A reassessment of the oxidation state of iron in MORB glasses

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The oxidation state of Fe, $Fe^{3+}/\Sigma Fe$ (where $\Sigma Fe = Fe^{2+} + Fe^{3+}$), in mid-ocean ridge basalt (MORB) glasses reflects the oxygen fugacity of the melt and possibly the mantle source. $Fe^{3+}/\Sigma Fe$ affects the temperature and composition of crystallising phases and the speciation of degassing volatiles. One might therefore expect the $Fe^{3+}/\Sigma Fe$ value of MORB, the most common rock on the surface of the Earth, to be accurately known; this is not the case.

The mean $Fe^{3+}/\Sigma Fe$ of MORB glasses from a wide range of localities was originally determined by redox titrations to be 0.07(1) (n = 78; [1]). This value was later re-evaluated, also using redox titrations, to be 0.12(2) (n = 104; [2]). A recent determination using Fe K-edge X-ray absorption near edge structure (XANES) spectroscopy revised the value further upwards to 0.16(1) (n = 103; [3]).

We find, using XANES, that $Fe^{3+}/\Sigma Fe$ of MORB glasses from global sources, is 0.12(2) (n = 41). Synthetic samples of MORB were equilibrated at oxygen fugacities between -4.7 and +11.1 log units relative to the quartz-fayalite-magnetite buffer. The $Fe^{3+}/\Sigma Fe$ of the standards were determined by Mössbauer spectroscopy. The $Fe^{3+}/\Sigma Fe$ of natural MORB glasses were determined relative to these standards using the energy of the pre-edge peak (centroid) in the XANES spectra. The present study and that of [3] are essentially identical in their design and execution. The anomalously high value of 0.16(1) in [3] is due to a calibration error arising from the fitting of their Mössbauer spectra and a resulting error in the $Fe^{3+}/\Sigma Fe$ values of their standards.

The latest redox titration and XANES results thus agree that $Fe^{3+}/\Sigma Fe$ is 0.12 for MORB glasses.

[1] Christie *et al*. (1986) *EPSL* **79**, 379-411. [2] Bezos & Humler (2004) *GCA* **69**, 711-725. [3] Cottrell & Kelley (2011) *EPSL* **305**, 270-282.