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The oxidation state of iron in basaltic glasses

A.J. BERRY¹, H.ST.C. O'NEILL¹, M.C. ROWE², J.F.W. MOSSELMANS³, AND C. RIVARD⁴

¹Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia
(*correspondence: Andrew.Berry@anu.edu.au)

²School of Environment, University of Auckland, New Zealand

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

⁴European Synchrotron Radiation Facility, B.P. 220, Grenoble 38043, France

The oxidation state of Fe, $\text{Fe}^{3+}/\Sigma\text{Fe}$ (where $\Sigma\text{Fe} = \text{Fe}^{2+} + \text{Fe}^{3+}$) in basaltic glasses reflects the oxygen fugacity ($f\text{O}_2$) of the melt. $\text{Fe}^{3+}/\Sigma\text{Fe}$ is frequently determined by redox titrations, Mössbauer spectroscopy, and XANES spectroscopy (which has the advantage of micron spatial resolution). The average $\text{Fe}^{3+}/\Sigma\text{Fe}$ of mid-ocean ridge basalt (MORB) glasses determined by XANES, calibrated against standards for which $\text{Fe}^{3+}/\Sigma\text{Fe}$ was determined by Mössbauer, is 0.098(17). This is consistent with the most recent value determined by redox titration [1]. Our interpretation of the Mössbauer spectra of the standards removes the problem of resolving $\text{Fe}^{3+}/\Sigma\text{Fe}$ values less than ~ 0.1 in basaltic glasses, produces isomer shift and quadrupole splitting values for Fe^{3+} that are independent of $\text{Fe}^{3+}/\Sigma\text{Fe}$ (as is the case for Fe^{2+}), and gives $\text{Fe}^{3+}/\Sigma\text{Fe}$ values that are consistent with the thermodynamically expected dependence on $f\text{O}_2$. For $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.098$ the average $f\text{O}_2$ of MORB will be very close to that of the quartz-fayalite-magnetite (QFM) buffer.

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ value of a basaltic melt may be changed by degassing of volatiles. Degassing of H_2O and CO_2 will have no effect on $\text{Fe}^{3+}/\Sigma\text{Fe}$, however, degassing of S, which is dissolved in basaltic melts as either sulfide (S^{2-}) or sulfate (S^{6+}), as SO_2 (S^{4+} ; the dominant S species in volcanic gases) is a redox reaction that will involve Fe. For reduced magmas degassing of SO_2 will lower $\text{Fe}^{3+}/\Sigma\text{Fe}$; for oxidised magmas degassing will increase $\text{Fe}^{3+}/\Sigma\text{Fe}$. In both cases the changes in $f\text{O}_2$ reflected by the change in $\text{Fe}^{3+}/\Sigma\text{Fe}$, will inhibit further degassing. For a reduced magma with 10% FeO, in which S is dissolved as S^{2-} , the degassing of 1000 ppm S as SO_2 would decrease $\text{Fe}^{3+}/\Sigma\text{Fe}$ from 0.098 to 0. The final $\text{Fe}^{3+}/\Sigma\text{Fe}$ of a glass will not record the redox state of the original magma. The redox effects of degassing have been recorded by coupled differences in S content and $\text{Fe}^{3+}/\Sigma\text{Fe}$ between melt inclusions and erupted magmas from Kilauea and the Cascades.

[1] Bezos & Humler (2004) *GCA* **69**, 711-725.