Oxy-amphibole equilibria in Ti-bearing calcic amphiboles: Experimental investigation and petrologic implications for mantle-derived amphiboles

ROBERT K. POPP,[1],* HEATHER A. HIBBERT,[2] AND WILLIAM M. LAMB[1]

[1]Department of Geology and Geophysics, Texas A&M University, College Station, Texas 77843, U.S.A.
[2]5502 Morgan Hill Ext., South Woodstock, Vermont 05071, U.S.A.

ABSTRACT

An experimental study was carried out to investigate the equilibrium between Fe oxy-component and hydroxy-component in Ti-bearing calcic amphiboles, as described in the dehydrogenation/oxidation reaction

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + 1/2 \, H_2,$$
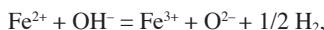
for which the equilibrium constant (K) can be expressed as

$$K = f_{H_2}(28.94)\frac{(X_{Fe^{3+}})^2(X_\square)^2}{(X_{Fe^{2+}})^2(X_{OH})^2} \cdot \Phi = K_x \cdot \Phi \quad .$$

where $\square$ = H-vacancy on the O3 anion position, Φ is the activity coefficient term, and K_x represents the thermodynamic mole fraction term (i.e., the K expressed as mole fractions rather than activities).

The variation in K_x was quantified experimentally by annealing experiments on amphiboles of two different compositions: a mantle-derived kaersutite from Greenland, and a crustal pargasite from the Tschicoma Formation from the Jemez Mountains, New Mexico, volcanic complex. The conditions of the experiments ranged from 700–1000 °C, 1–10 kbar, and f_{H_2} from that of the HM to GM solid buffer assemblages. The results, combined with similar data for a titanian pargasite from Vulcan's Throne, Arizona (Popp et al. 1995a), define the variation in log K_x as a function of T, P, and amphibole composition as given by the equation:

$$\log K_X = 4.23 - \frac{4380}{T(K)} + \left\{ 1.37 \cdot \left[(Ti + Al_{total}apfu) - 2.49 \right] \right\} + \left\{ \frac{88}{T(K)} \cdot \left[P - 1(kbar) \right] \right\}$$

If the T, P, and amphibole composition are known, values of log K_x calculated from the equation predict the equilibrium logf_{H_2} of any experiment to within ~0.1 to 0.3 log units. It is assumed that a similar uncertainty in log f_{H_2} would also to apply to the conditions of formation of natural amphiboles in the same composition range. If log f_{O_2} at the time of equilibration can be estimated independently for natural samples (e.g., mantle-derived amphiboles), the H_2O activity also can be estimated.

An alternate approach for estimating H_2O activity from amphibole-bearing mantle rocks is to use a variety of H_2O-buffering equilibria among end-member components in olivine, two-pyroxenes, amphibole, and other phases: e.g., 2 tr +2 fo = 5 en + 4 di + 2 H_2O.

A self-consistent thermodynamic database (THERMOCALC, Holland and Powell 1990) can be used to determine the a_{H_2O} of such univariant H_2O-buffering equilibria as a function of P and T.

A mantle amphibole assemblage from Dish Hill (sample DH101-E, McGuire et al. 1991) was used to calculate a_{H_2O} using the two different methods. The mean value of log a_{H_2O} determined from seven different dehydration reactions is –1.70, with a 1σ range of ±0.50. That range of water activity is in good agreement with the value of log $a_{H_2O} = -1.90 \pm 0.3$ obtained using the dehydrogenation/oxidation equilibrium, along with an estimate of log f_{O_2}.

The use of xenolith amphiboles to infer values of a_{H_2O} in the mantle requires that the H content of the amphibole does not change significantly during ascent or eruption. Changes in H content have significantly different effects on the dehydration and dehydrogenation equilibria, such that, comparison of the a_{H_2O} estimates from the two different methods may permit quantification of H loss.

Keywords: Experimental petrology, amphiboles, redox, fluid phase, activity of H_2 and H_2O, phase equilibria