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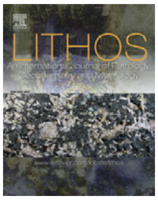

Calibration of a Ti-in-muscovite geothermometer for ilmenite- and Al_2SiO_5-bearing metapelites

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ABSTRACT

The Ti-in-muscovite geothermometer was empirically calibrated as $\ln[T(^{o}C)] = 7.258 + 0.289 \ln(Ti) + 0.158 [Mg/(Fe + Mg)] + 0.031 \ln[P(kbar)]$ using ilmenite- and Al_2SiO_5-bearing assemblages in metapelites under P–T conditions of 450–800 °C and 0.1–1.4 GPa. The calibration was conducted for muscovites containing Ti = 0.01–0.07, Fe = 0.03–0.16, Mg = 0.01–0.32 and Mg/(Fe + Mg) = 0.05–0.73, respectively, on the basis of 11 oxygen per formula unit. Such compositional range covers more than 90% natural muscovites, and the random error of this thermometer is estimated to be of ±65 °C. The geothermometer was validated against a set of independently determined temperature conditions between different degrees in samples from different prograde, inverted and contact metamorphic terranes. Application of this thermometer beyond the calibration conditions is not encouraged.

1. Introduction

Accurately retrieving the metamorphic P–T conditions is a fundamental issue in understanding the tectono-thermal evolution of a metamorphic terrane or an orogenic belt. For this regard, metapelites are important study targets due to their sensitivity in reflecting metamorphic P–T conditions and their ubiquitous occurrence. Muscovite occurs in almost all the low- to medium-grade metapelites; thus it has been used in calibrating the garnet-muscovite Fe–Mg exchange thermometer (e.g., Wu and Zhao, 2006), the plagioclase-muscovite K–Na exchange thermometer (e.g., Green and Usdansky, 1986) and even the topaz-muscovite F–OH exchange thermometer (e.g., Halter and Williams-Jones, 1999). However, such thermometers are useless when garnet and/or plagioclase are absent from the rocks, which is not uncommon in metapelites. Therefore, calibrating a thermometer based solely on the chemical composition of metapelitic muscovite coexisting with ilmenite and an Al_2SiO_5 polymorphs, is not only compensatory but also easier to use.

In recent years, some (nominally) single-mineral geothermometers based on trace or minor elements have been calibrated and applied in deciphering metamorphic temperature conditions in recent years, such as the Ti-in-zircon (e.g., Watson et al., 2006; Ferry and Watson, 2007), Zr-in-rutile (e.g., Degeling, 2002; Ferry and Watson, 2007; Tomkins et al., 2007; Watson et al., 2006; Zack et al., 2004), Ti-in-quartz (e.g., Wark and Watson, 2006; Thomas et al., 2010), Y-in-garnet (e.g., Pyle and Spear, 2000) and Ti-in-biotite (e.g., Henry and Guidotti, 2002; Henry et al., 2005) geothermometers.

The effect of pressure on Ti content of phengite in eclogites has been drawn much attention. For example, Auzanneau et al. (2010) experimentally calibrated a Ti-in-phengite geobarometer based on the buffer reaction among phengite, rutile and quartz or coesite, but the experimental P–T conditions (800–1050 °C/1.5–8.0 GPa) are too high for most metamorphic rocks formed in the crustal level. Furthermore, the chemical compositions of the phengites in eclogites are different from metapelitic muscovites. To investigate the temperature dependence of the intracrystalline coupled exchange $Ti^{VI}Al^{IV} = Si^{VI}Al^{IV}$ in muscovite, the model buffer reaction (1) among muscovite, rutile and quartz

$$\underset{Ms}{2\,K(Al_2)(AlSi_3)O_{10}(OH)_2} + \underset{Rt}{TiO_2} = \underset{Ti-Ms}{K(AlTi)(Al_2Si_2)O_{10}(OH)_2} + \underset{Qz}{SiO_2} \tag{1}$$

has been extensively studied by Chambers and Kohn (2012) for metapelitic muscovites in the temperature range of 400–1000 °C, but it is concluded that at least this model reaction (Reaction 1) cannot be used as a thermometer (Chambers and Kohn, 2012). On the contrary, we find that the Ti contents of the metapelitic muscovites coexisting with ilmenite and Al_2SiO_5 polymorphs are temperature dependent.

In this paper, we have empirically calibrated a Ti-in-muscovite thermometer considering natural ilmenite- and Al_2SiO_5-bearing metapelites metamorphosed at 450–800 °C and 0.1–1.4 GPa, based on a model buffer reaction among muscovite, ilmenite, Al_2SiO_5 and quartz. The validity of this thermometer has been demonstrated by applying it to different prograde, inverted and thermal contact metamorphic terranes. Symbols of the minerals used in this paper are after Whitney and Evans (2010).

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2. Calibration

The concentration of Ti atoms in muscovites in ilmenite- and Al_2SiO_5-bearing metapelites gradually increases with temperature in prograde metamorphic terranes (e.g., Lang and Rice, 1985; Ríos et al., 2003; di Vincenzo et al., 2004; Weller et al., 2013), inverted metamorphic terranes (e.g., Dasgupta et al., 2004; Stephenson et al., 2000) and thermal contact aureoles (e.g., Delor et al., 1984; Holdaway et al., 1988). These observations suggest the possibility of calibrating the Ti-in-muscovite geothermometer. It is found that the net-transfer reaction (Reaction 2)

$$\underset{\text{Ms}}{2\mathrm{K(Al_2)(AlSi_3)O_{10}(OH)_2}} + \underset{\text{Ilm}}{\mathrm{FeTiO_3}} + \underset{\text{Qz}}{\mathrm{SiO_2}} = \underset{\text{Ti-Ms}}{\mathrm{K(AlTi)(Al_2Si_2)O_{10}(OH)_2}} + \underset{\text{Fe-Ms}}{\mathrm{K(FeAl)Si_4O_{10}(OH)_2}} + \underset{\text{And/Sil/ky}}{\mathrm{Al_2SiO_5}} \tag{2}$$

may constitute the basis of the Ti-in-muscovite geothermometer.

The most reliable method to calibrate geothermometers and geobarometers is conducting reversed phase equilibrium experiments. In fact, earlier workers have done some experiments concerning the systematic change of the chemical compositions of phengite or muscovite with changing *P*–*T* conditions. Hermann and Spandler (2008) conducted melting experiments of synthetic metapelites to discover the mineralogic change of subducted metapelites under *P*–*T* conditions of 600–1050 °C at 2.5–4.5 GPa, and found the negative relation between the Si content and temperature and the positive relation between the Si atoms and pressure (as suggested by Massonne and Schreyer, 1987, 1989) of the product phengite. Auzanneau et al. (2006) made melting experiments on a natural metagreywacke at *P*–*T* conditions of 800–900 °C and 0.5–5 GPa, to locate the eclogite–amphibolite facies transition boundary. Later, Auzanneau et al. (2010) did crystallization experiments on natural metagreywacke and metapelite and found that Ti content in the produced phengite is strongly inversely correlated with pressure, thus they concluded that Ti content of phengite may be used as a geobarometer for high temperature eclogites. Meanwhile, they found that the Ti content in phengite is positively correlated to temperature.

However, the above mentioned experimental data are not ideal in constructing the Ti-in-muscovite geothermometer because (1) in most cases the produced mica is phengite, not muscovite; (2) the experimental temperatures of most of the runs are too high for common metapelites (Fig. 1a); (3) the produced phengite is quite dissimilar in composition with the common metapelitic muscovite (Fig. 1a, b) and (4) these experiments are not strictly reversed.

Therefore, we calibrated this thermometer using an empirical calibrating method, and overall considering 90 ilmenite- and Al_2SiO_5-bearing metapelitic samples from the literature (Supplementary Table 1 and references therein). Among these samples, 48 samples contain ilmenite but no rutile, whereas the other 42 samples contain both ilmenite and rutile. These rocks were metamorphosed under *P*–*T* conditions of 450–800 °C and 0.1–1.4 GPa, respectively, determined simultaneously by applying the garnet-biotite geothermometer (Holdaway, 2000) and the GASP geobarometer (Holdaway, 2001) as suggested by Wu and Cheng (2006). The cation ranges are $Ti = 0.01–0.07$, $Fe = 0.04–0.16$, $Mg = 0.01–0.32$ and $Mg/(Fe + Mg) = 0.05–0.73$, respectively, for muscovites on the basis of 11 oxygen per formula unit. It should be stated that such compositional range covers more than 90% natural muscovites (Supplementary Table 1 and references therein). Selection of calibration samples fits the following criteria: (a) there is clear description of textural equilibria among the mineral assemblage muscovite + Al_2SiO_5 + ilmenite + quartz + garnet + biotite + plagioclase for every sample in the literature; (b) no retrograde reaction textures are found in these rocks; (c) at least nine components (SiO_2, TiO_2, Al_2O_3, FeO, MnO, MgO, CaO, Na_2O and K_2O) were analyzed by electronic microbe and the high quality data are available; and (d) if there is chemical zoning profile in a garnet, only chemical composition of the rims was used to determine metamorphic *P*–*T* conditions. These criteria ensure that the muscovites used in the calibration grew simultaneously with the other minerals and thermodynamic equilibria of the assemblages have attained. Rocks containing only rutile but no ilmenite were discarded from the calibration data set, because the rutile-related buffer reaction (Eq. 1) cannot be calibrated as a thermometer (Chambers and Kohn, 2012).

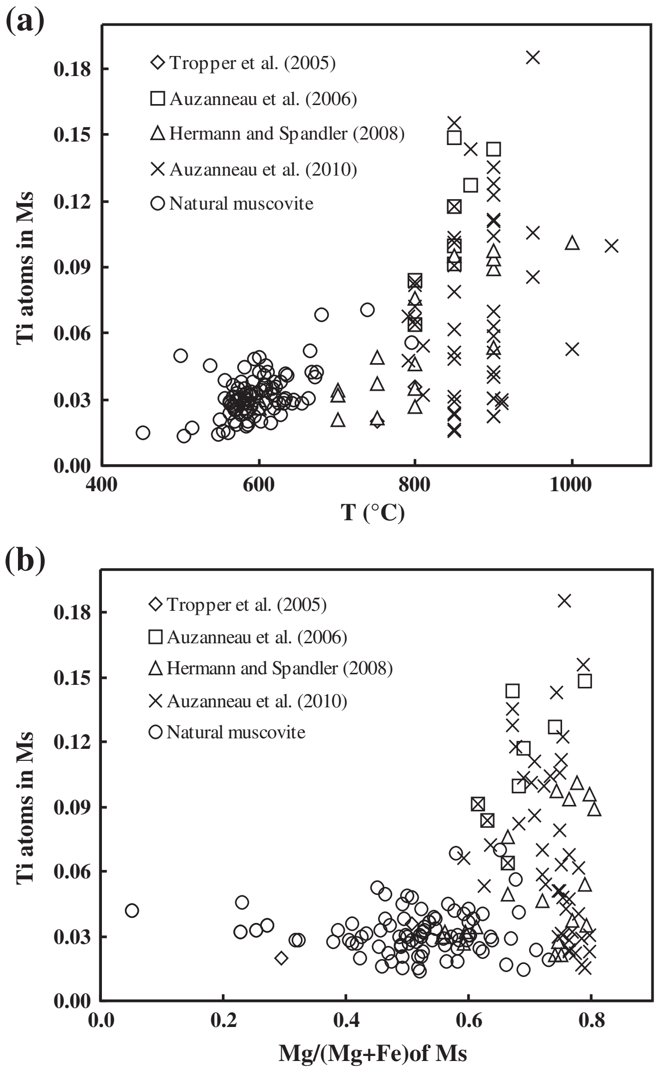

Fig. 1. Compositional variations between the natural (Supplementary Table 1) and the experimental muscovites (Tropper et al., 2005; Auzanneau et al., 2006; Hermann and Spandler, 2008; Auzanneau et al., 2010). (a) Temperature versus Ti atom of the muscovites; (b) Mg/(Mg + Fe) ratio versus Ti atom of the muscovites.

The Ti-in-muscovite geothermometer is empirically calibrated through three dimensional surface fitting as

$$\begin{aligned}\ln\left[T\left({}^{o}\mathrm{C}\right)\right] &= 7.258(\pm 0.04) + 0.289(\pm 0.01)\ \ln(\mathrm{Ti}) + 0.158(\pm 0.03)\\ &\quad \times [\mathrm{Mg}/(\mathrm{Fe}+\mathrm{Mg})] + 0.031(\pm 0.01)\ \ln[P(\mathrm{kbar})]\end{aligned} \tag{3}$$

in which Ti, Mg and Fe are the respective cation numbers per formula unit of the muscovites on the 11 oxygen basis, and *T* is in °C. The multiple correlation coefficient of the regression is $R = 0.932$ in the calibration. This formulation is similar in format to the Ti-in-biotite thermometer (Henry and Guidotti, 2002; Henry et al., 2005). Errors in the parentheses in Eq. (3) are fitting but not analytical errors.