Why most “dry” rocks should cool “wet”

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ABSTRACT

A new consideration of oxygen isotope resetting among metamorphic minerals is made accounting for (1) the possibility of $f_{\text{H}_2\text{O}}$-buffering by typical mineral assemblages during cooling and (2) experimental data that show that high $f_{\text{H}_2\text{O}}$ 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$_2$O-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 $f_{\text{H}_2\text{O}}$ 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 $f_{\text{H}_2\text{O}}$-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 $f_{\text{H}_2\text{O}}$ 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$_2$O-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$_2$O-absent) than when “wet” ($P_{\text{H}_2\text{O}} = 1$ 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 $f_{\text{H}_2\text{O}}$ 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 $f_{\text{H}_2\text{O}}$ is much greater than 1 bar. Because high oxygen diffusion rates correlate with high $f_{\text{H}_2\text{O}}$ in experiments (Farver and Giletti 1985; Farver and Lund 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 $f_{\text{H}_2\text{O}}$ 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 $f_{\text{H}_2\text{O}}$ 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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