

Carbonate clumped isotope closure temperatures

BENJAMIN H. PASSEY* AND GREGORY A. HENKES

Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218 (*bhpassey@jhu.edu)

Carbonate clumped isotope thermometry can potentially reveal information about the passage of inorganic carbon through the shallow- and mid-crust on its journey to and from the Earth's deep interior. The ordering of rare isotopes of C and O into the same carbonate groups creates 'multiply-substituted' isotopologues such as $\text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$ (~67 ppm natural abundance). These isotopologues are surrounded in the mineral lattice by isotopically normal isotopologues such as $\text{Ca}^{12}\text{C}^{16}\text{O}_3$ (~982,000 ppm), and solid-state diffusion of C and O over unit cell distances will act to create and remove multiple substitutions. This short length scale of diffusion leads to the possibility of cooling rate-dependent carbonate clumped isotope closure temperatures in the ~100-300 °C range, much lower than traditional mineral oxygen isotope closure temperatures, and a range useful for studying shallow- and mid-crustal processes. We determined Arrhenius parameters for solid-state reordering of C-O bonds in calcite through a series of laboratory heating experiments. We present a closure temperature equation for carbonate clumped isotope thermometry analogous to Dodson's solution first order loss [1], where the closure temperature is a function of cooling rate and the Arrhenius parameters for solid-state C-O bond reordering. The sensitivity of closure temperature to cooling rate is sufficient for order of magnitude inference of cooling rate, provided the Arrhenius parameters of the studied minerals are well known. The inferred cooling rate of Carrara marble is ~3 °C per 10 ka, which is within error of independent estimates of the cooling history of the Alpi Apuane metamorphic core complex.

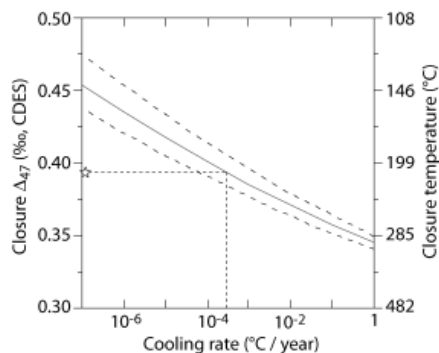


Figure 1: Carbonate clumped isotope closure Δ_{47} and closure temperatures as a function of cooling rate. Solid curved line is the best-estimate closure temperature relationship based on kinetics observed in the laboratory for an optical calcite. The curved dashed lines reflect uncertainty in Arrhenius parameters propagated through the closure temperature model. Star and horizontal dashed line show the mean Δ_{47} value of Carrara marble analyzed in four different laboratories [2]. CDES: 'Carbon dioxide equilibrium scale' [2].

[1] Dodson (1973) *Contrib. Mineral. Petrol.* **40**, 259-274.

[2] Dennis et al. (2011) *GCA* **75**, 7117-7131.

Metamorphic 'cascade effects' due to nucleation-related overstepping

DAVID R.M. PATTISON

Department of Geoscience, University of Calgary, Calgary, Alberta, Canada, pattison@ucalgary.ca

Nucleation difficulty can lead to overstepping of metamorphic reactions. Overstepping can result in multiple reactions being energetically possible, both stable and metastable. The only criterion that has to be satisfied is that each possible reaction lowers the free energy of the system. Overstepping can therefore lead to a 'cascade effect', in which several reactions involving the same reactant phases proceed simultaneously in a small temperature interval. Two different types of cascade effect are recognized. The first, termed the 'Bushveld-type' in respect of its documentation in the Bushveld aureole (Waters & Lovegrove, *J Met Geol*, 2002), arises from delayed nucleation of a product phase and subsequent production of that product phase from several different reactants. In the Bushveld example, the low-entropy chloritoid to staurolite/andalusite reactions were overstepped to the point that they were overtaken in terms of reaction affinity by high-entropy muscovite+chlorite-consuming reactions. Nucleation of staurolite and andalusite by the latter reactions eliminated the principal kinetic barrier to the progress of the overstepped chloritoid-consuming reactions, such that several staurolite- and andalusite-producing reactions ran in parallel in a small temperature interval, creating a reaction cascade. Fluid release accompanying initial reaction may also have contributed to the cascade effect by facilitating dissolution of chloritoid. The second type of cascade effect, termed the 'Nelson-type' in respect of its documentation in the Nelson aureole (Pattison et al., *J Met Geol*, 2009; 2011) involves a catalytic trigger related to the sudden build-up or influx of fluid in rocks that have overstepped two or more stable reactions. The result is simultaneous production of different product phases from the same reactant minerals. In the Nelson aureole, the clustering of the garnet, staurolite and andalusite isograds, contrary to their predicted wider spacing according to equilibrium thermodynamics, and the textural evidence that each of these porphyroblasts formed from reaction of the matrix with no evidence of the predicted consumption of the earlier-formed porphyroblasts, suggests the simultaneous operation of several chlorite-consuming reactions. Once the nucleation-related barriers to initial garnet formation were overcome, fluid was released into the grain boundary network, enhancing rates of intergranular transport and possibly further nucleation. This created a positive feedback and a vigorous reaction interval involving production of several porphyroblast phases from the same matrix reactants.