

## Effects of quench methods on Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios: Discussion

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In a recent paper with the above title, Dyar et al. (1987) stated, "The poor precision of wet-chemical Fe<sup>3+</sup> measurements is disconcerting, but is of particular concern in reduced specimens containing small amounts of Fe<sup>3+</sup>. . . . In such cases, the Fe<sup>3+</sup> values or calculated ratios (i.e., Fe<sup>3+</sup>/Fe<sup>2+</sup> or Fe<sup>3+</sup>/Fe<sub>tot</sub>) can have a very high uncertainty (50–100%). This is not a trivial problem in experimental studies requiring reducing conditions. One particular application for which this could present a problem is in the calculation of magmatic *f*<sub>O<sub>2</sub></sub> values from volcanic glass compositions. A 10% change in the ratio Fe<sup>3+</sup>/Fe<sup>2+</sup> changes the *f*<sub>O<sub>2</sub></sub> estimate calculated by the method of Kilinc et al. (1983) by one log unit." (p. 799; my emphasis). Intuitively, this last assertion should seem implausible to the reader, and indeed it is in error, on the high side, by a factor of about 5.

The empirical equation of Kilinc et al. (1983) relating the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio, oxygen fugacity, temperature, and silicate-melt composition is

$$\ln(X_{\text{Fe}_2\text{O}_3}^{\text{liq}}/X_{\text{FeO}}^{\text{liq}}) = a \ln f_{\text{O}_2} + b/T + c + \sum_i d_i x_i, \quad (1)$$

where *a*, *b*, *c*, and *d<sub>i</sub>* values are constants and *x<sub>i</sub>* values are the mole fractions of Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and total Fe, expressed as FeO, in the melt. At constant temperature and composition, Equation 1 reduces to

$$\ln(X_{\text{Fe}_2\text{O}_3}^{\text{liq}}/X_{\text{FeO}}^{\text{liq}}) = a \ln f_{\text{O}_2} + K_1 \quad (2)$$

or

$$\ln f_{\text{O}_2} = \frac{1}{a} \ln(X_{\text{Fe}_2\text{O}_3}^{\text{liq}}/X_{\text{FeO}}^{\text{liq}}) - K_2, \quad (3)$$

where *K*<sub>2</sub> = *K*<sub>1</sub>/*a*. From Table 4 of Kilinc et al. (1983), *a*

= 0.2185 and so 1/*a* = 4.58. Therefore,

$$f_{\text{O}_2} = \exp[4.58 \ln(X_{\text{Fe}_2\text{O}_3}^{\text{liq}}/X_{\text{FeO}}^{\text{liq}})] \times K_3, \quad (4)$$

where *K*<sub>3</sub> = 1/*e*<sup>*K*<sub>2</sub></sup>.

Now *X*<sub>Fe<sub>2</sub>O<sub>3</sub></sub><sup>liq</sup>/*X*<sub>FeO</sub><sup>liq</sup> of Kilinc et al. (1983) is not equal to Fe<sup>3+</sup>/Fe<sup>2+</sup> of Dyar et al. (1987), but the two ratios are related by a simple constant so that a 10% change in one necessitates a 10% change in the other. The difference can therefore be ignored for the purposes of this exercise.

Assume Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios of 0.10 and 0.09—a 10% difference. From Equation 4, the calculated *f*<sub>O<sub>2</sub></sub> values are 10<sup>-4.58*K*<sub>3</sub></sup> and 10<sup>-4.79*K*<sub>3</sub></sup>, a difference of 0.2 log units. For a Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio of 0.05—a 100% difference—the calculated *f*<sub>O<sub>2</sub></sub> is 10<sup>-5.96*K*<sub>3</sub></sup>, a difference of 1.4 log units. This is not much larger than the estimated RMS prediction error for Equation 4 of 0.5 log *f*<sub>O<sub>2</sub></sub> units.

I hasten to add that there is still a large problem here because more recent work has shown that when Fe<sup>3+</sup> contents are low, uncertainties in the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio may commonly be much higher than the 50–100% Dyar et al. have identified (Fudali et al., 1987).

### REFERENCES CITED

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