Titanium in biotite from metapelitic rocks: Temperature effects, crystal-chemical controls, and petrologic applications

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ABSTRACT

An extensive natural biotite data set from western Maine constrains the temperature and crystal-chemical controls on the saturation Ti levels in biotites from metapelites. The geologically and petrologically well-characterized metamorphic terrain associated with the M3 metamorphism of the Acadian Orogeny of western Maine is ideal for this approach in that metamorphism occurred at roughly isobaric conditions of 3.3 kbar, and chemical equilibrium was closely approached. The data set from these metapelites exhibits systematic variations in Ti contents over a continuum of metamorphic grades (garnet through sillimanite-K-feldspar zones), mineral assemblages, and bulk compositional ranges. Samples were selected so that competing substitutions are restricted to those in metapelites with quartz, aluminous phases (chlorite, staurolite, or sillimanite), Ti phases (ilmenite or rutile), and graphite. Due to crystal-chemical factors, in any given metamorphic zone, an inverse linear relationship exists between Ti and Mg contents. Decreasing octahedral Ti and increasing tetrahedral Si in Mg-rich biotite helps alleviate size disparity between octahedral and tetrahedral sheets. For a biotite with a given Mg content, Ti most dramatically increases above staurolite zone conditions. Our constrained data set allows us to calculate a Ti saturation surface for natural biotite as a function of temperature and Mg content at 3.3 kbar. The Ti saturation surface can be used to establish several important metamorphic features in similar metamorphic settings. These include a general approach to equilibrium, local and/or subtle departures from equilibrium due to minor alteration to chlorite, and relative and absolute geothermometry based on Ti in biotite inclusions in refractory minerals and in matrix biotite.

INTRODUCTION

Biotite is an important mineral in metamorphic rocks over a wide range of bulk compositions and metamorphic grades. One of the more interesting biotite substituents is Ti. This quadrivalent cation is preferentially partitioned into biotite relative to other typical metapelitic silicate minerals, and substitutes for octahedrally coordinated divalent or trivalent cations (e.g., Guidotti 1984). The common petrographic observation that reddish-brown coloration in biotite is more intense in high-grade biotite relative to lower-grade biotite in similar lithologies is generally attributed to the greater amount of Ti solid solution at higher temperature (e.g., Faye 1968; Guidotti 1984). In fact, the degree to which Ti substitutes in biotite is more than a simple functional relationship with temperature, but involves relatively complex interactions among temperature, pressure, biotite crystal chemistry, and coexisting mineral assemblages (e.g., Guidotti et al. 1977, 1988; Dymek 1983; Labotka 1983; Guidotti 1984; Tracy and Robinson 1988).

Experimental investigations have helped quantify several of the parameters that influence Ti concentrations in biotite. Earlier experimental work has demonstrated that Ti solubility in phlogopite increases with temperature and decreases with pressure (Forbes and Flower 1974; Robert 1976; Arima and Edgar 1981; Tronnes et al. 1985). For instance, Robert (1976) showed that Ti solubility is relatively low, 0.07 Ti atoms per formula unit (apfu; based on a 22 oxygen atom normalization) at 600 °C and 1 kbar, and increases significantly to 0.2 Ti apfu at 800 °C, 1 kbar, and to 0.7 Ti apfu at 1000 °C, 1 kbar. In turn, with an increase in pressure to 7 kbar, the Ti concentration in phlogopite drops to 0.2 Ti apfu at 1000 °C (Robert 1976). Furthermore, limited experimental data on Fe-Mg biotite indicate that Ti contents generally increase as Fe and/or $f_{O_2}$ increase (Arima and Edgar 1981; Abrecht and Hewitt 1988). Patiño Douce and Johnston (1991) examined Ti concentrations in biotite from a series of partial-melting experiments on natural peraluminous metapelitic starting materials at 825–975 °C and 7–13 kbar. Based on these experiments, Patiño Douce (1993) noted that Ti increases with temperature in a non-linear fashion over these conditions, and he calculated that for Fe-Mg aluminous biotite ($X_{Mg} = 0.5$) a pressure increase from 5 to 15 kbar results in a decrease of Ti by 0.24 apfu at 900 °C and by 0.1 apfu at 800 °C. Despite such advances, difficulty persists in extrapolating these experimentally derived relations to the thermal and baric conditions and bulk compositions found over the general range of natural metapelitic rocks.

An additional complication is that the exact nature of Ti substitution mechanism(s) is uncertain. A number of crystallo-