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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

1. 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 re-equilibration 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 re-equilibration 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 (Bargen 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, $\theta > 60°$, melt will be confined

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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 (Bargen 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°) 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, 2007) but there is some very preliminary 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 terrestial 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 meterorites (Lodders et al., 1993) we performed a low pressure wetting experiment that contained S in addition to Si in the metal melt.

2. 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 $T > 1830$ °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 multianvil cell assembly can be found in Keppler and Frost (2005). The run durations were varied between 0.75 and 71 h. Experiments were quenched by turning off the electrical power to the furnace.

The recovered 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 2D 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