The effect of fO_2 and composition on sulphur solubility and speciation in hydrous silicate systems

K. KLIMM[1], S.C. KOHN[1], R. BOTCHARNIKOV[2] AND M.E. SMITH[3]

[1]Department of Earth Sciences, University of Bristol, UK (K.Klimm@bristol.ac.uk)
[2]Institute for Mineralogy, University of Hanover, D
[3]Department of Physics, University of Warwick, UK

The release of volcanic gases is monitored worldwide. The flux of SO_2 in the plume and the S/Cl ratio vary systematically with the style of volcanic activity [1]. In order to relate these volcanic gas signatures to processes inside the volcanic edifice the mechanisms of sulphur incorporation in melts and the transfer into a fluid phase has to be known. Sulphur has several oxidation states and fO_2 is a crucial control on the sulphur solubility and hence the transfer of sulphur from a magma into a vapour phase.

In this study the sulphur solubility and speciation was determined for various hydrous iron-free silicate glasses equilibrated with sulphur at geological relevant P-T-fO_2 conditions. Glass compositions include “simple” (e.g. $K_2Si_4O_9$, $Rb_2Si_4O_9$) and more complex compositions (Albite, Trondhjemite). Experiments were performed in CSPV and IHPV at fO_2s ranging from QFM-0.7 to QFM+4.

The total sulphur solubility is a function of the degree of polymerisation of the silicate glasses and increases with increasing NBO/T. At reducing conditions (QFM) highly depolymerized glasses dissolve twice the amount of S (up to ~2 wt. %) compared to oxidising conditions (QFM+4). In runs that were saturated with sulphur, sulphate/sulfide blebs were identified, indicating the presence of an immiscible sulphate/sulfide liquid.

The oxidation state of sulphur dissolved in the glasses and the relative abundances of S-species were determined by XANES. Stable S-species in the glasses are sulfide (S^{2-}) and/or sulfate (S^{6+}) as previously demonstrated [2]. The occurrence of sulfite (S^{4+}) in the XANES experiments is demonstrated to be due to beam damage. The S^{6+}/S^{2-} ratio in the glass is a function of fO_2. At fO_2 > QFM+1.5 sulphur is dissolved as S^{6+}. At fO_2 ~ QFM sulphur is dissolved as a mixture of S^{6+} and S^{2-}. The lowest fraction of S^{6+} was ~0.25 at a fO_2 ~ QFM-0.7. The relatively steep change of S^{6+}/S^{2} ratio with fO_2 is in the range of QFM-1. This is at two orders of magnitude lower fO_2 than previously reported for Fe-bearing systems (QFM+1, [2]). Thus, for a fixed fO_2 at ~QFM sulphur is dissolved as mostly S^{2-} in Fe-bearing systems and as S^{6+} in Fe-free systems. This is of importance for natural processes that result in a dramatic change of the prevailing Fe/S ratio (e.g. slab melting, metasomatism, immiscible S-liquids) and has to be implicated in models aiming to quantify the sulphur flux at volcanoes.

Reference

[1] Aiuppa *et al*. (2004*) EPSL* **222,** 469
[2] Carroll & Rutherford (1985) *Am. Mineral.* **73,** 845

Jarosite and goethite identified by Mössbauer spectroscopy on the surface of Mars: Mineralogical evidence for aqueous processes

G. KLINGELHÖFER[1], R.V. MORRIS[2], D. RODIONOV[1,3], C. SCHRÖDER[1], IRIS FLEISCHER[1], A. YEN[4] AND D. MING[2]

[1]Institut Anorganische u. Analytische Chemie, Johannes Gutenberg Universität Mainz, 55099 Mainz, Germany (klingel@mail.uni-mainz.de)
[2]NASA Johnson Space Center, Houston, TX 77058, USA
[3]Space Research Institute IKI, Moscow, Russia
[4]Jet Propulsion Laboratory, Pasadena, CA 91109 , USA

The Mars Exploration Rovers (MER) Spirit and Opportunity have explored the Martian surface at Gusev Crater and Meridiani Planum for more than 3 Earth years, traveling more than ~ 10km (Opportunity) and ~ 7km (Spirit), each carrying our Mössbauer Spectrometer (MBS) MIMOS II [1]. Each of the instruments have analyzed more than 100 targets during their ongoing missions (>1100 sols). More than 15 different minerals have been identified so far by the Mössbauer instruments on board the two rovers [2,3,4]. Mössbauer spectroscopy identified the secondary Fe^{3+}-bearing minerals jarosite, hematite, and nanophase iron oxides in the sulfate-rich outcrop rocks at Meridiani Planum [3]. The sulfate rich outcrop material covers the whole area Opportunity traveled across so far, without significant changes in the mineralogical composition. At Gusev Crater rocks are much more diverse, ranging from little altered basaltic material in the plains to pervasively altered basalt in the Columbia Hills [2,4]. Secondary minerals include the Fe^{3+}-bearing minerals hematite, goethite, nanophase iron oxides, and an unspecified iron sulfate phase. The relation between primary and secondary minerals varies over short spatial scales. Recent results from Gusev Crater indicate the presence of hematite in greater abundance than in many targets at Meridiani.

In particular the minerals jarosite and goethite [5] found at Meridiani Planum and Gusev Crater, respectively, are clear mineralogical evidence for aqueous weathering processes active at both landing sites in the past.

References

[1] Klingelhöfer *et al., J. Geophys. Res.* **108(E12)** (2003) doi:10.1029/2003JE002138.
[2] R.V Morris *et al*. (2004) *Science* **305**, 833-836.
[3] G. Klingelhöfer *et al*. (2004) *Science* **306,**
[4] R.V. Morris *et al*. (2006) *JGR* **111**, E02S13.
[5] G. Klingelhöfer *et al*. (2005) *Hyperfine Interactions* **166**, 549-554.