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Why most "dry" rocks should cool "wet"

MATTHEW J. KOHN[1,*]

Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550, U.S.A.

ABSTRACT

A new consideration of oxygen isotope resetting among metamorphic minerals is made accounting for (1) the possibility of f_{H_2O}-buffering by typical mineral assemblages during cooling and (2) experimental data that show that high f_{H_2O} correlates with high diffusion rates. Isotope closure temperatures in buffered rocks are intermediate between simpler predictions based on "wet" (1 kbar hydrothermal) and "dry" ($P \leq 1$ atm, H_2O-absent) diffusion experiments, but are typically within ~50 °C of closure temperature estimates that use "wet" diffusion rates, yet 200–300 °C different from "dry." Even though many rocks may be "dry" in that they lack a hydrous fluid that is physically present during cooling, buffering of f_{H_2O} results in quasi-"wet" diffusion rates. Re-evaluation of published data shows that most rocks indeed exhibit substantial isotope resetting that is best matched by predictions of f_{H_2O}-buffering models. Wet- and dry-diffusion models somewhat overestimate and greatly underestimate resetting respectively. Previous interpretations invoking "dry" diffusion rates may derive from erroneous fractionation factors or faster cooling rates than assumed. The rare preservation of isotope closure temperatures that are higher than predicted may reflect faster than expected cooling rates or extraordinarily low f_{H_2O} in conjunction with anhydrous assemblages.

INTRODUCTION

Oxygen isotope analyses in metamorphic rocks may be applied to two related yet mutually exclusive endeavors: thermometry and speedometry. Isotopic thermometry assumes that diffusional reequilibration is negligible, so that the peak isotopic compositions of some minerals are retained, whereas speedometry assumes that diffusional resetting of isotope compositions occurs during cooling and uplift and that the degree of resetting reflects cooling rates. In several studies, "dry" conditions (i.e., absence of H_2O-rich fluids) have been invoked to explain why the major minerals in some rocks apparently retain peak metamorphic (Sharp et al. 1988; Hoffbauer et al. 1994; Massey et al. 1994; van Haren et al. 1996) or high-T (Farquhar et al. 1996) oxygen isotope compositions. Such a conclusion is consistent with two observations. (1) Experimentally determined oxygen diffusion rates are many orders of magnitude slower when conditions are "dry" ($P \leq 1$ atm, H_2O-absent) than when "wet" (P_{H_2O} = 1 kbar, hydrothermal). If "dry" diffusion rates apply, closure temperatures for diffusional reequilibration are so high that peak or near-peak compositions should invariably be retained for rocks that form at T of approximately ≤800 °C. (2) Fluids are unlikely to be present physically in many metamorphic rocks during cooling because they readily back-react to form retrograde minerals (Yardley 1981; Frost and Bucher 1994; Yardley and Valley 1997). In the absence of long-term infiltration, fluids sensu stricto are unlikely to facilitate diffusional reequilibration.

In evaluating whether diffusional reequilibration of oxygen isotopes is likely to occur under "dry" vs. "wet" conditions, it is important to recognize that most metamorphic rocks have mineral assemblages that may buffer f_{H_2O} during cooling. Thus, while a rock may be "dry" in the physical sense that it lacks a macroscopic fluid, it may still be "wet" in the thermodynamic sense that f_{H_2O} is much greater than 1 bar. Because high oxygen diffusion rates correlate with high f_{H_2O} in experiments (Farver and Giletti 1985; Farver and Yund 1990, 1991; Fortier and Giletti 1991; Watson and Cherniak 1997), diffusional exchange among minerals in nature may be controlled by the buffer capacity of the assemblages. As shown in this study, buffering will result in sufficiently high f_{H_2O} in most rocks that intracrystalline oxygen diffusion rates are more closely approximated by "wet" rather than "dry" experiments. Comparison of natural data to predictions that account for f_{H_2O} buffering further confirms that most mineral compositions reflect extensive rather than negligible resetting. That is, most physically "dry" rocks indeed cool "wet" (thermodynamically and diffusionally).

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[*] Present address: Department of Geological Sciences, University of South Carolina, Columbia, South Carolina 29208, U.S.A. E-mail: mjk@geol.sc.edu

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EFFECT OF f_{H_2O} ON DIFFUSION RATES

Hydrothermal experiments for minerals including ortho-, chain-, sheet-, and tectosilicates show that oxygen diffusion rates are much higher at P_{H_2O} = 70–10 000 bars than at atmospheric pressure and nominally anhydrous conditions (Farver and Giletti 1985; Farver and Yund 1990, 1991; Fortier and Giletti 1991; Watson and Cherniak 1997; Fig. 1). Although the origin of this correlation has been ascribed to H^+ activity (Elphick and Graham 1988), theoretical considerations (Zhang et al. 1991; McConnell 1995) and detailed diffusion experiments (Farver and Yund 1990, 1991) implicate water rather than protons. More importantly, the bulk oxygen diffusion rate (D_{Ox}) in quartz and silica-rich glasses is approximated closely as the product of the diffusion rate of molecular water and its concentration. Thus in many materials, diffusion of water rather than lattice oxygen is likely responsible for measured D_{Ox} (Farver and Yund 1990, 1991; Zhang et al. 1991; Doremus 1996). The significance of water in diffusional exchange of oxygen may well explain why H_2O content and D_{Ox} are both lower in ortho- vs. chain- and tecto-silicates (Farver and Yund 1990, 1991; Bell and Rossman 1992; Watson and Cherniak 1997). For simplicity, experiments and fast diffusion rates corresponding to P_{H_2O} approximately ≥100 bars will be referred to as "wet," whereas experiments and slow diffusion rates corresponding to $P \leq 1$ atm will be referred to as "dry."

The facilitation of diffusion by water has important implications for rocks because water has low solubility in most minerals, yet high diffusion rates (Zhang et al. 1991). Water contents are typically in the few parts per million to 100s of parts per million range (Bell and Rossman 1992), and water diffusivities are 3–5 orders of magnitude faster than measured D_{Ox} (Zhang et al. 1991). If a source or sink of water is available during cooling, for example from hydrous minerals, then diffusional exchange of intracrystalline H_2O allows water concentrations to track readily any changes in f_{H_2O}. Water will simply migrate through minerals, and react at grain boundaries to produce or consume hydrous minerals. Thus, while a free fluid phase may not be present during cooling, intracrystalline water concentrations may change via diffusion and trace reactions among solid phases on their boundaries. This process not only will facilitate the buffering of water fugacities but also will control D_{Ox}, because D_{Ox} is dependent on intracrystalline water (Farver and Yund 1990, 1991; Zhang et al. 1991; McConnell 1995; Doremus 1996).

Although this conceptual model (linking f_{H_2O}-buffering to diffusional resetting via intracrystalline water) follows directly from previous work, it raises several concerns that can be summarized as follows.

(1) Must an aqueous fluid be present physically to enhance oxygen diffusion rates? Because there have been no experiments that buffer f_{H_2O} yet also lack a fluid, there is no direct experimental evidence that bears on this issue. Nonetheless, many studies implicate intracrystalline water in enhancing D_{Ox} (Farver and Yund 1990, 1991; Zhang et al. 1991; McConnell 1995; Doremus 1996), implying that the presence of a macroscopic fluid at the grain surface is unnecessary. For example, Doremus (1996) has shown for quartz glass that D_{H_2O}(intragranular) and D_{Ox} are intrinsic properties of the material, unrelated to surface effects. This conclusion is also implicit in the time-independence of D_{Ox} determined for minerals in hydrothermal diffusion experiments.

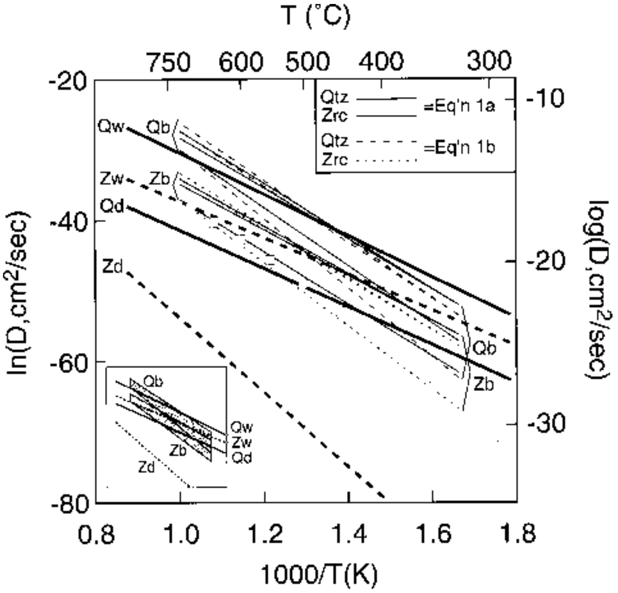

FIGURE 1. Plot of oxygen diffusivities (D values) vs. temperature for quartz and zircon from experiments and calculations. Qw and Qd are the experimentally determined "wet" (P_{H_2O} =1 kbar) and "dry" (P <1 bar) diffusion rates for quartz; Zw = "wet" and Zd = "dry" diffusion rates for zircon. Experiments for "wet" conditions (thick solid lines) yield diffusivities at geological conditions that are 5–10 orders of magnitude faster than "dry" experiments (thick dashed lines). In the three model rocks with H_2O-buffering assemblages, the distribution of calculated D values can be regressed against $1/T$ to determine fictive diffusion terms (D_0 and E), with which diffusion calculations can be made. Open squares and the thin dotted line show specific calculations for Zrc (Eq. 1b) and the best-fit linear regression through them. The buffered-diffusivities for quartz and zircon (thin lines labeled Qb and Zb) show that D values are higher at peak metamorphic conditions than hydrothermal experiments, but drop to lower values more rapidly. Inset summarizes calculations (gray boxes) compared with experiments. Experimental diffusion data from Dennis (1984), Farver and Yund (1991), and Watson and Cherniak (1997).

An analogy can be drawn between the effect of f_{H_2O} on oxygen diffusivities and the effect of a_{SiO_2} on melt properties. In the absence of quartz, the activity of silica can be described readily by using thermodynamics of mineral equilibria (e.g., Ghiorso and Carmichael 1987). If a physical property of the melt, such as viscosity, is dependent on a_{SiO_2}, then changes to that property resulting from changes to a_{SiO_2} can be monitored via mineral equilibria, even in the absence of an SiO_2-phase. Inasmuch as f_{H_2O} can be calculated thermodynamically and interrelated with oxygen diffusivities, it follows that changes in diffusivities resulting from changes in f_{H_2O} also can be monitored via mineral equilibria, even in the absence of a fluid phase.

(2) Are rates of reaction and transport of the diffusing species sufficiently fast to buffer f_{H_2O}? Rate kinetics for heterogeneous reactions involving the breakdown or formation of hy-

drous minerals are non-limiting to temperatures of 300 °C or less (e.g., Lasaga 1984). Diffusion of molecular water in quartz is extremely fast and has a length scale on the order of millimeters to 10s of centimeters (e.g., Zhang et al. 1991). The characteristic response time of dissolved water concentrations in quartz to changes in external f_{H_2O} is on the order of hours to days at 350–500 °C (Cordier et al. 1988). Thus, it is reasonable that f_{H_2O}-buffering occurs.

(3) Does intragranular water behave thermodynamically? Silver et al. (1990) have shown that molecular water in silicate glasses follows a Henry's Law behavior, and is thus predictable thermodynamically. Cordier and Doukhan (1989) found a correlation between intracrystalline water contents in quartz and imposed f_{H_2O}, a relationship that also is predicted theoretically by Zhang et al. (1991) and McConnell (1995).

(4) Are typical dissolved water contents sufficient to enhance diffusion? Zhang et al. (1991) demonstrated the importance of parts per million-level water contents on enhancing D_{Ox}, and noted that the self-diffusion of hydrous species can dominate D_{Ox} even at parts per billion levels.

(5) Can typical modes of hydrous minerals accomodate the expected changes in intracrystalline water contents? Intracrystalline water contents of ~100 ppm supply only enough water to produce ~0.1 modal% of a hydrous mineral that contains ~10 mol% H_2O (e.g., a mica). In rocks with at least several percent hydrous minerals, an essentially inexhaustible supply or sink of water is thus available. In fact, the changes in mineral modes are likely so small that petrographic identification of the process is probably not feasible.

Assuming the above arguments are correct, oxygen diffusion rates during cooling will be determined by two factors: the dependence of diffusion rates on f_{H_2O}, which has been measured experimentally, and the buffering of f_{H_2O} by the mineral assemblage, which can be calculated thermodynamically. An analogous conclusion can be reached if high H^+ activity causes high oxygen diffusivity. Protons have a high diffusivity, yet a low concentration in most minerals (Elphick and Graham 1988). If a rock has hydrous minerals, then a source or sink of protons is likely available, rapid H^+ diffusion facilitates equilibration, and buffering of a_{H^+} during cooling ensures buffering of oxygen diffusion rates.

With respect to the standard expression for the temperature-dependence of diffusion rate, $D = D_0e^{-E/RT}$ (where D is bulk oxygen diffusion rate, D_0 is the pre-exponential term, E is activation energy, R is the gas constant, and T is temperature in kelvins), f_{H_2O} potentially could affect both D_0 and E by changing intracrystalline water concentrations (if water is indeed the diffusing species) and/or the energetic barrier to atom movement. Most studies of wet- vs. dry-diffusion show changes to E, D_0, or both. Complete mathematical models relating D_0 and E to f_{H_2O} are lacking for common minerals, and detailed investigations of the effect of f_{H_2O} on diffusivity have been conducted only at 973 K (Farver and Yund 1990, 1991; Farver 1994). Consequently, two phenomenological models are considered here: that variations in f_{H_2O} affect only E, or only D_0. Such an assumption is consistent with data for feldspar and quartz (Giletti et al. 1978; Dennis 1984; Farver and Yund 1991; Ryerson and McKeegan 1994), as oxygen diffusion in quartz shows only a change in D_0, whereas feldspar shows a strong change in E but no resolvable change to D_0. Diffusion data for quartz at 973K (Farver and Yund 1991) show the strongest dependence of D on f_{H_2O}—log(D) is proportional to log(f_{H_2O}) with a proportionality constant of 1.0. As described in the Appendix, assuming that either D_0 or E is affected (but not both), this linear dependence implies either:

$$D = \left[D_0 e^{-E/RT}\right] * \left[\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right] \tag{1a}$$

or

$$D = D_0\exp-\left[\frac{E - 973R\ln\left(\dfrac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)}{RT}\right]$$

$$= \quad \left[D_0 e^{-E/RT}\right] * \left[\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right]^{973/T} \tag{1b}$$

where D_0 and E are the pre-exponential term and activation energy from wet diffusion experiments, $f_{H_2O}(P,T)$ is the fugacity at P and T (as buffered by the assemblage), and $f_{H_2O}(1\text{kbar},T)$ is the fugacity at the reference P of the hydrothermal experiments (typically $P_{H_2O} = 1$ kbar). Ordinarily, closure temperatures estimated by these two alternative models do not differ by more than a few degrees. Although diffusion rates are commonly described as being dependent solely on T, D_0, and E, the new phenomenological equations show explicitly how D may depend on f_{H_2O}. Indeed, accurate diffusion modeling of rocks should now address not only changes in T, but also in P and the mineral assemblage, because these both affect f_{H_2O} during cooling.

The models presented here assume a relatively strong dependence of D on water fugacity. Some minerals have a smaller f_{H_2O}-dependence of D, for example alkali feldspar and calcite (Farver and Yund 1990; Farver 1994), which show a linear dependence of D on $(f_{H_2O})^{0.5}$ and $(f_{H_2O})^{0.9}$, respectively. If a different dependency is accommodated by decreasing the exponent of $f_{H_2O}(P,T)/f_{H_2O}(1\text{kbar},T)$, calculated diffusivities become more similar to the measured wet diffusion data. Consequently, use of Equations 1a and 1b maximizes differences between closure temperatures calculated assuming f_{H_2O}-buffering as opposed to assuming either wet diffusion rates (i.e., $P_{H_2O} = 1$ kbar throughout cooling) or a weaker dependence of D on f_{H_2O}. Similarly, if buffering of f_{H_2O} simply does not occur, then intracrystalline water contents will likely correspond to peak metamorphic conditions and remain constant during cooling. This scenario contrasts with a buffered case, in which f_{H_2O} and intracrystalline water contents rapidly decrease during cooling. For a specific peak f_{H_2O}, buffering will therefore result in less diffusive exchange. Not all minerals exhibit a simple dependence of D_{0x} on f_{H_2O}. For example, zircon and magnetite exhibit a discontinuous dependence of D on f_{H_2O}, with nearly identical (and fast) D values at P_{H_2O} ranging from 70 to 10 000 bars (Giletti and Hess 1988; Watson and Cherniak 1997) but slow D values at 1 atm (Watson and Cherniak 1997). For these minerals, the models should nonetheless be reasonably accurate for two reasons: (1) at high T the difference between buffered and wet diffusivities is not very large (within ~1 order of magnitude) and (2) the change from wet to dry diffusivities occurs at sufficiently low T that the minerals are already closed to diffusional exchange. Because this study focuses on the maximal retardation of diffusional resetting that may occur because of f_{H_2O}-buffering, Equations 1a and 1b are preferred over alternative expressions for D that are more similar to wet diffusion rates.

Although the above theory provides a basis for interpreting high-f_{H_2O} rocks, modeling relatively low-f_{H_2O} rocks, such as granulites, is complicated by the possible occurrence of CO_2-rich fluids and their influence on D_{Ox}. Sharp et al. (1991) showed that D_{Ox} in quartz at P_{CO_2} = 100–7200 bars is ~100 times slower than under wet conditions, and ~100 times faster than at P_{CO_2} <1bar. They suggested that D_{Ox} at high P_{CO_2} is enhanced by a fast-diffusing species associated with CO_2, analogous to the interpretation that D_{Ox} in hydrothermal experiments is enhanced by fast-diffusing molecular water. These results imply that CO_2-rich fluids probably play a minor role in influencing oxygen diffusion in most rocks, even in granulites. The activity of water would have to be less than approximately 0.01 for the effect of dissolved water on D_{Ox} to become subsidiary to that of CO_2. Few granulites are so dry, but for those rocks with f_{H_2O} approximately <100 bars and $P_{CO_2} \geq$ 100 bar, diffusion rates based on the determinations of Sharp et al. should be used.

BUFFERING OF F_{H_2O}: CALCULATED EFFECTS

The basic model

Three model rocks are considered: (1) a water-saturated middle amphibolite-grade metapelite containing the assemblage Grt+Chl+Qtz at 575 °C and 5.5 kbar; (2) a moderately wet upper amphibolite-grade metapelite containing Kfs+Ms+Sil+Qtz at 650 °C and 6 kbar; and (3) a moderately dry granulite-grade metabasite containing Cpx+Opx+Hbl+Pl at 750 °C and 8 kbar. Other minerals can be present without affecting the fugacity calculations or the principal results described below. It is assumed that retrograde infiltration of aqueous fluids does not occur, because potentially this would stabilize a different assemblage, and because isotope exchange with the fluid could change isotopic compositions of minerals with fast oxygen diffusivities. Water fugacities are assumed to be 3250, 3900, and 1490 bars, which correspond to P_{H_2O} values of 5.5 kbar, ~5.4 kbar, and ~2 kbar, and a_{H_2O} of 1.0, ~0.84, and ~0.15, respectively. The low water activity for the metabasite was chosen to be representative of that determined by mineral equilibria in granulites (Valley et al. 1990). For these assemblages, f_{H_2O} can be calculated according to the following reactions, as normalized to 1 mol of H_2O:

$$1/4 \text{ Chlorite} + 1/2 \text{ Quartz} = 3/8 \text{ Pyrope} + H_2O$$

$$\text{Muscovite} + \text{Quartz} = \text{Potassium feldspar} + \text{Sillimanite} + H_2O$$

$$3/4 \text{ Tremolite} + 1/4 \text{ Pargasite} = 1/4 \text{ Albite} + 1/4 \text{ Ca-Tschermak's pyroxene} + 7/4 \text{ Diopside} + 3/2 \text{ Enstatite} + H_2O$$

Results are virtually unaffected by use of alternative reactions, for example one involving quartz, tremolite, enstatite, and diopside in the metabasite, or by Fe-end-members. A P-T path must be assumed (because f_{H_2O} depends strongly on pressure), and for simplicity a linear path for each rock to surface conditions of 1 bar and 25 °C was used. At each point along the P-T path, f_{H_2O} is determinable from the expression:

$$-RT\ln(f_{H_2O}) = \Delta G^\circ + RT\ln(K_{eq}) \qquad (2)$$

where

$$\Delta G^\circ = \Delta H(1 \text{ bar}, T) - T\Delta S(P, T) + P\Delta V(\text{solids at } P,T) \qquad (3)$$

Note that K_{eq} reflects only the activities of the solids and of the fluid at standard state. Values for K_{eq} can be determined from the assumed peak P-T conditions and f_{H_2O}, combined with tabulated thermodynamic properties (Holland and Powell 1990). At peak conditions, $RT\ln(K_{eq})$ = 3.37, 0, and –11.15 KJ, respectively. Although K_{eq} may change somewhat during cooling (e.g., through Fe-Mg or K-Na exchange), the sense of shift will be opposite for the different end-member reactions. Because both Fe-Mg or K-Na end-member reactions can be written for a given rock, calculations that assume constant K_{eq} probably monitor expected f_{H_2O} accurately. Alternatively, mineral modes could be specified in a less general model that allows fully quantitative characterization of f_{H_2O} at each P-T condition. However, when applied to model metapelites, this approach did not yield results that differ substantially from the more simple, single-reaction modeling.

Model results

Results of the numerical calculations using Equations 1 and 2 (Table 1, Fig. 1) show that diffusion rates are faster at peak metamorphic conditions than determined in hydrothermal experiments. This is expected because hydrothermal experiments ordinarily are conducted at P_{H_2O} = 1 kbar, whereas even in the driest rock considered, f_{H_2O} at peak conditions corresponds to P_{H_2O} > 1 kbar. However, as temperature drops, buffering causes f_{H_2O} to decrease below that of the experiments. In fact, the models were considered only to T = 300 °C, because at that point predicted f_{H_2O} is so low that the model rocks are not only physically but also thermodynamically dry, and diffusional exchange will become unimportant. In all cases, oxygen diffusion rates in buffered rocks are initially faster but eventually slower than determined in hydrothermal experiments. This is reflected in a steeper slope in the distribution of D vs. $1/T$ (Fig. 1). The values for calculated ln(D) can be regressed against $1/T$ to obtain apparent D_0 and E terms, which then can be used in diffusion calculations. These retrieved D_0 and E terms are only apparent because they incorporate diffusivities that correspond to different values of f_{H_2O} and depend on the buffering assemblage and P-T history specific to each model. Nonetheless, they accurately reflect the calculated change of diffusivity with temperature, and so allow the effects of f_{H_2O}-buffering on diffusive exchange and isotopic closure to be determined.

One test of the effect of f_{H_2O} buffering is to determine closure temperatures (T_c) according to the approach of Dodson (1973). This approach assumes that diffusion is the sole means of isotopic exchange during cooling, and that changes in bulk mineral composition are driven by changes of composition on grain surfaces, which maintain equilibrium at all times during

TABLE 1. Calculated f_{H_2O} and D of quartz during cooling in three buffered assemblages

T (˚C)	P (bars)	f_{H_2O}	Quartz D (1a)	Quartz D(1b)	Quartz D(wet)	Quartz D(dry)
			Granulite-facies Metabasite			
750	8000	1490	2.06e-13	2.00e-13	1.14e-13	1.57e-18
700	7450	727	2.49e-14	2.49e-14	2.63e-14	4.12e-19
600	6350	134	1.83e-16	1.53e-16	8.42e-16	1.80e-20
500	5250	16	4.00e-19	1.69e-19	1.11e-17	3.52e-22
400	4150	0.9	1.50e-22	1.24e-23	4.04e-20	2.13e-24
300	3050	0.02	3.83e-27	9.53e-30	2.07e-23	2.17e-27
			Upper Amphibolite-facies Metapelite			
650	6000	3900	2.89e-14	3.17e-14	5.16e-15	9.38e-20
600	5520	2260	3.10e-15	3.59e-15	8.42e-16	1.80e-20
500	4560	590	1.52e-17	1.64e-17	1.11e-17	3.52e-22
400	3600	95	1.55e-20	1.01e-20	4.04e-20	2.13e-24
300	2640	7.5	1.45e-24	2.27e-25	2.07e-23	2.17e-27
			Middle Amphibolite-facies Metapelite			
575	5500	3250	1.79e-15	2.31e-15	3.14e-16	7.56e-21
500	4750	970	2.50e-17	3.09e-17	1.11e-17	3.52e-22
400	3750	120	1.99e-20	1.45e-20	4.04e-20	2.13e-24
300	2750	7.0	1.36e-25	2.04e-25	2.07e-23	2.17e-27

cooling. No assumption regarding mineral modes is necessary (e.g., an infinite reservoir is not required; Kohn and Valley 1998), and closure temperatures are a simple analytical function of diffusion parameters (D_0 and E), grain size, and cooling rate. Because wet, dry, and buffered diffusion rates can be described by different values of D_0 and E, calculated values of T_c are quantitatively different. The effect of f_{H_2O}-buffering is therefore compared to wet and dry calculations, holding grain size and cooling rate constant (Table 2). For simplicity, only quartz and zircon are considered, because they are common in a wide variety of rocks, but have disparate oxygen diffusion rates.

For the f_{H_2O}-buffering values of D_0 and E, the average T_c for quartz in amphibolite-facies rocks is ~482 ± 6 °C, essentially identical to the calculated T_c using the wet diffusion data (483 °C), but nearly 300 °C lower than predicted using dry diffusion data (764 °C). The average T_c for quartz in the granulite-facies metabasite (~550 °C) is higher than in amphibolite-facies rocks because of lower f_{H_2O} and slower diffusivities, but T_c is nonetheless much lower than predicted from dry diffusion coefficients. Zircon shows similar behavior: values of T_c range from 475 to 560 °C in the buffered assemblages (depending on f_{H_2O}), compared to a wet T_c of ~480 and a dry T_c of ~890 °C. Calculations for several other minerals such as feldspar, amphibole, muscovite, biotite, and pyroxene (not shown) further corroborate the result: buffering of f_{H_2O} affects diffusion rates and ordinarily produces a T_c between that estimated by wet vs. dry diffusion rates; however the f_{H_2O}-buffered T_c is ordinarily within 50–75 °C of the wet T_c, yet ≥200–300 °C different from the dry T_c.

A more realistic model considers the diffusional resetting of all minerals in a metapelite that buffers f_{H_2O}, and reaffirms the similarity in T_c in calculations that use buffered vs. wet diffusion rates. Previous modeling (Giletti 1986; Eiler et al. 1992; Jenkin et al. 1994) has shown the importance of intracrystalline diffusion rates, grain sizes, and cooling rates on final mineral fractionations when wet diffusion rates are assumed. The model here uses the approach of Eiler et al. (1992) as modified computationally by Kohn and Valley (1998). The model employs the apparent D_0 and E values determined above in buffered systems, and thus allows comparison to both wet and dry calculations. An average pelitic bulk composition at kyanite+staurolite-grade was assumed (Spear et al. 1990; Kohn 1993), and f_{H_2O} can be calculated based on the buffering reaction: 3 Staurolite + 25 Quartz = 8 Garnet + 46 Kyanite + 12 H_2O.

A cooling rate of 10 °C/Ma and mineral grain radii of 0.5

TABLE 2. Calculated T_c for quartz and zircon during "dry," "wet," and buffered cooling

	Quartz			Zircon		
Model type	D_0 (cm²/s)	E (KJ)	T_c (˚C)	D_0 (cm²/s)	E (KJ)	T_c (˚C)
"dry" (P_{H_2O}<1 bar)	3.0×10^{-7}	221	764	1.33	448	894
"wet" (P_{H_2O}=1 kbar)	2.9×10^{-1}	243	483	5.5×10^{-6}	210	478
Buffered, Grt+Chl pelite						
Eq. 1a	1.1×10^{4}	305	476	0.21	273	474
Eq. 1b	1.3×0^{6}	335	478	2.5	297	497
Buffered, Kfs+Ms pelite						
Eq. 1a	2.1×10^{3}	298	484	3.8×10^{-2}	265	481
Eq. 1b	7.6×10^{4}	322	488	2.9	294	488
Buffered, Hbl+Pyx metabasite						
Eq. 1a	5.6×10^{4}	342	539	1.1	309	541
Eq. 1b	2.3×10^{8}	406	557	4.4×10^{3}	373	561

Note: The D_0 and E terms are based on regressions of calculated lnD vs. 1/T at 7–10 different T's; r-values are ≥0.995. Although the calculated lnD at 1/T = 973 K is identical for either Equation 1a or 1b, the predicted D values at 973 K using the regressed parameters are slightly different because of differences in curvature in the distribution of points. T_c is the closure temperature (Dodson 1973) calculated assuming a cooling rate of 10 °C/Ma and radii for quartz and zircon of 0.5 mm and 0.05 mm. A slab geometry was used for quartz because diffusion parallel to the *c* axis is several orders of magnitude faster than perpendicular to *c*, whereas an infinite cylinder geometry was used for zircon to accommodate grain shape. The diffusion parameters for quartz are based on exchange with water at 1 kbar (Farver and Yund 1991), and with O_2 at P_{O_2} ≤1 bar (Dennis 1984). The diffusion parameters for zircon are based on exchange experiments with SiO_2 in air, and with water at P_{H_2O} = 70–10 000 bars (Watson and Cherniak 1997).

mm were assumed, which are all typical of rocks described in the literature. This more complete model shows that the dependencies of mineral $\delta^{18}O$ on temperature in a buffered rock (thick solid lines, Fig. 2) are quite similar to those exhibited by a simpler model that uses wet diffusion rates (thin solid lines, Fig. 2), but deviate radically from models that use dry diffusion rates (dashed lines, Fig. 2). The main exception is plagioclase, whose composition is strongly affected by closure of the micas at higher temperatures; nonetheless, the value for T_c in the buffered rock (~330 °C) is closer to that of the wet model T_c (~255 °C) than to the dry (~535 °C). Thus, although natural rocks may lack a physically present fluid phase during cooling, they should in theory exhibit diffusional resetting similar to but somewhat less than that predicted on the basis of simple wet diffusion rates.

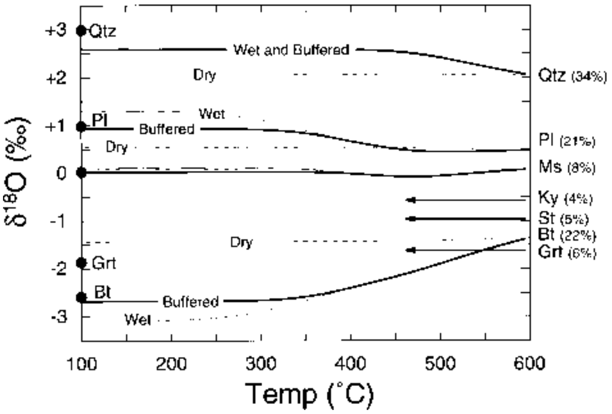

FIGURE 2. Plot of the diffusional resetting of minerals in a typical kyanite+staurolite-grade metapelite, showing effects of buffering of f_{H_2O} on final isotope compositions compared with simpler, constant-f_{H_2O} "wet" and "dry" diffusion models (thin solid and dashed lines, respectively). Because garnet, staurolite, and kyanite have such slow diffusivities, their compositional trajectories are independent of f_{H_2O} at these conditions, and are simply shown by horizontal arrows. The f_{H_2O}-buffering model results in final isotope compositions that are more similar to "wet" diffusion models than to "dry" diffusion predictions. Compilation of published data for metapelites (dots) is most consistent with extensive isotopic resetting, implying that f_{H_2O} was maintained or buffered to high values during cooling, as expected thermodynamically. Percentages are the mineral modes used in the model.

COMPARISON TO PUBLISHED DATA

Example 1

The expected degree of isotopic resetting in the compositionally average metapelite (Fig. 2) can be compared with published data for pelitic bulk compositions (Table 3). Because grain sizes and mineral abundances in individual samples are rarely reported, specific comparisons are substantially uncertain. However, by averaging reported mineral fractionations for ~200 samples, a reasonably accurate comparison with the theoretical model should be possible. It should be noted that retrograde infiltration, which could bias some mineral compositions, cannot be precluded for every rock used in these averages. The assemblages that are reported do not obviously indicate infiltration, and it is hoped that if retrograde infiltration did occur in a few samples, this merely increased the scatter of the data, rather than shifting the compositional means.

Critical to this comparison are the assumed values of the fractionation factors. Most values (Table 4) are based on carbonate exchange experiments (Chiba et al. 1989; Clayton et al. 1989; Chacko et al. 1996). The values for kyanite and the ferromagnesian minerals are based on analysis of petrologically well-characterized metapelites (Kohn and Valley 1998), and account for isotopic effects resulting from cation substitutions in natural minerals (garnet and biotite) compared to experiments on end-member phases (grossular and phlogopite). This set of factors is internally consistent with experimental determinations, yet for some minerals is quite different from other derivations (Bottinga and Javoy 1975; Zheng 1993; Hoffbauer et al. 1994), a point that is considered in more detail below. The fractionation factor for kyanite is consistent with the empirical determination of Sharp (1995).

The model is less sensitive to the choice of wet diffusion coefficients. Either different hydrothermal studies showed similar D values for the same mineral, or there has only been one detailed hydrothermal study for any given mineral. Wet diffusion rates were taken from Giletti et al. (1978), Fortier and Giletti (1991), Farver and Yund (1991), and Coghlan (1990) for feldspar, muscovite, biotite, quartz, and garnet. Where experiments were lacking (staurolite and kyanite), the empirical model of Fortier and Giletti (1989) was used. Dry diffusion data are more sparse, and were taken from the detailed studies of Dennis (1984) for quartz and from Ryerson and McKeegan (1994) for feldspar; for all other minerals, the dry diffusion rate simply was assumed to be 5 orders of magnitude slower than the wet rate, similar to the difference determined for quartz (~5 orders of magnitude) and smaller than the difference observed for zircon (~10 orders of magnitude). Note that most of the oxygen diffusion data of Sharp et al. (1991) for quartz are not relevant, because they are enhanced by high P_{CO_2}. At low P_{CO_2} (and low f_{H_2O}), diffusion rates determined by Sharp et al. (1991) are indistinguishable from those of Dennis (1984).

Average measured fractionations (dots, Fig. 2) are shown relative to muscovite, which should change composition very little during cooling (Kohn and Valley 1998; Fig. 2). These measured compositions support the hypothesis that substantial

TABLE 3. Fractionation factors used for modeling

Mineral:	Qtz	Alb	An	Ms	Ky	St	Opx	Bt	Cpx	Hbl	Grt	Mt
A:	0.0	1.0	2.0	1.5	2.0	2.3	2.4	2.6	2.8	2.8	2.8	6.3

Note: "A" is the constant in the approximate fractionation equation: $\Delta(Qtz\text{-}i) \sim A_i \times 10^6/T^2$ (Δ in per mil and T in kelvins). The A-terms for Qtz, Ms, Pl, Cpx, Opx, and Mt are based on carbonate-exchange experiments (Chiba et al. 1989; Clayton et al. 1989; Rosenbaum et al. 1994; Chacko et al. 1996), the terms for Ky, St, Bt, and Hbl are based on empirical analysis of restricted bulk compositions (Kohn and Valley 1998). The empirically derived terms for garnet, hornblende, and biotite are similar to experimental results for grossular, tremolite, and phlogopite, but account for the isotope effects of cation substitutions (Fe+Mg+Mn for Ca in garnet, and Na, Al, and Ti substitutions in hornblende and biotite).

TABLE 4. Average oxygen isotope fractionations among minerals in amphibolite-facies metapelites

Mineral (i)	Fsp	Ms	Grt	Bt	Mt
D(Qtz-i)	2.0	3.0	4.8	5.7	9.5

Note: Fractionations are all in per mil relative to quartz. Data from Garlick and Epstein (1967), Shieh and Taylor (1969), Schwarcz et al. (1970), Fourcade (1972), Hoernes and Friedrichsen (1974, 1978, 1980), Shieh and Schwarcz (1974), O'Neil and Ghent (1975), and Hoernes and Hoffer (1979).

isotope resetting is common during cooling (Deines 1977; Giletti 1986). The degree of resetting is closely approximated by the f_{H_2O}-buffered model but distinct from the dry diffusion model; the buffered model is a better match than the wet diffusion model. This comparison supports the contention that diffusional resetting in amphibolite-facies rocks occurs under f_{H_2O}-buffered conditions, even if a hydrous fluid was not present during cooling.

Example 2

A second evaluation of the conditions of resetting can be made based on the fractionations of minerals that have the same closure temperatures. Although general models have emphasized the effect of mineral modes on final oxygen isotope fractionations in rocks that contain many minerals with different values of T_c (Giletti 1986; Eiler et al. 1992; Jenkin et al. 1994), if two minerals have the same T_c, then they should preserve a fractionation corresponding to that T_c irrespective of mineral modes (Kohn and Valley 1998). Hydrothermal diffusion experiments (Fortier and Giletti 1991; Giletti and Hess 1988; Farver and Yund 1991) suggest that Ms-Bt have a common T_c of ~300 °C, and that Qtz-Mt both have a T_c of ~480 °C. If diffusion rates are commensurate with hydrothermal experiments, then measured fractionations should on average correspond to these values of T_c. However, if dry diffusion rates apply, then fractionations should reflect peak metamorphic conditions for all except the highest temperature rocks (≥750 °C), which should show Qtz-Mt closure at 750–800 °C.

Data from the literature (Fig. 3a) show that Ms-Bt pairs cluster around an apparent temperature of ~300 °C, whereas Mt-Qtz has an apparent temperature of ~540 °C. These data demonstrate substantial diffusional resetting, which is consistent with relatively high f_{H_2O} during cooling. If instead rocks were dry

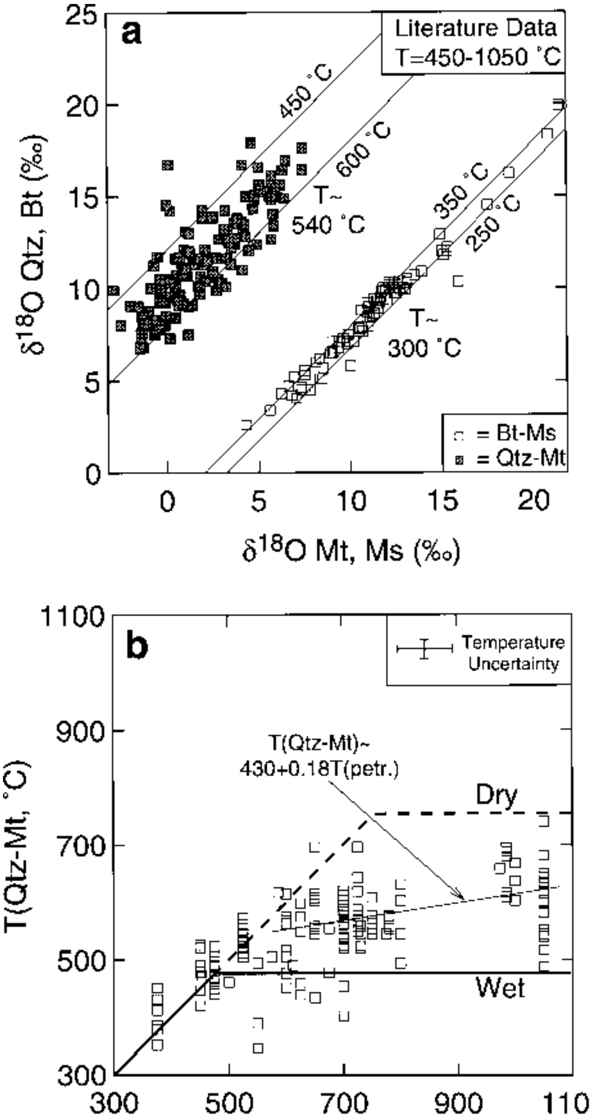

FIGURE 3. (a) Plot of $\delta^{18}O$ of Qtz vs. Mt (solid squares) and of Bt vs. Ms (open squares) using published data from rocks whose peak metamorphic conditions range from greenschist through granulite facies. The relatively low apparent temperatures exhibited by these mineral pairs support the hypothesis that f_{H_2O} was buffered to high levels during cooling, and that dry diffusivities are not relevant. **(b)** Plot of the apparent Qtz-Mt T vs. petrologic *T* illustrating substantial isotopic resetting of high-*T* rocks (amphibolite- and granulite-facies). Thick solid and dashed lines show expected relationships if diffusional exchange occurs at wet and dry rates respectively. At *T*(petrologic) = 550 °C, *T*(Qtz-Mt) is intermediate between expected wet and dry values. Regression of T(Qtz-Mt) vs. *T*(petrologic) >550 °C yields the thin solid line and equation. The positive slope to the line could reflect an increase in rock dryness with increasing grade, which would cause higher-*T* rocks to have slower intracrystalline oxygen diffusion rates, and hence higher closure temperatures. The large data scatter could result from differences in grainsizes, water fugacities, and cooling rates in different samples. Data for both plots from Garlick and Epstein (1967), Shieh and Taylor (1969), Wilson et al. (1970), Schwarcz et al. (1970), Fourcade (1972), Hoernes and Friedrichsen (1974, 1978, 1980), Shieh and Schwarcz (1974), O'Neil and Ghent (1975), Hoernes and Hoffer (1979), Brown and O'Neil (1982), Matthews and Schliestedt (1984), Jiang et al. (1988), Sharp et al. (1988), Cartwright and Valley (1992), Bröcker et al. (1993), Eiler and Valley (1994), and Farquhar et al. (1996). Values of petrologic *T* based on reported peak temperatures (Shieh and Taylor 1969; Wilson et al. 1970; Brown and O'Neil 1982; Matthews and Schliestedt 1984; Sharp et al. 1988; Cartwright and Valley 1992; Bröcker et al. 1993; Farquhar et al. 1996), regional geothermometry (Frey et al. 1980; Annovitz and Essene 1990; Lal 1993; Ouzegane and Boumaza 1996), and typical temperatures for metamorphic zones (biotite-zone = 450 °C, garnet = 500–550 °C, staurolite = 575 °C, kyanite = 600–625 °C, sillimanite = 650 °C, sillimanite-Kfs = 675 °C).

during cooling, Δ(Ms-Bt) would be ~1.0-1.7‰, rather than nearly constant at ~2.7‰ (range = 1.9 to 3.5‰). Comparison of Qtz-Mt apparent T (T_{QM}) with independently estimated peak metamorphic T (T_{PM}), shows that above ~550 °C, T_{QM} is substantially reset compared to T_{PM}, and reflects closure at a T between the theoretical limits imposed by wet and dry diffusion rates (Fig. 3b). For the 67 granulite-grade samples, Δ(Qtz-Mt) would be ≤6.6‰ ($T \geq 700$ °C) for dry conditions vs. ~11.1‰ (~480 °C) for wet, whereas measured Δ(Qtz-Mt) averages ~8.9‰ (~570 °C). The Qtz-Mt data also show a slight but statistically significant increase in T_{QM} with increasing T_{PM}. This trend may reflect a decrease in a_{H_2O} and/or f_{H_2O}-buffering capacity with increasing grade, as theoretical calculations for the low-f_{H_2O} metabasite show higher values of T_c compared to high-f_{H_2O} metapelites (Table 2). The observed pattern is that most mineral compositions reflect closure at a temperature similar to or higher than that expected from wet diffusion data, but substantially lower than expected from dry diffusion data, which supports f_{H_2O}-buffering during cooling (Table 2, Fig. 2).

Example 3

A final example concerns the resetting of minerals in granulites from the Georgetown inlier, Queensland, Australia (McNaughton and Wilson 1980). These samples are particularly germane because granulites are widely viewed as being "dry," and because several studies have reached different conclusions about these specific rocks. Oxygen isotope data for these granulites have been used as evidence that (1) diffusional resetting is extensive during cooling (McNaughton and Wilson 1980); (2) little diffusional resetting occurs because conditions were dry (Sharp and Moecher 1994); and (3) cooling rates from peak metamorphic conditions to ~500 °C were 10–20 °C/Ma (Farver 1989). Although various aspects of the data can indeed be used to support all three results, these conclusions are generally unexpected for two reasons. First, in many granulites, f_{H_2O} is low, but much greater than 1 bar (e.g., Valley et al. 1990). Although diffusional resetting should be less extensive than would be calculated using wet diffusion coefficients (Sharp and Moecher 1994), dry diffusion rates are unlikely to be relevant. Second, geochronologic data (Black et al. 1979; Black and Withnall 1993) show a peak metamorphic age of ~1550 Ma and Rb-Sr Ms and Bt cooling ages of ~1400 Ma and ~800 Ma, indicating slow cooling (0.5–3 °C/Ma). This example explores whether numerical models that incorporate fugacity-buffering can resolve some of the disparate conclusions drawn for this data set and also offer insights into the processes of resetting that occur in such dry rocks as granulites.

The analyzed rocks contain the typical granulite-facies assemblage of Quartz + Plagioclase + Orthopyroxene + Hornblende ± Clinopyroxene, and equilibrated at a peak T of ~790 °C (McNaughton and Wilson 1980). Mineral modes and $\delta^{18}O$ values have been reported for all rocks, and the grain sizes were reported for one sample (McNaughton and Wilson 1980; Farver 1989). Of the five samples originally described, one was not modeled because it apparently does not contain hydrous minerals, and so its f_{H_2O}-buffering capacity could not be evaluated. For each of the other four rocks, nine models were constructed assuming wet, dry, and f_{H_2O}-buffered diffusivities, and cooling rates of 0.5 °C/Ma, 3 °C/Ma, and 15 °C/Ma. The assumed peak f_{H_2O} was the same as used in the metabasite model above, reflecting a reduced a_{H_2O} that is typical of granulites (Valley et al. 1990).

Model results (Table 5; Fig. 4) show that quartz compositions are the most sensitive to variations in f_{H_2O} and cooling rate, and that most data can be matched closely by fugacity-buffering models with a slow cooling rate of 0.5–3 °C/Ma. As found previously (Farver 1989), wet models consistently overestimate the amount of diffusional resetting, unless cooling rates were ~15 °C/Ma, and hence much faster than suggested by the geochronologic data. Conversely, none of the dry diffusion models match the observed data, unless cooling rates were so extraordinarily slow (<<0.1 °C/Ma) that the age of the rocks exceeds that of the Earth. Overall, neither "wet" nor "dry" models fit the data well, whereas the f_{H_2O}-buffering models match the measurements accurately.

DISCUSSION

Rocks that retain peak metamorphic compositions

Despite the foregoing support for extensive diffusional resetting under f_{H_2O}-buffered conditions, some rocks clearly retain oxygen isotope fractionations that are not reset by diffusion during cooling. For example, although many diopside-calcite marbles from the central Adirondack Mountains, New York, show a decrease in diopside $\delta^{18}O$ with decreasing grain size (Edwards and Valley 1998), as expected from hydrothermal experiments of oxygen diffusivity in diopside (Farver 1989), other nearby marbles of essentially identical mineralogy show no such dependence (Sharp and Jenkin 1994; Edwards and Valley 1998). The simplest explanation of these conflicting data is that the marbles had different values of peak f_{H_2O}, which affected oxygen diffusivities differentially (Edwards and Valley 1998). Most importantly for this study, there is no evidence that these marbles had a mineral assemblage at the peak of metamorphism that was capable of buffering f_{H_2O}. Some of the

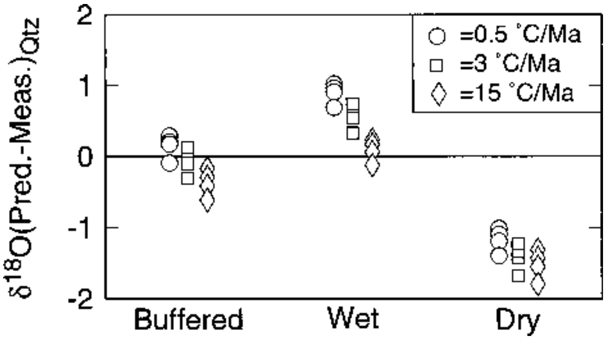

FIGURE 4. Results of f_{H_2O}-buffering, wet, and dry models as applied to quartz compositions of granulites from the Georgetown inlier, Queensland, Australia. In these mafic bulk compositions, quartz $\delta^{18}O$ is most sensitive to input parameters (cooling rate, diffusivities, etc.). Buffered models agree well with measured data (the difference between predicted and measured compositions is nearly zero) using observed cooling rates of 0.5–3 °C/Ma, whereas wet models do not match the data unless cooling rates were ~15 °C/Ma, and hence much faster than determined geochronologically. Dry models do not fit the data.

TABLE 5. Theoretical models of quartz $\delta^{18}O$ compositions in Australian granulites

		3˚C/Ma			0.5˚C/Ma			15˚C/Ma		
Sample	$\delta^{18}O$ Meas.	Buff	Wet	Dry	Buff	Wet	Dry	Buff	Wet	Dry
E011	8.40	**8.37**	8.98	7.08	8.62	9.38	7.32	8.13	8.64	6.92
E014B	9.39	**9.29**	9.94	7.98	**9.56**	10.35	8.18	9.06	**9.59**	7.82
E072	9.50	9.20	9.83	7.90	**9.46**	10.24	8.09	8.96	**9.47**	7.75
E078	8.30	**8.42**	9.02	7.18	8.68	9.43	7.29	**8.19**	8.68	7.06

Note: Bold values for model quartz $\delta^{18}O$ are within 0.2‰ of measured values. Measured and predicted values for other minerals are as follows:
E011: $Pl_m = 5.44$, $Pl_p = 5.16–5.66$, $Hbl_m = 4.19$, $Hbl_p = 3.83–4.31$, $Cpx_m = 4.07$, $Cpx_p = 4.14–4.31$, $Opx_m = 4.35$, $Opx_p = 4.64–4.66$;
E014B: $Pl_m = 5.84$, $Pl_p = 5.94–6.38$, $Hbl_m = 5.28$, $Hbl_p = 4.87–5.21$, $Opx_m = 5.31$ $Opx_p = 5.55–5.56$;
E072: $Pl_m = 5.42$, $Pl_p = 5.90–6.34$, $Hbl_m = 5.32$, $Hbl_p = 4.74–5.14$, $Cpx_m = 5.23$, $Cpx_p = 5.00–5.14$, $Opx_m = 5.42$, $Opx_p = 5.48–5.49$;
E078: $Pl_m = 5.47$, $Pl_p = 5.34 –5.80$, $Hbl_m = 4.32$, $Hbl_p = 3.99–4.46$, $Cpx_m = 4.27$, $Cpx_p = 4.28–4.46$, $Opx_m = 4.44$, $Opx_p = 4.78–4.81$.

marbles could have developed extremely low f_{H_2O} that, if retained throughout cooling, would lead to less resetting than expected from either hydrothermal experiments or fugacity-buffering models. This effect may also explain the high-*T* oxygen isotope fractionations evidenced in some granulites (Farquhar et al. 1996). If these rocks lacked hydrous buffering assemblages, then peak f_{H_2O} and diffusion rates might have been quite low, minimizing diffusional resetting. Although most granulite-facies rocks do show extensive diffusional resetting, the dependence of isotope resetting on f_{H_2O}-buffering (this study), and the general decrease in hydrous phase abundances and a_{H_2O} in granulite-facies rocks (Valley et al. 1990) explains the slight overall increase in values of apparent Qtz-Mt *T* with increasing grade above ~550 °C (Fig. 3).

Minerals from schists of the Langtang region of central Nepal also retain surprisingly small oxygen isotope fractionations (Massey et al. 1994), despite the presence of micas and the thermochemical potential for f_{H_2O}-buffering. However, new insights into the special geologic setting of these samples impacts evaluation of these data. Rocks from the same structural level of the central Himalaya have peak metamorphic ages as young as 5–6 Ma, corresponding to *T* ~550 °C and *P* ~6–8 kbar (Harrison et al. 1997). Given that average cooling rates were extraordinarily rapid (~100 °C/Ma), it is perhaps not surprising that peak metamorphic oxygen isotope compositions might be quenched in.

Comparison of isotopic and petrologic temperatures

In compiling data from the literature, it was found that calculated oxygen isotope temperatures were commonly reported to correspond well with expected peak metamorphic conditions, which would seem to favor dry diffusion rates over wet. However, the Qtz-Mt and Ms-Bt data from a broad spectrum of rocks unequivocally correspond to temperatures well below the peak of metamorphism (Fig. 3: Qtz-Mt ≤ 600 °C in granulite-facies rocks, and Ms-Bt ~300 °C in amphibolite-facies rocks). Indeed, inaccurate fractionation factors, especially for the micas, may have led to the conclusion in some studies that peak metamorphic compositions are retained as a result of dry diffusion. For example, fractionation factors that have been used for biotite (Bottinga and Javoy 1975) and muscovite (Zheng 1993; Hoffbauer et al. 1994) in isotopic thermometry are significantly in error, as shown both experimentally (Chacko et al. 1996) and by analysis of rocks whose minerals are resistant to isotopic exchange because of unusual mineral assemblages and modes (Kohn and Valley 1998). Use of the inappropriate fractionation factors increases apparent temperatures by tens to hundreds of degrees Celsius, implies retention of peak metamorphic isotope compositions, and leads to inferences that diffusion rates and rocks were dry. In contrast, if experimentally derived fractionation factors are used, the good correspondence between measurements and f_{H_2O}-buffered models (Fig. 2) corroborates widespread and substantial diffusive resetting of mineral oxygen isotope compositions under f_{H_2O}-buffered conditions.

Implications for *P-T-t-*f_{H_2O} paths

Assuming the f_{H_2O}-buffering models are applicable, then the degree of resetting of oxygen isotopes could in principle be used to constrain f_{H_2O} during cooling (if the *P-T-t* path is known), or the *P-T-t* path (if f_{H_2O} is known). In practice, in uninfiltrated rocks, the degree of diffusional resetting is rather insensitive to either peak f_{H_2O} or cooling rates. For example, in sample E011, very large ranges in peak f_{H_2O} of 450–5000 bars and in cooling rate of 0.5–15 °C/Ma affect predicted quartz $\delta^{18}O$ by only 0.35‰ and 0.49‰, respectively. Although qualitative distinctions may be possible between high- vs. low-f_{H_2O}, or rapid- vs. slow-cooling, phase equilibria and geochronology should remain the preferred methods for determining these parameters. Instead, the new models offer the possibility of investigating petrologic processes in rocks where the peak f_{H_2O} and cooling rate are already known. Deviations from models may identify open-system processes, which can then be investigated further with additional isotope and petrologic techniques.

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APPENDIX 1: DEVELOPMENT OF PHENOMENOLOGICAL DIFFUSION EQUATIONS

If only D_0 is influenced by changes of f_{H_2O} with a proportionality constant, α, then:

$$D = D_0^* e^{-E/RT} \qquad \text{(A1a)}$$

where

$$D_0^* = D_0\left[\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right]^{\alpha} \qquad \text{(A1b)}$$

If only E is affected:

$$D = D_0 e^{-E^*/RT} \qquad \text{(A2a)}$$

where

$$E^* = E - \alpha * 973R\ln\left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right) \qquad \text{(A2b)}$$

Assuming α = 1.0, expanding and simplifying yields expressions 1a and 1b in the text:

$$D = \left[D_0 e^{-E/RT}\right] * \left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)^{1.0} \qquad \text{(A3a)}$$

and

$$D = D_0 \exp\text{-}\left[\frac{E - 973R\ln\left(\dfrac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)}{RT}\right]$$

$$= \left[D_0 e^{-E/RT}\right] * \left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)^{1.0*973/T} \qquad \text{(A3b)}$$

A more general description of the fugacity-dependence of the diffusion coefficient would allow for changes in both D_0 and E. In this case:

$$D = D_0^* e^{-E^*/RT} \qquad \text{(A4)}$$

where

$$D_0^* = D_0\left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)^{\beta} \qquad \text{(A5a)}$$

and

$$E^* = E - \gamma * 973R\ln\left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right) \qquad \text{(A5b)}$$

yielding the general equation:

$$D = \left[D_0 e^{-E/RT}\right] * \left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)^{\beta} * \left(\frac{f_{H_2O}(P,T)}{f_{H_2O}(1\text{kbar},T)}\right)^{\gamma * 973/T} \qquad \text{(A6)}$$

The constraint that log(D) varies linearly with log(f_{H_2O}) at T = 973K with a proportionality constant of α further requires that:

$$\beta + \gamma * \frac{973}{T} = \alpha \qquad \text{(A7)}$$

There is no explicit requirement that β or γ be positive, zero, or negative, but experimental data (Giletti et al. 1978; Farver 1989, 1994; Dennis 1984; Farver and Yund 1990, 1991; Ryerson and McKeegan 1994; Watson and Cherniak 1997) show that, relative to wet diffusion rates, the dry value for D_0 either increases ($\beta < 0$), stays the same ($\beta = 0$), or decreases proportionately to f_{H_2O} ($\beta = 1$), whereas retrieved E stays the same ($\gamma = 0$) or increases ($\gamma > 0$). Thus $\beta \leq 1$, and $\gamma \geq 0$. The maximum variation in f_{H_2O} corresponding to continuous variations in D is ~3 orders of magnitude (e.g., Farver and Yund 1991), whereas the maximum change in E between wet and dry diffusion rates for any mineral is ~350 KJ (Giletti et al. 1978 vs. Ryerson and McKeegan 1994, for feldspar). Because the change between wet and dry values of E corresponds to a much larger range of f_{H_2O} than used by Farver and Yund (1991), substituting $\ln[f_{H_2O}(P,T)/f_{H_2O}(1\text{kbar},T)] = 73$ and $E^*\text{-}E = -350$ KJ into Equation A5b gives the strong maximum limit: $\gamma << 7$. Numerical calculations were found to be extremely insensitive to the specific value of γ above the T_c of the mineral. For example, at $\gamma = 7$, the theoretical closure temperature of quartz in the upper amphibolite-facies metapelite was estimated to be 481 °C, essentially identical to that derived using the simpler equations in the text. Because the calculations are so insensitive to the values of γ and β, the use of the simpler equations is believed to be accurate.