

The quintet completed: The partitioning of sulfur between nominally volatile-free minerals and silicate melts

SARA CALLEGARO^{1,2,*}, KALOTINA GERAKI³, ANDREA MARZOLI¹, ANGELO DE MIN⁴,
VICTORIA MANETA⁵, AND DON R. BAKER⁵

¹Department of Geosciences, University of Padova, via Gradenigo 6-35131 Padova, Italy

²Centre for Earth Evolution and Dynamics, University of Oslo, Sem Sælands vei 2A, 0371 Oslo, Norway

³Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, U.K.

⁴Department of Mathematics and Geoscience, University of Trieste, via Weiss 2, 34128 Trieste, Italy

⁵Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Quebec, Canada

ABSTRACT

Magmatic systems are dominated by five volatiles, namely H₂O, CO₂, F, Cl, and S (the igneous quintet). Multiple studies have measured partitioning of four out of these five volatiles (H₂O, CO₂, F, and Cl) between nominally volatile-free minerals and melts, whereas the partitioning of sulfur is poorly known. To better constrain the behavior of sulfur in igneous systems we measured the partitioning of sulfur between clinopyroxene and silicate melts over a range of pressure, temperature, and melt composition from 0.8 to 1.2 GPa, 1000 to 1240 °C, and 49 to 66 wt% SiO₂ (13 measurements). Additionally, we determined the crystal-melt partitioning of sulfur for plagioclase (6 measurements), orthopyroxene (2 measurements), amphibole (2 measurements), and olivine (1 measurement) in some of these same run products. Experiments were performed at high and low oxygen fugacities, where sulfur in the melt is expected to be dominantly present as an S⁶⁺ or an S²⁻ species, respectively. When the partition coefficient is calculated as the total sulfur in the crystal divided by the total sulfur in the melt, the partition coefficient varies from 0.017 to 0.075 for clinopyroxene, from 0.036 to 0.229 for plagioclase, and is a maximum of 0.001 for olivine and of 0.003 for orthopyroxene. The variation in the total sulfur partition coefficient positively correlates with cation-oxygen bond lengths in the crystals; the measured partition coefficients increase in the order: olivine < orthopyroxene < clinopyroxene ≤ amphibole and plagioclase. At high oxygen fugacities in hydrous experiments, the clinopyroxene/melt partition coefficients for total sulfur are only approximately one-third of those measured in low oxygen fugacity, anhydrous experiments. However when the partition coefficient is calculated as total sulfur in the crystal divided by S²⁻ in the melt, the clinopyroxene/melt partition coefficients for experiments with melts between ~51 and 66 wt% SiO₂ can be described by a single mean value of 0.063 ± 0.010 (1σ standard deviation about the mean). These two observations support the hypothesis that sulfur, as S²⁻, replaces oxygen in the crystal structure. The results of hydrous experiments at low oxygen fugacity and anhydrous experiments at high oxygen fugacity suggest that oxygen fugacity has a greater effect on sulfur partitioning than water. Although the total sulfur clinopyroxene-melt partition coefficients are affected by the Mg/(Mg+Fe) ratio of the crystal, partition coefficients calculated using S²⁻ in the melt display no clear dependence upon the Mg# of the clinopyroxene. Both the bulk and the S²⁻ partition coefficients appear unaffected by ¹⁸O in the clinopyroxene structure. No effect of anorthite content nor of iron concentration in the crystal was seen in the data for plagioclase-melt partitioning. The data obtained for orthopyroxene and olivine were too few to establish any trends. The partition coefficients of total sulfur and S²⁻ between the crystals studied and silicate melts are typically lower than those of fluorine, higher than those of carbon, and similar to those of chlorine and hydrogen. These sulfur partition coefficients can be combined with analyses of volatiles in nominally volatile-free minerals and previously published partition coefficients of H₂O, C, F, and Cl to constrain the concentration of the igneous quintet, the five major volatiles in magmatic systems.

Keywords: Clinopyroxene/melt sulfur partitioning, equilibrium melts, magmatic volatiles, synchrotron micro X-ray fluorescence