each experiment was calculated relative to the iron-wüstite (IW) buffer, using the relation $\Delta IW = -2*\log(X_{Fe}/X_{FeO})$, which is used in many studies of metal-silicate partitioning, and in this study ranged from 1.7 to 2.4 logfO$_2$ units below the iron-wüstite buffer (Table 1). For the regression calculations (see below), absolute oxygen fugacity is utilized, and calculated according to the relation $\Delta IW = -2\log(a_{Fe}/a_{FeO})$, where oxygen fugacity for the IW buffer at P and T was calculated using the expression of Righter et al. (1997), the activity of Fe in metal (using Swartzendruber et al., 1991 for the FeNi system) and the activity of FeO in the glass (from Holzheid et al., 1997).

5. Discussion

5.1. Partition coefficients

Because this study focused on Ge, we will discuss the new results for this element in detail. Partition coefficients were calculated using the relation, D(Ge) metal/silicate = $c_{metal}/c_{silicate}$ where D = partition coefficient of Ge and c = wt.% concentration of Ge in the metal and silicate respectively (Table 1). The samples in MgO capsules show a general increase of D(Ge) metal/silicate as temperature increases while the graphite samples show a decrease of D(Ge) metal/silicate as temperature increases (Fig. 2). Differences in absolute value of D(Ge) metal/silicate between the graphite capsule and MgO capsule series can be attributed to variables such as fO$_2$ or metallic liquid composition (e.g., S or C content), and thus direct comparison of these two series will not allow isolation of any specific variable. For example, the drop in D(Ge) in the MgO series from 1800 to 1900 °C may be due to a higher FeO content in the silicate melt (higher fO$_2$) compared to the rest of the samples in the series. In order to isolate the effects of T and melt composition we will re-calculate the D(Ge) metal/silicate in both series as described further below.

5.2. Effect of temperature (graphite capsule series)

The graphite capsule series of experiments was carried out at constant pressure, silicate melt composition, and metallic melt composition. As mentioned earlier, the carbon content is essentially constant in the graphite capsules series across this temperature range. The fO$_2$'s calculated for experiments in this series are very similar,

$\Delta IW = -1.72$ to -1.76, and therefore a small re-calculation can be applied to the results to normalize them to the same relative fO$_2$, that of the 1500 °C run. This is done by making a small adjustment to the partition coefficient by n/4 ΔIW (T) $-\Delta IW$ (1500 °C), where n is the valence of the element in the silicate melt. In the case of Ge, there is evidence that Ge has a 2+ valence (Kegler and Holzheid, 2010). In addition, as will be seen in Section 5.4.3, regression of all data available for Ge results in a fO$_2$ coefficient that implies a 2+ valence. Therefore, for these calculations a 2+ valence will be assumed for Ge (assumption of 4+ valence has an insignificant difference for the graphite series, and results in a smaller adjustment in the MgO series). Once this adjustment is made, the graphite capsule series is suitable for examining the effect of temperature on the magnitude of D(Ge) metal/silicate, since all other variables (pressure, silicate melt NBO/T, fO$_2$ and metal composition) are constant (Fig. 3). A linear fit to the corrected lnD(Ge) metal/silicate values shows a clear decrease in D(Ge) metal/silicate at higher temperatures (Fig. 3).

5.3. Effect of silicate melt composition (MgO series)

The effect of temperature measured using the graphite series (Fig. 3) can then be applied to the MgO series, thus isolating any melt compositional effects. The effect of variable fO$_2$ is also applied to the MgO capsule series, where fO$_2$ varies more between runs that it does for the graphite series ($\Delta IW = -1.97$ to -2.36). Therefore the MgO series D(Ge) values are re-calculated to both the fO$_2$ and temperature of the 1500 °C experiment (#72109 which is $\Delta IW = -1.97$; Table 1; and again assuming 2+ Ge), and since they are carried out at constant pressure and metallic liquid composition, the re-calculated values (Table S1) allow isolation of the effect of silicate melt composition over an interval from basaltic to peridotitic melts (NBO/T ~2.0 to 3.41; Fig. 4). In contrast to temperature, a more mafic silicate melt composition causes a small increase in D(Ge) metal/silicate, by about a factor of 2 between NBO/T = 2.0 and 3.4. This is different from the effect measured by Jana and Walker (1997a) for several synthetic basaltic compositions (Fig. 4). The difference is most likely due to the fact that the fO$_2$ in each of their five experiments was slightly different thus masking effects due only to melt composition. Siebert et al. (2011) also show a slight decrease in D(Ge) at higher values of NBO/T. It is possible that melt structural and/or compositional changes can
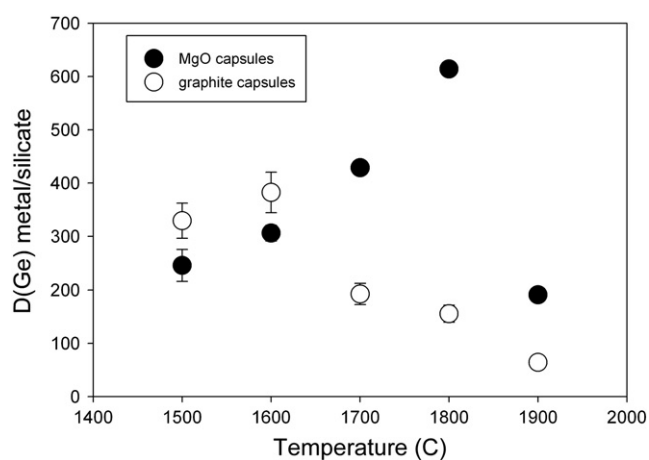

Fig. 2. Results of both temperature series (graphite and MgO capsules) with partition coefficient vs. temperature. MgO capsule samples have variable composition and fO$_2$ while the graphite capsule samples have nearly constant composition and fO$_2$. The effects of temperature and melt composition must be isolated by making small corrections for temperature and fO$_2$, as is demonstrated in Figs. 3 and 4.
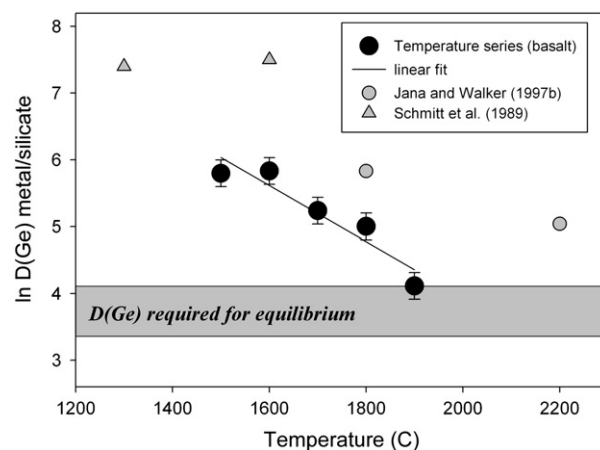

Fig. 3. Illustration of the temperature effect in the graphite capsule series, with each experiment being renormalized to a constant fO$_2$ of $\Delta IW = -1.7$ to allow for direct comparison. Also shown are the data of Schmitt et al. (1989) at 1300 °C and 1600 °C, and calculated using their expressions for a relative fO$_2$ of IW-1.7. And data from Jana and Walker (1997b) measured for samples equilibrated at 5 GPa and 1800 °C and 2200 °C for a basalt composition. Although the Schmitt et al. (1989) data show nearly no change with temperature, our data and the Jana and Walker (1997b) points show a clear decrease in D(Ge) metal/silicate with increasing temperature. Horizontal shaded area is the D(Ge) required to explain the Ge content of Earth's primitive upper mantle (~1 ppm) by a metal-silicate equilibrium scenario (28–63; see text).
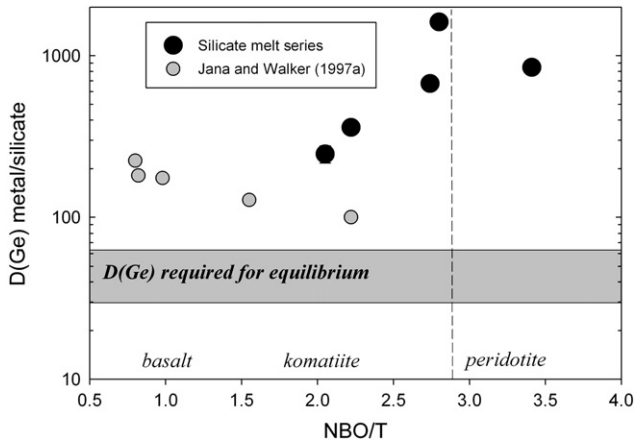
Fig. 4. Illustration of the effect of silicate melt composition in the MgO capsule series. The partition coefficients have been re-calculated to the same fO₂ and temperature, according to the method described in the text. Silicate melt composition is represented by NBO/T, which is meant to be a gauge of melt structure, but is here used as a proxy for activity coefficient variation that may exist for Ge in the silicate melt. Also shown are the previous results of Jana and Walker (1997a) across variable NBO/T values for some basaltic melts. The results of Jana and Walker (1997a) indicate a decrease in D(Ge) metal/silicate from NBO/T values of 0.7 to 2.2. Our new data indicate an increase in D(Ge) from NBO/T values of 2.0 to 3.41 (peridotite) melts. Horizontal shaded area is the D(Ge) required to explain the Ge content of Earth's primitive upper mantle (~1 ppm) by a metal-silicate equilibrium scenario (28–63; see text).

cause non-linear effects on D(i) metal/silicate, as was shown for Ni by Ertel et al. (1997). Quantification of this effect as non-linear will be considered below in Section 5.4.

5.4. Application to the Earth

5.4.1. Mantle concentrations and D(Ge) metal/silicate required for equilibrium

Mantle siderophile element (i) concentrations resulting from core formation depend upon several factors: the initial siderophile element concentration of the bulk planet, core size, and the magnitude of the metal-silicate partition coefficient (e.g., Righter, 2003). These three factors can be combined to quantify the content of a planetary mantle after core formation. The expression determining the concentration of a side-rophile element in a planet's mantle is (from mass balance constraints):

$$C_{LS}^i = \frac{C_{bulk}^i}{x\left[p + (1-p)D_{SS/LS}^i\right] + (1-x)\left[D_{LM/LS}^i\right]} \quad (1)$$

where x is the silicate fraction of the planet and p is the fraction of the silicate portion that is molten; C_{sil}^i and C_{bulk}^i are concentrations of i in the magma ocean and bulk planet, respectively; $D_{SS/LS}^i$ and $D_{LM/LS}^i D_{LM/LS}^i$ are the partition coefficients for element i between solid silicate (SS), liquid metal (LM) and liquid silicate (LS), and $D_{met/sil}^i$ can be calculated using an equation such as presented in the next section for Ge. This expression applies only to the case where the metallic core is completely molten. Given this equation one can see that the concentration of element i in the silicate melt will be dependent upon the values of $D_{SS/LS}^i$ and $D_{LM/LS}^i$ The partition coefficient for Ge during silicate melting ($D_{SS/LS}^{Ge}$) is close to 1 (Capobianco and Watson, 1982; Malvin and Drake, 1987; McFarlane et al., 1994); since D(Ge) metal/silicate is much higher than this value, the metal phase will be the main control on C_{LS}^i, and Eq. (1) simplifies to:

$$C_{sil}^i = \frac{C_{bulk}^i}{\left[x + (1-x)\left(D_{met/sil}^i\right)\right]} \quad (2)$$

Eq. (2) can be used to calculate the concentration of a siderophile element in a magma ocean after core formation, or it can be used to constrain the magnitude of D required to explain a known mantle siderophile content, assuming one has independent estimates of the core size and bulk composition.

In order to calculate the D(Ge) metal/silicate required for equilibrium (or target D(Ge) metal/silicate) for early Earth, determining the approximate abundance of Ge in the core and mantle is necessary. For Earth we have samples of the primitive upper mantle and the concentration of Ge has been measured (~1 ppm, Jagoutz et al., 1979). In order to calculate the concentration in the core, a bulk composition must be assumed for Earth. If the bulk composition is the same as CI carbonaceous chondrites (32 ppm Ge; Newsom, 1995) and Ge is depleted by a factor of 2 to 3 according to the volatility trend of siderophile elements (see Fig. 5), the bulk composition would be 32/3 = (to 32/2) 11 to 16 ppm Ge. This bulk composition, together with the known mantle abundance of ~1.1 ppm (Jagoutz et al., 1979; McDonough and Sun, 1995), would result in a core with 31 to 48 ppm of Ge, thus making the required D(Ge) metal/silicate = 28–43 if the content in the mantle was set by metal-silicate equilibrium. If the bulk composition is the same as EH carbonaceous chondrites (42 ppm Ge; Newsom, 1995) and as above Ge is depleted by a factor of 2 to 3 according to the volatility trend of siderophile elements (Fig. 5), the bulk composition would be 42/3 (or 42/2) = 14 to 21 ppm Ge. This bulk composition would result in a core with 41 to 63 ppm of Ge, thus making the required D(Ge) metal/silicate = 38 to 58 if the content in the mantle was set by metal-silicate equilibrium. We will use this range of D values – 28 to 63 – as the target D(Ge) metal/silicate for a scenario where Ge is explained by metal-silicate equilibrium. These calculations include a correction for the volatility (as above) of Ge and assume a 32 mass % core and 68 mass % mantle.

5.4.2. Qualitative assessment

Is there a set of P-T-fO₂-X conditions at which D(Ge) metal/silicate may attain the "target value" of 28–63 required for an equilibrium
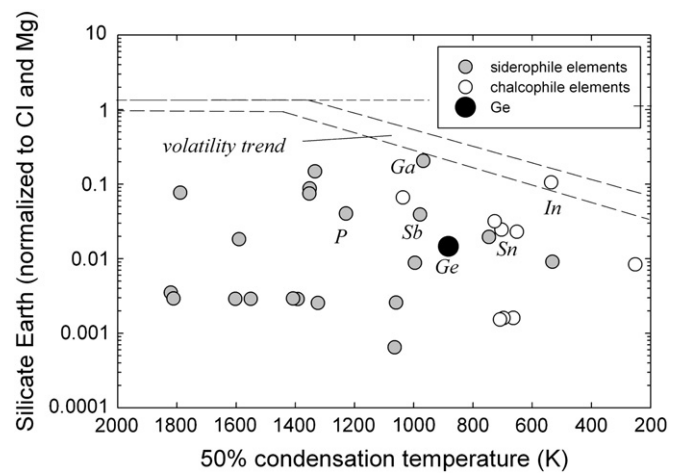

Fig. 5. Concentrations of siderophile elements in the terrestrial primitive upper mantle, relative to CI chondrites, plotted against 50% condensation temperature for the metal. Depletions of volatile siderophile elements are due in part to volatility, as shown by dashed region. Germanium (as well as antimony, tin, and phosphorus) plots below the volatility trend indicating that a further depletion is likely due to core formation. Condensation temperatures for elements are commonly tabulated in 50% values which indicate the temperature at which the element falls to 50% of its initial value in the gas (e.g., Wasson, 1985); the abundances of the volatile elements are thought to be a reflection of condensation processes in the early solar nebula. Primitive mantle and chondrite values are from McDonough and Sun (1995), except for primitive mantle Cd, In, Ga, As and Sn which are from Witt-Eickschen et al. (2009), 50% condensation temperatures are from Lodders (2003). For Ge, a volatility correction of 2 to 3 is required, with the range delineated by the shaded region. This correction is smaller than previous corrections based on previous condensation temperatures and abundance data for some volatile elements from McDonough and Sun (1995) and Wasson (1985).

scenario? Metal-silicate partition coefficients for siderophile elements for a terrestrial planet growing during core formation will change as a function of pressure, temperature, oxygen fugacity, and metal and silicate composition. For Ge there are several studies in addition to the current results that give an indication that the combined effects of increasing temperature, pressure and metallic sulfur content will all lead to reduction of the partition coefficient to values approaching that required for equilibrium explanation (Figs. 3, 4, 6 and 7).

The graphite series data suggest temperature causes a decrease in D(Ge) metal/silicate (Fig. 3). Such a decrease is in agreement with two previous studies: Jana and Walker (1997b) measured a lower D(Ge) at 2200 °C than at 1800 °C at nearly constant melt composition, pressure (5 GPa), and relative fO$_2$, and Siebert et al. (2011) measured a clear decrease in D(Ge) across nearly 1000 °C. The calculations of Capobianco et al. (1993) disagree with all three of these experimental studies, as they predicted an increase in D(Ge) at higher temperatures. Considering just our data, the target value D(Ge) metal/silicate (28–63) could be reached at T between 2000 °C and 2200 °C (Fig. 3).

Re-calculated values of D(Ge) to constant T and fO$_2$ for experiments in the MgO series show that silicate melt composition has a significant influence on the magnitude of D(Ge) metal/silicate (Fig. 4). Previous work on a different set of melt compositions (SiO$_2$- and Al$_2$O$_3$-rich; Jana and Walker, 1997a) showed that partition coefficients can be lowered by a factor of 2.5 when increasing NBO/T from 0.7 and 2.0. Siebert et al. (2011) also show a slight decrease in D(Ge) with higher values of NBO/T. In this study our data show a small increase in D(Ge) metal/silicate between NBO/T of 2.0 to 3.4 (Fig. 4). The effects of melt composition appear to be small, and perhaps non-linear with respect to NBO/T, and this will be modeled in more detail in the next section.

Findings from Jana and Walker (1997b) show that the presence of S decreases D(Ge) metal/silicate. Consequently, an addition of 5–10 wt.% S could lower the D(Ge) metal/silicate down to the target value for temperatures between 1500 °C and 1800 °C (Fig. 6). This reduction caused by S is also qualitatively in agreement with effect of S on D(Ge) solid metal/liquid metal measured by Chabot et al. (2003) and Chabot et al. (2006) and others. Ge much prefers S-free metal rather than S-bearing, and this helps to reduce any partition coefficient involving an S-bearing metallic liquid.

Schmitt et al. (1989) first studied the dependence of D(Ge) metal/silicate on oxygen fugacity, and found solubility consistent with Ge^{2+} in the silicate melt. Later work by Capobianco et al. (1999) demonstrated the importance of Fe/Ni ratio of the metallic phases.

Fig. 7. Comparison to our results at 1 GPa to those of Schmitt et al. (1989) at 1 bar, and Walker et al. (1993) at 10 GPa. The data from Schmitt et al. (1989) was re-calculated for ΔIW = −1.7 to allow for direct comparison to our graphite series results. Our new D (Ge) metal/silicate, obtained for similar silicate and metallic melt compositions at 1 GPa, are lower by a factor of 10 than the 1 bar experiments. And high pressure results – 10 GPa – are even lower than our 1 GPa data, but the high pressure data have not been recalculated to the same fO$_2$, so this is a more qualitative comparison. Overall, however, the comparison indicates pressure will cause a reduction in D(Ge) metal/silicate. Horizontal shaded bar is the D(Ge) required to explain the Ge content of Earth's primitive upper mantle (~1 ppm) by a metal-silicate equilibrium scenario (see text).

They showed that even though some data exhibited a low slope of D (Ge) metal/silicate vs. fO$_2$ indicating Ge^{2+} in the melt, when activity variations in Fe–Ni alloys are considered the re-calculated slope is consistent with Ge^{4+} in the melt. However, more recent work has discovered that Ge is likely dissolved in silicate melts as 2+ (Kegler and Holzheid, 2010).

Finally, comparison to the results obtained by Schmitt et al. (1989) shows that our new D(Ge) metal/silicate, obtained for similar silicate and metallic melt compositions at 1 GPa, are lower by a factor of 10 than the 1 bar experiments (Fig. 7). For this plot, the data from Schmitt et al. (1989) was calculated for ΔIW = −1.7 to allow for direct comparison. The reduction of D(Ge) metal/silicate with pressure is also evident in data from Hillgren et al. (1996) and Walker et al. (1993) for 10 GPa; even considering the high sulfur metallic liquids of Walker et al. (1993) (which will lower the D(Ge) even more), the higher pressure Ds are lower than the lower pressure Ds at comparable ΔIW and silicate melt composition (Fig. 7). Siebert et al. (2011) demonstrated that the exchange coefficient Kd between Fe and Ge (for the equilibrium Fe + GeO = Ge + FeO) decreases slightly at higher pressures. On a related note, the volumetric data of Holzapfel et al. (2001) for GeO$_2$ indicate enhanced siderophile behavior at high pressure, whereas this assessment indicates the opposite. It is possible, as also noted by Holzapfel et al. (2001) that Ge dissolves as GeO in silicate melts and its behavior at high pressures may different. This may be additional evidence that Ge is present in 2+ valence in silicate melts relevant to core formation.

5.4.3. Quantitative assessment

Enough experimental data exist to constrain the several controlling variables of D(Ge) metal/silicate, and calculation of metal-silicate partition coefficients can be done using an approach guided by chemical thermodynamics where:

$$\ln D(\text{met / sil}) = a \ln fO_2 + b/T + cP/T + d \ln(1-Xs) \quad (3)$$
$$+ e \ln(1-Xc) + f(NBO/T - 2)$$
$$+ g(NBO/T - 2)^2 + h.$$

The a, b, c, and h terms relate to valence, enthalpy (H/R), volume (V/R), and entropy (S/R), respectively, the d and e terms relate to
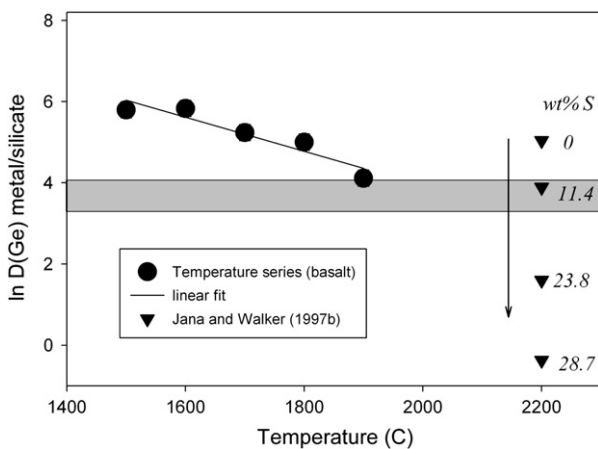

Fig. 6. Illustration of the effect of S content of the metallic liquid on D(Ge) metal/silicate, from the study of Jana and Walker (1997b). Shown for comparison are our temperature series (graphite capsules) results. It is easy to see that even a small to moderate amount of S in the metallic liquid will decrease D(Ge) metal/silicate substantially. Horizontal shaded area is the D(Ge) required to explain the Ge content of the Earth's primitive upper mantle (~1 ppm) by a metal-silicate equilibrium scenario (28–63; see text).
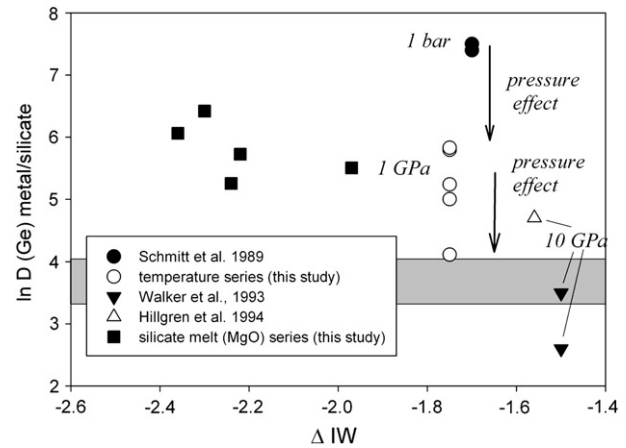
activity expressions for these elements in a metallic liquid (X_S and X_C = mole fraction of S and C in the metallic liquid, respectively), and the f and g terms relate to the non-linear dependence of D(Ge) on silicate melt composition, as shown above and in Fig. 4. Because there is evidence that Ge exists at 4+ above IW, and we want to use the expression for core formation processes which are typically below IW, we have not used 11 experiments from Capobianco et al. (1999) that were done at high fO_2 > IW buffer. Also, the d and e terms are proxies for activity coefficients, used in place of those such as employed by Capobianco et al. (1999) for Fe–Ni–Ge systems or Wade and Wood (2005) for one bar steelmaking conditions. The f and g terms are a departure from the previous work on other siderophile elements. In many previous studies, D was shown to have linear dependence on silicate melt structure and composition and has been regressed against NBO/T (e.g., Righter et al., 1997; Walter and Thibault, 1995). In this case, given the non-linear dependence upon NBO/T and the minimum near 2, we have added these two terms that mimic a parabolic function to allow this non-linearity to be fit in the regression if necessary.

Results of the regression are: a = −0.39(0.04); b = −17430 (2700); c = 520(70); d = 8.09(0.67); e = 3.56(1.59), f = −0.118 (0.05); g = −0.124 (0.04); h = 7.48(1.21); comparison of predicted vs. measured ln D(Ge) values are shown in Fig. 8. The derived temperature dependence is similar to that demonstrated for other moderately siderophile elements (Righter et al., 2010; Supplementary information), and in agreement with the decreases measured in this study, Jana and Walker (1997b), and Siebert et al. (2011). The pressure dependence is positive, as also predicted by Holzapfel et al. (2001) albeit for GeO$_2$. Despite this, the D(Ge) metal/silicate decreases with increasing pressure and temperature, as it does for many other siderophile element such as Ni, Co, or Mn (e.g., Righter, 2011). The effect of C and S in metallic liquids is predicted to decrease D (Ge) metal/silicate for each element, also in agreement with work on Ge in metallic systems (e.g., Chabot et al., 2006). And finally, the valence of Ge is predicted to be close to 2+, as also demonstrated independently by Kegler and Holzheid (2010). As mentioned above, some oxidized experiments from Capobianco et al. (1999) were not included in the regression since the valence of Ge may be 4+ at more oxidized, and thus not relevant to core formation conditions.
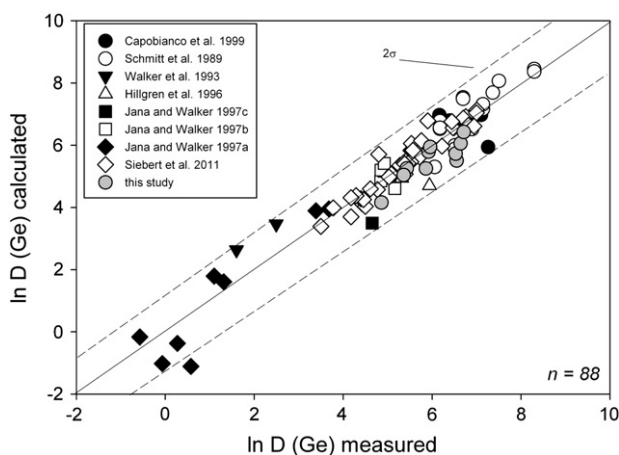

Fig. 8. lnD(Ge) metal/silicate (measured) vs. lnD(Ge) metal/silicate (calculated) for all available D(Ge) metal/silicate data from the literature: Capobianco et al. (1999), Hillgren et al. (1996), Jana and Walker (1997a, b), Schmitt et al. (1989), Siebert et al. (2011), Walker et al. (1993) and this study. Note that 11 of the oxidized experiments from Capobianco et al. (1999) that were > IW were left out of the regression analysis since the valence of Ge may be higher than that relevant to core formation. Total number of experiments is 88. Dashed lines indicate 2σ error on the regression. Coefficients from the regression analysis are a = −0.39(0.04), b = −17430(2700), c = 520(70), d = 8.09(0.67), e = 3.56(1.59), f = −0.118(0.05), g = −0.124 (0.04), h = 7.48(1.21).

Using Eq. (3) and the derived regression coefficients, models for Earth's mantle Ge content can be tested. If we fix relative fO_2 at IW-1, metallic liquid Xs = 0.05 and Xc = 0.11, and peridotite with NBO/T = 2.8, we are left with temperature and pressure as variables (Table 2). D(Ge) metal/silicate of 68 (+130/−34) is attained at a temperature of 3200 °C and pressure of 30 GPa, similar to the PT range calculated for magma ocean conditions explaining the Ni, Co, Mo, W, P, Mn, V, Cr, Cu, Ga and Pd concentrations in Earth's upper mantle (Fig. 9; Righter, 2011). This D(Ge) overlaps the range of required D (Ge) of 28–63 calculated above for an equilibrium solution to the Ge content of the PUM, and produces a mantle Ge content of 0.7 to 1.3 (Table 1). Because the combined effects of pressure and temperature on D(Ge) are offsetting, the value of D(Ge) does not change much with depth into a molten Earth and only decreases by a factor of ~10% for example, along the peridotite liquidus of Wade and Wood (2005).

Even though the depth of a magma ocean is not well defined by D (Ge), the combined effects of P, T, fO$_2$, and core and mantle compositions lead us to conclude Earth's mantle Ge can be explained by a metal-silicate equilibrium scenario, rather than late accretion or heterogeneous accretion. Our modeling results show that D(Ge) metal/silicate can be consistent with metal-silicate equilibrium explanation for the Ge content of the PUM only at magma ocean conditions of an intermediate depth 30 (±5) GPa and 3200 (±400) °C (Fig. 9; uncertainties are based on allowed match to the PUM Ge content given the range of D(Ge) from 28 to 63 and 20% error on the calculated partition coefficient). These conclusions will undoubtedly require revision when the effects of Si and O dissolution in Fe metallic liquids are quantified; Ge is known to avoid Si in Fe alloys (Chabot et al., 2010), and thus Si in Earth's core would likely cause D(Ge) metal/silicate to decrease further, and allow easier fits to mantle concentrations. Similarly, the volatility trend may require revision (as it did recently for In, Ga, Sn and As; Witt-Eickschen et al., 2009) with additional analyses of Ge in peridotites.

5.5. Application to Moon, Mars and Vesta

5.5.1. Controls on [Ge] during mantle melting

Estimating the mantle concentration of Ge from planetary basalts derived from melting of that mantle is relatively straightforward because the bulk partition coefficient for Ge during melting is close to 1 (Capobianco and Watson, 1982; Malvin and Drake, 1987; McFarlane et al., 1994). As a result, the concentrations of Ge in the melts are similar to those in the mantle, as can be seen in the case of the Earth (Fig. 10). The other variable with respect to melting and Ge concentration in basalt is the role of gasses and degassing. For example, Taran et al. (1995) show that many siderophile and chalcophile elements are also volatile and their concentrations can be lowered in the basaltic magmas during degassing. Germanium is among this group of elements with a volatility intermediate between Sn and Zn. Therefore, the role of degassing must be considered and defined when interpreting Ge contents of basaltic rocks.

5.5.2. Moon

Modeling core formation in the Moon is somewhat unconstrained due to uncertainties in the Moon's bulk composition and the size of the core (e.g., Righter, 2002). Nonetheless some constraints can be placed if assumptions are made such as fixing the size of the core at 2 mass %, and fixing the bulk composition to be that of the Earth's upper mantle. The latter constraint is based on the idea that the Moon formed from the mantle of a large differentiated impactor (Righter, 2002). The approach of Righter (2002) is followed, since it is the most recent siderophile element modeling attempt for the Moon. We can estimate the Ge of the lunar mantle using for lunar samples using analyses of basalts (Dickinson et al., 1989; Wolf et al., 1979; Fig. 10), and using the terrestrial mantle–basalt trends as a guide (Fig. 10). We can see that the lunar basalts show a large range of Ge contents. The

Table 2
Summary of conditions and results of modeling Ge in mantles of Earth, Moon, Mars and asteroid 4 Vesta.

	Core mass	Bulk Ge [a]	ΔIW [b]	NBO/T mantle	X sulfur in core	X carbon in core	T (°C)	P (GPa)	D(Ge) met/sil [c]	Mantle Ge (ppm) [d]	Mantle Ge calc (low)	Mantle Ge calc [e]	Mantle Ge calc high
Earth	32	32 (11–16)	−1.0	2.8	0.04	0.11	3200	30	68	1.0	0.4	0.7	1.3
Moon	2	1	−2.5	2.55	0	0	1730	4.5	1870	0.01	0.01	0.03	0.05
Mars	21	15(5)	−1.5	2.55	0.17	0	1830	14	140	0.25-0.85	0.08	0.16	0.33
4 Vesta	14	12.1	−2.4	2.6	0.1	0.05	1550	0.01	620	0.2	0.08	0.14	0.25

[a] Bulk Ge is CI for Earth, PUM for Moon (as per Righter, 2002), Lodders and Fegley (1997) for Mars, and CV–L mix of Righter and Drake (1997) for Vesta. Numbers in parentheses are volatility corrected values, based on volatility factors of 2 to 3 for Earth and 3 for Mars (see Fig. 5 caption).
[b] Relative oxygen fugacity for Moon, Mars and Vesta are based on studies of Karner et al. (2006), Righter and Chabot (2011), and Righter and Drake (1997) for Vesta, respectively.
[c] Calculated from Eq. (3).
[d] Mantle concentrations of Ge are estimated from the basalt data in Fig. 10.
[e] Calculated mantle Ge contents are using Eqs. (2) and (3), with error from regression representing the low and high values.

high Ge contents of the Dickinson et al. (1989) analyses are likely due to impact processes or metasomatism, rather than indigenous melting processes for the Moon. The lowest Ge concentrations are likely due to degassing as they are for Sb, Re and other volatile elements (Norman et al., 2004; Taran et al., 1995). There are some lunar samples that are as high as 0.01 ppm, suggesting that the lunar mantle Ge content is very low compared to the Earth. The value of 0.01 ppm Ge in the lunar mantle is used in the modeling, as is a bulk lunar Ge content of 1 ppm (similar to Earth's upper mantle). With a small core (2 mass %), and conditions of 4.5 GPa, 1730 °C, ΔIW = −2.5, peridotite and low $Xs = Xc = 0$, the calculated D(Ge) metal/silicate = 1870 (+3400/−1025), which produces a mantle with 0.03 (+0.05/−0.01) ppm Ge (Table 2). This is in general agreement with the estimated value of 0.01 ppm—any such calculations for the Moon have an inherent uncertainty with respect to the bulk composition. If the bulk composition is <1 ppm Ge, and considering volatility of Ge, the mantle value would likely be <0.05 ppm and thus a mantle with 0.01 ppm Ge could be achieved easily with a small core. On the other hand calculated D(Ge) at a slightly higher fO_2 (IW-1.5) but all the same conditions as above, would result in D(Ge) of 350, and a mantle Ge content of 0.1 ppm, so the best solutions are achieved at conditions lower than IW-1.5. These calculations indicate that Ge (like Sb) is present in the lunar mantle at low concentrations that might be expected from extraction of most Ge into a small metallic core.

5.5.3. Mars

Eight siderophile elements have been previously modeled for Mars pointing to a deep magma ocean scenario for early Mars allowing metal-silicate equilibrium at PT conditions of 14 ± 3 GPa and 1830 ± 200 °C (Righter and Chabot, 2011). The Ge content of the Martian
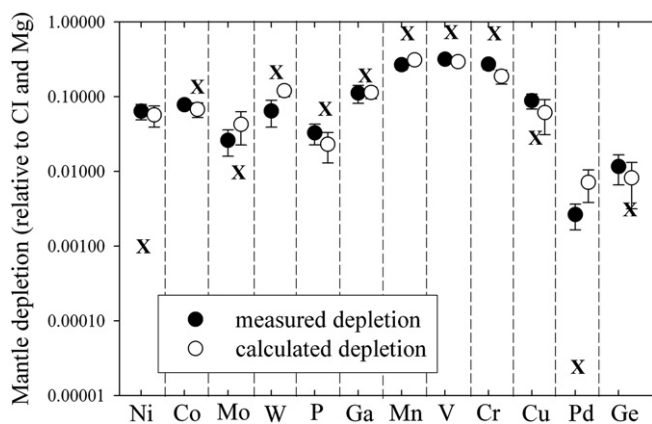

Fig. 9. Depletion of Ge in the PUM, as well as 11 other siderophile elements (from Righter, 2010), compared to depletions for partition coefficients calculated for P = 30 GPa, T = 3200 ° C, relative fO_2 = IW-1, NBO/T = 2.8, Xs = 0.11, and Xc = 0.04. Also shown (as 'X') are the depletions calculated for low pressure conditions such as might be expected in a heterogeneous accretion scenario (e.g., Capobianco et al., 1993).
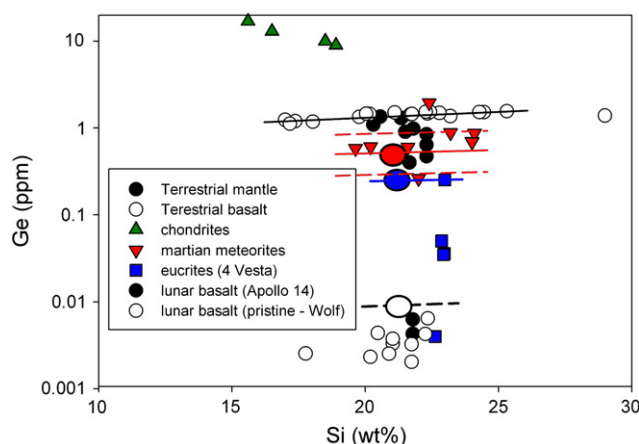
mantle can be estimated using Ge–Si trends of Martian meteorites and the terrestrial mantle-basalt array as a guide (Fig. 10). The resulting mantle Ge content is 0.25 to 0.85 ppm (Fig. 10), with the large range due to some scatter in the Ge data. Using the bulk Mars Ge composition of 15 ppm (Lodders and Fegley, 1997), and calculated D(Ge) metal/silicate at 14 GPa, 1930 °C and for Xs = 0.17, and Xc = 0, peridotite (Mars mantle NBO/T = 2.55), and ΔIW = − 1.5, results in D (Ge) metal/silicate of 140 (+260/−80) and a mantle content of 0.16 (+0.33/−0.08) ppm Ge (Table 2). This value has been adjusted for volatility since Ge is volatile and could be depleted in the Martian mantle by a factor of 3 (see Righter and Chabot, 2011). The measured and calculated Ge contents overlap, indicating that the Ge content of the Martian mantle is also consistent with the intermediate depth magma ocean scenario proposed by Righter and Chabot (2011).

5.5.4. HED parent body or asteroid 4 Vesta

Some eucrites have been analyzed for Ge, and can be used to estimate the Ge content of the HED parent body mantle (e.g., Righter and Drake, 1997). This results in a Ge content of ~0.2 ppm (Fig. 10), assuming magmatic volatility has affected the lowest Ge content basalts. Righter and Drake (1997) were able to explain Ni, Co, Mo, W and P contents of the HED mantle using a 70% L–30% CV chondrite mixture (12.1 ppm Ge), a core size of 14 mass %, 1 bar pressure, 1550 °C, peridotite silicate melt, Xc = 0.05, X_S = 0.1, and ΔIW = − 2.4 (Table 2). If these conditions are used to calculate D(Ge) metal/

Fig. 10. Summary of analyses of Ge (ppm) and Si (wt.%) for the Earth, Moon, Mars and asteroid 4 Vesta (eucrites). Terrestrial data serve as a guide for interpretation of data from the Moon, Mars and 4 Vesta. Estimates of the mantle Ge content from these latter three bodies are plotted as larger circles—details are explained in the text. Larger uncertainty for Mars reflects more scatter in the data from Martian meteorites. Data sources are as follows: Earth: peridotites—Jagoutz et al. (1979); basalts—DeArgollo and Schilling (1978), Hertogen et al. (1980), Wasson and Baedecker (1970). Moon: basalts— Dickinson et al. (1989), Wolf et al. (1979). Mars: Lin et al. (2008), Warren et al. (1999), and sources complied in Meyer (2010). 4 Vesta: eucrite sources cited in Kitts and Lodders (1998).

silicate, the resulting D(Ge) metal/silicate is 620 (+1140/−340), which results in a mantle Ge content of 0.14 (+0.25/−0.08) ppm. Furthermore, the resulting core Ge content is ~58 ppm which is well within the range of iron meteorite groups such as the IIAB and IIIAB irons (e.g., Chabot and Haack, 2006) and mesosiderites (Kong et al., 2008).

6. Summary

We have studied the partitioning behavior of Ge (and ten other siderophile elements), at variable temperatures and silicate melt compositions including peridotitic liquids. The last decade has seen a large increase in publication of metal-silicate partitioning data for siderophile elements, and a generally stated conclusion is that high temperature conditions make siderophile elements less siderophile. Our previous work showed that many si\derophile elements become more siderophile at high temperatures (Righter et al., 2010), consistent with the prediction of Capobianco et al. (1993) where increases in D(met/sil) with temperature were predicted based on the van't Hoff equation. However, Capobianco et al. (1993) predicted an increase in D(Ge) metal/silicate with temperature and we show here that there is a clear decrease.

In addition to the temperature effect, there is a slight silicate melt compositional effect that causes an increase in D(Ge) metal/silicate partition coefficients in experiments with melts of low degree of polymerization. This is contrary to the decrease demonstrated by Jana and Walker (1997a) for a few synthetic silicate melt compositions and Siebert et al. (2011) at higher degrees of melt depolymerization. The combination of these three results indicates that Ge solubility may be a non-linear function of silicate melt polymerization.

Finally, the new results for Ge, together with previous studies, indicate that the Ge content of Earth's primitive upper mantle is generally consistent with metal-silicate equilibrium in the early Earth at conditions of 30(±5) GPa, 3200(±400) °C, $\Delta IW = -1$, and between peridotite melt and S- and C-bearing metallic liquid. These conditions are not unique, but rather illustrate that the Ge contents of the PUM (and Martian and asteroid 4 Vesta mantles) can be explained by high temperature and/or pressure conditions of a magma ocean, rather than by late chondritic additions after core formation, or by heterogeneous accretion. Nonetheless, much work remains to explore D(Ge) at higher pressures (>10 GPa), and in systems with O and Si dissolved in the metallic liquid iron. Further work may also focus on better defining the bulk Ge content of the Earth and other differentiated bodies (Mars, Moon, 4 Vesta) and in general the volatility of Ge and other siderophile elements.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2011.02.015.

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