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## The oxidation state of iron in basaltic glasses

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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  $\sim 0.1$  in basaltic glasses, produces isomer shift and quadrupole splitting values for  $\text{Fe}^{3+}$  that are independent of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (as is the case for  $\text{Fe}^{2+}$ ), 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  $\text{H}_2\text{O}$  and  $\text{CO}_2$  will have no effect on  $\text{Fe}^{3+}/\Sigma\text{Fe}$ , however, degassing of S, which is dissolved in basaltic melts as either sulfide ( $\text{S}^{2-}$ ) or sulfate ( $\text{S}^{6+}$ ), as  $\text{SO}_2$  ( $\text{S}^{4+}$ ; the dominant S species in volcanic gases) is a redox reaction that will involve Fe. For reduced magmas degassing of  $\text{SO}_2$  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  $\text{S}^{2-}$ , the degassing of 1000 ppm S as  $\text{SO}_2$  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.