Effects of quench methods on Fe^{3+}/Fe^{2+} 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^{3+} measurements is disconcerting, but is of particular concern in reduced specimens containing small amounts of Fe^{3+}. . . . In such cases, the Fe^{3+} values or calculated ratios (i.e., Fe^{3+}/Fe^{2+} or Fe^{3+}/Fe_{tot}) 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_{O_2} values from volcanic glass compositions. *A 10% change in the ratio* Fe^{3+}/Fe^{2+} *changes the f_{O_2} 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^{3+}/Fe^{2+} ratio, oxygen fugacity, temperature, and silicate-melt composition is

$$\ln(X^{liq}_{Fe_2O_3}/X^{liq}_{FeO}) = a \ln f_{O_2} + b/T + c + \Sigma_i d_i x_i, \quad (1)$$

where a, b, c, and d_i values are constants and x_i values are the mole fractions of Al_2O_3, CaO, Na_2O, K_2O, and total Fe, expressed as FeO, in the melt. At constant temperature and composition, Equation 1 reduces to

$$\ln(X^{liq}_{Fe_2O_3}/X^{liq}_{FeO}) = a \ln f_{O_2} + K_1 \quad (2)$$

or

$$\ln f_{O_2} = \frac{1}{a} \ln(X^{liq}_{Fe_2O_3}/X^{liq}_{FeO}) - K_2, \quad (3)$$

where $K_2 = K_1/a$. From Table 4 of Kilinc et al. (1983), a

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

$$f_{O_2} = \exp[4.58 \ln(X^{liq}_{Fe_2O_3}/X^{liq}_{FeO})] \times K_3, \quad (4)$$

where $K_3 = 1/e^{K_2}$.

Now $X^{liq}_{Fe_2O_3}/X^{liq}_{FeO}$ of Kilinc et al. (1983) is not equal to Fe^{3+}/Fe^{2+} 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^{3+}/Fe^{2+} ratios of 0.10 and 0.09—a 10% difference. From Equation 4, the calculated f_{O_2} values are $10^{-4.58} K_3$ and $10^{-4.79} K_3$, a difference of 0.2 log units. For a Fe^{3+}/Fe^{2+} ratio of 0.05—a 100% difference—the calculated f_{O_2} is $10^{-5.96} K_3$, 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_{O_2} units.

I hasten to add that there is still a large problem here because more recent work has shown that when Fe^{3+} contents are low, uncertainties in the Fe^{3+}/Fe^{2+} 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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