Pressure, sulfur, and metal-silicate partitioning: The effect of sulfur species on the parameterization of experimental results

NEIL R. BENNETT1,* AND YINGWEI FEI1

1Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015, U.S.A.

ABSTRACT

Performing well-controlled metal-silicate partitioning experiments at conditions directly simulating those of a deep magma ocean is difficult. It is therefore common to perform experiments at lower pressures and temperatures, which are used to determine the effects of salient variables. Often, these effects are determined by multiple linear regression of a data set covering a large range of \( P-T \)-composition space. In particular, these data sets often contain the results of experiments performed both with and without sulfur in the system. Data are often regressed, however, using a relationship based only upon the formation of oxide species in the silicate melt. Several studies have suggested that when sulfur is present in the system, siderophile trace metals may also dissolve into silicate melt as S-bearing species. We have derived a relationship for regressing experimental metal-silicate partitioning data that considers the formation of both oxide and sulfide species in the silicate melt. Using model data sets, we have assessed the ability of this relationship, and the more typical single-species relationship, to accurately parameterize data in which the formation of S-bearing species is important. We have also applied this new relationship to experimental results on the metal-silicate partitioning of gold and find it is able to reconcile the conflicting pressure dependencies of \( \ln D_{\text{met/sil}}^{\text{Au}} \) found in previous studies.

Keywords: Sulfur, core formation, chalcophile, siderophile, speciation, high pressure

INTRODUCTION

Many studies seek to constrain the conditions of planetary core formation by comparing the composition of primitive mantle estimated from the rock record with that predicted by forward models based upon experimental results. The experiments used in these forward models equilibrate trace-element doped metal and silicate melts at high pressure and temperature, from which metal-silicate partition coefficients \( D^{\text{metal}} \) are determined. Alternatively, for the most siderophile (iron-loving) elements, silicate melts are saturated in the trace element of interest, and \( D^{\text{metal}} \) is calculated from the resulting solubility data. Most metal-silicate partitioning data have been produced at pressures below \( \sim 27 \) GPa due to the difficulty of achieving higher pressures using large-volume press techniques. Although these conditions overlap with lower estimates for the maximum depth of core-segregation from a magma ocean (e.g., Li and Agee 1996; Righter et al. 1997), it is significantly below the maximum pressures invoked in some studies (e.g., 40–80 GPa; Corgne et al. 2009; Rubie et al. 2011; Siebert et al. 2013). Considerable extrapolation of the experimentally determined metal-silicate partition coefficients to relevant conditions is therefore required. This is typically achieved by parameterizing the available data using multiple linear regression, as a function of pressure \( (P) \), temperature \( (T) \), composition, and in some cases oxygen fugacity \( (f_{O_2}) \). These parameterizations are based on reactions where the element of interest dissolves in silicate melt as an oxide species. For systems containing sulfur, however, it has been suggested for several elements that the formation of sulfur-bearing complexes is important (e.g., Botcharnikov et al. 2010; Laurenz et al. 2013; Mungall and Brenan 2014; Bennett et al. 2016). Here, we consider whether these elements require a different approach to parameterization, to account for the coupled effects of pressure that arise from both the partial molar volume of reaction and changes to the distribution of sulfur between metal and silicate phases. We derive a new form for parameterizing the data from sulfur-bearing experiments and demonstrate the potential for erroneously extrapolating \( D_{\text{metal}}^{\text{metal}} \) with pressure when sulfur-bearing data are parameterized in the traditional manner. We also use existing metal-silicate partitioning data for Au to explore the ability of our new relationship to explain real-world observations. To better test the veracity of this new relationship, however, experiments are needed that target the \( P-T \) composition conditions and elements for which coupled pressure-sulfur effects are expected to be most apparent.

SULFUR IN SILICATE MELTS AND THE EXISTENCE OF METAL-SULFUR COMPLEXES

Although oxygen is the dominant anion in silicate melts over most terrestrial conditions, sulfur can dissolve in significant quantities as conditions become suitably reducing (\( \leq 16 \) wt% \( S \)) (Namur et al. 2016; Wood and Kiseeva 2016). Below the fayalite-magnetite-quartz buffer (FMQ) sulfur dissolves as \( S^2- \) and is often considered to replace oxygen bonded to iron (e.g., Mavrogenes and O’Neill 1999; Mérich et al. 2009). Significant increases in \( S \) solubility with more reducing conditions, however, do not manifest until below ~IW-2 and depend upon temperature (Namur et al. 2016). As conditions become highly reducing, the sulfur content of silicate melt can exceed the iron content and Namur et al. (2016) suggest in these instances that reaction with Mg and Ca is a significant solution mechanism for \( S \). This assertion is supported by the Raman spectra of silicate melts in equilibrium with sulfide liquid, which display increasingly intense peaks corresponding to MgS and CaS with decreasing \( f_{O_2} \) (IW-3.6 to -8.4) and increasing \( S \) content (Namur et al. 2016). Terrestrial core-formation is associated with rela-

* E-mail: nbennettgeo@gmail.com

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