How mountains are made out of molehills: The link between geological episodes and events as revealed by kinetic studies

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Rates of reaction and diffusion measured in the laboratory are increasingly being used to determine the durations of a variety of processes ranging from evolution of plumbing systems under volcanoes, through partial melting in the crust to stages of exhumation of metamorphic rocks and mountain ranges. The results are often unexpectedly short timescales of days to millenia, rather than millions of years. More conventional bulk isotopic data from these same rocks often date events separated by millions of years. However, confidence in the modern kinetic rates measured in the laboratory, combined with other geological observations, now indicate that the shorter timescales obtained from kinetic modelling relate in many cases to durations of individual episodes that make up the larger events that were more conventionally demarcated. The short duration of episodes are consistent with time scales of thermal relaxation and other physical processes. Indeed, the durations determined from kinetic modelling can be used as an added fingerprint to identify the nature of processes that produced particular chemical and textural features recorded in rocks. Examples from igneous as well as metamorphic systems will be discussed.

These improvements in the temporal resolution of geological processes have been made possible in part by advances in analytical methods that allow us to manipulate and measure concentration gradients over scales of a few nanometers. Scaling laws, such as the relation $x^2 \sim Dt$ for diffusion, allow us to translate the enhanced spatial resolution (x) to increased resolution of time (t), or duration of processes. These analytical advances allow us to (i) reliably determine smaller diffusion coefficients and other rate constants in the laboratory and (ii) measure rates at conditions close to those at which processes occur in nature, so that the large source of uncertainty that arose from extrapolation is largely eliminated. Some examples of such experimental studies will be shown from our recent works.

Two (nearly) single-mineral monitors of the activity of rutile, 2: Applications

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We have recently calibrated two exchange reactions involving Ti in micas that have equilibrated with rutile and quartz [1]. These calibrations allow estimation of:

(1) a(Rt) in rutile-absent rocks, if pressure and temperature are known and SiO_2 (either quartz or coesite) is present;

(2) Ti contents of mica coexisting with rutile and SiO_2, if pressure and temperature are known;

(3) temperature, if rutile and SiO_2 are present and pressure is known.

Although Ti in mica can serve as a thermometer in rutile-bearing assemblages, it is much less sensitive to T than Ti-in-Qtz, Zr-in-Rt or Ti-in-Zrc (assuming Zrc is present). Rather, we anticipate that the main application of this equilibrium will be for estimating a(Rt) in conjunction with Ti-in-Qtz and Ti-in-Zrc thermometry in rocks that lack rutile, and especially in high-variance or inclusion assemblages which limit the use of traditional geothermometers. For example, Hopkins *et al.* [2] calculated Ti-in-Zrc temperatures of ~700°C for Hadean zircons that lack rutile, but contain inclusions of muscovite (~0.4 wt% TiO_2) and quartz. When combined with our Ti-in-Ms calibration, a(Rt) for the Ms-Qtz inclusions is estimated to be ~0.85. Iterative solution of T from Ti-in-Zrc and a(TiO_2) from Ti-in-Ms increases the best-fit calculated temperature by ~15°C. This result further supports the key conclusion that Hadean zircons formed in relatively low-T magmas.

The Ti content of mica can also serve as a useful check on equilibrium mineral compositions and assemblages. Our literature search uncovered several discrepancies in HP and UHP micas: the measured Ti content was 2-3 times lower than predicted from the inferred P-T conditions. These results imply that most phengite in HP and UHP rocks forms at low-T on the prograde path, and that many measured phengite compositions are not in equilibrium with the peak mineral assemblage.

In summary, while Ti-in-mica may not become a widespread thermometer, it can be used to diagnose chemical disequilibrium where T is already known, and refine temperatures determined using trace element thermometers for all mica + quartz-bearing assemblages.

[1] Kohn & Chambers (2009) *GCA,* this volume. [2] Hopkins *et al*. (2008) *Nature*, v. **456**, p. 493-496.