

# Magnetite scavenging and the buoyancy of bubbles in magmas. Part 1: Discovery of a pre-eruptive bubble in Bishop rhyolite

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**Abstract** Little is known about the presence, distribution and size of bubbles in rhyolitic magmas prior to eruption. Using X-ray tomography to study pumice from early-erupted Bishop rhyolite, we discovered a large vesicle with abundant magnetite crystals attached to its walls. Attachment of magnetite crystals to bubble walls under pre-eruptive conditions can explain the cluster of magnetite crystals as a result of bubbles rising and collecting magnetite crystals. Alternatively, bubbles may have nucleated on magnetite crystals and then coalesced to form one large bubble with multiple magnetite crystals attached to it. We argue that the clusters of magnetite crystals could not have formed during or after eruptive decompression, and conclude that this vesicle corresponds to a bubble present prior to eruptive decompression. The inferred presence of pre-eruptive bubbles in the Bishop magma confirms the interpretation that the magma was volatile-saturated prior to eruption. The pre-eruptive size of this bubble is estimated based on three independent approaches: (1) the current size of the vesicle, (2) the total cross-sectional area of the magnetite crystals, and (3) the bubble size required for the aggregate to be

neutrally buoyant. These approaches suggest a pre-eruptive bubble 300–850  $\mu\text{m}$  in diameter, with a preferred value of 600–750  $\mu\text{m}$ .

## Introduction

The Bishop Tuff (California) has become an important laboratory for the understanding of magmatic processes in large silicic magma systems, and a wealth of information on its geology and petrology has accumulated since the seminal works of Sheridan (1965) and Hildreth (1979), particularly on the abundance and composition of volatile species prior to eruption (Anderson et al. 1989, 2000; Wallace et al. 1995, 1999). Despite much progress, whether the Bishop magma was volatile-saturated and contained bubbles prior to ascent and eruption is still contentious. It is important to establish if the Bishop magma contained pre-eruptive bubbles (i.e. bubbles that existed prior to the onset of ascent and eruption), particularly because

- (1) *Bubbles reveal gas saturation.* It is difficult to recognize pre-eruptive bubbles, as they are obscured by the overwhelming amount of bubbles formed during eruptive decompression. Some of the largest vesicles in pumice plausibly formed before eruption (Sparks and Brazier 1982; Whitham and Sparks 1986), but they may also have formed by coalescence during eruptive decompression (Klug and Cashman 1994). The best evidence to date for gas saturation is indirect. For active volcanoes, observed volatile fluxes indicate excess  $\text{SO}_2$  emissions, which can be interpreted to reflect the existence of an exsolved gas phase

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prior to eruption (Andres et al. 1991; Wallace 2001). In the Bishop case, the inference of an exsolved gas phase in the pre-eruptive condition derives from the observation of a decrease in dissolved CO<sub>2</sub> in melt inclusions with increasing differentiation (Wallace et al. 1995). However, this interpretation presumes a closed system, and this is problematic for the Bishop magma in view of the reverse zoning observed in sanidine phenocrysts (Lu 1991; Anderson et al. 2000; Gualda and Anderson 2006). The recognition of pre-eruptive bubbles would definitively demonstrate that the Bishop rhyolitic magma was gas-saturated prior to eruption.

- (2) *Bubbles influence magma density, dynamics and eruption.* The mass and volume fraction of bubbles in magma affects the magma bulk density and its tendency to convect (Marsh 1981; Thomas et al. 1993). At a particular bubble mass fraction, the number density and size distribution of bubbles will influence eruption, because with bigger bubbles, the bubble separation distance will be greater, and this will increase the diffusion distance for exsolution of volatile species, resulting in increased supersaturation between bubbles, possibly leading to homogenous nucleation of bubbles.
- (3) *Bubbles may migrate relative to melt and crystals, and cause mass and heat transport.* Rising bubbles will carry volatile species upwards, and this flux may be important for the compositional and thermal evolution of magma. In addition, rising bubbles will transport a boundary layer of melt surrounding each bubble and this may affect the non-volatile compositional evolution of magma.
- (4) *Bubbles affect pre-eruptive coalescence of crystals as well as bubbles.* Crystals will tend to become attached to bubble walls because of surface wetting characteristics, and this will differ from one mineral to another. Attachment of bubbles to crystals modifies the density, buoyancy and rates of movement of aggregates of crystals and bubbles. Thus, the proportions of crystals remaining in bubble-bearing magma may differ from the proportions of crystallizing minerals. As a result, bubbles may influence differentiation.

Against the importance of bubbles stands the difficulty of documenting their existence, size distribution and roles. Finding pre-eruptive bubbles within the overwhelming number of vesicles in a pumice clast is a daunting task. Importantly, there is no guarantee that there is a fingerprint that makes the recognition of pre-eruptive bubbles possible.

Aggregation of bubbles and crystals may be one process that affords an opportunity to document pre-eruptive bubbles. The bubble may disappear or become obscured during eruptive decompression. However, a cluster of crystals may remain and attest to a pre-eruptive collection of crystals that was attached to the gas/melt interface.

In this first contribution, we identify and characterize one such aggregate, in the form of a peculiar vesicle with abundant magnetite crystals attached to its walls, imaged using X-ray tomography. We argue that this aggregate formed in the pre-eruptive magma. From the size of the vesicle and the magnetite crystals attached to it, we deduce the likely size and bulk density of the bubble + magnetite aggregate in the pre-eruptive magma. In the final sections, we discuss the importance of this discovery, and point to the possibility that such a cluster might have been neutrally buoyant in the pre-eruptive magma.

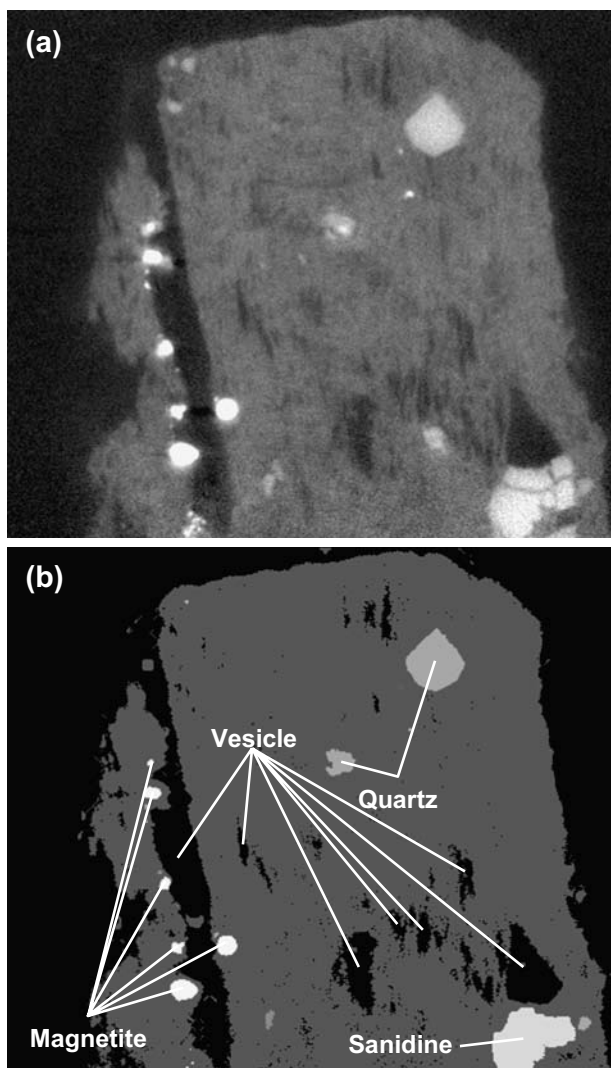
In the accompanying contribution, we review the fundamentals of the energetics of crystal–bubble surface interactions, and derive expressions for the attachment energies and forces, which show that magnetite will be preferentially attached to bubbles, and that forces are strong enough that millimeter-sized bubbles may become neutrally buoyant due to the attachment of crystals.

## Methods and sample description

The studied sample comes from fall unit F8 of the early-erupted Bishop Tuff (Wilson and Hildreth 1997). Sample F8-15 is the densest (0.90 g/cm<sup>3</sup>), most crystal-rich (13 wt% crystals), and least porous (63% porosity) of the five pumice clasts we have been studying (Gualda et al. 2004; Gualda and Anderson 2006; Gualda and Rivers 2006).

Tomographic images were acquired at the GSECARS beamline at APS (Advanced Photon Source), Argonne National Laboratory, using a monochromatic 22 keV X-ray beam. The imaged sample is a cylinder of pumice approximately 1 cm in diameter and height. The resulting images correspond to 3D maps of the linear attenuation coefficient—proportional to the mean atomic number and density—in which each cubic volume element (voxel) is 17.1 μm along each edge. Magnetite, sanidine, quartz, glass and vesicles, in this order of decreasing brightness (i.e. attenuation) in the images (Fig. 1), can be identified (Gualda and Rivers 2006).

In order to yield quantitative textural information on the size and abundance of crystals and vesicles, the original images were classified and separated using



**Fig. 1** **a** Reconstructed tomographic slice of sample F8-15 showing the vesicle with magnetite crystals attached to its walls. Image brightness is proportional to X-ray attenuation, which is a function of the mean atomic number and the density of the material. *Dark area* surrounding the pumice is air; large vesicles are clearly visible as *dark areas* surrounded by *gray matrix*, which corresponds to vesiculated rhyolitic glass. Attenuation by quartz, sanidine and magnetite increases in this order. **b** Classified image, in which each pixel has been assigned to a phase. Magnetite, sanidine and quartz crystals are indicated. For details, see Gualda et al. (2004). Field of view is ca.  $8 \times 7$  mm

Blob3D (Ketcham 2005), following the steps described by Gualda and Rivers (2006).

## Results and discussion

The studied sample contains a region in which abundant magnetite crystals form an elongate array (Figs. 1, 2, Video 1), in sharp contrast with the scattered distribution of magnetite crystals in the remainder of

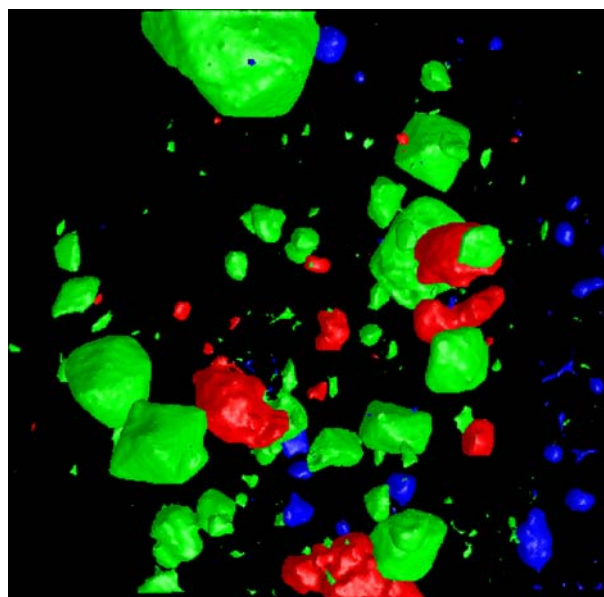
the sample, and also in other samples we have studied (see Gualda and Rivers 2006). In fact, the abundance of magnetite in this sample (4.0% of the total crystal volume) is very high when compared to the amounts seen in the other pumice clasts (i.e.  $<1.2\%$  of the total crystal volume). Importantly, almost half of the magnetite volume present in sample F8-15 occurs as magnetite crystals that comprise this elongate array, while the remainder ( $\sim 2.0$  vol%) is scattered throughout the sample (Fig. 2, Video 1). The magnetite crystals in the array are in contact with the walls of a large elongate vesicle (Figs. 1, 3, Video 2).

The characteristics of this magnetite–vesicle aggregate are unique among the pumice samples studied by us. In the following section, we discuss the texture of this aggregate in detail and suggest a preferred mechanism for its origin, as well as refute some alternative explanations.

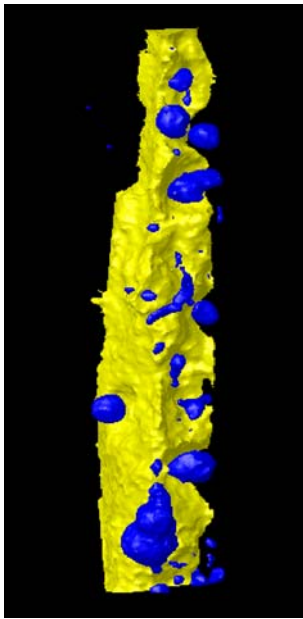
### Origin of the magnetite–vesicle aggregate

#### *The case for magnetite aggregation under pre-eruptive magmatic conditions*

Perhaps the most striking feature of this aggregate is the fact that only magnetite crystals are in contact with the walls of this vesicle, even though silicates are many



**Fig. 2** Three-dimensional view of Sample F8-15; glass and vesicles were suppressed for clarity. Magnetite crystals are shaded *dark gray* (*blue* in the online version), quartz crystals are shaded *light gray* (*green*), and feldspar *intermediate gray* (*red*). A few large magnetite crystals are observed, but most of the magnetite crystals are concentrated in an elongated array (right side of the view). Field of view is equivalent to that in Fig. 1. An animated version of this figure is available online as Video 1



**Fig. 3** Detailed three-dimensional view of the large vesicle (shaded *light gray*; *yellow* in the online version) surrounded by an array of magnetite crystals (shaded *dark gray*; *blue*). Magnetite crystals are in contact with the vesicle walls, but most of the crystal volumes are embedded within the glass (suppressed for clarity). More detailed views are shown in Figs. 4 and 5. Elongated cluster of magnetite crystals is ca.  $4.3 \times 0.7$  mm. An animated version of this figure is available online as Video 2

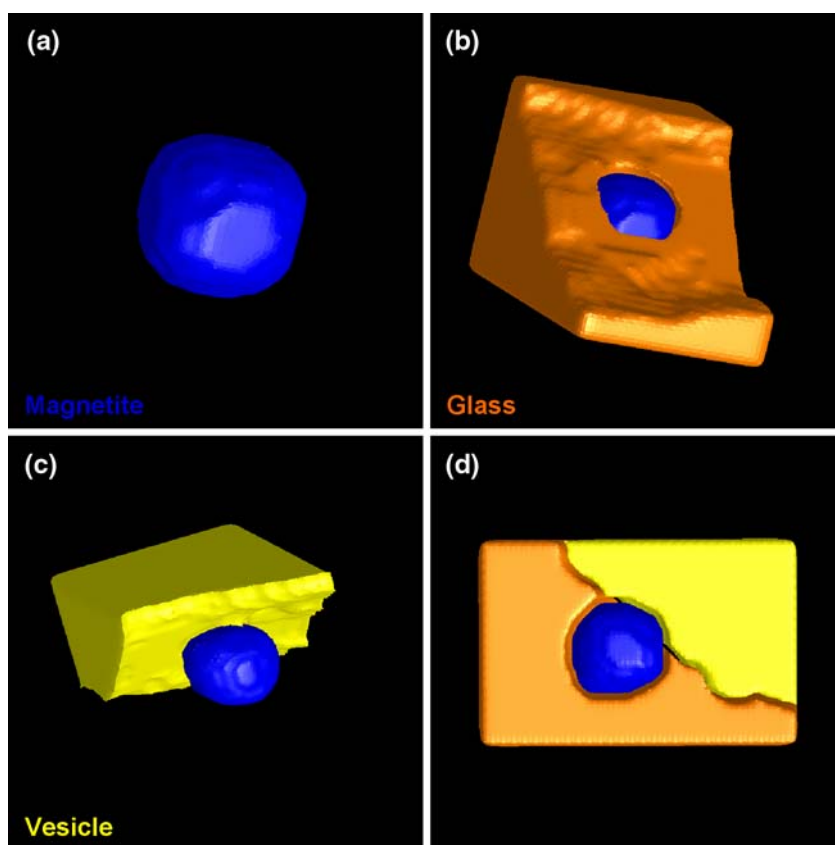
times more abundant (both by number and by volume) than magnetite (Gualda and Rivers 2006). This affinity between magnetite crystals and bubbles is not unexpected if the aggregate formed under magmatic conditions, particularly in light of the experiments of Hurwitz and Navon (1994) and Mangan and Sisson (2000), which show that bubbles tend to nucleate heterogeneously onto magnetite crystals used as seeds. Importantly, in these experiments, sanidine and quartz crystals do not serve as efficient seeds for bubble nucleation. These observations are expected based on surface energy considerations, and we demonstrate in the accompanying paper (Gualda and Ghiorso, in review) that the attachment of any crystals to bubbles is always thermodynamically favored over their isolated occurrence, because it leads to a reduction of the surface free-energy of the system. We also show, however, that this energy reduction is much larger for magnetite than for silicates like quartz and sanidine. We argue that attaching a magnetite crystal to a bubble wall leads to a reduction in surface free-energy that is at least five times larger—possibly much larger—than attaching any of the silicate minerals to a bubble (Gualda and Ghiorso, in review). Hence, the occurrence of only magnetite crystals around this vesicle is compatible with the magmatic origin of the observed aggregate.

One critical observation favoring the magmatic origin of this aggregate is that the magnetite crystals are partly embedded within the glass that makes up the pumice matrix (Fig. 1), such that the crystals must have been embedded when the glassy matrix was still molten. Detailed inspection of individual magnetite crystals (Figs. 4, 5) reveals that magnetite crystals have most of their volumes embedded in glass (see also Videos 3 and 4), with only a small fraction of the crystal surfaces actually exposed to gas-filled vesicle. In fact, from the configuration in Fig. 4d, it is possible to measure the wetting angle between crystal and melt (Fig. 6). The contact surface between vesicle and glass is somewhat irregular, which leads to some uncertainty in the measurement of the wetting angle. Our measured values are within the range  $45^\circ$ – $50^\circ$ . The geometry of the contact between magnetite, glass and vesicle in Fig. 5d is much more irregular, and prevents simple determination of the wetting angle. Relatively little is known about the wetting angle of magnetite in rhyolitic melts (Hurwitz and Navon 1994; Mangan and Sisson 2000), but Mangan and Sisson (2005) report wetting angles in the range  $36^\circ$ – $50^\circ$  in decompression experiments. The agreement between the values reported by Mangan and Sisson (2005) and our observations is remarkable. It is almost surprising that the contact relations would be preserved, but it seems unlikely that this would represent a coincidence. We believe the preservation of the wetting angle adds to the evidence that the magnetite–vesicle aggregate formed under magmatic conditions, and, in fact, it represents a preserved bubble–magnetite aggregate.

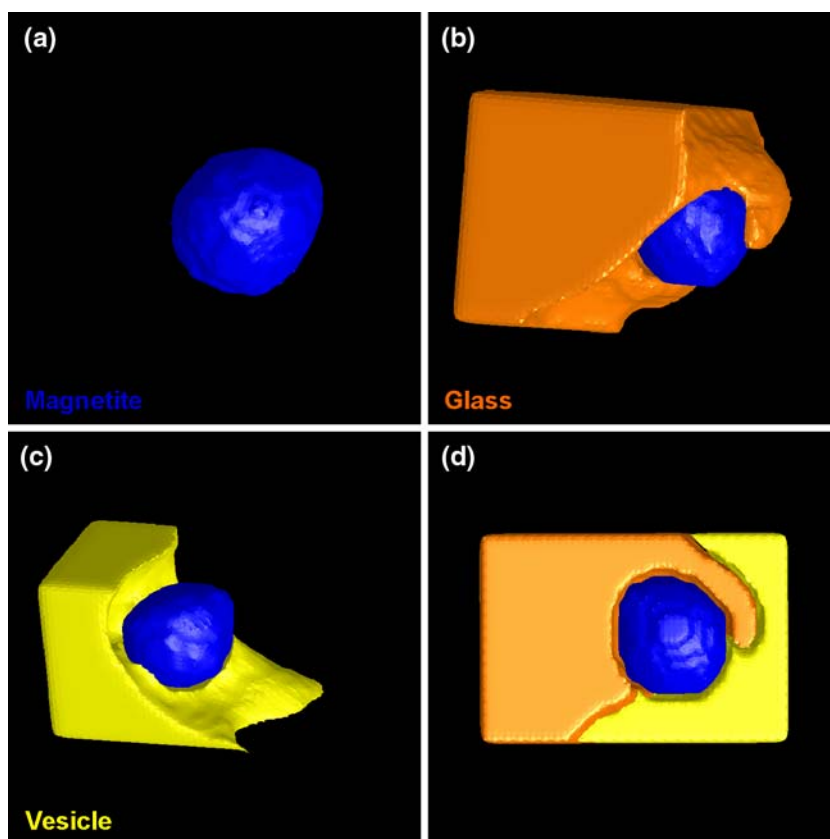
Two plausible end-member processes for the attachment of magnetite clusters to vesicles under magmatic conditions are as follows. (1) Bubbles form from the melt without crystals attached to them; due to the relative movement of crystals and bubbles, magnetite crystals are gradually captured by the bubbles. (2) Bubbles nucleate on magnetite crystals; migration and growth of magnetite–bubble pairs leads to encounters between distinct pairs, which results in bubble coalescence; the final product is a large bubble with abundant magnetite crystals attached to it. Hurwitz and Navon (1994) argue that bubbles nucleate on crystal seeds in their experiments, in part based on the observations that “in many cases two or more bubbles are attached to a single microlite” and “in a few samples, it was clear that while all bubbles are associated with microlites, many microlites are free of bubbles” (Hurwitz and Navon 1994, p. 272), which would favor (2). In the case presented here, however, the situation is quite distinct, with bubbles usually devoid of magnetite crystals, and magnetite crystals devoid of

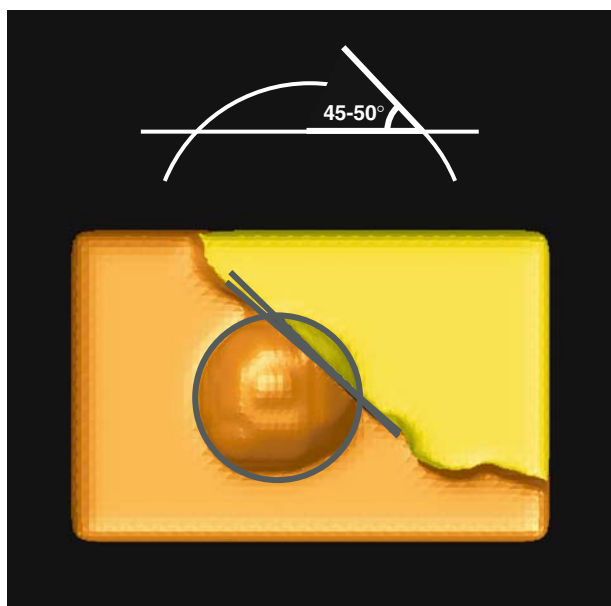


**Fig. 4** Detailed three-dimensional view of a small region including one magnetite crystal within the cluster shown in Fig. 3. **a** Only the magnetite crystal is shown (shaded *dark gray*; *blue* in the online version). **b** Magnetite crystal and glass (shaded *intermediate gray*; *orange*) are shown, and it can be seen that the crystal is mostly embedded within the glass. **c** Magnetite crystal and vesicle (shaded *light gray*; *yellow*) are shown, and reveal that the crystal is in contact with the vesicle as well. **d** Magnetite crystal, and part of the vesicle and glass, are shown, and clearly illustrate the contact relations between them. Volume shown is ca.  $1 \times 0.7 \times 0.7$  mm. An animated version of this figure is available online as Video 3



**Fig. 5** Detailed three-dimensional view of a small region including a second magnetite crystal within the cluster shown in Fig. 3. Views are analogous to those in Fig. 4. Magnetite is shaded *dark gray* (*blue* in the online version), glass *intermediate gray* (*orange*), and vesicle *light gray* (*yellow*). While the contact between glass and vesicle is more complicated than in Fig. 4, the same general contact relations are observed, with the magnetite crystal mostly embedded within the glass, but also in contact with the vesicle. Volume shown is ca.  $0.9 \times 0.6 \times 0.5$  mm. An animated version of this figure is available online as Video 4





**Fig. 6** Detailed three-dimensional view of the contact between glass and vesicle in the region surrounding the crystal in Fig. 4 (same view as Fig. 4d, crystal suppressed for clarity). From the observed configuration, a wetting angle can be measured. Values obtained are in the range 45°–50°, which is remarkably similar to what was observed by Mangan and Sisson (2005), reinforcing the idea that the magnetite–bubble cluster formed under magmatic conditions

bubbles, which indicates that (1) is the more likely mechanism (Gualda and Ghiorso, in review).

If the evidence for attachment of magnetite and bubble under magmatic conditions is accepted, one important question is whether the attachment took place before or during eruption. We argue that the clusters of magnetite crystals could not have formed during eruptive decompression. During ascent and eruption (Wilson et al. 1980), relative movement of crystals would be mainly due to shearing of the magma and even the largest quartz phenocrysts would sink only a few microns relative to the surrounding melt. Eruptive shearing of the magma would be laminar, and we cannot envision how laminar shear could selectively extract and concentrate magnetite crystals into a cluster free of quartz and other silicate minerals. Also, extensive nucleation, growth, and expansion of bubbles during eruptive decompression would increase the distances between crystals and inhibit clustering. Thus, we conclude that the vesicle presented here was present as a bubble prior to eruptive decompression.

A simple calculation reveals an order of magnitude estimate of the time required for a bubble to collect enough magnetite crystals and form an aggregate similar to the one described here. Using a melt viscosity of  $4 \times 10^5$  Pa s (Anderson et al. 2000),

densities of  $0.46 \text{ g/cm}^3$  for the gas, and  $2.2 \text{ g/cm}^3$  for the melt, and assuming Stoke's rise, a bubble  $700 \mu\text{m}$  in diameter would rise at a rate of  $1.52 \times 10^{-9} \text{ m/s}$ , which corresponds to  $130 \mu\text{m/day}$ . We assume a column of melt swept clean of initial magnetite by a bubble of constant size. The rise distance ( $h$ ) needed to provide the mass of attached magnetite ( $M$ ) is:

$$h = \frac{M}{C \times \pi \times r^2} \quad (1)$$

where  $C$  is the mass concentration of magnetite in the magma before scavenging. The value of  $M$  can be calculated from the individual volumes of the magnetite crystals observed in the aggregate ( $M = 10^{-3}$ ), while  $C$  can be estimated from the modal abundances presented in Gualda and Rivers (2006) to be ca.  $0.005 \text{ g/cm}^3$ . For a bubble  $700 \mu\text{m}$  in diameter (see “Bubble size prior to eruption” section), the rise distance is  $0.5 \text{ m}$ , and this would take roughly 10 years. It is generous to assume that all magnetite crystals in the path would be collected by the bubble. Furthermore, the bubble will slow down as it approaches neutral buoyancy. Hence, the time for formation of an aggregate like the one we describe here is likely much larger than 10 years, and probably many orders of magnitude greater than that for magma decompression, ascent and eruption (Wilson et al. 1980). We regard this as supporting evidence that the bubble–magnetite aggregate was present in the pre-eruptive magma.

#### *Bubble growth and melt oxidation, an alternative*

At least three alternative explanations must be considered. First, it has been argued that bubble growth may lead to local oxidation of the melt (Candela 1986), which could promote magnetite crystallization. The main weakness of this hypothesis is that, given the eutectoid nature of the Bishop magma (Hildreth 1979; Anderson et al. 2000), crystallization of a significant amount of magnetite simultaneously with volatile exsolution would also require crystallization of quartz and feldspar to maintain the eutectic melt composition, and there is no evidence for such crystallization. Furthermore, in order to grow  $1 \text{ mg}$  of magnetite,  $0.72 \text{ mg}$  of Fe would be necessary. Given the low abundance of FeO in the early-erupted Bishop melt ( $0.50 \text{ wt\%}$  in residual glass, Hildreth 1977;  $0.65 \text{ wt\%}$  in melt inclusions, Anderson et al. 2000), Fe would have to diffuse from as far as  $2\text{--}3 \text{ mm}$  to crystallize on the walls of the growing bubble. The diffusivity of Fe in a rhyolitic melt containing  $6 \text{ wt\%}$  water can be well approximated by Si diffusivities measured experimen-

tally by Baker (1991), and corresponds to  $3.6 \times 10^{-14} \text{ m}^2/\text{s}$  at  $725^\circ\text{C}$ , which is appropriate for the early-erupted Bishop (Hildreth 1979). The time necessary to diffuse Fe from such distances is thus calculated to be ca. 5 years. Hence, even if the magnetite crystals formed on the bubble walls in response to oxidation of the melt, it would have taken years to fully develop a feature like the one described here. This again would imply a pre-eruptive origin for the bubble–magnetite aggregate, and the discussion in “Bubble size prior to eruption” section would be unchanged.

#### *The case against fragmentation*

Some sanidine crystals have relatively large vesicles associated with them. However, these textures are very distinct from the one described here. We have argued that quartz crystals were extensively fragmented prior and during eruption, as evidenced by the presence of irregular quartz fragments fully coated by glass (Gualda et al. 2004), and by the fractal size distributions of quartz even prior to any lab processing (Gualda 2006; Gualda and Rivers 2006). The similarity between the size distributions of quartz and sanidine led us to infer that sanidine has been subjected to a similar fragmentation history (Gualda and Rivers 2006). To a large extent, fragmentation of quartz and sanidine crystals seems to be related to bursting of melt inclusions (Gualda, unpublished data), which could lead to an association between vesicles and fragments of quartz and sanidine.

Several fragmented crystals are observed in the sample studied here (see, for instance, sanidine crystal in the bottom right of Fig. 1). When fragmentation is more extreme, textures may at first inspection resemble the one described here. In detail, however, these textures are quite distinct. One example is presented in Fig. 7 (see also Video 5). It can be readily seen that the individual sanidine crystals are in fact crystal fragments that lie entirely within the vesicle. In magmatic conditions, the wetting angle between sanidine and melt is significantly smaller than that of magnetite and melt. This means that sanidine crystals should be more strongly embedded within the glass than magnetite, which is clearly not the case. Hence, we conclude that these clusters of broken sanidine crystals are not magmatic in origin, but probably related to the decompression and eruptive history.

#### *The case against post-deposition precipitation*

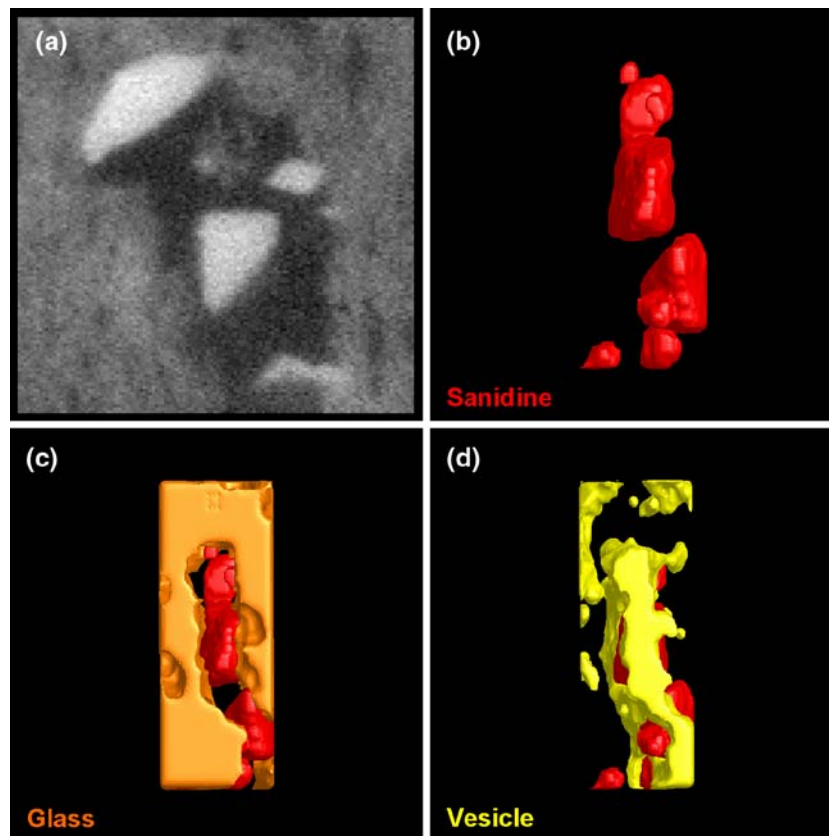
A final alternative possibility to consider is the growth of magnetite from gas onto the walls of a cavity during

cooling of the deposit, after eruption and deposition. First and foremost, such an origin would be hard to reconcile with the observation that magnetite crystals are embedded within the glass. Nonetheless, precipitation of oxide–hydroxides along cavities within pumice clasts is sometimes observed in samples from the same stratigraphic horizon as that discussed here (i.e. fall unit F8). We selected one such pumice clast with a very prominent veinlet of dark material. Qualitative EDS analyses of the dark material reveal that it is composed of Mn and Fe, while no X-ray diffraction pattern could be obtained, suggesting that it corresponds to an amorphous Fe–Mn oxide or hydroxide (analyses performed by Ian Steele at The University of Chicago, unpublished data). Furthermore, we obtained an X-ray tomography dataset of a small fragment (ca. 10 mm diameter) of pumice containing this kind of material under conditions similar to those employed for the sample studied here. The precipitated material appears as a thin film deposited along the surface of the sample, which is characterized by relatively low X-ray absorption. All these characteristics differ significantly from those seen in the magnetite–vesicle aggregate discussed previously, and reinforce our conclusion that this latter aggregate formed in bubbly magma.

#### Bubble size prior to eruption

The recognition of a pre-eruptive bubble not only shows that the early-erupted Bishop magma was at least locally volatile-saturated, but also gives rise to a unique opportunity to estimate the size of this bubble in the pre-eruptive magma. The pre-eruptive bubble was smaller than the present vesicle because of growth and expansion during eruptive decompression. We use three independent approaches to calculate the pre-eruptive radius of the bubble.

- (1) *Vesicle volume.* In the first case, we use the total volume of the vesicle as currently observed. Because the shape of the vesicle is probably much modified from its original shape, we consider a spherical bubble of the same volume as the observed vesicle. Neglecting the effect of growth of the bubble and considering only expansion due to a decompression from about 200 to 15–30 MPa, we can calculate a pre-expansion bubble diameter. The vesicle volume is measured to be  $1.45 \text{ mm}^3$ , which corresponds to a sphere of 1.4 mm in diameter, and this yields a pre-eruptive diameter of 600–750  $\mu\text{m}$  (Table 1). Because bubble growth during ascent is neglected, this is a maximum estimate of the pre-eruptive size.



**Fig. 7** **a** Reconstructed tomographic slice through a small region including several sanidine crystal fragments within a vesicle; irregular shapes of the sanidine crystals (*light gray*) are indicative that they correspond to crystal fragments, and it can be seen that they are located within the vesicle. **b–d** Detailed three-dimensional view of the same region. **b** Only the sanidine crystal fragments are shown (shaded *dark gray*; *red* in the online

version). **c** Sanidine crystals and glass (shaded *intermediate gray*; *orange* in the online version) are shown, and it can be seen that the crystal fragments are not embedded in the glass. **d** Sanidine crystals and vesicle (shaded *light gray*; *yellow* in the online version) are shown, and reveal that the crystals lie entirely within the vesicle. Volume shown is ca.  $0.8 \times 2 \times 3$  mm. An animation including views **b–d** is available online as Video 5

However, it should be pointed out that the vesicle analyzed here is not fully enclosed by the pumice (i.e. the vesicle is open to the edge of the sample), such that it is possible that the bubble possessed a somewhat larger diameter, and we guess that  $600 \mu\text{m}$  is probably close to a minimum estimate of the true volume of the original spherical bubble.

- (2) *Magnetite crystal population.* The second approach used is based on the population of magnetite crystals attached to the vesicle walls. The cross-sectional area of each crystal can be calculated from the individual crystal volumes, measured using Blob3D. We then consider that the bubble surface is totally occupied by magnetite crystals—a rather extreme assumption—and use the total cross-sectional area of the population of magnetite crystals to calculate a bubble surface area and diameter. The total volume of magnetite

attached to the vesicle is  $0.20 \text{ mm}^3$ , distributed among  $\sim 60$  individual crystals. The inferred equivalent pre-eruptive bubble diameter is about  $300 \mu\text{m}$  (Table 1). Evidently, this represents the minimum pre-eruptive diameter of the bubble prior to eruption.

- (3) *Neutral buoyancy.* While isolated bubbles are positively buoyant and crystals are negatively buoyant, bubble–crystal aggregates may become neutrally buoyant, and it is likely that neutrally buoyant pre-eruptive bubble–crystal aggregates will be preferentially preserved over more rapidly rising individual pre-eruptive bubbles. We can use the total mass of magnetite in the population of crystals attached to the vesicle to yield the bubble size needed for neutral buoyancy of the crystal–bubble aggregate (Table 1). The measured crystal volumes can be converted into a total mass of 1 mg of magnetite on the vesicle walls. At con-



**Table 1** Bubble size estimates based on vesicle volume, magnetite volume, and neutral buoyancy of the magnetite-bearing bubble

Size estimate based on vesicle characteristics	
Vesicle volume	1.45 mm <sup>3</sup>
Diameter of sphere of equal volume	1.4 mm
Pre-expansion diameter (neglecting growth during ascent)	600–750 μm
Size estimate based on the attached magnetite population	
Number of crystals	60
Crystal diameters	50–500 μm
Total cross-sectional area	1.15 mm <sup>2</sup>
Equivalent diameter (assuming crystals completely cover bubble surface)	300 μm
Size estimate based on buoyancy of the magnetite-bearing bubble	
Magnetite volume	0.2 mm <sup>3</sup>
Magnetite mass	1 mg
Bubble volume required for buoyancy	0.6 mm <sup>3</sup>
Bubble diameter required for buoyancy	850 μm

ditions of 750°C and 200 MPa (H<sub>2</sub>O gas density = 0.46 g/cm<sup>3</sup>), the bubble diameter required for neutral buoyancy of the aggregate is 850 μm. This size is remarkably close to our estimate of bubble enlargement due to decompression.

Generalizing the above considerations, based on two independent minimum estimates, we suggest that the Bishop magma included some pre-eruptive bubbles that were at least several hundred micrometers in diameter. Such a size is consistent with expectations based on correlations between crystal or bubble size and the crystal/melt or gas/melt distribution factor (Anderson 2002).

Importantly, our study not only shows that the vesicle we describe most likely corresponds to a pre-eruptive bubble of several hundred micrometers in diameter, but also that it may have been neutrally buoyant. This latter conclusion has important consequences for the fate of pre-eruptive bubbles in the Bishop magma, and their role in its compositional and dynamical evolution, as partly discussed in the accompanying paper (Gualda and Ghiorso, in review).

## Conclusions

Using X-ray tomography of early-erupted Bishop pumice, we describe a vesicle with approximately 60 magnetite crystals attached to its walls. The texture of this aggregate, in particular the fact that the magnetite crystals are partly embedded in the glassy matrix, is best explained by formation under magmatic conditions. The timescale for the formation of this aggregate (i.e. years to decades) is incompatible with accumulation during decompression and eruption of magma (i.e. days to weeks, Anderson 1991; Wilson and Hildreth 1997), such that the aggregate must have been present in the pre-eruptive magma and, thus, the vesicle

corresponds to a pre-eruptive bubble. The recognition of this pre-eruptive bubble nicely confirms the inferred presence of an exsolved gas phase suggested based on indirect evidence (Wallace et al. 1995, 1999).

We use three independent approaches to estimate the size of this pre-eruptive bubble in the Bishop magma: (1) we use the vesicle volume to yield a bubble volume prior to decompression, (2) we approximate the bubble surface area as the total cross-sectional area of the magnetite crystal population from the individual crystal volumes, and (3) we calculate the bubble volume necessary for neutral buoyancy of the crystal–bubble aggregate. Our results imply a bubble of several hundred micrometers diameter, forming a nearly neutrally buoyant aggregate with ~60 magnetite crystals.

The recognition and characterization of a pre-eruptive bubble in the Bishop magma provides us with new information about the presence and size of bubbles in the pre-eruptive magma. Importantly, it also reveals a textural association between vesicles and magnetite crystals that may prove to be diagnostic of pre-eruptive bubbles in the Bishop magma and elsewhere.

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