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The dynamic nature of $a\mathrm{TiO_2}$: Implications for Ti-based thermometers in magmatic systems

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ABSTRACT

In recent decades, new Ti-based thermometers have found widespread use in geosciences, providing a convenient and powerful tool for investigating crystallization temperatures of quartz and zircons in magmatic systems. However, an often-overlooked aspect is the constraint of TiO_2 activity ($a\mathrm{TiO_2}^{\text{liquid-rutile}}$). Many studies assume $a\mathrm{TiO_2}$ to be constant or equate the presence of Ti-rich phases, such as ilmenite, with fixed activity levels. Using solubility models and data from natural systems, we demonstrate that $a\mathrm{TiO_2}$ is a dynamic parameter, influenced by temperature, mineral assemblage, and TiO_2 content in the melt. Focusing on examples from several volcanic fields (Bishop Tuff, Fish Canyon Tuff, Yellowstone, and Shiveluch), we discuss the impact of these factors on $a\mathrm{TiO_2}$ and highlight how inadequate constraint of $a\mathrm{TiO_2}$ can lead to erroneous interpretations of magma storage conditions.

INTRODUCTION

Temperature profoundly controls chemical systems by governing exsolution and solubility, and thus is critical for phase saturation, fluid exsolution, crystal structure and chemistry. In Earth sciences, accurately determining the temperatures of these processes, e.g., through mineral-based thermometry, is essential for understanding the evolution of igneous, metamorphic, and hydrothermal systems. Titanium (Ti) thermometry finds extensive use in petrology, particularly for common phases like quartz (e.g. Wark and Watson, 2006; Huang and Audétat, 2012) and zircon (e.g. Ferry and Watson, 2007; Loucks et al., 2020), known for their resistance to weathering and alteration. In situ Ti contents can be easily analyzed via laser-ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) or electron probe microanalysis (EPMA).

All TiO_2-based thermometers fundamentally hinge on constraining the titanium oxide activity in the melt from which minerals crystallize (**aTiO$_2^{\text{liquid-rutile}}$**, [the TiO_2 activity in the melt with respect to rutile saturation] hereinafter aTiO$_2$). aTiO$_2$ is usually inferred from the presence of Ti-rich phases (e.g., rutile, ilmenite, Schiller and Finger, 2019), and assumed to be static. Small variations in aTiO$_2$ are typically deemed to have a minor impact on estimated temperatures.

In this paper, we discuss the underlying concepts of aTiO$_2$ and its substantial influence on the application of widely used thermometers. We argue that aTiO$_2$ is unlikely to remain constant in evolving magmatic systems and may exhibit significant temporal variations, underlining the importance of understanding the different methods to constrain aTiO$_2$. Ultimately, a comprehensive and integrated approach considering multiple lines of evidence is necessary to establish and confidently utilize Ti-based geothermometers.

RUTILE SOLUBILITY MODELS

Solubility models based on experimental constraints help understand the behavior of Ti and $a\mathrm{TiO_2}$. Models for Ti solubility were first developed by Hayden and Watson (2007) and later revised by Zhang et al. (2020), showing temperature (T) as a primary control of Ti solubility:

$$log(Ti, ppm) = 6.5189 - \left(\frac{3006.5}{T(K)}\right) - 461 * \left(\frac{P^{0.2}}{T(K)}\right) + 0.1155 * FM \quad \text{(Eq. 1)}$$

Where P is pressure and FM is a compositional factor. is The compositional factor FM is less relevant for comparisons within the same system, as it varies significantly only between different melts (e.g., FM varies from ~4 in basalts to 1.5 in rhyolites, Hayden and Watson, 2007). Fractionation-induced variations in FM have negligible influence on Ti solubility since FM is multiplied by ~0.1, and melt compositions rarely span the entire range from basalt to rhyolite within the same system. Pressure variations (of more than several kilobars) affect $\mathrm{TiO_2}$ solubility, but are unlikely within a given reservoir, making temperature the main varying factor.

In line with most solubility models, we consider $a\mathrm{TiO_2}$ in the melt relative to rutile saturation, i.e. $a\mathrm{TiO_2} = 1$ when the system is rutile saturated. Thermodynamically, $a\mathrm{TiO_2}$ is calculated as:

$$aTiO_2^{liquid-rutile} = \frac{XTiO_2^{liquid} * \gamma\mathrm{TiO_2}^{liquid}}{XTiO_2^{liquid-saturated} * \gamma TiO_2^{liquid-saturated}} \quad \text{(Eq. 2)}$$

Where $\mathrm{XTiO_2}$ is the $\mathrm{TiO_2}$ mole fraction in the melt, and γTiO2 is the activity coefficient, influenced by melt composition, pressure and temperature (Borisov and Aranovich, 2020 – see the Supplemental Material).

It is evident that $a\mathrm{TiO_2}$ depends strongly on $\mathrm{XTiO_2}$ in the saturated melt, which according to the solubility equation, is primarily influenced by temperature. If the $\mathrm{TiO_2}$

content of the melt remains constant, $a\mathrm{TiO_2}$ should increase as the system's temperature decreases (Fig. 1).

MELT TIO_2 CONCENTRATIONS AND $a\mathrm{TIO_2}$ IN NATURAL SYSTEMS

Evolving magmas may not maintain a constant TiO_2 concentration in the melt. TiO_2 concentrations can either (1) increase due to precipitation of non-Ti-bearing minerals such as quartz and feldspar, resulting in the removal of other oxide components and the associated relative increase in TiO_2 content (Fig. 2), or (2) decrease due to formation of Ti-bearing phases (e.g., rutile, ilmenite, titanite, or major minerals containing minor TiO_2 such as pyroxenes and amphiboles). Consequently, $a\mathrm{TiO_2}$ should not remain constant in an evolving magma reservoir.

By definition, a magma is at $a\mathrm{TiO_2}^{\text{liquid-rutile}} = 1$ when rutile is present. However, rutile is almost never found in volcanic rocks, and rare in plutons. Hence, $a\mathrm{TiO_2}$ must typically be lower than 1, and can be estimated by different techniques: (1) from co-crystallizing Fe-Ti oxides (Ghiorso and Gualda, 2013), providing $a\mathrm{TiO_2}$ estimates over the temperature range of oxide crystallization, or (2) using thermodynamic software, such as MELTS or PerpleX (Connolly, 2005; Gualda et al., 2012). When both methods are applied to the same unit, results are not always consistent, e.g., in the Bishop Tuff, rhyolite-MELTS generally yields lower $a\mathrm{TiO_2}$ than those from oxides (Fig. 2), despite being calibrated on this unit (Gualda et al., 2012). The inability of thermodynamic software to accurately predict saturation and composition of Fe-Ti oxides suggests that insufficient thermodynamic data currently hinders accurate determination of $a\mathrm{TiO_2}$ through these programs.

When comparing multiple examples based on Fe-Ti oxides (Fig. 1), some systems exhibit increasing $a\mathrm{TiO_2}$ with decreasing temperature, consistent with the expected down-temperature increase in TiO_2 solubility. Others show the opposite, recording a down-

temperature decrease in $a\mathrm{TiO_2}$, suggesting efficient $\mathrm{TiO_2}$ removal from the melt by Ti-bearing phases to compensate for the increase in $a\mathrm{TiO_2}$ resulting from cooling (Fig. 3). We used this data to model $a\mathrm{TiO_2}$ evolution in four natural systems (Bishop Tuff, California, western USA; Fish Canyon Tuff, Colorado, western USA; Shiveluch, Kamchatka, Russia; and Yellowstone, western USA; Fig. 1) as a function of different rates of TiO2 change with decreasing temperature ($\partial\mathrm{TiO_2}/\partial\mathrm{T}$ in ppm/°C; see supplemental Material). More negative $\partial\mathrm{TiO_2}/\partial\mathrm{T}$ indicates greater fractionation of Ti phases and thus decrease of $\mathrm{TiO_2}$ with decreasing temperature. Two observations are noteworthy: (1) the trends in Fig. 1 cannot be fitted with constant $\partial\mathrm{TiO_2}/\partial\mathrm{T}$, but require that $\partial\mathrm{TiO_2}/\partial\mathrm{T}$ varies with temperature, and (2) the contrasting trends in $a\mathrm{TiO_2}$ (e.g., Yellowstone and Shiveluch) occur over similar temperature and $\partial\mathrm{TiO_2}/\partial\mathrm{T}$ ranges, but are associated with high-$a\mathrm{TiO_2}$ (Shiveluch) and low-$a\mathrm{TiO_2}$ systems (Yellowstone). Our calculated values align with observations in these systems: for example, the hotter late-erupted Bishop Tuff, following a higher $\partial\mathrm{TiO_2}/\partial\mathrm{T}$ trend, contains ~0.5% of ilmenite and titanomagnetite, while the early-erupted Bishop Tuff contains only ~0.05% of these Ti-bearing oxides (Hildreth, 1979).

Unlike high-$\mathrm{TiO_2}$ systems near rutile-saturation, low-$\mathrm{TiO_2}$ systems are very sensitive to crystallization of Ti-bearing phases, as even minor $\mathrm{TiO_2}$ removal can decrease $a\mathrm{TiO_2}$ (Fig. 3). However, $\mathrm{TiO_2}$ removal from the melt through crystallization does not necessarily stabilize or decrease $a\mathrm{TiO_2}$ unless it occurs on a scale that compensates for the decreasing solubility and passive enrichment from non-$\mathrm{TiO_2}$-bearing phase crystallization. The logarithmic relationship between solubility and temperature suggests that $a\mathrm{TiO_2}$ in most magmas increases with decreasing temperature (Fig. 3), unless the crystallizing mineral assemblage decreases the $\mathrm{TiO_2}$ content by more than ~ 5 ppm/°C.

DO MINERALS BUFFER $a\mathrm{TIO_2}$ IN MAGMAS?

Ilmenite has been suggested to crystallize at $a\mathrm{TiO_2}$ ~ 0.5 (Schiller and Finger, 2019) based on rhyolite-MELTS and PerpleX, and its presence is commonly used to constrain a system's $a\mathrm{TiO_2}$. However, the presence of ilmenite in rutile-saturated rocks (e.g., Pikes Peak batholith, Colorado, Fonseca Teixeira et al., 2022) and experiments (Ryerson and Watson, 1987) demonstrate that ilmenite can crystallize at much higher $a\mathrm{TiO_2}$ than 0.5. Co-existing Fe-Ti oxides indicate ilmenite precipitation at $a\mathrm{TiO_2}$ between 0.3 and 0.9 (Fig. 1), suggesting ilmenite saturation requires a minimum $a\mathrm{TiO_2}$ near 0.3 and can occur up to $\mathrm{TiO_2}$ saturation. Among the units with Fe-Ti oxide estimates (Fig. 1), none consistently exhibit $a\mathrm{TiO_2}$ <0.3. We suggest that extremely low values (e.g., 0.1) are unlikely near the solidus due to the temperature effect on solubility. A system starting at low $\mathrm{TiO_2}$ (e.g., 500 ppm at 1100°C, equivalent to $a\mathrm{TiO_2}$ ~0.03) would reach $a\mathrm{TiO_2}$ = 0.6 at the solidus (660°C, Fig. 1) through the temperature effect alone. The only way to reach $a\mathrm{TiO_2}$ as low as 0.1 near the solidus is through significant fractionation of $\mathrm{TiO_2}$-bearing phases, which is unlikely at extremely low $a\mathrm{TiO_2}$. When disregarding the effect of Ti-free (or Ti-poor) silicate crystallization, only extremely $\mathrm{TiO_2}$-poor melts (<100 ppm $\mathrm{TiO_2}$) could reach $a\mathrm{TiO_2}$ ~ 0.1 at 660 °C. We are not aware of any evolved igneous systems of such compositions.

Unlike rutile, ilmenite stability depends not only on $a\mathrm{TiO_2}$, but also on other constituents, including oxygen fugacity, ferrous/ferric and Fe/Mg ratios (Frost, 1991), affecting the saturation and the mass of ilmenite crystallization. Hence, rocks with rutile do not necessarily contain ilmenite, and ilmenite presence cannot be used to assign a static $a\mathrm{TiO_2}$ value.

ERRORS FROM FIXED $a\mathrm{TIO_2}$

Slightly over- or underestimating $a\mathrm{TiO_2}$ is often suggested to yield insignificant deviations from the true temperature (Fu et al., 2008). While this assumption can be valid, it

must be assessed carefully. Small discrepancies in $aTiO_2$ are particularly relevant in low-$aTiO_2$ systems, e.g., at $aTiO_2$ = 0.9 and 3 kbar, a quartz crystal with 50 ppm Ti yields 692 °C based on Huang and Audétat (2012). If $aTiO_2$ is overestimated by 0.1, the same quartz gives a temperature of 705 °C (deviation of <15 °C). At lower $aTiO_2$, the same discrepancy in $aTiO_2$ leads to higher deviations, e.g., 60 °C difference for quartz with 50 ppm Ti at $aTiO_2$ of 0.2 and 0.3.

Temperature ranges of quartz crystallization (from saturation to low-T, interstitial quartz) are typically calculated assuming fixed $aTiO_2$. However, as discussed above, $aTiO_2$ is unlikely to be constant unless the system is rutile-saturated, leading to significant discrepancies in Ti-in-quartz temperatures (Fig. 4). We compare Ti contents in quartz for a fixed $aTiO_2$ of 0.5 and a dynamic $aTiO_2$ value in the same system (Fig. 4 – see Suppl. Data for additional information). For a single point, the highest deviation (~100 °C) is at high-$aTiO_2$ (Shiveluch). However, the largest error in the estimated temperature range occurs for Bishop Tuff, where the range is ~100 °C larger at $aTiO_2$=0.5 than with a dynamic $aTiO_2$, leading to potential misinterpretations of the system's crystallization range. Furthermore, low-Ti quartz or zircon may be falsely interpreted as crystallized below the solidus (e.g., temperatures as low as 620 °C for Yellowstone). For the Fish Canyon Tuff, Ti-in-quartz temperatures at dynamic *a*TiO2 are consistently 50 °C cooler, and are more consistent with quartz crystallization needing to be at lower temperatures than those measured by Fe-Ti oxides and amphibole-plagioclase thermometry immediately pre-eruption (~760 °C ; Whitney and Stormer, 1985; Johnson and Rutherford, 1989; Bachmann and Dungan, 2002) to explain the resorbed appearance of quartz in this unit (Bachmann et al., 2002).

Dynamic $aTiO_2$ also affects the cathodoluminescence (CL) response of crystals and must be considered when interpreting CL images. Quartz with weak CL zoning might be interpreted as having formed over a narrow temperature range. However, if $aTiO_2$ increases

sufficiently to compensate for the temperature decrease, quartz Ti contents vary minimally, resulting in weakly zoned crystals despite significant temperature variation. In summary, assuming a constant $a\mathrm{TiO_2}$ of 0.5 can lead to significant temperature discrepancies, and it is impossible to ascertain the scale of this effect without an accurate estimation of the $a\mathrm{TiO_2}$ evolution.

THE ROLE OF $a\mathrm{TIO_2}$ IN THE BISHOP TUFF

One of the main sources of controversy in studies on the Bishop Tuff is the origin of Ti-rich (80-100 ppm) rims in quartz crystals of the late-erupted Bishop Tuff, in abrupt contact to lower-Ti (40-50 ppm) cores (Peppard et al., 2001; Wark et al., 2007). Mafic recharge has been suggested to have induced the rim crystallization by elevating the temperatures and adding enough CO_2 to allow quartz saturation at temperatures of ~800 °C (Wark et al., 2007). However, recharging the upper crustal magma reservoir with a less-differentiated, more Ti-rich melt would also affect Ti concentrations, e.g., mixing of early-erupted Bishop Tuff with 5-13% of a Long Valley (California) andesite (Bailey, 1962) results in an increase of melt TiO_2 from ~0.07 wt% to 0.12-0.19 wt%, comparable with late-erupted Bishop Tuff glass compositions (Suppl. Data). At a recharge mass fraction of ~13 %, $a\mathrm{TiO_2}$ post-mixing would be at 0.8 at 750°C. A quartz with 100 ppm of Ti, at $a\mathrm{TiO_2} = 0.8$ would crystallize at the same ~ 750°C (based on Huang and Audétat, 2012), 50 °C lower than the temperatures originally calculated by Wark et al. (2007), and more compatible with experimental and modelled phased stabilities in the late-erupted Bishop Tuff (Gardner et al., 2014). Hence, only limited increase of temperature or addition of CO_2 would be required to explain conditions recorded by the late-erupted Bishop Tuff: simply increasing the $a\mathrm{TiO_2}$ in the magma chamber to 0.8 could explain crystallization of the high-Ti quartz rims (although such deeper, more mafic recharge would certainly add heat and CO_2 to the system as well). Hence, we concur with

previous publications (e.g. Evans et al., 2016) that adding a small fraction of a less-differentiated melt from deeper in the system to the Bishop Tuff rhyolitic composition allows for the formation of high-Ti quartz rims . This highlights the role of $a\mathrm{TiO_2}$ regarding its most important parameters: temperature and $\mathrm{TiO_2}$ content in the melt.

CONCLUSIONS

Constraining $a\mathrm{TiO_2}$ in geological systems is a challenge, requiring careful consideration of various observations. Rutile reliably indicates $\mathrm{TiO_2}$ saturation. While it does not guarantee constant saturation throughout crystallization, substantial removal of $\mathrm{TiO_2}$ is needed to lower $a\mathrm{TiO_2}$ in rutile-saturated or near-saturated conditions. In rutile-undersaturated systems, ilmenite has traditionally been used to indicate $a\mathrm{TiO_2} = 0.5$, but this contradicts observations in natural and experimental samples. The presence of ilmenite suggests that $a\mathrm{TiO_2}$ should be ***at least*** 0.3. Substantial precipitation of ilmenite and other Ti-bearing phases can lead to decreasing $a\mathrm{TiO_2}$ trends, counteracting the effect of cooling.

Further constraints can be derived from Ti concentrations in quartz and zircon. In quartz-saturated granitic systems close to haplogranite eutectic or minimum composition, the lowest Ti content of <u>magmatic</u> quartz (excluding dark-CL fluid inclusion trails and hydrothermal rims) can be approximated to solidus temperatures (650-680°C; Tuttle and Bowen, 1958; Luth et al., 1964; Piwinskii, 1968). Combining these observations not only allows us to estimate *a*TiO2 at the final stage of magmatic crystallization but also to infer potential evolution paths.

The overall Ti content also helps constrain probable $a\mathrm{TiO_2}$ values, e.g., Ti-rich quartz (>200 ppm) likely formed at high $a\mathrm{TiO_2}$ (>0.8). Similarly, zircon crystals with >30 ppm Ti likely precipitated at high $a\mathrm{TiO_2}$. In contrast, low Ti quartz and zircons can mean low T and/or low $a\mathrm{TiO_2}$. CL provides valuable insights, as abrupt changes signal events such as

recharge (Wark et al., 2007) and depressurization (Gualda and Ghiorso, 2013), that affect temperature, $a\mathrm{TiO_2}$, or both. In such cases, $a\mathrm{TiO_2}$ should be considered separately for quartz and zircon before and after the change. For example, significant $a\mathrm{TiO_2}$ increase following recharge and mixing may result in weak or even reverse Ti zoning in quartz (as seen in many volcanic systems). It is therefore essential to account for $a\mathrm{TiO_2}$ variations in evolving magmatic systems to be able to recover meaningful temperatures from Ti-based mineral thermometers.

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FIGURES

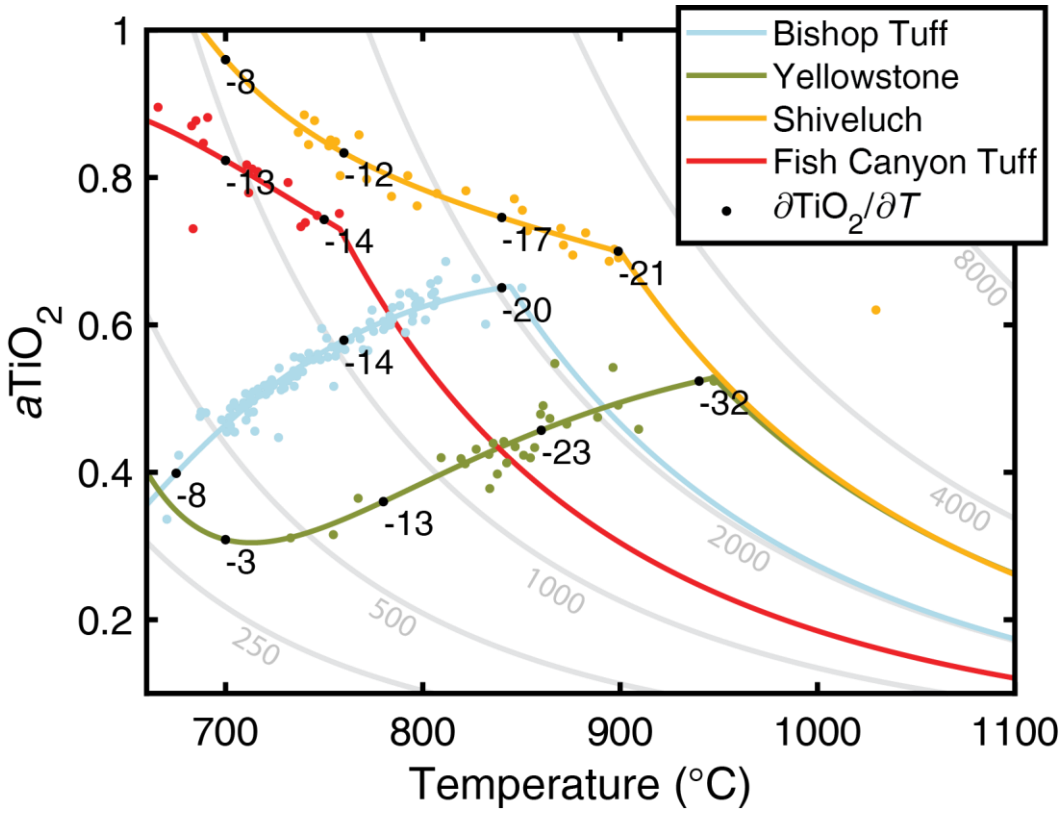

Fig. 1: TiO_2 activity ($aTiO_2$) in natural systems from co-existing magnetite-ilmenite pairs (Ghiorso and Gualda, 2013): Bishop Tuff (California, USA; full sequence, Hildreth, 1977), Yellowstone (western United States; Lava Creek and Huckleberry Ridge Tuffs, Hildreth, 1981, Cougar Point Tuff, Cathey and Nash, 2004), Shiveluch (Kamchatka, Russia; 2001-2004 eruptions, Blundy et al., 2006), and Fish Canyon Tuff (Colorado, USA;outflow sheet, Whitney and Stormer, 1985). Grey lines mark solubility relationships in melts with constant TiO_2 (in ppm). Colored lines mark best-fit $aTiO_2$-temperature (T) relationships as function of variable $\partial TiO_2/\partial T$ (variation in ppm TiO_2 per 1°C decrease); black numbers show $\partial TiO_2/\partial T$ along this trend.

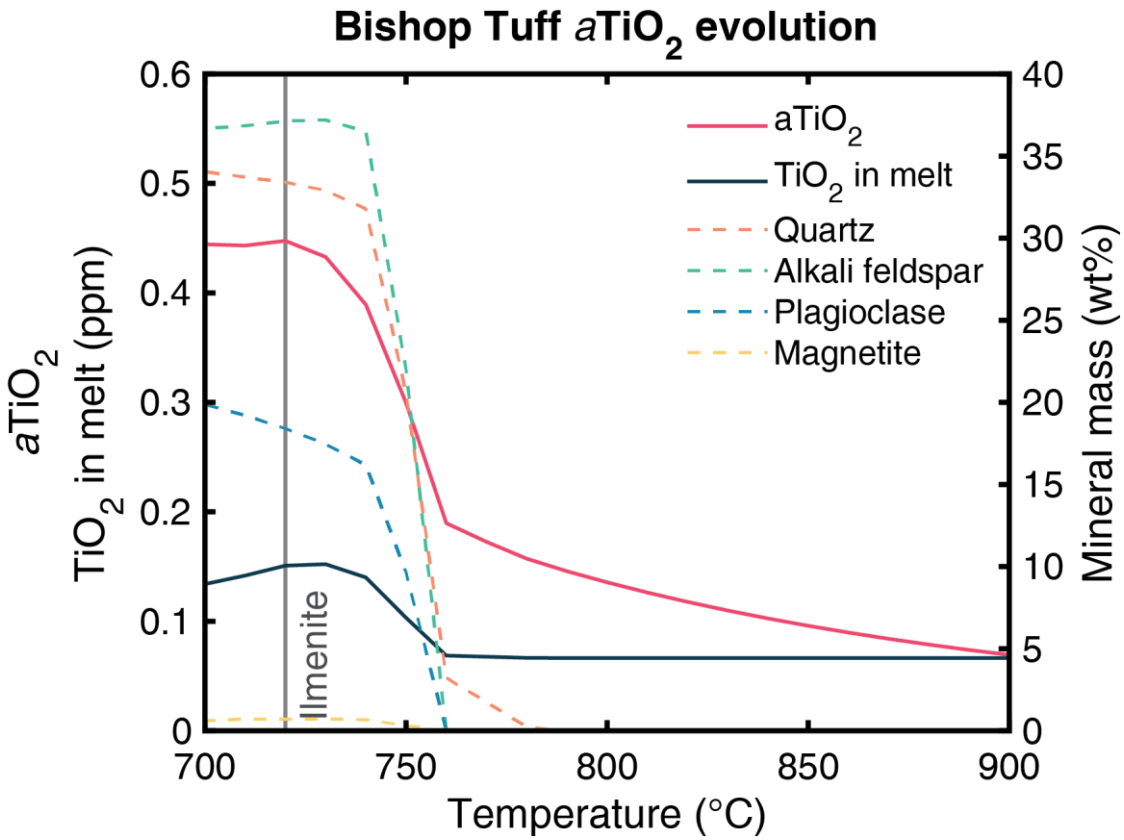

Fig. 2: Left axis: $a\mathrm{TiO_2}$ and $\mathrm{TiO_2}$ in the Early Bishop Tuff calculated with MELTS for Excel (Gualda and Ghiorso, 2015). Right axis: mass of crystallized phases. The vertical line marks the start of ilmenite precipitation.

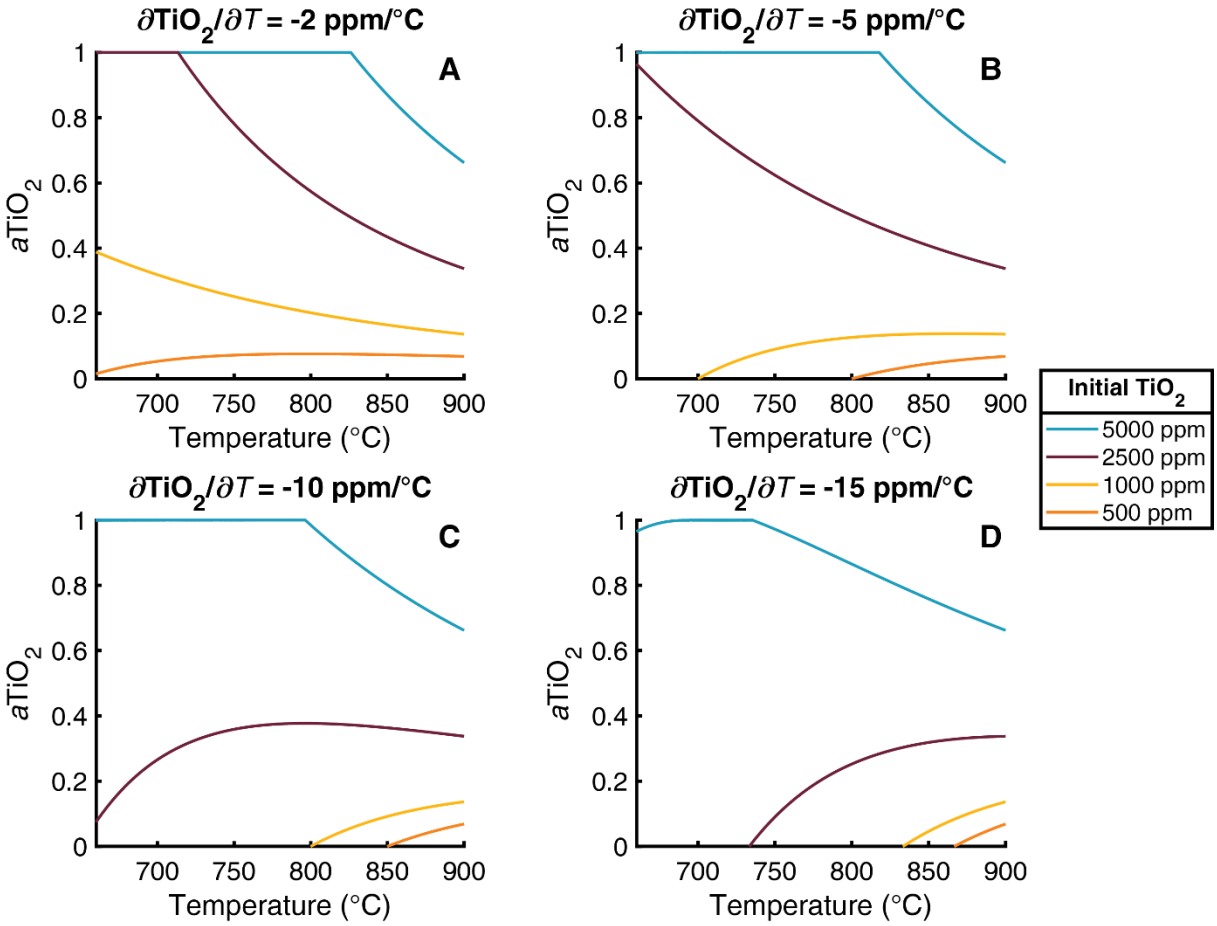

Fig. 3: $a\mathrm{TiO_2}$ evolution for melts with different initial $\mathrm{TiO_2}$ contents at different $\partial\mathrm{TiO_2}/\partial\mathrm{T}$ calculated for an average Yellowstone-Heise composition (Troch et al., 2020) and calculating $a\mathrm{TiO_2}$ with the method from (Borisov and Aranovich, 2020).

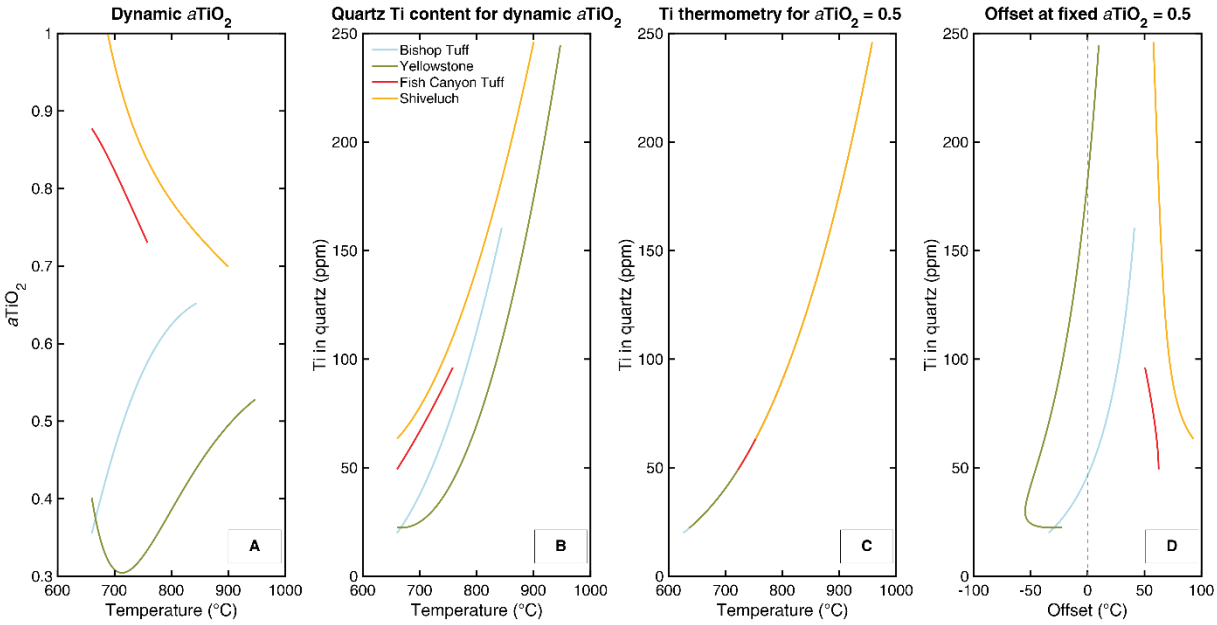

Fig. 4: (A) $a\mathrm{TiO_2}$ evolution for examples from Fig. 1. (B) Hypothetical Ti content in quartz co-crystallizing with Fe-Ti oxides, based on Huang and Audetat (2012) and $a\mathrm{TiO_2}$ activities in (A). (C) Ti-in-quartz thermometry for fixed $a\mathrm{TiO_2}$ = 0.5. Note how all lines from B collapse into a single trend. (D) Temperature offset between dynamic and fixed $a\mathrm{TiO_2}$.