

A Raman calibration for the quantification of SO_4^{2-} groups dissolved in silicate glasses: Application to natural melt inclusions

**YANN MORIZET^{1,*}, EMANUELA GENNARO^{2,3}, SÉBASTIEN JEGO², ZOLTAN ZAJACZ⁴, GIADA IACONO-MARZIANO²,
MICHEL PICHAVANT², IDA DI CARLO², CLÉMENT FERRAINA², AND PRISCILLE LESNE²**

¹Laboratoire de Planétologie et Géodynamique de Nantes (LPGN) UMR 6112 CNRS, Université de Nantes, Nantes Atlantique Universités,
2 rue de la Houssinière, 44322 Nantes, France

²Institut des Sciences de la Terre D'Orléans (ISTO) UMR 7327 CNRS, Université d'Orléans BRGM, Campus Géosciences,
1A rue de la Férolierie, 45071 Orleans Cedex 2, France

³Dipartimento Scienze della Terra e del Mare (DiSTeM), Università di Palermo, via Archirafi, 22, 90123 Palermo, Italy

⁴Department of Earth Sciences, University of Toronto, 22 Russell Street, Toronto, Ontario M5S 3B1, Canada

ABSTRACT

Sulfur is an important volatile element involved in magmatic systems. Its quantification in silicate glasses relies on state-of-the-art techniques such as electronprobe microanalyses (EPMA) or X-ray absorption spectroscopy but is often complicated by the fact that S dissolved in silicate glasses can adopt several oxidation states (S^{6+} for sulfates or S^{2-} for sulfides). In the present work, we use micro-Raman spectroscopy on a series of silicate glasses to quantify the S content. The database is constituted by 47 silicate glasses of various compositions (natural and synthetic) with S content ranging from 1179 to 13 180 ppm. Most of the investigated glasses have been synthesized at high pressure and high temperature and under fully oxidizing conditions. The obtained Raman spectra are consistent with these f_{O_2} conditions and only S^{6+} is present and shows a characteristic peak located at $\sim 1000 \text{ cm}^{-1}$ corresponding to the symmetric stretch of the sulfate molecular group ($\nu_1 \text{SO}_4^{2-}$). The intensity of the $\nu_1 \text{SO}_4^{2-}$ peak is linearly correlated to the parts per million of S^{6+} determined by EPMA. Using subsequent deconvolution of the Raman spectra, we established an equation using the ratio between the areas of the $\nu_1 \text{SO}_4^{2-}$ peak and the silicate network species (Q^n) in the high-frequency region:

$$\text{ppm S}^{6+} = 34371 \frac{A\text{SO}_4^{2-}}{A\text{Q}^n} \pm 609.$$

We tested our calibration on several silicate glasses equilibrated under moderately reducing conditions ($\text{QFM}+0.8 \leq f_{\text{O}_2} \leq \text{QFM}+1.4$) in which S is dissolved as both SO_4^{2-} and S^{2-} . We also analyzed several olivine-hosted melt inclusions collected from Etna for which the f_{O_2} and S speciation are unknown. For these samples, the S content estimated by the Raman calibration is systematically lower than the total S measured by EPMA. We combined both methods to estimate the S^{2-} content not accounted for by Raman and derive the S speciation and f_{O_2} conditions. The derived f_{O_2} is consistent with the imposed f_{O_2} for synthesized glasses and with current assumed f_{O_2} conditions for basaltic melt inclusions from Etna.

Keywords: Micro-Raman spectroscopy, S content, silicate glass, melt inclusions, S speciation, redox conditions