

New Ti-in-quartz diffusivities reconcile natural Ti zoning with time scales and temperatures of upper crustal magma reservoirs

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ABSTRACT

Titanium-in-quartz thermometry and diffusion chronometry are routinely applied to felsic magmatic systems. These techniques can be used to determine for how long, and at what temperatures, shallow crustal magmatic systems remain partially molten, both of which are fundamental for assessing volcanic hazards. We have conducted new Ti-in-quartz diffusion experiments at 1 bar, in air, between 900 and 1490 °C, and analyzed the products by secondary ion mass spectrometry (SIMS) depth profiling. The results show that Ti diffusivity is two to three orders of magnitude lower than previously determined [$\log_{10}D = -8.3 \pm 0.4 \text{ m}^2 \text{ s}^{-1} - [311 \pm 12 \text{ kJ mol}^{-1}/(2.303RT)]$], where R is the universal gas constant ($\text{kJ K}^{-1} \text{ mol}^{-1}$) and T is the temperature in Kelvin. Application of these new diffusivities brings time scales determined by Ti-in-quartz diffusion chronometry, using quartz primarily from ignimbrites, into agreement with those determined from zircon U-Pb ages from the Bishop Tuff system (California, USA). This indicates that quartz crystallized early and recorded all, or much of, the thermal history of this magmatic system. These new data also show that sharp Ti zoning profiles can be maintained in quartz within slowly cooled rocks without necessitating that the quartz crystallization temperature is significantly lower than the experimentally determined H_2O -saturated granite solidus, or that such samples underwent ultrafast cooling, as has recently been proposed for the granitoids from the Tuolumne Intrusive Suite (California, USA). Finally, our data also indicate that, at least regarding the Bishop Tuff, temperatures must have remained at near-solidus conditions for the entire pre-eruptive evolution of the system, thus relaxing interpretations of “cold storage” for this magmatic system.

INTRODUCTION

Understanding the processes forming large silicic volcanic eruptions is crucial for assessing their potential societal and environmental impacts. Because such eruptions have rarely been observed in modern times, preserved deposits from eruptions in the geological record may be our best tools for predicting the nature of eruptions in the future. Quartz commonly forms in the silicic magmatic systems that feed these eruptions, and thus it has the capability to provide useful insights into their thermal, chemical, and temporal evolution. Measured titanium (Ti) contents of quartz in volcanic and plutonic rocks are routinely used for determining crystallization temperatures (the TitaniQ geothermometer;

Wark and Watson, 2006), and Ti concentration profiles, typically interpreted as partially resulting from diffusion, have been employed to determine time scales between quartz growth and eruption (e.g., Wark et al., 2007; Gualda et al., 2012; Chamberlain et al., 2014). Similar Ti diffusion-based techniques have been applied to a wide range of problems in the geosciences, such as to resolve time scales of metamorphic events (Spear et al., 2012), times necessary to form porphyry ore deposits (Mercer et al., 2015), and recently for reexamining quartz crystallization temperatures (Ackerson et al., 2018). Although the TitaniQ geothermometer has been revised and debated (Thomas et al., 2010, 2015; Huang and Audétat, 2012), to date

no independent confirmation of the original Ti diffusivities (Cherniak et al., 2007) has been attempted. To address this, we conducted a series of Ti-in-quartz diffusion experiments, showing 2–3 orders of magnitude slower diffusion than the previous determination.

NEW TITANIUM-IN-QUARTZ DIFFUSION EXPERIMENTS

To make our experiments as closely comparable as possible to those of Cherniak et al. (2007), we employed similar experimental procedures (full details are given in the GSA Data Repository¹). The main difference was that we used TiO_2 - SiO_2 mixes or Ti-doped SiO_2 as the Ti source, rather than pure rutile. This followed preliminary experiments where we found that the use of pure rutile led to considerable interface degradation. Quartz crystals were packed into the powders and annealed in air between 900 and 1490 °C, and analyzed via secondary ion mass spectrometry (SIMS) depth profiling. Depths of ablation pits were measured using white-light interferometry to assign a spatial dimension to the data, and diffusivities as a function of temperature and experimental duration were extracted using standard one-dimensional solutions to the diffusion equation. Fitting the measured diffusion coefficients to the general Arrhenius relationship gives $\log_{10}D = -8.3 \pm 0.4 \text{ m}^2 \text{ s}^{-1} - [311 \pm 12 \text{ kJ mol}^{-1}/(2.303RT)]$, where R is the universal gas constant ($\text{kJ K}^{-1} \text{ mol}^{-1}$) and T is the temperature in Kelvin. These Ti diffusivities are two to three orders of magnitude lower than those determined by Cherniak et al. (2007) within our experimental temperature range (Fig. 1).

As far as we can tell, neither analytical nor experimental artifacts can reconcile our results

¹GSA Data Repository item 2020197, descriptions of experimental and analytical and modeling methods, as well as results and further discussion, is available online at <http://www.geosociety.org/datarepository/2020/>, or on request from editing@geosociety.org.

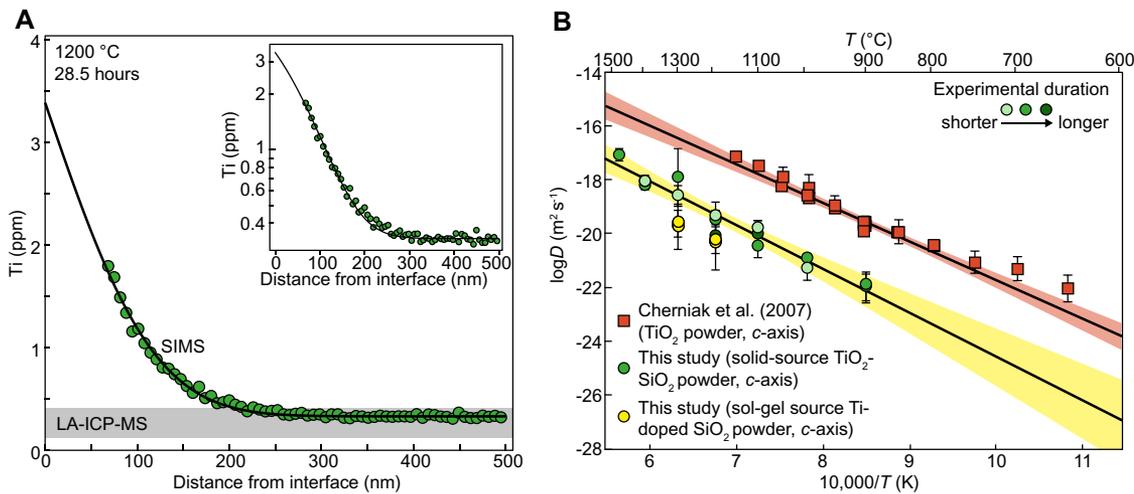


Figure 1. Experimental results. (A) Example Ti diffusion profile obtained by secondary ion mass spectrometry (SIMS) depth profiling. Solid line is fit of constant boundary solution of Fick's second law to the data. Uncertainties on individual data points associated with the Ti content of the standard are $\pm 7\%$. Gray bar is the range of background Ti contents in the starting material (as measured by LA-ICP-MS—laser ablation–inductively coupled plasma–mass spectrometry). Inset: Data recast into semi-log plot. **(B)** Comparison of Ti diffusivity

ity (D) data obtained in this study and the Ti diffusivities of Cherniak et al. (2007), including 95% error envelopes calculated as the product of the standard error of the regression line and the inverse of the Student's *t*-distribution. *T*—temperature. Error bars on individual data points represent one standard deviation. Data obtained using sol-gel source powders show slightly slower diffusivities than those obtained using solid-source powders. Data from solid-source powder experiments from this study are color-coded to show experimental duration (lighter color corresponds to shorter experiment).

(relatively low Ti diffusivity) with those of Cherniak et al. (2007) (relatively high Ti diffusivity), given the following considerations:

(1) Potential artifacts from SIMS depth profiling, notably ion beam mixing, can lengthen diffusion profiles and thus increase calculated diffusion coefficients (Williams and Baker, 1981). In this case, our calculated diffusivities would be too high, so true diffusivities would be even lower. However, our successful time series suggest that this effect is negligible in most cases.

(2) Rutherford backscattering spectroscopy, used by Cherniak et al. (2007), has high detection limits relative to SIMS, thus diffusion profiles of minor and trace elements can be artificially shortened because the ends of the profiles are effectively cut off. If this were the case, the Cherniak et al. (2007) diffusivities would be too low, so true diffusivities would be even higher.

(3) Long, low-concentration tails on our diffusion profiles can be ruled out, given that the background Ti contents at the tail end of our measured diffusion profiles were generally within the Ti concentration range of the starting materials (Fig. 1A). Therefore, we can preclude the possibility that a much faster diffusion mechanism has reequilibrated the background portion of the diffusion profiles to higher Ti concentrations.

(4) Regarding experimental differences between our experiments and those of Cherniak et al. (2007), our low-Ti sources led to considerably lower, and variable, Ti concentrations at the crystal surfaces in this study. This was following preliminary experiments in which the experimental design of Cherniak et al. (2007) was copied as closely as possible, using pure TiO₂ (rutile) powder as the diffusant source.

Without exception, this approach always led to visible interface degradation, suggesting some form of significant surface reaction (see the Data Repository). The variable surface concentrations are likely a result of variable, and potentially incomplete, contact between the powder source and crystal. This is not considered problematic for three reasons. First, in a concentration-independent diffusion regime, the interface concentration should not considerably affect the length scales of diffusion nor the extracted diffusion coefficients (discussed in the Data Repository). Second, if this were indeed an issue, we would expect this to be reflected in time-series experiments, and our time-series runs were successful. Third, the grain-boundary diffusivity of Ti in quartz (albeit in piston-cylinder experiments) is around five orders of magnitude higher than our Ti diffusivities (Bromiley and Hiscock, 2016). Furthermore, it is unlikely from a theoretical perspective that Ti diffusion in quartz is concentration dependent, and indeed neither the results of this study nor those of Cherniak et al. (2007) show any indication of concentration dependence, which would be clearly visible in profile shapes deviating from error functions (e.g., Crispin and Van Orman, 2010; Jollands et al., 2018).

TIME SCALES OF MAGMA CHAMBER EVOLUTION

The evolution of magmatic systems that generate rhyolites is proposed to occur on the order of 10^4 – 10^6 yr (Spera, 1980; Jellinek and DePaolo, 2003; Bachmann and Bergantz, 2004). The nature of the eruptible portion of the system during this time is a matter of debate: some models propose continuous, prolonged extraction of magma from a mush, thus form-

ing a long-lived, crystal-poor magma reservoir (Bachmann and Bergantz, 2004); whereas others suggest that magma mobilization occurs rapidly via an “unzipping” process (Burgisser and Bergantz, 2011). Regardless, crystals carried by the erupting magma may hold a record of processes beginning with their initial nucleation, through their growth, and to their final cooling on Earth's surface. Whether due to thermal or chemical oscillations or to variable growth rates, magmatic quartz is generally zoned in trace elements (Wark et al., 2007; Gualda et al., 2012; Chamberlain et al., 2014; Pamukcu et al., 2016), including Ti. Because of this zoning, there exist chemical potential gradients within the crystals, which drive diffusive fluxes. If the diffusivity of Ti is well known, the spatial extent of the relaxation of these gradients can be used to determine the residence time (generally a maximum, assuming an initial step function) of the crystal in the magmatic system, which sheds some light on the longevity of magmatic systems as a whole.

Titanium-in-quartz geospeedometry was first applied to measured Ti profiles in quartz from the Bishop Tuff (California) by Wark et al. (2007), followed by more extensive studies on the same deposit (Chamberlain et al., 2014; Gualda et al., 2012). The extracted time scales between quartz (over)growth and eruption were consistently short, on the order of years to hundreds of years, relative to the ~80–200 k.y. history of the magma system retrieved from the difference between ages derived from U-Pb zircon geochronology and the age of eruption (Coath and Reid, 2000; Simon and Reid, 2005). The time scales are also long relative to those potentially representing the last pre-eruption recharge (months to years, from Fe-Mg in orthopyroxene diffusion chronometry; Chamberlain et al., 2014) and the eruption

itself (on the order of hours to days; Wilson and Hildreth, 1997; Myers et al., 2018).

When applied to previously published data, the Ti-in-quartz diffusion data reported here bring the Bishop Tuff quartz residence time scales into agreement with time scales of the evolution of the whole system determined from different techniques (Fig. 2). This indicates that Ti-zoned quartz from this locality crystallized early, and that previously measured diffusion profiles record the entirety, or most of, the residence time of the system. As a general guide, time scales determined using the previously determined Ti-in-quartz diffusivities of Cherniak et al. (2007), for systems around 700–800 °C, can be brought in line with our data by multiplying by ~1000. It is notable that some time scales become apparently too long with the application of the new diffusivities if the same modeling approach is followed (Fig. 2). In previous time-scale determinations, it has been reasonable to subsume any issues related to analysis (synthetic smearing out of diffusion zones by analytical techniques) and modeling (initial conditions that

are not perfect step functions; Pamukcu et al., 2016) into the general concept of maximum time scales. In other words, the derived times could only be shortened, but not lengthened, by improved analyses and modeling, which has generally been reasonable considering how short these retrieved time scales were. Using the data set presented here, these issues become considerably more important as Ti now appears to be able to cover the full residence time of the quartz within the magmatic system. Regardless of these complications that will need to be overcome, in light of our new data, Ti diffusion in quartz appears to be a viable tool to retrieve the full residence times of magmatic evolution, and thus could provide complementary information to that determined from zircon.

GRANITE CRYSTALLIZATION TEMPERATURES

Titanium-in-quartz diffusion chronometry has been applied to crystallizing granites with the consideration that temperature, and hence Ti diffusivity, changes over time. Such model-

ing yields temperature-time paths, and in turn sheds light on cooling rates. Results obtained from this approach are generally non-unique—changing the initial temperature and cooling rate can give the same length and geometry of diffusion profiles. Recently, such Ti diffusion modeling was applied by Ackerson et al. (2018) using short (tens of microns) Ti diffusion profiles in quartz from the Tuolumne Intrusive Suite (Sierra Nevada batholith, California, USA). Using the Cherniak et al. (2007) Ti diffusivities, these Ti profiles are too steep to be formed at temperatures $T > 650$ °C without invoking unrealistically fast cooling rates (>300 °C m.y.⁻¹). These modeled profiles, along with Ti-in-quartz thermometry, were used to argue that quartz from the Tuolumne Intrusive Suite formed at a much lower temperature (~500 °C) in order to retain sharp Ti zoning, and by extension, that the H₂O-saturated granite solidus may be considerably lower than the experimentally well-determined value (650–750 °C at 0.1–1 GPa; Tuttle and Bowen, 1958; Luth et al., 1964; Johannes, 1984).

Although the argument put forth by Ackerson et al. (2018) was understandable in the framework of the Ti diffusivities reported by Cherniak et al. (2007), those presented in this study reconcile the experimentally determined 650–750 °C granite solidus (Johannes, 1984; Luth et al., 1964; Tuttle and Bowen, 1958) with the Ti zoning in quartz observed in the Tuolumne Intrusive Suite. Using our Ti diffusion data and following the modeling approach of Ackerson et al. (2018), the measured profiles from the Tuolumne Intrusive Suite can be modeled using an initial temperature of 700 °C and cooling rates of 2–20 °C m.y.⁻¹ (Fig. 3); i.e., without invoking unrealistic cooling rates or low initial temperatures.

COLD OR WARM STORAGE?

Titanium diffusion in quartz has implications for the concept of “cold storage” (Cooper and Kent, 2014; Rubin et al., 2017), whereby a magmatic system is proposed to reside below 650–750 °C for most (~90% of more) of its history, with only periodic heating events. Because characteristic length scales of diffusion profiles are proportional to \sqrt{Dt} , where $Dt = \int D(t) dt$ (D is the diffusion coefficient, and t is time), a reduction in temperature leading to a lower diffusion coefficient would need to be compensated by increased time. If this were the case for the Bishop Tuff, the time scales necessary to generate the measured Ti profiles would need to be considerably longer than any proposed evolution times of this magmatic system—the time scales calculated at 750–800 °C are already at the limit defined by zircon and modeling constraints (Fig. 2). Titanium diffusion profiles are instead consistent with this magma body, at least, remaining at high temperature for tens to hundreds of thousands of

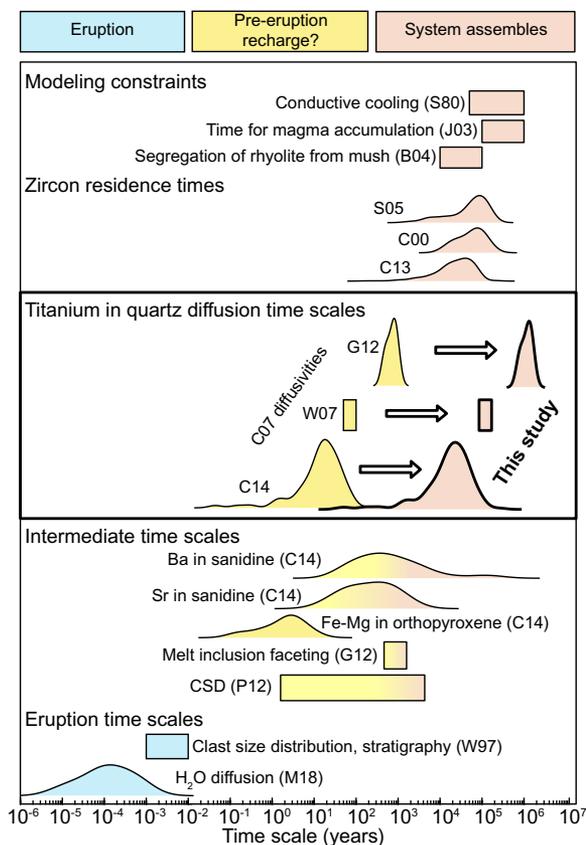


Figure 2. Time scales of magmatic evolution for the Bishop Tuff (California, USA). (Top panel, upper half) Time scales for evolution of magmatic system (or similar systems) constrained by various modeling techniques. S80—time for solidification of pluton (Spera, 1980); J03—compiled times for accumulation of magmatic systems given known subduction rates and volcano spacing (Jellinek and DePaolo, 2003); B04—time to segregate crystal-poor magma from mush (Bachmann and Bergantz, 2004). (Top panel, lower half) Time scales of zircon residence (kernel density plots), determined as U-Pb age minus eruption age (assuming 767 ka; Chamberlain et al., 2013) from three studies: S05—Simon and Reid (2005); C00—Coath and Reid (2000); C13—Chamberlain et al. (2013). (Middle panel) Ti-in-quartz diffusion time scales determined using the diffusivities from Cherniak et al. (2007; C07), reevaluated (shown by arrows) using data from this study. G12—profiles measured on internal zoning using X-ray microfluorescence (Gualda et al., 2012); W07—profile both extracted from cathodoluminescence (CL) map and measured

using electron probe (Wark et al., 2007); C14—>150 profiles extracted from CL maps, mostly from close to outermost rims (Chamberlain et al., 2014). Time scales become 100x–1000x longer with the application of our data. (Bottom panel) Other time-scale determinations. Ba and Sr in sanidine diffusion, and Fe-Mg in orthopyroxene (C14—Chamberlain et al., 2014) may record a recharge event. Time scales of melt-inclusion faceting (G12—Gualda et al., 2012) and crystal size distribution (CSD) time scales (P12—Pamukcu et al., 2012) are not consistent with reevaluated quartz residence times. At the bottom are time scales of eruption, based on clast sizes and detailed mapping and stratigraphy (W97—Wilson and Hildreth, 1997), and behavior of reentrants and melt inclusions in quartz (M18—Myers et al., 2018).

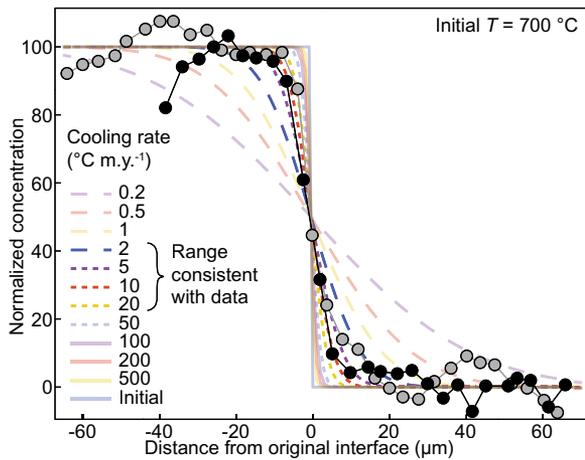


Figure 3. Assessment of quartz crystallization temperatures. Reproduced Ti in quartz concentration profiles (from Ackerson et al., 2018, their figure 3) are refitted using Ti diffusivities from this study. Ti concentrations from two separate profiles (gray and black dots, respectively) were normalized between 0 and 100 by Ackerson et al. (2018). Profiles are consistent with an initial temperature (T) of 700 °C and 2–20 °C m.y.⁻¹ cooling rate, rather than 500 °C initial T and/or cooling rates >300 °C m.y.⁻¹.

years (the “warm storage” model; e.g., Barboni et al., 2016), rather than undergoing any considerable thermal oscillations.

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