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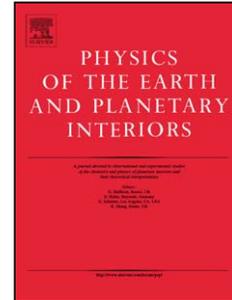
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The wetting ability of Si-bearing liquid Fe-alloys in a solid silicate matrix - Percolation during core formation under reducing conditions?

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Abstract

The wetting characteristics of liquid Fe-Si alloys in a matrix of the respective predominating stable silicate mantle mineral (forsterite or silicate perovskite) at pressures of 2 - 5 and 25 GPa and temperatures of 1600 - 2000 °C were studied by determining the liquid metal - solid silicate contact angles. The median angle values from texturally-equilibrated samples were found to be independent of pressure, temperature, silicate mineralogy and the Si content in the metal fraction and range between 130° and 140° which is far above the critical wetting boundary of 60°. This shows that within the studied range of conditions dissolved Si does not lower the surface energies between Fe-rich liquids and silicate mantle grains. As a consequence, under reducing conditions the presence of Si in the metal phase of planetary bodies would not have enhanced percolative flow as an effective metal - silicate separation process.

Keywords: percolation; wetting angle; core formation;

Introduction

A central issue in the context of planetary core formation is the mechanism by which core forming Fe-rich metal separated efficiently from the silicate mantle. The nature of this process is important because it will have influenced the time duration of core formation and the geochemical signatures of the two resulting reservoirs (Stevenson 1990; Poirier 1994).

A number of arguments support the idea that metal-silicate separation occurred through the formation of a terrestrial magma ocean that allowed metal to pond at its base and sink through the underlying solid mantle as diapirs (Stevenson, 1990; Li and Agee, 1996; Righter and Drake, 1997; Rubie et al., 2003). In such a model metal-silicate equilibration would occur at the base of the magma ocean but reequilibration during the passage of the liquid metal through the underlying solid mantle would be minimal (Karato and Murthy, 1997). A further mechanism that may have significantly aided the relatively rapid process of core formation on terrestrial planets is the percolation of liquid metal through solid silicate mantle (Stevenson, 1990). Percolation is an attractive mechanism to explain core formation on small bodies where temperatures during accretion may be below the silicate liquidus and for larger bodies, such as the Earth, in the later stages of accretion, when a significant portion of the mantle may have been crystallised. In both cases percolation could have drastically influenced the geochemistry of the core and mantle because in contrast to liquid metal separating as large diapirs, percolative flow would allow reequilibration of core forming liquids during their entire transit through the solid mantle.

In texturally equilibrated solid - liquid systems the occurrence of percolative flow is largely controlled by the melt fraction and the solid - solid (γ_{ss}) and solid - liquid (γ_{sl}) interfacial energies of the phases involved (von Bagen and Waff, 1986). The ratio of the interfacial energies determines the geometry of a melt pocket in a solid matrix by controlling the contact angle

between the melt and the confining grains, known as the dihedral angle θ (Bulau et al., 1979; Laporte and Provost, 2000):

$$\frac{\gamma_{ss}}{\gamma_{sl}} = 2 \cos \frac{\theta}{2}$$

If the dihedral angle θ is below the so-called wetting boundary of 60° an interconnected melt network can be formed and melt can migrate through the solid matrix independently of the melt fraction. If, on the other hand, $\theta > 60^\circ$, melt will be confined to disconnected pockets unless a critical melt fraction (at least 6 %) is exceeded. In the latter case, percolation can occur; however, the melt will not be completely removed from the matrix because a pinch-off melt fraction will be reached where a certain quantity of melt, slightly below the critical melt fraction, is trapped at grain boundaries (von Bargar and Waff, 1986; Yoshino et al., 2003). Therefore, only in cases where $\theta \leq 60^\circ$ can core separation by percolation through a solid silicate matrix be completed efficiently.

Pure liquid Fe has a high dihedral angle ($>100^\circ$) in silicate assemblages (Jurewicz and Jones, 1995). However, in addition to Ni it is known that the Earth's core also contains approximately 10 % of one or more light alloying elements with Si, S, O, C, and H being the most likely candidates (Poirier, 1994). Previous studies have systematically examined the effects of Ni, S and O on liquid metal-silicate matrix dihedral angles over a wide range of pressure, temperature and silicate mineralogy (Minarik et al., 1996; Ballhaus and Ellis, 1996; Shannon and Agee, 1998; Terasaki et al., 2005). It has been shown that S and especially O can strongly reduce the wetting angles so that values $\leq 60^\circ$ can be reached at pressures < 3.5 GPa (Minarik et al., 1996; Gaetani and Grove, 1999). At pressures representative of most of the Earth's upper mantle, transition zone and the upper part of the lower mantle, high O and S contents do not result in dihedral angles $< 60^\circ$ (Shannon and Agee 1998; Terasaki et al., 2005; Terasaki et al., 2007) but

there is some evidence to suggest this situation may change in the deep lower mantle (Takafuji et al., 2004). The effects of Si on the wetting behaviour of liquid Fe-alloys in a silicate matrix have not been systematically examined at concentrations compatible with it possibly being the major light element in the Earth's core. Poirier (1994) recognized this deficiency and suggested that, based on the low surface energy of pure silicon (Iida and Guthrie, 1988), Fe-alloys containing Si may have lower surface tensions than pure liquid Fe as suggested by the studies of Ixanov et al. (1978) and Utigard (1994). Some heterogeneous accretion models propose an early reducing phase of core formation during which Si would have been extracted into the core (O'Neill, 1991; Javoy, 1995; Wade and Wood, 2005). Some models even propose that such conditions prevailed over the entire core formation process (Wänke, 1981; Javoy, 1995; Allègre et al., 1995) with Si therefore accounting for the majority of the light element in the core (Allègre et al., 1995; McDonough and Sun, 1995). Such models are supported by the observation that the Earth's mantle is apparently depleted in Si relative to chondritic meteorites. If the presence of Si in core-forming Fe-rich liquids increased their ability to wet a silicate matrix and allowed porous flow to occur, this would be an important factor lending at least some support to such models. In this study we report wetting angles between Fe-rich melts with variable Si contents and typical silicate mantle minerals covering a wide P - T range relevant to core formation on terrestrial planets under reducing conditions. As such data would also help to clarify whether Si could have aided percolative core formation on some small reduced differentiated asteroids such as the parent body of the aubrite meteorites (Lodders et al., 1993) we performed a low pressure wetting experiment that contained S in addition to Si in the metal melt.

Experiments and analytical techniques

Mixtures of Fe-Si alloys and synthetic silicate minerals were employed as starting materials. Forsterite was used in experiments performed up to 5 GPa and for experiments at 25 GPa enstatite was the precursor for Mg-Si perovskite. The Fe-Si alloys had Si contents of 9 and 17 wt% and 5 wt% of the respective alloy was added to the silicates. For the S-bearing run at 2.7 GPa, powdered Fe, Fe-Si-alloy (17 wt%) and FeS were mixed in proportions such that the resulting Fe-alloy contained 5 wt% Si and 5 wt% S. This mixture was placed in the centre of a capsule between two layers of synthetic forsterite.

High-pressure experiments were performed using a piston-cylinder press at 2 GPa and 1600 °C and a multi-anvil apparatus at conditions of 2.7, 5 and 25 GPa and 1600 - 2000 °C. In the piston-cylinder experiment talc-pyrex was used as the pressure medium with a graphite furnace. For the 2.7 and 5 GPa experiments a 500-tonne Walker style multi-anvil press was used with a Cr-doped MgO octahedral pressure medium of 18 mm edge length and tungsten carbide cube truncations of 11 mm (18/11 assembly). At 25 GPa a 1200-tonne Kawai-type press with a 10/4 assembly was employed. To ensure reducing conditions graphite sample containers were wrapped in Re foil and a few runs at $T > 1830^{\circ}\text{C}$ were performed with polycrystalline and single crystal MgO capsules. Stepped LaCrO_3 heaters were employed in order to minimize thermal gradients across the sample. At 25 GPa a Re foil furnace was used. In all high-pressure experiments the temperatures were chosen such that they lay between the melting temperatures of the Fe-alloy and of the silicate phase and temperature was monitored with D-Type W-Re thermocouples. Further details of the multi-anvil cell assembly can be found in Keppler and Frost (2005). The run durations were varied between 1 and 71 hours. Experiments were quenched by turning off the electrical power to the furnace.

The samples were imbedded in epoxy resin and final polishing was performed with colloidal silica in order to produce a slight relief between differently oriented silicate grains for better imaging contrast. Imaging, phase identification and semi-quantitative chemical analyses were carried out with a SEM/EDX system (LEO 1530). Textures, especially silicate grain boundaries, could be best documented using low angles of incidence (70°) for the electron beam and thus combining orientational and Z-contrast back scattered electron (BSE) signals from the sample. From such BSE images with clearly visible liquid metal pocket - forsterite triple junctions the dihedral angles were measured with the angle tool of Corel Draw software. As a 2-D section of a sample cuts through melt-grain junctions in various orientations a single measurement will give an apparent angle value, which may be an over- or underestimation of the true angle measured perpendicular to the solid-solid-liquid contact. To account for this effect, the median value of an observed angle population in a sample was taken as this has been shown to be a good approximation of the true wetting angle (Jurewicz and Jurewicz, 1986). Accordingly, the measurement error for a population was determined from the 95 % confidence interval around the median (Table 1). To achieve a statistically adequate result a large number of angles, if possible > 100 , should be analysed (Stickels and Hucke, 1964). In our study the number of angles measured on each sample containing a forsterite matrix ranges from 100 - 211, with the exception of three samples where only 76, 78 and 90 angles could be obtained from the respective sections. However, in these cases we also think that the numbers of analyses should be sufficient and that a representative median value is approached for the following reasons. In the case of the sample with 211 measurements, we used two sections oriented at 90° to each other and the medians of the obtained populations, consisting of 91 and 120 analyses, differ from the bulk median by only -3° and $+1^\circ$ respectively. In another sample, with a total of 150 measurements, we tested the median after every 10 analyses from 50 onwards and the deviation from the final median value ranges from 0° to $+2.5^\circ$. In the samples with the Mg-Si perovskite matrix, polishing with colloidal silica solution produced a strong relief between the metal and

silicate phases, while the silicate grain boundaries are still not clearly visible. This hampered the identification of melt-grain junctions and the small number of measurable angles (9) gives only a very qualitative result. In the S-bearing run angles could only be determined for a S-rich Fe-melt that had separated and the number of 61 is also quite low so that we treat it as qualitative result only.

Results

S-free samples

Initial experiments of the 5 GPa series were performed with Fe-bearing olivine, but as a consequence of the low redox conditions, 3-4 log units below the iron-wüstite oxygen buffer, tiny metallic Fe droplets formed and pinned the grain boundaries thus inhibiting grain growth and the attainment of textural equilibration. For subsequent experiments, pure forsterite was employed. In these cases dry three-grain contacts of forsterite with angles close to 120° as well as the smoothly-curved forsterite grain boundaries provided a good indication that the matrix phase had reached textural equilibrium (Fig. 1 a, b). In a previous high-pressure study on the wetting behavior of Fe-S alloys in an olivine matrix (Terasaki et al., 2005) a time series of experiments performed over run durations of up to 24 hours indicated that textural equilibrium was approached after 12 hours at 1600°C . In our study experiments were performed for various time durations between 0.45 and 71 hours but measured dihedral angles remained unchanged over these durations. Given that significant grain growth occurred, even in the shortest runs, textural equilibrium was evidently reached quite rapidly.

Typical textures from recovered samples, including both forsterite and Mg-Si perovskite experiments, are shown in Fig. 1. In the 5 GPa forsterite samples, the majority of the quenched metal is present in pockets with convex-shaped contacts towards the silicate grains (Fig. 1a, 1b).

Additionally, smaller melt pockets occur as nearly spherical inclusions within the recrystallized forsterite grains. In one sample, crystal growth was so rapid that metal was only observed as such inclusions. In the Mg-Si perovskite sample shown in Fig. 1c most of the metallic melt has been overgrown by perovskites and a relatively small amount of melt remained at grain junctions. The schematic sketch added as an inset in Fig. 1c shows the grain boundary junctions in the area of the metal blebs more clearly. Both features - round inclusions and convex pockets that are seen in all samples- are general indicators for high liquid - solid surface tensions (Bulau et al., 1979; Laporte and Provost, 2000; Walte et al., 2007), as are other characteristics such as an uneven melt distribution and abnormal grain growth, that result from the low melt mobility of high dihedral angle systems (Walte et al., 2007). Such behaviour causes the equilibrium texture to deviate from those observed in low dihedral angle systems.

In some of the samples Si metal was observed to oxidize. Using MgO capsules, oxidation phenomena were observed in all cases, whereas in graphite capsules this effect was minimized. In the 5 GPa series, Si loss from the metal phase occurred to different degrees (Table 1a) and was generally accompanied by the formation of enstatite occurring either as irregular patches in the forsterite matrix (Fig. 1b) or completely enclosing some of the metal pockets. Such metal-silicate contacts including at least one enstatite grain were excluded from the dihedral angle measurements. At 1830°C, Si loss from the alloy was most extreme and resulted in a pure Fe melt (Fig. 1d). For comparison with the wetting behaviour of the Fe-Si alloys we also measured the pure Fe-liquid/forsterite wetting angles in this sample.

In test runs at 25 GPa using a LaCrO₃ furnace we observed strong oxidation of the metal phase that was then Si-free after the experiment. In some cases excess SiO₂ (stishovite) was formed either in direct contact with the metal phase or within the perovskite matrix. Moreover,

even Fe was oxidized and partly incorporated in the perovskite that shows reaction zones around metal pockets while tiny Fe-metal droplets pin the perovskite grain boundaries. With such intensive chemical reaction, textural equilibrium was clearly not achieved. By replacing the LaCrO_3 furnace with a Re-foil heater, redox conditions in the experiment were drastically lowered and no Si loss from the metal phase or FeO-rich reaction rims in perovskite were observed.

In some samples the metal phase shows an internal texture with patches of variable Si content that most likely result from phase separation during quenching. In order to obtain the bulk metal composition, such metal pockets were analysed using a scanning mode over a rectangular area.

The median values of the wetting angles are listed in Tab. 1. Up to 5 GPa within a forsterite matrix all values lie within an interval of 130° - 140° and are thus far above the wetting boundary of 60° . No dependency of the wetting characteristics on P, T or Si content of the Fe-alloy was observed, within error. Moreover, at 1830°C the contact angle of pure Fe (119°C) is actually lower than for all the Si-bearing Fe-alloys studied in this work. For the Mg-Si perovskite matrix at 25 GPa, even though a statistically-adequate evaluation was not possible, from the few measurements and the texture it is obvious that liquid - solid interfacial energies are high and wetting angles are likewise $\geq 140^\circ$. As can be seen in Fig. 1c the metal blebs have very rounded shapes that appear to be almost unaffected from their position at various grain contacts (left and central melt pocket) or as inclusions (right melt pocket). This independence of melt pool shapes from grain boundaries gives further support that solid - liquid surface tensions in this system are high (Walte et al., 2007) and that wetting angles must be at least as high as in the olivine matrix at lower pressures, where melt pools are found at triple junctions more frequently.

Si- and S-bearing run at low pressure

In the experiment where S was added to the Fe-Si-alloy the run product contained a S-rich metallic liquid in addition to a Si-rich liquid. A third liquid which was a 55:45 mixture of Re and Fe, resulting from contamination by the foil capsule, was also present in some areas. Interestingly this Re-rich liquid appeared to fully wet the forsterite grain boundaries.

From the starting Fe-S-Si mixture two melts formed which is in qualitative agreement with the phase diagram (Raghavan, 1988) except that the S content of the Si-rich melt was only 0.1 % (Table 1b) whereas the phase diagram would predict at least 1-2 wt %. This melt formed small round droplets between the forsterite grains and showed no sign of wetting the silicate matrix. We qualitatively estimate wetting angles in excess of 120°. The S-rich melt on the other hand was nearly Si-free and formed angular melt pockets at forsterite grain contacts with an approximate wetting angle of 94° (Table 1b). Angles in the range of 85 - 100° have also been reported for reduced Fe-rich metal melts with S-concentrations of 24 - 35 wt% at similar conditions of 2 GPa and 1350 °C by Ballhaus and Ellis (1996).

Discussion and Conclusions

Over the studied range of pressure (2 - 25 GPa), temperature (1600 - 2000°C) and liquid Fe compositions (Si contents of 9 - 17 wt%), Si does not lower the dihedral angle between liquid Fe-rich alloy and silicate minerals. Up to the highest Si content in the metal, dihedral angles remain high (132 - 140°) and lie far above the wetting boundary of 60°, as shown in Fig. 2. Therefore, in contrast to the suggestion of Poirier (1994), Si actually seems to raise the interfacial energy of liquid iron alloys. This is most likely because, in contrast to S and O (Iida and Guthrie, 1988; Terasaki et al., 2005), Si apparently does not behave as a surface-active element that reduces the surface tension of liquid Fe. As shown in Fig 2. anions such as S and O have significant effects on the liquid Fe surface tension, while metallic alloying components

such as Si do not. This is consistent with the observation that Ni, also, has little effect on the surface tension liquid Fe (Gaetani and Grove, 1999). As Si does not favourably influence the liquid wetting behaviour, it is likely that interfacial energies between Si-bearing Fe liquids and other silicate minerals are also high.

Under reducing core formation conditions, where significant amounts of Si would partition into the metal phase, efficient liquid metal separation cannot occur by percolation alone. Aubrite achondrites are a family of meteorites that seem to come from a reduced parent body where metal segregation has occurred (Lodders et al., 1993). Under strongly reducing conditions, which resulted in very low FeO contents of silicate minerals, the separated metal must have contained significant Si. Our results indicate that the presence of Si did not aid percolation of the Fe-rich liquid and segregation must therefore have occurred through large degree melting of the silicate matrix. Although the aubrite parent body also contained significant S, Si-Fe liquids have a large immiscibility gap with S-Fe liquids at these low-pressure conditions (Raghavan, 1988). This is supported by our results from 2.7 GPa that showed immiscible Si-Fe liquids to have low S contents that had no influence on the liquid interfacial energy. Perhaps more importantly, even though the coexisting S-Fe liquid has a lower surface tension, it still has a dihedral angle of $\sim 94^\circ$ that is still far above the wetting boundary. Although Fe-S melts have been observed to wet a silicate matrix at more oxidizing conditions (Gaetani and Grove, 1999) this clearly results from a higher solubility of O in the melt. Under reducing conditions even if the Si contents of the Fe-S melts are low, O contents are likely to be also low, thus ensuring a high metal-silicate dihedral angle even for high S contents.

The results, moreover, imply that Si would not have aided liquid metal percolation through the Earth's solid silicate perovskite bearing lower mantle as our preliminary qualitative data

indicate that dihedral angles remain very high under these conditions. Although lower interfacial energies have been claimed (Takafuji et al., 2004) for some O and Si bearing metallic Fe-liquids at very high pressures (> 70 GPa), this effect, if correct, most likely arises from the influence of dissolved O rather than Si.

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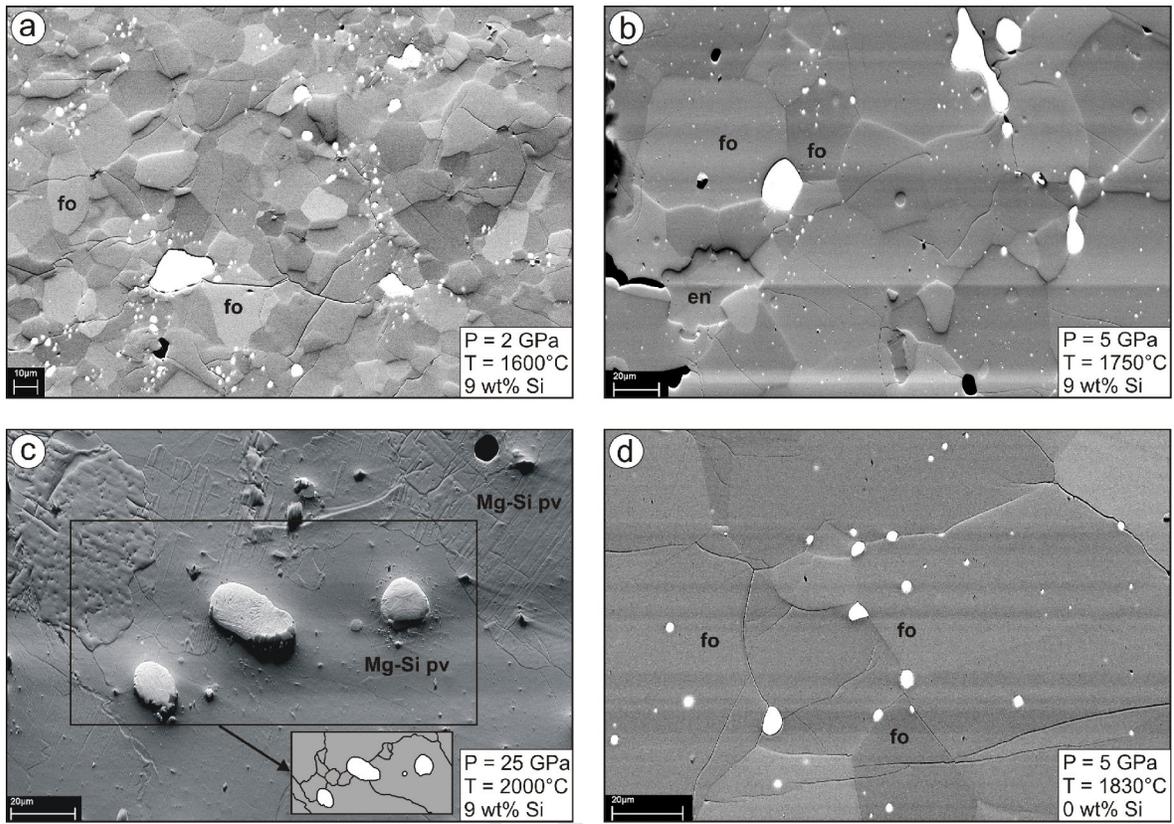
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Figure Caption

Fig. 1: BSE images of typical run products with quenched Fe-alloy melt pockets (white, bright grey in c) contained in a polycrystalline matrix of silicate grains (various grey colours). fo: forsterite, Mg-Si pv: Mg-Si perovskite, en: enstatite. All S-free metal compositions; the wt% values give the Si content in the metal phase of recovered samples. (a) Run product of the piston cylinder experiment at 2 GPa (Dh-1-P1). (b) The silicate phase of an experiment run at 5 GPa additionally shows enstatite, occurring in irregular shaped patches (negative relief) between the forsterite grains (V298) (c) At 25 GPa most of the metal melt occurs as inclusions within the Mg-Si pv. The black areas around the metal blebs are shadows resulting from the strong relief between metal and Mg-Si pv after polishing combined with a low angle of incident of the electron beam (S3533). In the inserted sketch the grain boundaries in the area of the metal blebs are indicated (d) At 5 GPa the highest temperature resulted in complete Si loss from the metal phase (V302).

Fig. 2: Dihedral angles between silicate and metal/metal sulphide melt as a function of the light alloying elements Si, S and O in the melt. All data are for olivine. Data for oxygen are from melts that also contained S. O and S experiments were performed in the range 1623 - 1850 K, while those for Si were performed between 1873 - 2096 K.



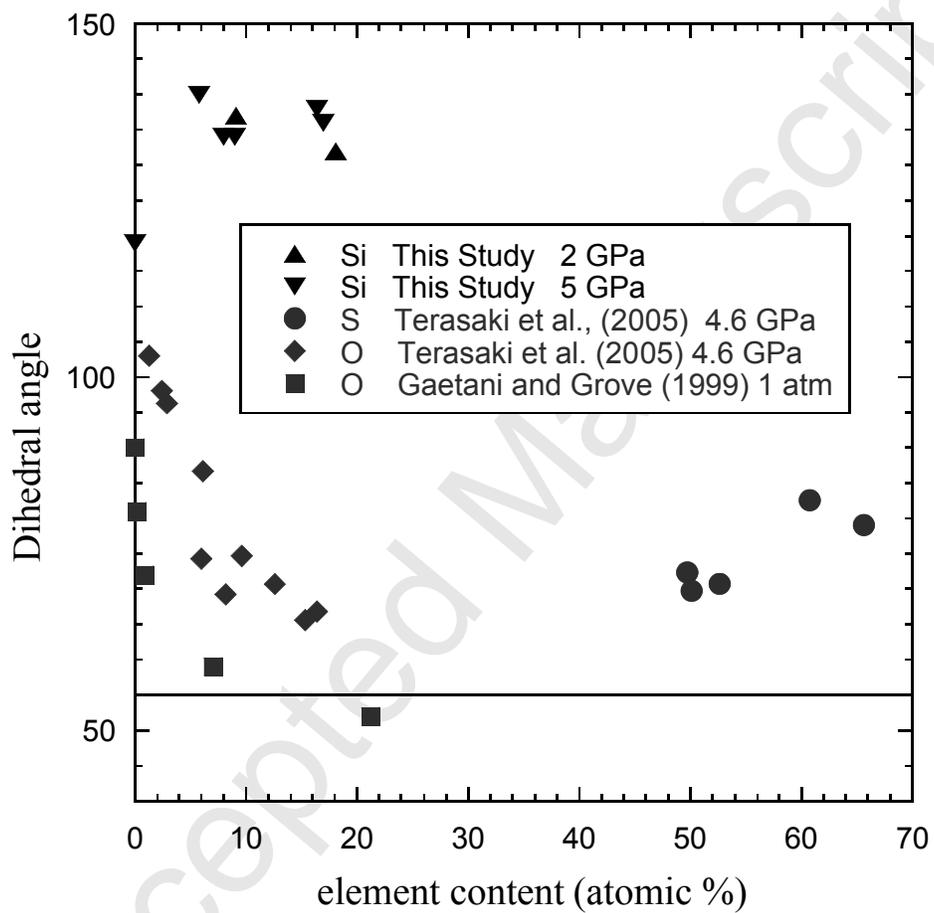


Table 1

Experimental conditions, starting compositions¹ and results.

a) Experiments with Fe-Si alloys

run no.	P (GPa)	T (°C)	Duration (h)	Initial Si content of the alloy (wt%)	Si content in recovered alloy (wt%) ²	Silicate phase ³	Wetting angle (median)	95% C.I. ⁴ -	95% C.I. ⁴ +	Number of angles measured
Dh-1-P1	2	1600	0.75	9.0	9.0	fo	137°	4°	4°	150
Dh-2-P1	2	1600	0.75	17.0	18.0	fo	132°	2°	5°	150
V297	5	1600	19.5	9.0	6.0	fo	140°	6°	3°	90
V298	5	1750	18.8	9.0	9.0	fo	134°	3°	1°	211
V299	5	1750	71.0	9.0	8.0	fo	134°	4°	3°	100
V300	5	1750	31.7	17.0	16.0	fo	138°	5°	5°	78
V313	5	1750	1.5	17.0	17.0	fo	136°	4°	4°	76
V302	5	1830	7.0	9.0	9.0	fo	119°	4°	4°	103
S3533 ⁵	25	2000	2.3	9.0	9.0	Mg-Si pv	≥ 140° ⁶			9

b) Experiment with two liquids: (1) FeS melt and (2) Fe-Si alloy

run no.	P (GPa)	T (°C)	Duration (h)	Initial comp. of metal mix (wt%)	recovered Fe- alloys (wt%) ²	Silicate phase ³	Wetting angle (median)	95% C.I. ⁴ -	95% C.I. ⁴ +	Number of angles measured
V360	2.7	1650	7.0	5.0 Si, 5.0 S	1) 0.1 Si, 36.5 S 2) 5.9 Si, 0.1 S	fo	94° > 120° ⁶	10°	7°	61 -

¹ Melt fraction of Fe-alloy: 5wt%² semiquantitative analysis with EDX device of SEM. Uncertainties of approximately 1 %³ fo: forsterite, Mg-Si pv: Mg-Si perovskite; phases identified with SEM⁴ Error for the median of the angle population based on the 95% confidence interval⁵ Re heater used⁶ semiquantitative value