THE EFFECTS OF OXYGEN, SULPHUR AND SILICON ON THE DIHEDRAL ANGLES BETWEEN FE-RICH LIQUID METAL AND OLIVINE, RINGWOODITE AND SILICATE PEROVSKITE: IMPLICATIONS FOR PLANETARY CORE FORMATION. H. Terasaki[1,2], D. C. Rubie[1] U. Mann[1], D. J. Frost[1], and Falko Langenhorst[1,3], [1]Bayerisches Geointitut (Universität Bayreuth, D-95444 Bayreuth, Germany, terasaki@mail.tains.tohoku.ac.jp, dave.rubie@uni-bayreuth.de), [2] Institute of Mineralogy, Petrology and Economic Geology (Tohoku University, Sendai 980-8578, Japan), [3]Institut für Geowissenschaften (Friedrich-Schiller-University Jena, Burgweg 11, D-07749 Jena, Germany).

Introduction: The separation of the Earth's core by porous flow through the solid silicate mantle has been considered improbable on grounds of the high dihedral angles measured between Fe-rich liquids and silicate minerals [1]. At the low Fe metal melt fractions that are relevant to efficient core/mantle separation, the occurrence of melt interconnectivity requires that the dihedral angle between metal and crystals is less than 60^o. There is evidence, however, that the solution of light elements, such as O and S, into Fe-rich liquids can lower dihedral angles significantly [2,3]. In comparison to the Earth, the Martian mantle is more FeO-rich (~ 18 wt %) and the Martian core is believed to contain more sulphur (~ 14 wt %), differences that might have made core formation by porous flow more feasible on Mars. In addition to O and S, Si is also often proposed as a plausible light element in the Earth's core [4]. Fe-Si alloying is particularly relevant to models of core formation that propose a stepwise increase in the redox state of the accreting material over time [5]. In order to investigate the effects of these light elements on the dihedral angles between Fe-rich liquid and silicate minerals, we have performed a series of high-pressure experiments between 3 and 26 GPa, conditions which encompass those of almost the entire Martian mantle. Olivine, ringwoodite and silicate perovskite have been studied over a range of silicate FeO concentrations relevant to core formation on both the Earth and Mars.

Experimental Procedure: High-pressure experiments were carried out using MA8 type multi-anvil apparatus. Relatively large high-pressure octahedral assemblies (18 and 25 mm edge lengths) were employed in conjunction with a 5000 tonne press in order to obtain large sample volumes and to minimize thermal gradients across the samples. Graphite capsules were employed and MgO capsules were used in addition for experiments on Si. Starting materials were mixtures of powdered iron-sulphide (S = 31, 39 and 50 at %) and synthetic olivine (Fe# = FeO/{FeO+MgO} [molar ratio] = 0, 0.1, 0.24 and 0.5) and pyroxenes (Fe# = 0 – 0.16) for perovskite experiments. Values of Fe# = 0.1 and 0.24 are applicable to the mantles of Earth and Mars respectively. $Fe_{91}Si_9$ and $Fe_{83}Si_{17}$ alloys were used for experiments on Si in conjunction with Fe-free silicates. All experiments were performed for between 6 and 72 hours. Imaging and chemical analyses were carried out using SEM/EDX and an electron microprobe. In order to observe microstructure of the Fe-S melt pockets with high magnification, high-resolution imaging was also carried out using transmission electron microscopy (TEM).

Results and Discussion: In the olivine and ringwoodite stability fields texturally-equilibrated dihedral angles decrease slightly with increasing sulphur content but decrease more significantly with increasing FeO content of the silicate phases (Fig. 1). Increasing the FeO content of silicates results in an increase in both the oxygen fugacity and oxygen solubility in the Fe-S melt. Oxygen is therefore much more effective at reducing the dihedral angle than sulphur. This is because of the effectiveness of dissolved oxygen, as a surface-active element, in reducing the metal-silicate interfacial energy.

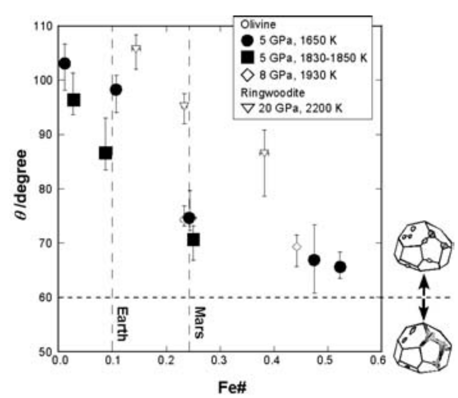


Figure 1. Dihedral angle as a function of Fe# in olivine and ringwoodite. The vertical dashed lines show the likely olivine composition in the mantles of Earth and Mars.

For silicate perovskite the measured dihedral angles also decrease (101^o to 79^o) with increasing FeO content in the perovskite phase as shown in Fig. 2. This tendency is in good agreement with results for olivine and ringwoodite and would seem to be also a result of an increase in the oxygen fugacity and consequently an increase in the measured oxygen content of the Fe-S liquid. In contrast to olivine and ringwoodite experiments, however, as the FeO content of perovskite is increased the concentration of Fe in the Fe-S liquid also increases. As it is unlikely that S is lost from the liquid the only explanation is that FeO in the silicates is being reduced during the experiments. Such a phenomena has only been observed in perovskite experiments and is likely related to the measured increase in the ferric Fe concentration of perovskite with increasing FeO content.

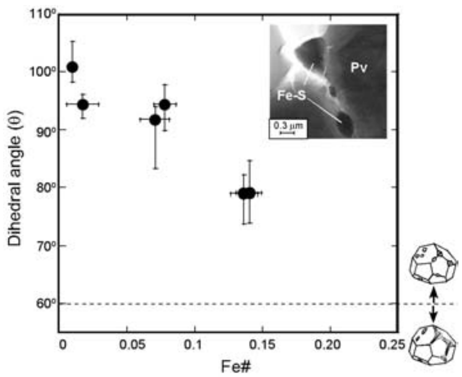
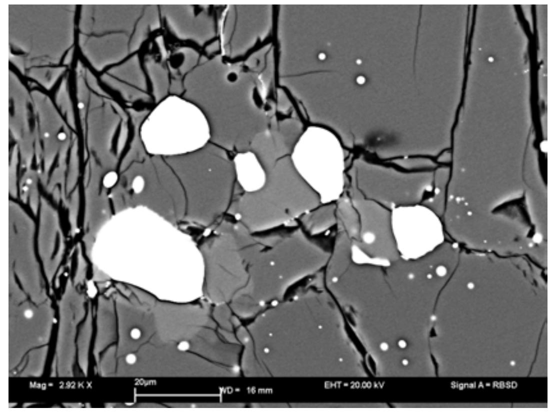


Figure 2. Dihedral angles between silicate perovskite and Fe-S melt (initially $Fe_{61}S_{39}$) as a function of the perovskite Fe#. The dashed line is the wetting boundary of 60°. The inset is a TEM image of Fe-S melt pockets from the experiment at 23 GPa and 2223 K.

As a result of higher oxygen concentrations in Martian core-forming metal liquids the dihedral angle between liquid iron-alloy and silicate crystals would have been much closer to the wetting boundary of 60° than in the Earth's interior. However, over the range of conditions investigated, which encompassed those of the entire Martian mantle, dihedral angles would still have remained above 60°.

Experiments on Fe-Si liquids were performed at 5 GPa and 1750-1850°C. Redox conditions in the experiments were very low and in initial experiments Fe-bearing silicates were reduced to produce tiny metallic Fe droplets that pin grain boundaries and inhibit textural equilibration. Consequently, Fe-free olivine was employed with run times of up to 72 hours to ensure that an equilibrated texture was achieved. Typical textures are shown in Fig. 3. Olvine grain boundaries cannot be seen in normal back scattered electron images (the dark lines in Fig. 3A are only cracks). EBSD (electron back scattered diffraction) images, however, clearly show Fe-Si alloys at well equilibrated olivine triple junctions (Fig. 3B). During the experiments some Si oxidized to form enstatite which can also be seen as the lighter grains in Fig. 3A. Measured dihedral angles between olivine and the Fe-rich liquid are 112° for $Fe_{91}Si_9$ and 107° for $Fe_{83}Si_{17}$. Si clearly has very little effect on interfacial energies between liquid Fe and olivine. Efficient core formation by porous flow in relatively-reduced planetary bodies (e.g. enstatite-chondrite-like) is therefore implausible.



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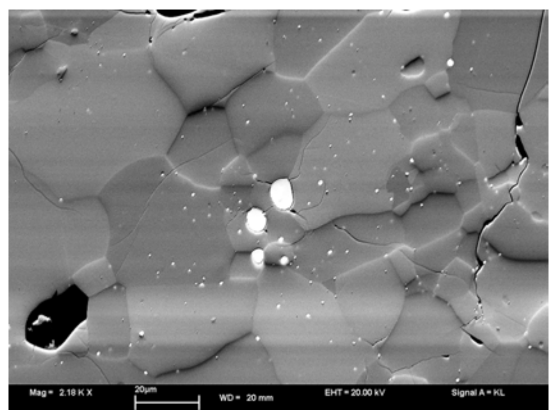

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Figure 3. A) Sample textures from back scattered electron images of forsterite with Fe-Si melt pockets at 5 GPa and 1750°C. K. Some lighter gains of enstatite can be seen adjacent to some melt pockets. B) EBSD image of Fe-Si metal at olivine grain boundaries.

References: [1] Stevenson D.J. (1990) *Origin of the Earth, Oxford University Press*, pp. 231-249. [2] Minarik W.G., Ryerson F.J. and Watson E.B. (1996) *Science*, 272, 530-533. [3] Gaetani G.A. and Grove T.L. (1999) *Earth Planet. Sci. Lett.,* 169, 147-163. [4] Poirier J.P., (1994) *Phys. Earth Planet. Int.*, 85, 319-337. [5] O'Neill H.St.C. (1991) *Geochim., Cosmochim. Acta*, 55, 1159-1172.