Effects of quench methods on Fe³⁺/Fe²⁺ 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 Fe³⁺ measurements is disconcerting, but is of particular concern in reduced specimens containing small amounts of Fe²⁺. . . . In such cases, the Fe³⁺ values or calculated ratios (i.e., Fe³⁺/Fe²⁺ or Fe³⁺/Fe₂⁺) 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 fO₂ values from volcanic glass compositions. A 10% change in the ratio Fe³⁺/Fe²⁺ changes the fO₂ 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 Fe³⁺/Fe²⁺ ratio, oxygen fugacity, temperature, and silicate-melt composition is

\[ \ln \left( \frac{X_{\text{Fe}^3+}}{X_{\text{Fe}^2+}} \right) = a \ln f_{O_2} + b/T + c + \sum d_i x_i, \]

where \( a, b, c, \) and \( d_i \) values are constants and \( x_i \) values are the mole fractions of \( \text{Al}_{2}O_{3}, \text{CaO}, \text{Na}_2O, \text{K}_2O, \) and total Fe, expressed as FeO, in the melt. At constant temperature and composition, Equation 1 reduces to

\[ \ln \left( \frac{X_{\text{Fe}^3+}}{X_{\text{Fe}^2+}} \right) = a \ln f_{O_2} + K_1 \]

or

\[ \ln f_{O_2} = \frac{1}{a} \ln \left( \frac{X_{\text{Fe}^3+}}{X_{\text{Fe}^2+}} \right) - K_2, \]

where \( K_2 = K_1/a. \) From Table 4 of Kilinc et al. (1983), \( a = 0.2185 \) and so \( 1/a = 4.58. \) Therefore,

\[ f_{O_2} = \exp[4.58 \ln \left( X_{\text{Fe}^3+}/X_{\text{Fe}^2+} \right)] \times K_3, \]

where \( K_3 = 1/e^{K_2}. \)

Now \( X_{\text{Fe}^3+}/X_{\text{Fe}^2+} \) of Kilinc et al. (1983) is not equal to \( \text{Fe}^3+/	ext{Fe}^2+ \) 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 \( \text{Fe}^3+/	ext{Fe}^2+ \) ratios of 0.10 and 0.09—a 10% difference. From Equation 4, the calculated \( f_{O_2} \) values are \( 10^{-4.39}K_3 \) and \( 10^{-4.79}K_3, \) a difference of 0.2 log units. For a \( \text{Fe}^3+/	ext{Fe}^2+ \) ratio of 0.05—a 100% difference—the calculated \( f_{O_2} \) is \( 10^{-5.39}K_3, \) 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 Fe³⁺ contents are low, uncertainties in the Fe³⁺/Fe²⁺ 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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