

# The role of hydrogen fugacity in controlling ferric–ferrous ratio and volatile content of kaersutitic amphibole: an experimental study

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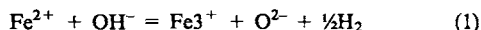
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## Introduction

Titanium-rich hornblendes (e.g., Ti-pargasite or kaersutite) have been widely recognized in mantle xenoliths that are entrained in alkali basalts. Recent documentation of an inverse 1:1 correlation between Fe<sup>3+</sup> and H-content in naturally occurring megacryst amphiboles and experimentally treated samples (e.g., Virgo *et al.*, *Terra Abstracts*, 6, (1), 50, 1994) requires that essentially all the ferric iron is accommodated by an oxygen-component described by the oxidation-dehydrogenation reaction:



Furthermore, Virgo *et al.* (1994) have concluded that Ti is accommodated in these amphiboles by a multivariate substitution that requires an inverse 1:1 correlation between Ti and OH. The simultaneous operation of the two oxy-amphibole substitution mechanisms controls the volatile content of kaersutitic amphiboles, such that the deficiency of H is equal to the sum of both the Fe<sup>3+</sup> and Ti occupancy.

Despite the general success of the existing experimental data in defining the stability of amphibole at supersolidus, mantle-type conditions, most experiments have not been carried out under  $f_{\text{H}_2}/f_{\text{O}_2}$  controlled conditions, nor have the bulk chemical compositions, ferric-ferrous ratios, or H<sub>2</sub>O<sup>+</sup> contents of the amphibole run products been systematically determined. New results of phase equilibrium experiments were obtained primarily in the subsolidus region for a Ti-pargasite megacryst sample from an alkali basalt from Vulcan's Throne, AZ. The conditions of experiments ranged from 1 atm to 10 kb, 500 to 1200°C, and oxygen fugacities from that of air to those defined by the IQF solid state buffer.

## Methods

The experiments were carried out in either horizontally mounted Rene-41 cold-seal pressure vessels or an internally-heated, argon-gas apparatus. Oxygen fugacity and hydrogen fugacity were controlled using the standard hematite-magnetite, nickel-nickel oxide, fayalite-magnetite-quartz, graphite-methane, and iron-quartz-fayalite solid buffer assemblages. The starting material and run products were analyzed thoroughly by petrographic analysis, powder X-ray diffraction, electron microprobe analyses, and <sup>57</sup>Fe Mössbauer spectroscopy. A vacuum fusion, U-furnace, manometry technique was used to analyze the H-contents of selected amphiboles.

## Results

At  $P_{\text{fluid}} = 1 \text{ kb}$ , there is a linear relationship between  $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$  and both  $\log f_{\text{H}_2}$  and  $\log f_{\text{O}_2}$  such that the Fe<sup>3+</sup>/Fe<sup>2+</sup> of amphibole at fixed temperature and  $\log f_{\text{H}_2}$  conditions can be predicted to within  $\sim 0.02$ . Figure 1 shows calculated ferric-ferrous ratios as a function of  $f_{\text{H}_2}$  within the subsolidus stability field of amphibole.

Notable features of the figure are the fact that a) contours of constant ferric-ferrous ratio do not parallel the solid buffer curves, and b) relatively high ferric iron contents are observed at solidus temperatures for redox conditions presumed appropriate to upper mantle assemblages (NNO  $\pm 1-1.5 \log$  units). As a consequence of a), if a whole-rock or melt composition follows a cooling path parallel to the buffer curves, as they are generally considered to do, an enclosed amphibole that changed ferric-ferrous ratio in response to the cooling would become more reduced rather than more oxidized. A consequence of b) is that the

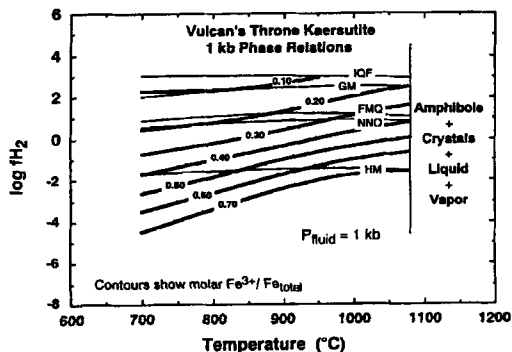


FIG. 1.

highly oxidized iron and low volatile contents of natural kaersutitic amphiboles may reflect pristine conditions of crystallization, rather than oxidation at the Earth's surface. The latter position is supported by Dyar *et al.* (1993, *Amer. Mineral.*, 78, 968–79), who concluded the rate of H-loss from amphibole is such that the operation of reaction (1) is not likely to produce significant changes in  $Fe^{3+}/Fe_{total}$  values on the time scale required for transport of alkali basalt melts to the surface.

Whereas the relations depicted above are applicable to the Vulcan's Throne amphibole composition, a more general expression is required if the results are to be applied to kaersutites of other bulk compositions. The

expression

$$K = \frac{f_{H_2} (X_{Fe^{3+}}^{amph})^5 (X_{oxy}^{amph})^2}{(X_{Fe^{2+}}^{amph})^5 (X_{hyoxy}^{amph})^2} \quad (2)$$

where  $X$  is mole fraction, has been shown to be the best operational representation of the equilibrium constant for exchange reaction (1). At 1 kb, the variation in  $\log K$  vs  $1/T(^{\circ}K)$  in the range 700–1000°C is given by

$$\log K = 8.202 - 11,371/T \quad (r_2 = 0.94) \quad (3)$$

Using values of  $K$  obtained from (3) and ferric-ferrous ratios from the experimental run products, the  $\log f_{H_2}$  conditions of the experiments can be predicted to within 0.45 log units, on average. It follows from equation (2) that at constant  $f_{H_2}$ , any variation in the amounts of  $OH^-$  and  $O^{2-}$  apfu will cause variation in  $Fe^{3+}/Fe_{total}$  of the amphibole. Thus, the Ti-content, which is controlled by an oxy-substitution, will exert control over the proportions of ferric and ferrous iron. Likewise, the actual numbers of  $Fe^{3+}$  and  $Fe^{2+}$  apfu, not only their proportions, will affect the  $OH^-$  and  $O^{2-}$  contents. Therefore, the use of ferric-ferrous ratios alone, without regard for such bulk composition effects, to infer the redox state in the environment of formation of kaersutitic amphiboles is not warranted.