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Quantifying the effect of solid phase composition and structure on solid–liquid partitioning of siderophile and chalcophile elements in the iron–sulfur system

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ABSTRACT

We report experimentally determined partition coefficients between solid and liquid phases for bulk compositions on either side of the Fe–FeS eutectic for a suite of siderophile, chalcophile, and lithophile elements. Experiments were performed at conditions of 1.5 and 2 GPa in pressure (*P*), 1323 K in temperature (*T*), and virtually identical eutectic sulfide liquid compositions in equilibrium with either solid face centered cubic Fe or solid FeS. This enabled isolation of the effect of solid phase composition and structure from pressure–temperature–melt composition effects. Solid phase–liquid metal partition coefficients (*D* values) for Ge, Re, Ni, Co, Cr, Mn, V, Sn, Pb, Re and W differ significantly if partitioning occurs between identical metallic liquids but different solid phases, whereas Zn, Cu and Mo are virtually unaffected. For all elements except Ge and Sn, measured solid Fe–liquid sulfide partition coefficients at 1.5 and 2 GPa are inconsistent with model predictions based on atmospheric pressure experiments, indicating that such models may not be appropriate for modeling core crystallization processes at non-ambient pressure.

The framework of a lattice strain-based model of solid–liquid metal partitioning (Stewart et al., 2009) enables us to quantify the effect of the solid phase. Changing the solid phase from Fe to FeS leads to systematic increases in r_0 (from 1.54 to 1.65 Å) and apparent Young's modulus *E* (from 112 to 178 GPa). These systematic changes can be used to predict element partitioning in eutectic solid FeS-bearing systems from measurements in eutectic solid Fe-bearing systems. Although changing the solid phase from face centered cubic Fe to FeS is an end member example, our data suggest that changes with pressure in the structure (e.g., to hexagonally close packed at high pressure) and composition (e.g. to higher S content at high pressure) of solid iron could affect the partitioning of elements between Fe and liquid metal during the solidification of planetary cores.

1. Introduction

Accurate knowledge of the partitioning behavior of trace elements in metal-light element systems is crucial to model processes of planetary differentiation and evolution. For example, interpretations of the trace element compositional trends observed in iron meteorites (Jones and Drake, 1983; Haack and Scott, 1993; Chabot et al., 2003; Chabot and Haack, 2006; Walker et al., 2008) and prediction of the geochemical signatures consequential to the crystallization of the Earth's inner core (e.g. Walker et al., 1995; Brandon et al., 1998, 1999, 2003; Brandon and Walker, 2005), rely heavily on the systematics of element partitioning between solid and liquid phases in semi-molten iron alloy systems (Chabot et al., 2003; Chabot and Jones, 2003; Chabot et al., 2005, 2007; Van Orman et al., 2008; Chabot et al., 2009; Stewart et al., 2009; Chabot et al., 2010, 2011; Hayden et al., 2011).

Partitioning in the presence of sulfur is of particular interest. On a planetary scale, sulfur is believed to be an important constituent of the cores of Mars (e.g. Wanke and Dreibus, 1988; Lodders and Fegley, 1997; Sanloup et al., 1999; Campbell et al., 2007; Stewart et al., 2007), Mercury (e.g. Stevenson et al., 1983; Harder and Schubert, 2001; Breuer et al., 2007; Margot et al., 2007; Chen et al., 2008; Hauck et al., 2013), Ganymede (Hauck et al., 2006; Williams, 2009), and the Moon (Weber et al., 2011; Rai and van Westrenen, 2012). Estimated sulfur contents in these bodies are such that core cooling leads to the crystallization of either Fe-rich metal (Earth, Moon) or iron sulfide (Mars, Mercury, Ganymede). On a smaller scale, many magmatic sulfide ore deposits are found to be compositionally zoned with parts enriched in Ir, Os, Ru and Rh along with Fe, while other parts are enriched in Pd, Pt and Au along with Cu (Li et al., 1996). This zonation is thought to be a consequence of the fractional crystallization of monosulfide solid solution from sulfide liquid (Naldrett et al., 1982; Li et al., 1992; Li and Naldrett, 1994; Zientek et al., 1994; Li et al., 1996).

Element partitioning between solid Fe and S-bearing metallic liquid has been studied extensively at atmospheric pressure conditions, as

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recently reviewed by Chabot et al. (2011). The majority of existing studies conclude that the composition of the metallic liquid (i.e., the concentration of S and/or other non-metals in the melt) is the dominant factor that controls solid–liquid partitioning. For example, increasing amounts of sulfur in the metallic liquid inhibit the partitioning into solid Fe for elements such as Cu and Ag, and favor the partitioning into Fe for other elements including Ni, Co, W, Mo, Ga, Ge, As and the PGEs (Chabot et al., 2011).

Jones and Malvin (1990) provided a parameterization method to predict element partitioning in Fe-light element systems between solid metal and molten metal phases, incorporating liquid properties only. In their method, the metallic liquid is assumed to consist of metal and non-metal bearing domains, and the fractions of these domains are the primary factors that control element partitioning. Subsequent work has shown this parameterization to be very successful in predicting partition coefficients (D values, defined as the ratio by weight of element concentrations in the solid and liquid phases) at 0.1 MPa, on the Fe-rich side of the eutectic composition in the simple systems Fe–Ni–X (X = S, P, C) and Fe–Ni–S–P (Chabot and Jones, 2003; Chabot et al., 2003, 2009, 2010).

A limited experimental data set exists for solid Fe–liquid sulfide partitioning at elevated pressure (e.g., Jones and Walker, 1991; Walker, 2000; Lazar et al., 2004; Van Orman et al., 2008; Walker and Li, 2008; Hayashi et al., 2009; Stewart et al., 2009; Chabot et al., 2011). These high-pressure studies vary significantly in terms of pressure, temperature, sulfur content of the metallic liquid and the suite of studied elements, limiting our ability to assess the effect of pressure on partitioning. For the Fe–S system, Chabot et al. (2011) recently presented results from partitioning experiments at 9 GPa which show that 0.1 MPa parameterizations of solid Fe–liquid sulfide partition coefficients based on liquid metal compositions do not hold at elevated pressures for many elements including Co, Pd, Sn, Sb and Au. The reason for this observation is unclear.

In parallel with the growth of high-pressure partitioning studies in semi-molten metallic systems, Stewart et al. (2009) demonstrated that the crystal-lattice strain model commonly used to describe silicate mineral–silicate melt partitioning (Blundy and Wood, 1994, 2003) can be successfully applied to D values in partially molten metallic systems at both 0.1 MPa and high pressure. The fact that this model can be successfully applied implies that the structure and/or composition of the solid metal may also play a non-negligible role in determining solid metal/molten metal partitioning. To date this model has not been tested in Fe–S systems with sulfide as the solid phase.

In summary, the effects of pressure, temperature, solid and liquid composition on element partitioning are not sufficiently well known to enable reliable modeling of the geochemical effects of metal solidification in planetary interiors. Here, we specifically investigate the effect of the composition and structure of the solid phase in the Fe–S system on solid phase/liquid sulfide melt partitioning. We obtained element partitioning data at pressures of 1.5 and 2 GPa for a suite of siderophile, chalcophile and lithophile elements including Ni, Co, W, Mo, V, Nb, Ta, Sn, Cu, Pb, Zn, Cr, Mn, and Ge. We performed pairs of experiments close to the eutectic temperature with two bulk compositions on either side of the eutectic composition. As a result, for each pair, the resulting melt compositions are nearly identical in S content (i.e., very close to eutectic compositions), but the solid phase has widely different composition and structure (i.e., either fcc Fe or FeS). This allows us to (a) assess how well predictive models of solid Fe–liquid sulfide based on 0.1 MPa data perform for experiments at 1.5–2 GPa (b) assess whether the crystal lattice strain model can also be applied to solid FeS–liquid sulfide partitioning data and (c) quantify the effect of the solid phase on partitioning, in isolation from pressure–temperature–melt compositional effects.

2. Experimental methods and analytical techniques

Starting mixtures were prepared from high-purity metallic powders of Fe and FeS (>99.5% purity) and doped with several hundred ppm levels of trace elements Ni, Co, W, Mo, V, Nb, Ta, Sn, Cu, Pb, Zn, Cr, Mn, Ge, and Re (added in the form of pure metallic powders and sulfides). The mixtures were intimately mixed under ethanol in an agate mortar for 30 min and then allowed to dry under a heat lamp. Nominal starting compositions are given in Table 1.

Experiments were performed using a Depths of the Earth QUICKPress piston cylinder apparatus at VU University Amsterdam, the Netherlands. Alumina was the chosen sample container for all experiments. The pressure cell consisted of concentric sleeves of natural talc (outer), pyrex glass (inner) and graphite furnace. Sample capsules were 3 mm in diameter and 4.5 mm in length with a ~2.7 mm^3 sample chamber. A W5Re/W26Re (type C) thermocouple was placed directly above the capsule to monitor the temperature. The temperature variation along the sample chamber is estimated to be no more than ~5 °C (Watson et al., 2002). Pressure calibration was based on locating the phase boundaries for the reactions fayalite + quartz = ferrosillite and albite = jadeite + quartz (Van Kan Parker, 2011; Van Sijl, 2011). The resulting friction correction is <3%, in agreement with previous calibrations of similar assemblies (McDade et al., 2002).

Following Walker (2000), experiments were heated to 1073 K at high pressure and allowed to sinter for 10 h before the temperature was raised at a rate of 50 K/min to the target value. All experiments were run for 24 h at final pressure–temperature conditions to ensure chemical equilibration between the solid and molten phases. Quenching was achieved by turning off the power to the furnace. Malvin et al. (1986) have shown that run durations as short as 5 h were sufficient to approach chemical equilibrium in this type of experiment. Furthermore, Chabot et al. (2011) demonstrated that at 1323 K and 9 GPa, the solid Fe/liquid sulfide melt trace element partition coefficients obtained from two experiments with 2 and 6 hour run durations agreed to within two standard deviations, suggesting equilibration at timescales much shorter than our run times.

The quenched experimental charges were mounted in epoxy resin and polished to a <1 μm finish using diamond polishing techniques. The polished mounts were then carbon-coated for chemical analysis. The experimental charges were analyzed for Fe and S concentrations with a JEOL JXA-8800 electron microprobe at VU University Amsterdam, using a 20 kV accelerating voltage and 15 nA beam current, and acquisition times of 20 s. Pure Fe metal and FeS_2 (pyrite) were the chosen standards for Fe and S respectively. On average between 10 and 15 analyses were undertaken for each phase to determine the bulk composition as accurately as possible, using a 20 μm defocused electron beam to analyze the molten phase. Concentrations of trace elements Ni, Co, Cr, Mn,V, Cu, Zn, Ge, Nb, Ta, Sn, Re, W, Mo and Pb were determined by LA-ICP-MS at the Institute of Geochemistry and Petrology of ETH Zurich, Switzerland. A beam-homogenized 193 nm ArF excimer laser ablation system

Table 1
Nominal chemical compositions of starting materials (wt.%).

	F2	S1
FeS	31.83	91.50
Fe	66.88	6.62
V	0.005	0.006
Cr	0.005	0.009
Mn	0.050	0.005
Co	0.150	0.150
Ni	0.150	0.210
Cu	0.200	0.350
Zn	0.005	0.040
Ge	0.050	0.450
Nb	0.005	0.010
Mo	0.005	0.050
Sn	0.150	0.220
Ta	0.005	0.010
W	0.090	0.060
Re	0.120	0.010
Pb	0.300	0.300