Revision 1

Implications of equilibrium and disequilibrium among crystal phases in the Bishop Tuff

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ABSTRACT

Eruption of the Bishop Tuff magma preserved equilibrium of exchange components and element concentrations among magnetite, ilmenite, biotite, apatite, zircon and liquid. Orthopyroxene and clinopyroxene were not in exchange equilibrium with the other MgFe-bearing phases, but they appear to have been in equilibrium among themselves. Internally consistent temperatures recorded by the FeTi-oxide, Ti-in-quartz, and Δ¹⁸O quartz-magnetite thermometers, coupled with evidence for magmatic corrosion of quartz and sanidine, indicate that an initially low- ⁰C, near-H₂O-saturated, high-SiO₂ rhyolite magma was heated up to ≥ 800 °C and its crystal cargo partially melted by recharge of hotter melt from below. Oxygen fugacity and compositions of biotite, ilmenite, magnetite, and silicate liquid initially adjusted by internal rearrangement of components and conservation of oxygen. Partial melting of feldspars liberated Sr and Ba back into the melt. Mixing during recharge eventually re-introduced
compatible elements (e.g., Mg, Ba, Sr) as well as foreign crystals of euhedral ortho- and
clinopyroxene, which evidently never totally re-equilibrated with the rhyolite liquid. Introduction
of CO₂ and accompanying reduction in the aH₂O during recharge raised crystallization
temperatures of quartz and sanidine in the rhyolite sufficient to allow marginal regrowth of these
phases with enhanced contents Ti, Ba and Sr.

**Keywords:** Bishop Tuff, Supervolcanoes, silicic magma, petrogenetic processes, disequilibrium

**INTRODUCTION**

Over the last decades, many studies focused on large silicic pyroclastic deposits
(ignimbrites) have reported the preservation of original thermal gradients of as much as 100-150
°C (~700 °C to >800 °C) from early to late-erupted material (over length scales of 10s to 100s of
meters; e.g., Lipman 1971; Hildreth 1979; Wolff et al. 1990; Mills et al. 1997; Matthews et al.
2012). These thermal gradients were revealed by microprobe analysis of the Fe-Ti oxides (co-
existing magnetite and ilmenite crystals), which systematically change composition from the
base to the top of stratigraphic sections. Assuming thermodynamic equilibrium, temperatures
were estimated from analyses of these opaque oxide minerals by use of then current
experimental/theoretical calibrations (e.g., Buddington and Lindsley 1964; Andersen et al. 1993;
Ghiorso and Evans 2008). For the Bishop Tuff, however, the assumption of quenched
Fe²⁺Ti(Fe³⁺)₂ exchange equilibrium between ilmenite and magnetite, and consequently the
reliability of extracted temperatures, was questioned (Lindsley et al. 1990, 1991; Ghiorso and
Sack 1991; Frost and Lindsley 1992) on the following grounds: (1) The granite-minimum
(“eutectic”) assemblage (Qtz, San, Plag, L, V) close to H₂O saturation could not be stable (as it
appears to be) over the measured 100 °C temperature range, and (2) the compositions of FeTi-
oxide minerals and pyroxenes failed to correlate in a manner appropriate for chemical
equilibrium. Barometry based on the oxides + pyroxene + quartz assemblage produce a range of
$P$ values (from $< 0$ to 5 kb) that are hard to reconcile with independent constraints. Lindsley et al. (1990, 1991), Ghiorso and Sack (1991) and Frost and Lindsley (1992) concluded that the ilmenite had undergone late- or post-eruption re-equilibration and that oxide temperatures substantially below the $824 \pm 15 ^\circ C$ two-pyroxene temperature were unreliable. Therefore, a sizeable thermal gradient may not have existed in the magma reservoir; it was instead an artifact of additional, poorly understood and late- or post-magmatic processes.

This paper presents a reassessment of thermodynamic equilibrium among the various Fe/Mg-bearing minerals of the Bishop Tuff (namely, ilmenite, magnetite, biotite, orthopyroxene and clinopyroxene) and the silicic melt using published data (no new data added here). It is customary for similar large silicic deposits to show evidence of local and partial equilibrium only (Pichavant et al. 2007). Here, we use Roozeboom plots, as commonly employed in metamorphic petrology, to assess thermodynamic exchange equilibrium among the coexisting phases. We emphasize that all selected oxide pairs used have passed the Hirschmann and Bacon (Mn/Mg) test (Hildreth and Wilson 2007). Hence, there would appear to be no a-priori reasons for rejecting or questioning the reliability of the temperature estimates based on the oxide pairs (Fig. 1).

The Fe/Mg ratios (expressed as mole fractions $X_{Mg}$) of magnetite, ilmenite and biotite, using analyses from Hildreth (1979) and Hildreth and Wilson (2007) plot in a manner strongly suggestive that these phases crystallized close to mutual element-exchange equilibrium (Fig. 2). Roozeboom plots ordinarily show curvature, and they are obliged to terminate at 0:0 and 1:1. Although the data are few, the Fe/Mg composition of the melt also appears to be in equilibrium with those minerals (Anderson et al. 2000). In any case, this conclusion follows from the role of melt as the medium for element transfer among the minerals. In contrast, orthopyroxene and
clinopyroxene, which are found mostly in the late-erupted, hotter and more crystal-rich parts in
the Bishop Tuff deposits, fail to pass this test of exchange equilibrium with the FeTi oxides and
biotite. The two pyroxenes show constant values of $X_{\text{Mg}}$ while the oxide minerals and biotite
exhibit clear positive correlations that extend in the case of the FeTi-oxides virtually to $X_{\text{Mg}} = 0$
(Fig. 2). Orthopyroxene and clinopyroxene do, however, appear to be in equilibrium with each
other. We note that the biotite compositions do not extend to low $X_{\text{Mg}}$ values, and so the
extrapolation to the origin of the graph is unclear. A correction for Fe$^{3+}$ might raise the
$X_{\text{Mg}}$ values of biotite in the hotter, more oxidized samples (Fig. 1 and 2). The minor element
compositions of apatite and zircon vary consistently with temperature (Hildreth and Wilson
2007, p. 974), so we include them among the equilibrium minerals.

IN DEFENSE OF FeTi-OXIDE THERMOBAROMETRY IN THE BISHOP TUFF

In the following, we cite further reasons for considering that the pre-eruptive temperature
range measured by Fe-Ti oxides in the Bishop Tuff is robust and reliable:

1. Only chilled, unoxidized glassy samples with homogeneous oxide pairs were used for $T$-$fO_2$
determination (Hildreth and Wilson 2007, p. 973).

2. The lowest estimated temperatures ($\sim 700$ °C) correspond to the expected temperature of the
haplogranite eutectic at low $P$ (1-2 kbar) in H$_2$O-rich systems (Tuttle and Bowen 1958;
Whitney 1988; Holtz et al. 1992). It is not necessary to postulate post-depositional re-
adjustment of ilmenite to account for these low temperatures (Lindsley et al. 1991). The low
$X_{\text{Mg}}$ values (low $T$) of the oxides show a remarkable clustering on the Roozeboom diagram
(Fig. 2). It is hard to believe that, with possibly one or two exceptions (Fig. 1), they
underwent the more random process of post-depositional re-equilibration. If ilmenite alone
(not magnetite) underwent a late-stage re-adjustment of the Ilm component, it is curious that
the Mg/Fe (Fig. 2) and Mn/Mg (Hildreth and Wilson 2007, Fig. 15) ratios retained their equilibrium proportions.

3. Alternative thermometers applied to the Bishop Tuff (Ti-in-quartz, $\Delta^{18}O$ quartz-magnetite thermometry, Hildreth and Wilson 2007) provide the same answer; a thermal gradient of $\geq 100 \, ^\circ C$ (from $\sim 700 \, ^\circ C$ to $\geq 800 \, ^\circ C$). We note the concomitant variations in H$_2$O concentrations in liquids from $\sim 5$-$6$ wt% in early-erupted samples to $\sim 4$ wt% in late-erupted samples (Anderson et al. 2000, Fig. 2) suggesting that the magma was not fully H$_2$O-saturated at $\sim 2$ kbar and high temperature. According to VolatileCalc (Newman and Lowenstern 2002), a rhyolite magma with 6 wt % H$_2$O and 100 ppm CO$_2$ at 700 °C (typical of the early-erupted material) yields an $X_{H_2O_{vapor}} \sim 0.95$, whereas one with 4 wt % H$_2$O and 600 ppm CO$_2$ (typical of the late-erupted material) at 820 °C yields an $X_{H_2O_{vapor}} \sim 0.59$.

4. Magnetite is modally more abundant than ilmenite in the Bishop Tuff by one to two orders of magnitude (Hildreth 1979). This means that for closed-system temperature changes, the magnetite composition should follow the Usp isopleth (Frost and Lindsley 1992). With magnetite to ilmenite tielines in the TiO$_2$-FeO-Fe$_2$O$_3$ chemographic diagram essentially rotating around magnetite, an increase in temperature of 100 °C leads predictably (Ghiorso and Evans 2008, Fig. 14) to a 6-7 mol.% decrease in the Ilm component of ilmenite, and a one-log unit increase in relative $f_{O_2}$. This is exactly what is observed in the Bishop Tuff (Fig. 1). The concomitant and correlated variations in $X_{Mg}$ of magnetite, ilmenite, biotite and melt can in principle be achieved by closed-system re-equilibration (crystal-liquid fractionation and conservation of oxygen) with increasing temperature. In this case, some partial melting of biotite is involved, and all phases increase in $X_{Mg}$. 
5. The fact that pyroxenes appear not to have been in exchange equilibrium with ilmenite, magnetite and biotite (Fig. 1), was previously noticed by Lindsley et al. (1990, 1991) and Ghiorso and Sack (1991). These authors attempted to apply the Opx-Qz-Mag-IIm equilibrium to an estimate of magma chamber pressure. However, they found an unrealistically large range (from < 0 to 5 kb). According to the P-T phase diagrams (Whitney 1988; Johnson and Rutherford 1989), pyroxenes are not expected to be stable in the lower temperature (< 770 °C at 2 kb for orthopyroxene; Evans and Ghiorso 1995, Figure 5a), water-rich, high-SiO2 rhyolite compositions that form most of the Bishop Tuff. In the general case, their place should be taken by biotite, cummingtonite, or hornblende, depending on magma composition. The pyroxenes cannot therefore be incorporated into any sort of “test” of the accuracy of Fe-Ti oxide thermobarometry; they are clearly not in chemical equilibrium with the oxides (Fig. 2). It is not unusual for the orthopyroxene also to be out of exchange equilibrium with cummingtonite and biotite (e.g., Schmitz and Smith 2004). The euhedral nature of the pyroxenes (Hildreth and Wilson 2007, p. 970) in our opinion, indicates a lack of surface reaction with the present melt in the short time available (e.g., Pichavant et al. 2007; Wark et al. 2007); their crystal faces developed earlier.

**EVIDENCE FOR MAGMATIC RECHARGE**

The elevated magmatic temperatures and the presence of pyroxenes in the late-erupted parts of the Bishop Tuff are consistent with a late recharge event that brought deep, less evolved magma and heat into contact with the high-SiO2 rhyolite reservoir (e.g., Wark et al. 2007). Recharge from below is found to be commonplace in large and small upper crustal reservoirs (e.g., Sparks et al. 1977; Hervig and Dunbar 1992; Spera and Bohrson 2004; Bohrson and Spera 2007; Hildreth and Wilson 2007; Ruprecht and Bachmann 2010; Druitt et al. 2012; Lohmar et al.
right up to a few decades prior to eruption (Wark et al. 2007; Gualda et al. 2012). A late partial mixing between the resident high-SiO$_2$ rhyolite and a hotter, pyroxene-bearing recharge (month to years before eruption) is consistent with evidence from fluid dynamics that the thermal gradient could not be preserved for long periods of time (i.e., more than a few decades or centuries for large bodies) in a crystal-poor magma chamber capable of undergoing convection (Ruprecht et al. 2008; Huber et al. 2012; Lohmar et al. 2012). These thermal gradients must be transient features.

A paradoxical observation of the Bishop Tuff system, and many other zoned ignimbrites (e.g., Carpenter Ridge Tuff; Whitney, 1988; Ammonia Tanks Tuff; Mills et al. 1997; Deering et al. 2011), is that the hottest part of the magma is also the most crystal-rich. Whereas part of the crystal assemblage comprises more mafic crystals, stable at higher temperatures, these refractory crystals do not account for all the crystal population; some of the low-temperature phases (feldspars and quartz) are still present. Sanidine and quartz crystals in the Bishop Tuff show obvious resorption textures and later growth of rims that are: (1) high in Ti in quartz (yielding higher temperature using the Ti-in-Quartz thermometer; Wark et al. 2007; Gualda et al. 2012) and (2) high in Ba in the sanidine (Anderson et al. 2000). Such high Ti-rims in quartz and high Ba rims in sanidine crystals are found in several other localities (both plutonic and volcanic; Hervig and Dunbar 1992; Wiebe et al. 2007; Matthews et al. 2012).

The presence of the low temperature minerals with reversely-zoned rims in the late-erupted parts of the deposits not only requires that some of them survived the reheating process, but that they were able to recrystallize shortly prior to eruption in a significantly hotter environment. It is reasonable to think that the short-lived heating event registered by the Ti rims in quartz (< 100 years; Wark et al. 2007), for reasons of kinetics alone, might fail to completely
dissolve the granitic mineral assemblage. Three minerals participate in the melting reaction (Qz + Sa + Pl $\rightarrow$ L), and the progress of the reaction involves the kinetics of dissolution of all three of them, as well as diffusion in the liquid of Si, Na, K, and Al. In all these processes, the slowest will dictate the pace. In particular, quartz dissolution is expected to be relatively slow (albeit poorly constrained) at low temperature and high viscosity close to its saturation level (Shaw 2006).

A more challenging observation to explain is the regrowth of quartz and sanidine at temperatures $\geq$ 780-800 °C. Two processes can be envisaged: (1) the total $P$ dropped significantly, or (2) the total $P$ remained roughly constant, but the $a$H$_2$O in the melt declined significantly (Whitney 1988; Johnson and Rutherford 1989).

A drop in total $P$ would require that the deepest parts of magma body ascended towards the surface. Such a process seems unlikely for the inferred geometry of the reservoir and rheological properties of these silicic magmas. Alternatively, the $P$ drop could be related to eruption and evacuation of the top of the reservoir. Such syn-eruptive crystal growth has been called upon in other systems (Lipman et al. 1997) and is an expected consequence of large-scale evacuation from shallow magma reservoirs (Bachmann et al. 2012). However, the Bishop Tuff appears to have been erupted within a few days (Hildreth and Wilson 2007), which would appear too short for such syn-eruptive growth to occur.

Assuming that the total $P$ remained constant, the second possibility to trigger growth of sanidine and quartz at higher $T$ is a drop of $a$H$_2$O. This may be brought about by the injection of CO$_2$ from magma below (Hildreth and Wilson 2007; Wark et al. 2007). The Bishop Tuff is known to have more CO$_2$ in its late-erupted melt inclusions (Wallace et al. 1999), and this correlates very well with Ba (Anderson et al. 2000, Fig. 6). Also, there is evidence in several
natural systems that deep recharge commonly carries abundant CO₂, fluxing the shallow, H₂O-rich upper crustal reservoir (Bachmann et al. 2009; Humphreys et al. 2009; Blundy et al. 2010).

The high-Ba rims in the Bishop Tuff sanidine crystals, within a system dominated by crystal fractionation (in which Ba is highly compatible), has been highlighted as a paradox. Anderson et al. (2000) noted that: (p. 465) “Mixing can explain the sense of the zoning (… of Ba in sanidine…), but not the form of the (…trace element…) correlation. Fractional crystallization can explain the form of the correlation but not the sense of the zoning!” However, the recharge - partial remelting model reported by previous contributions (Hildreth and Wilson 2007; Wark et al. 2007), and highlighted in this paper, accounts for the sense of zoning while still keeping a dominant crystal fractionation signature. The sanidine-rich zones in the deep part of the magma reservoir (mush with accumulation of crystals, including sanidine) can be expected to melt significantly upon recharge, releasing much Ba to the melt. A significant amount of this Ba does not come from the recharge, and hence would not produce a strong mixing trend. As sanidine become stable again (due to the same mechanisms that stabilize quartz, as discussed above) the rims incorporate large amounts of Ba, producing the observed reverse zoning. This dissolution-recrystalization could have happened several times during the growth of the Bishop Tuff magma body as evidenced by longer diffusion timescales calculated for Ti in the cores of some quartz crystals (> 1000 ky; Gualda et al. 2012) and for Ba in some sanidine crystals (10-100 ky depending on temperature of diffusion; Morgan and Blake 2006).

MODEL REFINEMENTS

We propose the following refinements of the model for the Bishop Tuff, largely building on previous work (Hildreth and Wilson 2007; Wark et al. 2007) and on par with multiple other
systems, large and small, old and young, in the volcanic and plutonic record (Murphy et al. 2000; Bachmann 2010; Sparks et al. 1977; Wiebe et al. 2004):

1. A large silicic mush is present in the upper crust (1.5-3 kb), from which high-SiO$_2$ rhyolitic liquid is extracted, pooling as a highly eruptible melt-dominated region in the upper level of the reservoir (Hildreth 2004; Bachmann and Bergantz 2008). This high-SiO$_2$ rhyolite is kept at low temperature near the H$_2$O-saturated haplogranite eutectic for most of the time (~ 700-720 °C), thermally buffered by the large amount of crystal mush around it (Huber et al. 2009) and multiply saturated with feldspars and quartz, as well as biotite and Fe-Ti oxides.

2. As this mush is periodically replenished by deeper recharge, some of the hotter, less differentiated melt can penetrate up into the base of the high-SiO$_2$ rhyolite cap. Hence, the upper part of the mush, transformed into a low-temperature cumulate by progressive melt extraction, can partially remelt and become mixed with the recharge and the base of the rhyolitic cap. Hence, higher temperature, and foreign crystals that are not in chemical equilibrium with the rest of the mineral assemblage (e.g., pyroxene in this case) can be imposed on the lower part of the reservoir.

3. Assuming that recharge is a potential eruption trigger (e.g., Sparks et al. 1977; Pallister et al. 1992; Nakagawa et al. 2002; Ruprecht and Bachmann 2010; Druitt et al. 2012), and that the timescales of < 100 years obtained from Ti diffusion in the reversely-zoned quartz in the Bishop Tuff are accurate (Wark et al. 2007), mixing did not have enough time to yield perfect homogenization (Huber et al. 2012). Therefore, the deposits record gradients in temperature, trace elements, and mineral modes that were transient; more mixing would have induced more homogeneous deposits, as are evident in others large
silicic provinces, particularly in the Taupo Volcanic zone (Dunbar et al. 1989; Matthews et al. 2012).

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FIGURE CAPTIONS

Figure 1: (a) $\Delta$ NNO (b) $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ Ilm and (c) $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ Mag as a function of temperature (Ghiorso and Evans 2008) for the Bishop Tuff (data from Hildreth 1979 and Hildreth and Wilson 2007). The temperature of the water-saturated haplogranite eutectic at 2 kb (Johannes and Holtz 1996) is shown for reference. Possibly some of the five lowest temperature data points (below 700 °C) suffered from late- or post-depositional re-equilibration.

Figure 2: Roozeboom plot ($X_{\text{Mg}}$ Ilmenite vs. $X_{\text{Mg}}$ for biotite, orthopyroxene, clinopyroxene and magnetite (for the oxide minerals, the iron component is $\text{Fe}^{2+}$ calculated from the formula; for biotite and the pyroxene iron is total Fe).

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Water-saturated haplogranite eutectic at 2 kb

Post-depositional reequilibration?