Sulfur solubility in the Earth magma ocean – testing the hypothesis of the "Hadean matte".

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Sulfur is one of the most abundant elements on Earth (1.7 wt.% (Palme and Zipfel, 2017), but most of Earth's sulfur is concentrated in the core (Dreibus and Palme, 1996) with estimates for the Bulk Silicate Earth (BSE) being a modest 200-250 μg/g (McDonough and Sun, 1995; Palme and O'Neill, 2013). Despite only being a trace element in Earth's mantle, sulfur punches well above its weight as it will be difficult to find a magmatic process on Earth that is not affected by sulfur and its geochemical behaviour. Through precipitation of sulfide, sulfur allows for the concentration of precious chalcophile (sulfur-loving) metals eventually leading to the formation of mineral deposits. Volcanic emissions of sulfur dioxide can have a severe impact on climate, as evidenced by the eruption of Mt. Pinatubo in June 1991, which introduced approximately 20 million tons of SO_2 into the atmosphere (Bluth et al., 1992) and caused short-term global cooling. The sequestration of sulfide liquid into the Earth's core during the early stages of Earth's accretion might have had a profound effect on the concentrations of many elements found in the BSE. To quantify any of these processes, the behaviour of sulfur in geological processes has been the focus of many research papers in the past 60+ years (see review by Baker and Moretti, 2011). An important milestone was achieved by Fincham and Richardson (1954) who showed that at an average mantle fO_2, sulfur is dissolved in the silicate melt predominantly as S^{2-}.

A way to assess the amount of sulfur in silicate melts, is to refer to sulfur solubility or sulfur concentration at sulfide saturation (SCSS), a term, introduced by Shima and Naldrett in 1975 (Shima and Naldrett, 1975). In the past 60 years there were produced more than 20 sulfur solubility and SCSS models, considering the effects of pressure, temperature, silicate and sulfide liquid compositions as well as oxygen and sulfur fugacities of the system (Baker and Moretti, 2011). Most models show that SCSS is positively correlated with temperature and fO_2, and negatively correlated with pressure and fS_2. Apart from a range of FeO < 5 wt%, SCSS is also increasing with the increasing FeO content of the silicate liquid and decreasing almost linearly with Fe/(Fe+Ni+Cu) of the sulfide liquid (Smythe et al., 2017). Despite thorough investigation of SCSS over the wide range of conditions, surprisingly, up until now, there were no studies that systematically addressed the pressure effect on SCSS at relatively high pressures (>10 GPa) applicable to the conditions of magma ocean. The only two models that considered high-pressure conditions had a very limited number of experiments at above 10 GPa which potentially increase the uncertainties while extrapolating to the transition zone and lower mantle pressures (Laurenz et al., 2016; Smythe et al., 2017).

In this issue, Blanchard et al. reports 25 multi-anvil experiments to study SCSS at pressures of 7-23 GPa (corresponding to approximately 200-700 km depths) and temperatures of 2173-2623 K (1900-2350 ^{o}C). Current-day mantle is significantly cooler, with mantle adiabat temperatures estimates of around 1500-1700 ^{o}C at 23 GPa (Mckenzie and Bickle, 1988). However, these temperatures could have been reached at the early stages of Earth history, when the planet was fully or partially molten. The starting mixtures contained two layers of silicate powders of peridotitic composition with a layer of FeS sulfide sandwiched between them.

To assess the effects of pressure and temperature on SCSS individually, Blanchard et al. conducted sets of experiments, fixing one parameter at a time. In the first set of experiments, a constant temperature of 2473 K was used, and pressures were varied between 7 and 23 GPa. In the second set of experiments, the authors fixed the pressure at 8 GPa and 11 GPa and varied temperatures between 2173 and 2623 K.

All experiments produced a sulfide blob and quenched silicate melt around it. The results were quite astounding. Between 7 and 23 GPa and at a constant temperature of 2473 K, SCSS drops by almost an order of magnitude from ~11,000 to 1650 μg/g and the trend is close to linear (see figure 2a in Blanchard et al.). The variations of SCSS with temperature are just as large. At a fixed pressure of 8 GPa, the authors observe an increase in SCSS between 3000 and 11,000 μg/g. Interestingly, we almost see a competing effect of pressures and temperatures as these two parameters simultaneously increase with the depth, but have the opposite effect on SCSS (e.g. Liu et al., 2007).

Multiple simulation models suggest that the Earth is likely to have accreted through several giant impacts (Agnor et al., 1999; de Vries et al., 2016). These impacts resulted in extensive melting and formation of deep magma oceans that most likely were present on Earth for a relatively long time, comparable to the intervals between multiple impacts (de Vries et al., 2016). Blanchard et al. model SCSS in a magma ocean up to 80 GPa (~2000 km) along peridotite melting temperature and along 80 GPa adiabat and show that with the increasing depth, the SCSS decreases down to ~450 ppm at 80 GPa, which agrees with previous models (Laurenz et al., 2016; Smythe et al., 2017). At pressures of 10-40 GPa, however, the new SCSS model predicts a higher sulfur solubility (by 20-60%) than previously thought. This may have implications for modelling the "Hadean matte", an hypothetical fraction of immiscible sulfide-rich liquid that presumably segregated from the magma ocean, and, due to its density sank into the core. The idea of putative Hadean matte was proposed by Hugh O'Neill (1991), who found an elegant explanation for the observed depletion of siderophile elements in the BSE. If there were one or more pulses of Hadean matte, depending on the P-T conditions, it would be possible to explain the depletion of chalcophile and, in particular, siderophile elements in the BSE (Rubie et al., 2016). If the initial S contents of Earth were close to chondritic, low SCSS at higher pressures (> 60 GPa) provide further support for the existence of an Hadean matte in equilibrium with the deep magma ocean, inferring that most of S on Earth will be sequestered into the core through immiscible sulfide liquid.

Thus, Blanchard et al. added another "brick" into the big picture of understanding how sulfur and sulfur-loving elements behave in geological processes. This article will allow better estimates of the processes occurred during the early accretion, before the Earth's mantle was fully solidified.

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