The relationship between apparent equilibrium temperature and closure temperature with application to oxygen isotope geospeedometry

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Abstract   Oxygen isotope fractionation between coexisting minerals in slowly cooled rocks conveys information about their cooling history. By using the fast grain boundary (FGB) model to simulate closed-system diffusive exchange of oxygen isotopes between coexisting minerals, I show that the apparent equilibrium temperatures (T_{ae}) by the mineral pair with the largest isotopic fractionation (PLIF) always lies between the closure temperatures (T_c) of those two minerals. Therefore, when the rate of oxygen diffusion and hence T_c for the PLIF chance to be comparable (such as in the case of quartz and magnetite), T_{ae} will serve as a good approximation of T_c regardless of variation in mineral proportions. The specialty of the PLIF in constraining T_{ae} within their T_c range can be generalized to other stable isotope systems and element partitioning. By approximating T_c with T_{ae} and inverting Dodson's equation, the cooling rate of plutonic or metamorphic rocks can be inferred.

Key words   apparent equilibrium temperature; closure temperature; oxygen isotope; geospeedometry; cooling rate; diffusion

1 Introduction

Inferring the thermal history of rocks from their mineralogical, chemical, isotopic and textural records is a major theme of igneous and metamorphic petrology. Oxygen isotope geothermometry uses the isotopic fractionation between coexisting minerals to calculate an "equilibrium" temperature. For slowly cooled rocks, however, this apparent equilibrium temperature (T_{ae}) does not correspond to the temperature of petrogenesis or peak metamorphism, but is controlled by diffusion kinetics and hence conveys information about the cooling history. A number of authors (Giletti, 1986; Eiler et al., 1992; Jenkin et al., 1994; Kohn and Valley, 1998a; Kohn, 1999) have developed increasingly more sophisticated models to investigate the diffusive exchange of oxygen isotopes during cooling. However, a quantitative connection between T_{ae} and the cooling rate is yet to be established.

On the other hand, the closure temperature (T_c) of mineral grains, a well-developed concept in thermochronology, is directly related to the instant cooling rate (q) through the Dodson (1973)'s equation:

$$T_c = \frac{E}{R \ln \dfrac{GD_0 R T_c^2}{a^2 q E}} \qquad (1)$$

where G and a are the geometry factor and the grain size (55 and radius for sphere; 27 and radius for cylinder; 8.7 and half thickness for tablet), E and D_0 are the activation energy and the pre-exponential factor for oxygen diffusion, and R is the universal gas constant.

It is clear that the substitution of T_c with T_{ae}, if justifiable, would provide a convenient method for retrieving cooling rate. In fact, Kohn and Valley (1998a, b) already suggested that T_{ae} by a mineral pair with similar closure temperatures would be indicative of their T_c. However, as will be shown in the present study, a crucial prerequisite for their suggestion to be valid has been neglected. Only some special mineral

pair validates $T_c = T_{ae}$ and is appropriate for the application of geospeedometry.

2 Methods

The Fast grain boundary (FGB) model of Eiler et al. (1992, 1994) since developed has been widely used to simulate the diffusive exchange of oxygen isotopes between coexisting minerals during continuous cooling (e.g. Peck et al., 2003; Bonamici et al., 2011). Assuming that grain boundary diffusion is sufficiently rapid for keeping the grain boundary isotopic compositions of minerals at equilibrium, the FGB model not only couples mass balance and diffusion, but also predicts that T_{ae} depends strongly on the modal abundances of minerals. In view of that it is theoretically well-founded with simulation results generally consistent with field observations, I also used the FGB model to in this study investigate the relationship between T_c and T_{ae}.

In my FGB modeling, the cooling curve of a given rock was assumed to be asymptotic:

$$T = \frac{T_0}{1 + t/\tau} \tag{2}$$

where T_0 is the onset temperature, t is the time, and τ is a time constant. Asymptotic cooling leads to an exponential decrease of oxygen diffusivity with time. Temperature-dependent oxygen diffusivities, oxygen isotope fractionation factors relative to quartz, and oxygen concentrations of minerals are presented in Table 1. Other input parameters include the modal abundances, grain sizes and $\delta^{18}O$ values of the minerals. Conclusions of the present study will not change in any fundamental manner if different sets of parameters are adopted.

Forward simulations are stopped at 50℃, where oxygen isotope exchange is slow enough for being considered as negligible. From the "frozen" isotopic compositions of minerals, T_{ae} by different mineral pair can be derived and compared with T_c values of minerals calculated from eqn (1).

3 Results and Discussion

3.1 Mineral pair with the largest isotopic fractionation

A series of hypothetical granitic rocks, containing varying amounts of quartz (Qz), albite (Ab) and magnetite (Mt) with a uniform grain size of 1 mm, were examined. These rocks cooled from 750 to 50℃ in 160 million years, with the cooling rate being 10℃/Ma at 600℃. Using these parameters and eqn (1),

closure temperature is found to be 505℃ for quartz, 219℃ for albite, and 526℃ for magnetite. The quartz-albite pair, which has the smallest oxygen isotope fractionation, yields highly variable apparent equilibrium temperatures (Fig. 1a). At low concentrations of albite and high concentrations of magnetite, T_{ae} even cannot be defined because the normal fractionation is reversed (i.e., Mt is more enriched in ^{18}O than Ab). Clearly, when a mineral pair gives high T_{ae}, this does not necessarily mean that the onset temperature has been preserved. The dramatic variation of T_{ae} by quartz-albite, as also observed in Eiler et al. (1992, 1993), is due to the disturbance from exchange with magnetite. By contrast, T_{ae} by the albite- magnetite pair generally falls within their T_c range, except in the presence of >90% quartz (Fig. 1b). At ~10% magnetite, both Qz-Ab and Ab-Mt (and certainly also the third pair, Qz-Mt) yield similar T_{ae} (503–524℃). Therefore, even if different mineral pairs show apparently consistent T_{ae} values, it is not guaranteed that they correspond to the onset temperature (750℃ in this case).

The most important finding from the modeling, however, is that T_{ae} by the quartz-magnetite pair unfailingly falls within their narrow T_c range (505–526℃), no matter how the modal abundances of minerals vary (Fig. 1c). Numerous simulations of other rocks, with some being compositionally more complicated, consistently show that T_{ae} by the mineral pair with the largest isotopic fractionation (abbreviated to PLIF) is always constrained between their two closure temperatures. Therefore, when the PLIF chances to have similar oxygen diffusivity and hence similar T_c values, T_{ae} will serve as a good approximation for T_c regardless of variation in mineral proportions.

3.2 Mineral pairs with similar closure temperature

Already Kohn and Valley (1998a) suggested that T_{ae} by two minerals with similar T_c would be close to the T_c values, with examples such as coexisting amphiboles (cummingtonite and hornblende), pyroxenes (orthopyroxene and clinopyroxene) and micas (biotite and muscovite). To assess the validity of their argument, I investigated a series of hypothetical rocks containing quartz (Qz, $a=0.5$ mm), magnetite (Mt, $a=1$ mm), biotite (Bt, $a=0.5$ mm) and muscovite (Mus, $a=0.5$ mm), which again cooled from 750 to 50℃ in 160 Ma. In these rocks, the PLIF pair of quartz and magnetite have similar T_c (477 and 526℃, respectively); biotite and muscovite also have similar T_c (293 and 336℃, respectively) but with much smaller oxygen isotope fractionation. It turns out that the two micas yield highly variable T_{ae} (as high as 792℃ and as low as 236℃), often significantly off their

Table 1   Thermodynamic and kinetic parameters used in FGB modeling

	$\Delta_{\text{Qz-mineral}} = A \times 10^6/T^2$	$\ln D = \ln D_0 - E/RT$				Oxygen concentration (mol/m³)
	A	D_0 (m²/s)	E (kJ/mol)	Orientation	G	
Quartz	0	2.9×10^{-5}	243	$// c$	8.7	88145
Calcite	0.38	7.0×10^{-9}	173	~isotropic	55	81235
Albite	0.94	2.3×10^{-13}	89.1	~isotropic	55	79944
Muscovite	1.5	7.7×10^{-9}	163	$\perp c$	27	85221
Anorthite	1.99	1.4×10^{-11}	110	~isotropic	55	79373
Phlogopite	2.16	1.4×10^{-8}	176	$\perp c$	27	80187
Biotite	2.4	9.1×10^{-10}	142	$\perp c$	27	77771
Apatite	2.51	9.0×10^{-9}	205	$// c$	8.7	81454
Hornblende	2.6	1.0×10^{-11}	172	$// c$	8.7	88235
Zircon	2.64	5.5×10^{-12}	210	~isotropic	55	101885
Almandine	2.71	6.0×10^{-9}	301	isotropic	55	104058
Diopside	2.75	1.5×10^{-10}	226	$// c$	8.7	90785
Titanite	3.66	2.1×10^{-12}	180	~isotropic	55	89702
Rutile	4.69	2.0×10^{-5}	330	$\perp c$	27	106270
Magnetite	6.29	3.5×10^{-10}	188	isotropic	55	89847

Note: Oxygen isotope fractionation factors are from Clayton et al. (1989) for albite, anorthite, and calcite; Chiba et al. (1989) for diopside and magnetite; Fortier and Lüttge (1995) for apatite; Chacko et al. (1996) for muscovite, phlogopite and rutile; Kohn and Valley (1998a) for biotite and hornblende; and Valley et al. (2003) for zircon, almandine and titanite. Oxygen self diffusivities (at ~100 MPa water fugacity) are from Farver and Yund (1991) for quartz; Farver (1994) for calcite; Giletti et al. (1978) for albite and anorthite; Fortier and Giletti (1991) for muscovite, phlogopite and biotite; Farver and Giletti (1989) for apatite; Farver and Giletti (1985) for hornblende; Watson and Cherniak (1997) for zircon; Coghlan (1990) for almandine; Farver (1989) for diopside; Zhang et al. (2006) for titanite; Moore et al. (1998) for rutile; Giletti and Hess (1988) for magnetite. Oxygen concentrations are calculated as ν/V, where ν is the stoichiometric coefficient of oxygen and V is the molar volume of minerals (Robie and Hemingway 1995).

T_c range (Fig. 2a). By contrast, T_{ae} by quartz and magnetite always lies between their closure temperatures (Fig. 2b). Therefore, the point made in Kohn and Valley (1998a) is incorrect. In reality, a non-PLIF mineral pair with similar closure temperature does not guarantee that their T_{ae} will be a good approximation of T_c. Whether it does so depends on their modal abundances—the higher abundances of the mineral pair, the more closely that T_{ae} approaches T_c.

3.3 Other stable isotope systems and element partitioning

In principle, the specialty of PLIF in constraining T_{ae} within their closure temperatures is not only applicable to oxygen isotopes, but can also be generalized to other stable isotope systems and element partitioning. With rapid developments in non-traditional stable isotope geochemistry, such as Mg and Si isotopes, appropriate PLIF may be discovered as good candidates for constraining the closure temperatures for Mg and Si self diffusion. For Fe-Mg exchange

reactions between ferromagnesian minerals, T_{ae} by the mineral pair with the largest difference in Fe^{2+}/Mg ratio is expected to lie between their T_c values in terms of Fe^{2+}-Mg interdiffusion.

4 Application to oxygen isotope geospeedometry

The approximate equivalence of apparent equilibrium temperature and closure temperatures for the PLIF with similar T_c can be exploited to develop a geospeedometry method based on oxygen isotope fractionation. By inverting eqn (1), the cooling rate at Tc is expressed as:

$$q = \frac{GRT_c^2 D(T_c)}{a^2 E} \tag{3}$$

where $D(T_c)$ is the oxygen diffusivity at T_c. Using T_{ae} by the PLIF as a proxy of T_c for both minerals, one will be able to obtain two cooling rate estimates, which bracket the actual cooling rate at T_{ae}.
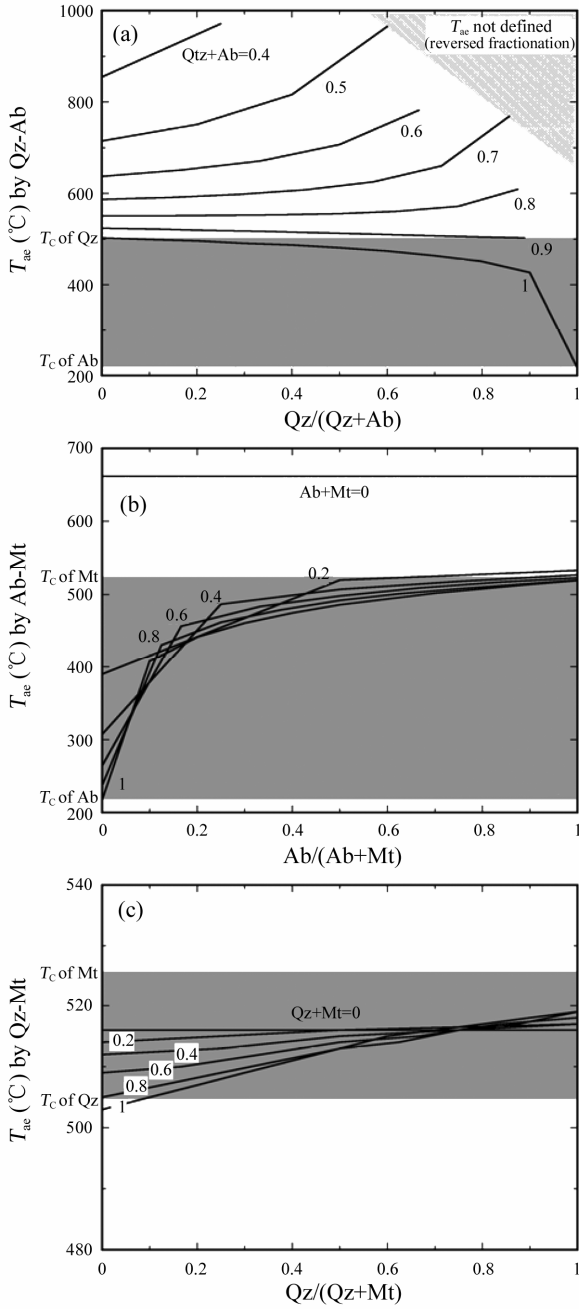
Fig. 1. Apparent equilibrium temperature by (a) quartz-albite; (b) albite-magnetite; and (c) quartz-magnetite pairs in hypothetical granitic rocks (Qz + Ab + Mt = 1) cooled from 750 to 50℃ in 160 Ma, based on simulations using the FGB model. Shaded areas indicate the closure temperature range of the respective mineral pair.

San Jose tonalite is a 108 km² pluton with an age of ~105 Ma, belonging to the Jurassic to Cretaceous Peninsular Ranges batholith of northern Baja California, Mexico (Johnson et al., 2003). A sample collected from the central portion of the pluton by Taylor and Epstein (1962) contained 62.3% plagioclase, 9.6% hornblende, 6.0% biotite, 17.1% quartz and 2.6%

magnetite. From the oxygen isotope compositions of the minerals (Taylor and Epstein, 1962; Taylor, 1968), Giletti (1986) suggested that San Jose tonalite had cooled at a rate of 100–200℃/Ma. However, as convincingly shown in Eiler et al. (1992, 1993), Giletti's model is fundamentally flawed in that it decouples mass balance and diffusion.

The coexistence of quartz and magnetite make the San Jose tonalite an ideal case for applying the oxygen isotope geospeedometry method proposed here. Based on and the calibration of Chiba et al. (1989) and the measured δ18O values of minerals, 9.7‰ for quartz and 2.0‰ for magnetite, I first find a T_{ae} of 633℃. By assigning T_c of both minerals with this T_{ae} value, with literature data of oxygen diffusivities (Farver and Yund, 1991; Giletti and Hess, 1988) and grain sizes (2.0 mm for quartz and 0.5 mm for magnetite; Giletti, 1986), the cooling rate for San Jose tonalite is estimated to be 556–1247℃/Ma, about 6 times higher than that erroneously estimated by Giletti (1986).
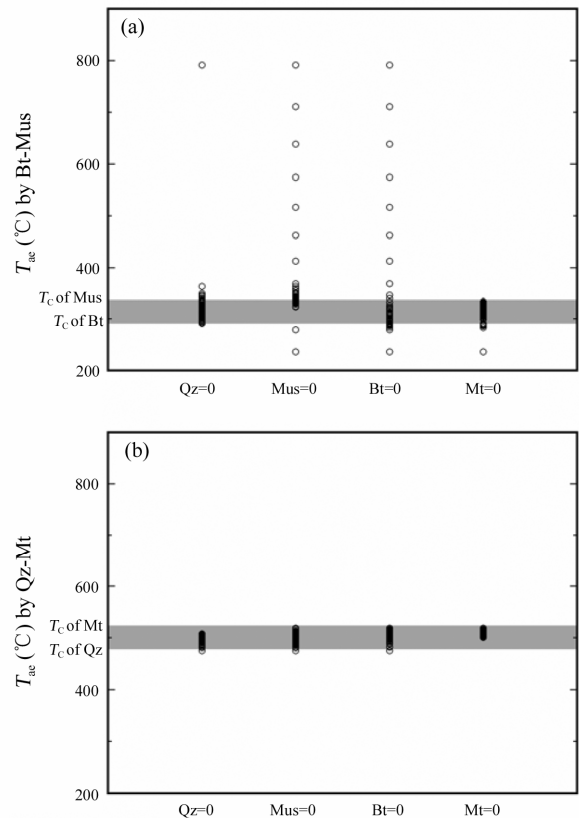

Fig. 2. Apparent equilibrium temperatures by (a) biotite-muscovite; and (b) quartz-magnetite pairs in hypothetical quartz-magnetite-biotite-muscovite systems (Qz+Mus+Bt+Mt=1) cooled from 750 to 50℃ in 160 Ma, based on simulations using the FGB model. Shaded areas indicate the closure temperature range of the respective mineral pair.

5 Concluding remarks

In summary, for slowly cooled plutonic and metamorphic rocks, the mineral pair with the largest isotopic fractionation (PLIF) robustly constrains T_{ae} between their closure temperatures. Therefore, when the rate of oxygen diffusion and hence T_c for the PLIF chance to be comparable, T_{ae} will serve as a good approximation of T_c regardless of variation in mineral proportions. One such pair is quartz and magnetite. By contrast, a mineral pair with similar T_c but small isotopic fractionation is susceptible to the disturbance from other minerals such, that their T_{ae} may not be indicative of T_c, especially when other minerals are of high abundance. The specialty of PLIF in constraining T_{ae} within their closure temperatures is not only applicable to oxygen isotopes, but can also be extended to other stable isotope systems (such as Mg isotopes and Si isotopes) and element partitioning.

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