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Magma Storage and Extraction Associated with Plinian and Interplinian Activity at Santorini Caldera (Greece)

T. H. Druitt^{1*}, M. Mercier¹, L. Florentin², E. Deloule², N. Cluzel¹,
T. Flaherty¹, E. Médard¹ and A. Cadoux^{3,4,5}

¹Laboratoire Magmas et Volcans, Université Blaise Pascal-CNRS-IRD, OPGC, 6 Avenue Blaise Pascal, 63178 AUBIERE Cedex; ²CRPG-CNRS, BP 20, 54501 Vandoeuvre les Nancy, France; ³Université d'Orléans, ISTO, UMR 7327, 45071 Orléans, France; ⁴CNRS, ISTO, UMR 7327, 45071 Orléans, France and ⁵BRGM, ISTO, UMR 7327, BP 36009, 45060 Orléans, France

*Corresponding author. Telephone: +33 4 7334 6718. E-mail: T.Druitt@opgc.univ-bpclermont.fr

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ABSTRACT

Santorini caldera has had a long history of plinian eruptions and caldera collapses, separated by 20–40 kyr interplinian periods. We have carried out a study to constrain magma storage/extraction depths beneath the caldera. We analysed H₂O in 138 olivine-, pyroxene- and plagioclase-hosted melt inclusions from plinian and interplinian products from the last 200 kyr, and CO₂, S, Cl, F and δD in various subsets of these. The dataset includes 64 inclusions in products of the Minoan plinian eruption of the late 17th century BCE. All the melt inclusions were ellipsoidal and isolated, with no textural evidence for volatile leakage. Mafic melt inclusions contain 1–4 wt % H₂O and up to 1200 ppm CO₂, 1200 ppm S, 2000 ppm Cl and 400 ppm F; silicic inclusions contain 2–7 wt % H₂O, up to 150 ppm CO₂, up to 400 ppm S, 2000–6000 ppm Cl and 600–1000 ppm F. The δD values of 27 representative inclusions (–37 to –104‰) are intermediate between mantle and slab values and rule out significant H₂O loss by hydrogen diffusion from olivine-hosted inclusions. H₂O, S and Cl behave compatibly in melt inclusion suites varying from mafic to silicic in composition, showing that entrapment of many melt inclusions took place under volatile-saturated conditions. Most Santorini melts are saturated in a free COHSCl vapour phase at depths of less than ~10 km; the only exceptions are basaltic melts from a single interplinian eruption, which were volatile-undersaturated up to K₂O contents of ~1 wt %. The rhyolitic melt of the Minoan eruption probably contained a free hypersaline liquid phase. H₂O + CO₂ saturation pressures were calculated using suitably calibrated solubility models to estimate pre-eruptive magma storage depths. Magmas feeding plinian eruptions were stored at >4 km (>100 MPa) and extracted over depth intervals of several kilometres. Plagioclase phenocrysts in rhyodacitic pumice from the Minoan eruption have cores containing melt inclusions trapped at depths up to 10–12 km (320 MPa), and rims (also orthopyroxene and clinopyroxene) containing inclusions trapped at 4–6 km (100–160 MPa). This records late-stage silicic replenishment of a <2 km thick shallow magma chamber, rather than extraction of melts syn-eruptively over the entire depth range. The plagioclase cores were carried from depth in the ascending melt, then overgrown by the rims in the shallow chamber. Exsolution of volatiles during ascent may have caused the replenishment melt to inject as a bubbly plume, causing mixing prior to eruption. This would explain (1) the homogeneity of the Minoan rhyodacitic magma, and (2) extraction of melt inclusions from the entire pressure spectrum during the first eruptive phase. Most silicic magmas feeding eruptions of the interplinian periods were stored in reservoirs at shallow depths (2–3 km) compared with those feeding the plinian eruptions (>4 km). Melt inclusions from the AD 726 eruption of Kamani Volcano yield a pre-eruptive storage depth of ~4 km, which is similar to that estimated from geodetic data for the inflation source during the 2011–2012 period of caldera

unrest; this supports a magmatic origin of the unrest. The level of pre-AD 726 magma storage beneath Kameni was deeper than that of earlier silicic interplinian eruptions, perhaps owing to changes in crustal stress caused by the Minoan eruption. Combined with previously published results, the melt inclusion data provide a time-integrated image of the crustal plumbing system. Mantle-derived basalts are injected into the lower crust, where they fractionate to produce evolved melts in bodies of hot crystal mush. Evolved residual melts separate from their parent mushes in the 8 to >15 km depth interval, then ascend rapidly into the upper crust, where they either crystallize or accumulate as bodies of eruptible, crystal-poor magma.

Key words: magma storage; melt inclusions; plinian; Santorini; volatiles

INTRODUCTION

The crustal magma plumbing system beneath a volcano exerts a strong control on eruptive behaviour and hazards (see reviews by [Cashman & Sparks, 2013](#); [Cashman & Giordano, 2014](#)). Pre-eruptive storage conditions determine initial magma properties such as pressure, temperature, volatile content and volatile composition, which in turn influence eruption dynamics ([Colucci *et al.*, 2014](#)). Magma ascending from deep to shallow crustal levels can inject to form high-level lenses of eruptible magma, or replenish and remobilize extant bodies of crystal mush, resulting in rapid build-up to eruption ([Annen *et al.*, 2006](#); [Bachmann & Berganz, 2008](#); [Druitt *et al.*, 2012](#); [Menand *et al.*, 2015](#)). Knowledge of past plumbing system architectures is useful for the interpretation of geodetic and seismic data during periods of unrest (e.g. [Blundy *et al.*, 2008](#); [Arienzo *et al.*, 2010](#); [Muir *et al.*, 2014](#)). Volatile contents of phenocryst-hosted melt inclusions (MIs) can be used to petrologically image the magma storage system if the degree of multi-species volatile saturation is known, and if accurate, appropriately calibrated, solubility laws exist ([Wallace, 2005](#); [Moore, 2008](#)). Melt inclusions have been used to probe magma storage levels beneath silicic caldera volcanoes prior to individual eruptions, such as Bishop, Oruanui and Kos Plateau ([Wallace *et al.*, 1995](#); [Lui *et al.*, 2005](#); [Bachmann *et al.*, 2009](#)). Temporal variations of pre-eruptive magma storage depth with time within tight chrono-stratigraphic contexts have, however, been documented at only a few caldera volcanoes such as Toba ([Chesner & Luhr, 2010](#)) and Mount Mazama ([Wright *et al.*, 2012](#)).

Santorini is a multi-cyclic caldera complex with an eruptive history spanning half a million years ([Druitt *et al.*, 1999](#)). Activity over the last ~360 kyr has consisted of multiple caldera-forming plinian eruptions, alternating with interplinian periods characterized by effusive activity and weak (mostly subplinian or less) explosive eruptions. Detailed knowledge of the eruptive, structural and chemical history of the complex makes Santorini a good target for using MIs to understand the factors that control magma storage and extraction beneath calderas. We address the following questions. First, over what range of depths were magmas extracted immediately prior to, and during, each plinian

eruption? Studies of ignimbrites such as Bishop and Oruanui ([Wallace *et al.*, 1995](#); [Liu *et al.*, 2005](#)) have shown that magma can be extracted from a surprisingly large range of depths, raising questions concerning the geometry of large silicic magma reservoirs ([Cashman & Giordano, 2014](#)). Second, are there differences between the pre-plinian storage levels and those during interplinian periods? The 15 month period of caldera unrest at Santorini between January 2011 and March 2012 involved inflation of the caldera floor and greatly increased levels of microseismicity, and has been attributed to the shallow injection of 10–25 million m³ of magma ([Newman *et al.*, 2012](#); [Parks *et al.*, 2012, 2015](#)). Is this hypothesis consistent with magma storage levels prior to historical eruptions of the volcano?

We report the H₂O contents of 138 phenocryst-hosted melt inclusions from Santorini, most of which were also analysed for CO₂, S, Cl and F. We also analysed a subset of inclusions for their D/H isotopic ratio to test for H₂O loss from olivine-hosted MIs by hydrogen diffusion ([Hauri, 2002](#); [Buchholz *et al.*, 2013](#)). By showing that MIs in nearly all Santorini magmas were trapped under volatile-saturated conditions, we invert the data via published solubility models to provide a time-integrated petrological snapshot of the crustal plumbing system over the last 200 kyr. Based on a set of 64 new volatile analyses of MIs from the Minoan plinian eruption of the late 17th century BCE, we place tight constraints on the thickness of the upper crustal magma reservoir that fed that eruption, as well as on the nature of an event of recharge by silicic melt that took place within about a decade prior to it.

VOLCANOLOGICAL BACKGROUND AND PREVIOUS STUDIES

Santorini volcanism

Santorini is the southernmost volcanic centre of the Aegean island arc ([Fig. 1](#)). It lies on continental crust about 25 km thick ([Tirel *et al.*, 2004](#)), which is partitioned into upper and lower sections, with the boundary lying at about 15 km depth ([Sachpazi *et al.*, 1997](#); [Konstaninou, 2010](#)). The volcano is situated within a 40 km wide NE–SW rift zone of normal to right-lateral transtensional faults ([Dimitriadis *et al.*, 2009](#); [Nomikou *et al.*, 2012](#); [Feuillet, 2013](#)). The caldera is

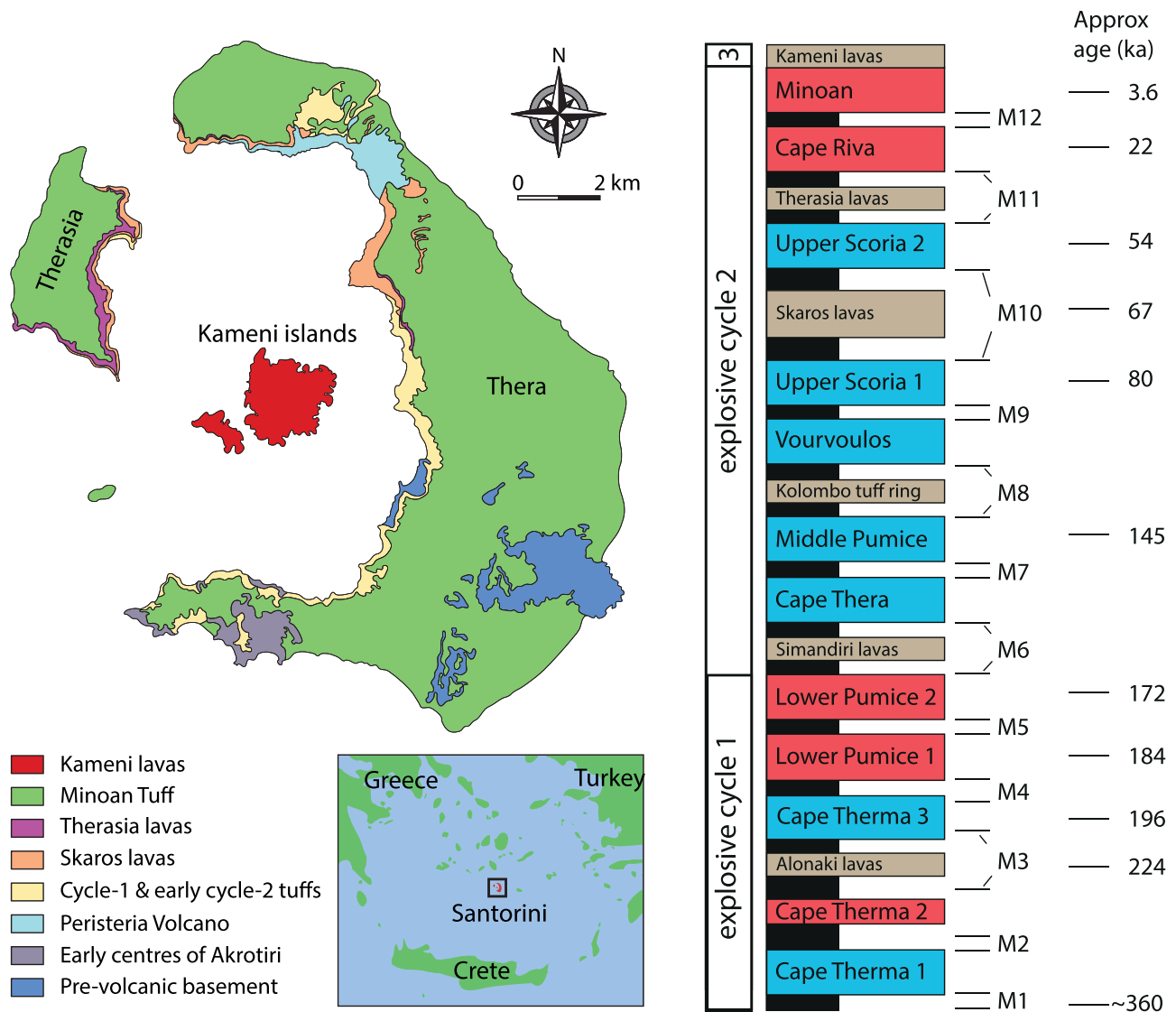


Fig. 1. Simplified geological map of Santorini, with inset showing the regional location. The schematic stratigraphic column shows the main eruptive units since the onset of major explosive volcanism, about 360 kyr ago. The activity since that time can be divided into three explosive cycles, cycles 1 and 2 each ending in a pair of major caldera-forming silicic eruptions, and cycle 3 inferred to have begun with the modern-day Kameni activity. Eruptions of mainly intermediate composition are shown as blue boxes, and those of mainly silicic composition are shown as red boxes. The silicic Cape Thera 3 unit is of much smaller magnitude than the other silicic units depicted. Black boxes are sequences of interplinian tephra (named M1 to M12, after Vespa *et al.*, 2006), and brown boxes are prominent lava or tuff successions within the interplinian sequences (after Druitt *et al.*, 1999). The ages derive from K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of onland products (Druitt *et al.*, 1999), as well as from O-isotope wiggle matching dating of deep-sea tephra [unpublished data cited by Vespa *et al.* (2006) and Gertisser *et al.* (2009)].

10 km north–south, 6 km west–east, and is an $\sim 45 \text{ km}^2$ multiple collapse structure that last subsided during the Minoan eruption of the late 17th century BCE (Druitt, 2014). Repeated eruptions have subsequently built up a largely submarine 3 km^3 intracaldera edifice, the sub-aerial summits of which form the Kameni Islands (Pyle & Elliot, 2006).

The evolution of the volcanic field has been described by Druitt *et al.* (1999). It is founded on a pre-volcanic island of Mesozoic limestones and Tertiary metapelites, draped and plastered by the volcanic products. The earliest dated volcanism (650–550 ka) discharged

amphibole-bearing silicic tuffs and lava flows. Between 530 and 430 ka, a stratocone complex (Peristeria Volcano) was constructed in the northern half of the volcanic field. Major explosive activity began at ~ 360 ka, and since then about 12 large-magnitude ($1\text{--}100 \text{ km}^3$ range) plinian eruptions have occurred. The plinian eruptions all had fallout phases, most discharged ignimbrite, and most were probably accompanied by caldera collapse. Direct field evidence exists for large collapses following the Lower Pumice 2, Cape Riva and Minoan eruptions (Druitt & Francaviglia, 1992). Plinian eruptions were separated by interplinian periods during which

prolonged effusive (and weakly explosive) activity built up intracaldera edifices, which then collapsed during the next plinian eruption. This alternation of plinian and interplinian activity has been repeated on average every 20–40 kyr. Sequences of interplinian pyroclastic products record many small-magnitude eruptions in the subplinian to violent strombolian (or less) range (some may be small-magnitude plinian). The interplinian sequences are termed M1–M12 (Fig. 1), and they range from basaltic to rhyodacitic in composition. They have been described by *Druitt et al. (1999)* and *Vespa et al. (2006)*; *Vaggelli et al. (2009)* described a scoria fall deposit from unit M12.

The volcanic products since 360 ka can be divided into two ~180 kyr magmatic cycles, each commencing with eruptions of mainly mafic to intermediate composition, and terminating with a pair of large silicic plinian eruptions: Lower Pumice 1 and Lower Pumice 2 at the end of cycle 1, and Cape Riva and Minoan at the end of cycle 2 (Fig. 1). The present-day Kameni interplinian activity (last eruption 1950) may constitute the start of a third volcanic cycle.

Santorini magmas range from basaltic (up to ~7 wt % MgO) to rhyodacitic in composition, and are transitional tholeiitic to calc-alkaline in character (*Druitt et al., 1999*). Typical phase assemblages (in all but the oldest, >550 ka, products) are olivine ± augite ± plagioclase in basalts (<53 wt % SiO₂), plagioclase + augite + magnetite ± olivine ± orthopyroxene in andesites (53–63 wt % SiO₂), and plagioclase + augite + orthopyroxene + magnetite + ilmenite + apatite ± pyrrhotite ± (rare) hornblende in dacites (63–68 wt % SiO₂) and rhyodacites (68–72 wt % SiO₂). Interstitial glasses in some rhyodacites are rhyolitic (>72 wt % SiO₂). The primary melt at Santorini has been estimated by back-calculation to have 9–12 wt % MgO (*Nichols, 1978*). This would fractionate 6–13 wt % of olivine and small amounts of Cr-spinel and clinopyroxene to generate the most primitive basalt erupted (~7 wt % MgO). Incompatible trace element contents (e.g. K, Rb, Th, La) in the intermediate and silicic magmas decrease with time, probably as a result of changing proportions of different mantle-derived mafic magma batches entering the crust (*Huijsmans et al., 1988*; *Druitt et al., 1999*; *Francalanci et al., 2005*; *Bailey et al., 2009*; *Vaggelli et al., 2009*; *Fabbro et al., 2013*). However, if a single time slice is considered, then Santorini magmas can be modelled well by fractional crystallization accompanied by ~10% of crustal assimilation (*Barton et al., 1983*; *Mann, 1983*; *Barton & Huijsmans, 1986*; *Huijsmans et al., 1988*; *Huijsmans & Barton, 1989*; *Druitt et al., 1999*; *Zellmer et al., 2000*).

Understanding of Santorini magmatism has been advanced by a recent series of phase equilibria studies on a parental basalt (~340 ka Balos basalt; *Andújar et al., 2015*), a silicic andesite *Andújar et al.* (in preparation), and silicic magmas of four plinian eruptions (Lower Pumice 1, Lower Pumice 2, Cape Riva and Minoan; *Cadoux et al., 2014*). The experiments were carried out at 100–400 MPa, 850–1040°C, redox conditions of QFM (quartz–fayalite–magnetite) to NNO

(nickel–nickel oxide) + 3–5, and melt H₂O contents of 2–10 wt %. Some of the main conclusions were as follows: (1) parental basalt containing 4–6 wt % H₂O fractionates via 60–80 wt % crystallization to silicic andesite at about 400 MPa, 1000°C and QFM; (2) silicic melts are generated by fractional crystallization at 200–400 MPa; (3) silicic melts feeding plinian eruptions are saturated with respect to H₂O + Cl ± CO₂, and in some cases a hypersaline liquid (brine) phase.

Abundant nodules of cumulate gabbro and diorite have been erupted on Santorini. Cumulate gabbros contain primocrysts of plagioclase, clinopyroxene, orthopyroxene, Fe–Ti oxides and rare olivine with intercumulus quartz, alkali feldspar, hornblende and biotite. Major element modelling reproduces the observed phase assemblages and proportions of the gabbros if they are assumed to be cumulates from andesites with 56–66% SiO₂ (*Druitt et al., 1999*).

Measurements of H₂O, S and halogens in Santorini MIs have been reported by several researchers (*Sigurdsson et al., 1990*; *Gardner et al., 1996*; *Cottrell et al., 1999*; *Michaud et al., 2000*; *Gertisser et al., 2009*; *Vaggelli et al., 2009*; *Cadoux et al., 2014*). However, there are no published data for H₂O in basaltic melts, no volatile data for interplinian products, and no measurements of CO₂ at all.

Previous estimates of pre-eruptive magma storage pressures

Previous estimates of storage pressures of <550 ka Santorini magmas have been made using mineral equilibria, phase equilibria experimentation, and geodetic modelling of deformation during the 2011–2012 period of unrest; they range from <100 to ~400 MPa (*Table 1*). Phase equilibria studies of the natural products have constrained pre-eruptive storage pressures for silicic pumices from the four main plinian eruptions (≥200 MPa; *Cadoux et al. 2014*), for a basalt from the ~340 ka Balos cinder cone (~400 MPa; *Andújar et al., 2015*), and for an andesite from a plinian eruption (~200 MPa; *Andújar et al.*, in preparation). *Gertisser et al. (2009)* estimated a pressure of 430 ± 10 MPa for the silicic Lower Pumice 2 magma body using the Al-hornblende barometer; however, the barometer as used is probably outside its conditions of application (*Johnson & Rutherford, 1989*; *Anderson & Smith, 1995*), and the amphibole in LP2 may be antecrystic (*Cadoux et al., 2014*).

METHODS

Field sampling

Our samples were collected mostly from pyroclastic products of the second explosive cycle, but we also included the two rhyodacitic eruptions terminating cycle 1 (Lower Pumices 1 and 2), as well as one sample from the (cycle 3) Kameni edifice (Fig. 1). The samples (described in *Table 2*) are representative of plinian

Table 1: Previous estimates of pre-eruptive storage depths of Santorini magmas

Unit	Composition	Pressure (MPa)	Depth (km)	Method	Ref.
Kameni	s	80–150	3.1–5.8*	cpx–plag equilibria	1
Skaros, Peristeria	m, i	170–340	6.6–13.1*	cpx–plag and ol–cpx equilibria	2
Lower Pumice 2	s	430 ± 10	16.6 ± 0.4*	Al in hb; equilibrium with qz	4
Minoan	s	≥200 to 50	>7.7 to ~1.9*	phase equilibria; melt inclusions	3, 5
Min, CR, LP2, LP1	s	≥200	>7.7*	phase equilibria	5
Minoan	s	190 ± 50	7.3 ± 1.9*	hb composition (mph-rich pumice)	5
Balos basalt	m	~400	~15.4*	phase equilibria	6
Unrest 2011–2012	?		3.3–6.3	geodesy	7–9
Silicic melt generation	s	200–400	7.7–15.4*	phase equilibria Fe/Mg ratios	10

References: 1, Barton & Huijsmans (1986); 2, Huijsmans & Barton (1989); 3, Cottrell *et al.* (1999); 4, Gertisser *et al.* (2009); 5, Cadoux *et al.* (2014); 6, Andújar *et al.* (2015); 7, Newman *et al.* (2012); 8, Parks *et al.* (2015); 9, Papoutsis *et al.* (2013); 10, Andújar *et al.* (in preparation). m, mafic; i, intermediate; s, silicic; mph, microphenocryst. Min, Minoan; CR, Cape Riva; LP2, Lower Pumice 2, LP1, Lower Pumice 1. ol, olivine; cpx, clinopyroxene; plag, plagioclase; hb, hornblende; qz, quartz

*Recalculated using a mean upper crustal density of 2640 kg m⁻³ (Konstantinou, 2010).

Table 2: Sample details

Unit	Eruptive phase	Sample	SiO ₂ (wt %)	Phenocryst phases	Description
Kameni*	AD 726	PKB3	67	pl, px, ox	Dacitic pumice from AD 726 eruption
Minoan*	4	S12-10	70	pl, px, ox	Rhyodacitic pumice; ignimbrite
	4	S82-11	70	pl, px, ox	Rhyodacitic pumice; ignimbrite
	4	S82-2	70	pl, px, ox	Rhyodacitic pumice; ignimbrite
	3	R2	70	pl, px, ox	Rhyodacitic pumice; low-grade ignimbrite
	2	S82-34b	70	pl, px, ox	Rhyodacitic pumice; pyroclastic surge
	1	S82-30	70	pl, px, ox	Rhyodacitic pumice; fallout
	1	S82-28	70	pl, px, ox	Rhyodacitic pumice; fallout
	1	S82-34a	61	pl, px, ox, hb (tr)	Mph-rich andesitic pumice, fallout
M12†		G1	54	ol, pl, px, ox	Andesitic scoria; fallout
Cape Riva*	1	S09-39	67	pl, px, ox	Dacitic pumice; fallout
M10a-FS3‡		S12-43	52	ol, pl, px, ox	Basaltic scoria; fallout
M10a-BP‡		S12-41	58	pl, px, ox	Andesitic scoria; fallout
M10a-Y/B6‡		S12-37	51	ol, pl, px, ox	Basaltic scoria; 5 cm fallout
Vourvoulos*	1	S12-67	66	pl, px, ox	Dacitic pumice; fallout
M8-MSF‡		S12-68	56	ol, pl, px, ox	Andesitic scoria; fallout
Middle Pumice*	1	S12-59	65	pl, px, ox, ol (tr)	Dacitic pumice; fallout
M7a§		S12-46	64	pl, px, ox	White dacitic pumice; 25 cm fallout
M7c§		S12-44	53	ol, pl, px, ox	Black basaltic scoria; 40 cm fallout
M6a§		S12-48	65	pl, px, ox	White dacitic pumice; 20 cm fallout
M6e§		S12-52	54	ol, pl, px, ox	Black andesitic scoria; 20 cm fallout
Lower Pumice 2*	1	S09-23	70	pl, px, ox	Rhyodacitic pumice; fallout
Lower Pumice 1*	1	S09-17	69	pl, px, ox	Rhyodacitic pumice; fallout

*Unit name and SiO₂ content from [Druitt *et al.* \(1999\)](#).

†Unit name and SiO₂ content from [Vaggelli *et al.* \(2009\)](#); sampled at the location in that paper.

‡Unit name, eruptive phase, and SiO₂ content from [Vespa *et al.* \(2006\)](#); sampled at the photograph locations in that paper.

§Details of M6 and M7 given by [Druitt *et al.* \(1999\)](#).

ol, olivine; px, pyroxene; ox, oxides; hb, hornblende; tr, trace quantities; mph, microphenocryst.

(Lower Pumice 1, Lower Pumice 2, Middle Pumice, Vourvoulos, Cape Riva and Minoan) and interplinian (M6, M7, M8, M10, M12, Kameni) eruptions; Vourvoulos is the smallest of the plinian units. The mafic interplinian units were laid down by violent strombolian to subplinian eruptions.

The samples consist of one or more fresh, glassy pyroclasts ranging from basaltic to rhyodacitic in composition, as analysed by previous researchers ([Druitt *et al.*, 1999](#); [Vespa *et al.*, 2006](#); [Vaggelli *et al.*, 2012](#)). In the case of olivine-bearing samples, we chose fallout lapilli one to a few centimetres in diameter that would have cooled rapidly during emplacement, and hence would contain olivine-hosted MIs less likely to be

affected by post-eruptive diffusive loss of H₂O ([Lloyd *et al.*, 2013](#)).

Sample preparation and selection

One or more clasts from each level were crushed and sieved, retaining the fractions between 0.5 and 1.0 mm and between 1.0 and 2.0 mm. Olivine, pyroxene and plagioclase crystals were handpicked under a binocular microscope, giving priority where possible to euhedral, glass-coated crystals. The MIs selected for study were vitreous (without daughter minerals or heavy oxide dusting), ellipsoidal, isolated (not connected to the crystal surface) and fracture-free ([Fig. 2](#)). Partially crystallized

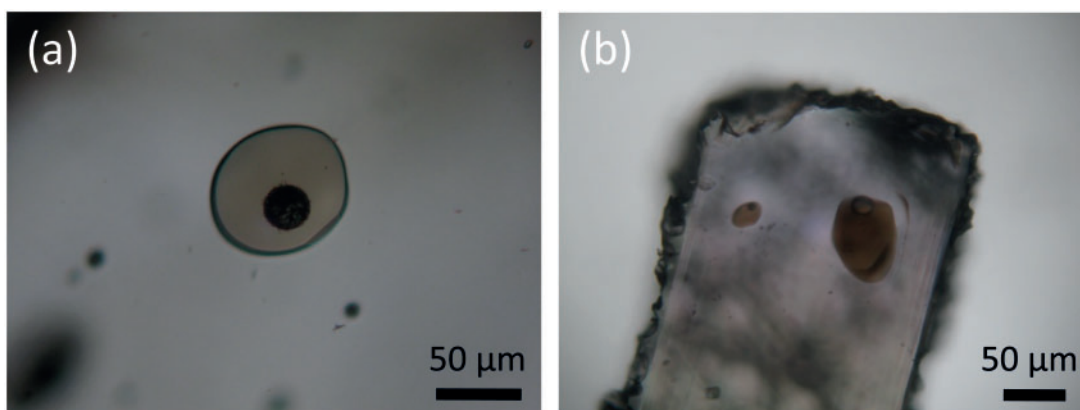


Fig. 2. Photomicrographs of representative melt inclusions hosted by (a) olivine (M8-MSF, S12-68, crystal 6, MI 1), and (b) plagioclase (Kameni AD 726, PKB3, crystal 4, MI 1).

MIs were observed, but not studied. Each crystal was mounted in resin, then polished on one face to expose the chosen MI. The crystal was then extracted, washed in acetone and pressed into indium and coated with gold for secondary ion mass spectrometry (SIMS) analysis. All polishing was done using corundum disks to avoid carbon contamination from diamond powder. Following SIMS analysis, the indium crystal mount was repolished and coated with carbon for major element, sulphur and halogen analysis by electron microprobe.

We also analysed the composition of the host mineral phase immediately in contact with each MI. In olivine or pyroxene, the crystal was spot analysed as close as possible to the MI. In plagioclase, we used back-scattered electron (BSE) imagery to recognize the plagioclase in equilibrium with the MI. Melt inclusions in plagioclase commonly occupy resorption re-entrants that were then sealed up by precipitation of further plagioclase. By analysing the plagioclase shell around the MI, we obtained a true equilibrium plagioclase–melt pair.

Analytical techniques

Major element compositions of MIs were analyzed by wavelength-dispersive spectrometry (WDS) on a CAMECA SX 100 electron microprobe at the Laboratoire Magmas et Volcans, Clermont-Ferrand using a 15 keV, 4–8 nA electron beam with a 10–20 µm spot size and calibrated using international glass standard A99. These conditions avoided significant Na diffusion under the electron beam, as confirmed by test analyses on a single, large H₂O-rich MI. The host olivine, pyroxene or plagioclase was analysed using a 15 keV, 15 nA focused beam, and calibrated on natural and synthetic minerals.

Volatile contents of the MIs were analysed by SIMS using the IMS 1280 system at the French national SIMS facility (Centre de Recherches Pétrographiques et Géochimiques, Nancy) during five analytical sessions: (1) M12 and Minoan; (2) Lower Pumice 1, Lower Pumice

2, M6, M7, Middle Pumice, M8, Vourvoulos and Kameni; (3) M10a and Cape Riva; (4) δD and some Minoan MIs; (5) additional Minoan MIs. A 4–6 nA primary beam of Cs⁺ ions was focused on a 10 µm diameter area, and the electron gun was used to avoid electrostatic charging. Negative secondary ions ¹²C, ¹⁷O, ¹⁶O¹H, ¹⁸O, ¹⁹F, ²⁷Al, ³⁰Si, ³²S and ³⁵Cl were measured at a mass resolution of 7850, with an energy offset of 30 ± 10 eV, by ion counting on EM in monocollection mode. A 10 µm × 10 µm raster was used for 80 s prior to analysis on each spot to pre-sputter through the gold coat and remove surface contamination. The sample chamber vacuum was kept below 2 × 10⁻⁹ torr using a liquid nitrogen trap. Each analysis consisted of between 15 and 20 scans, with counting times of 4 s per scan on each peak.

Concentrations of H₂O and CO₂ were calculated using best-fit regressions to plots of H₂O/SiO₂ vs ¹⁶O¹H/³⁰Si and of CO₂/SiO₂ vs ¹²C/³⁰Si, respectively. We used three sets of experimental standard glasses to calibrate the H₂O analyses (Fig. 3): (1) 13 basaltic glasses with 0–5.7 wt % H₂O; (2) four dacitic glasses with 0–6.4 wt % H₂O; (3) seven rhyolitic glasses with 0–6.6 wt % H₂O (Appendix A). These define three distinct calibration curves with slopes increasing as a function of melt polymerization (Fig. 3a) (Hauri, 2002). Each calibration curve was fitted by a quadratic polynomial

$$\left(\frac{\text{H}_2\text{O}}{\text{SiO}_2}\right) = A \left(\frac{{}^{16}\text{O}^1\text{H}}{{}^{30}\text{Si}}\right) + B \left(\frac{{}^{16}\text{O}^1\text{H}}{{}^{30}\text{Si}}\right)^2$$

where *A* and *B* are functions of SiO₂ content. The H₂O content of each MI was determined by calculating its value from the two calibration curves with SiO₂ contents (renormalized to 100 wt % dry) below and above that of the MI, then by linear interpolation between these two values as a function of SiO₂ content. Although the rhyolite calibration curve is not well constrained at H₂O/SiO₂ < 0.03, our silicic MIs all lie at values above this.

We used three sets of standard glasses for CO₂: a basaltic set containing 0–3800 ppm CO₂, an andesitic set containing 2600–4300 ppm, and a rhyolitic set containing

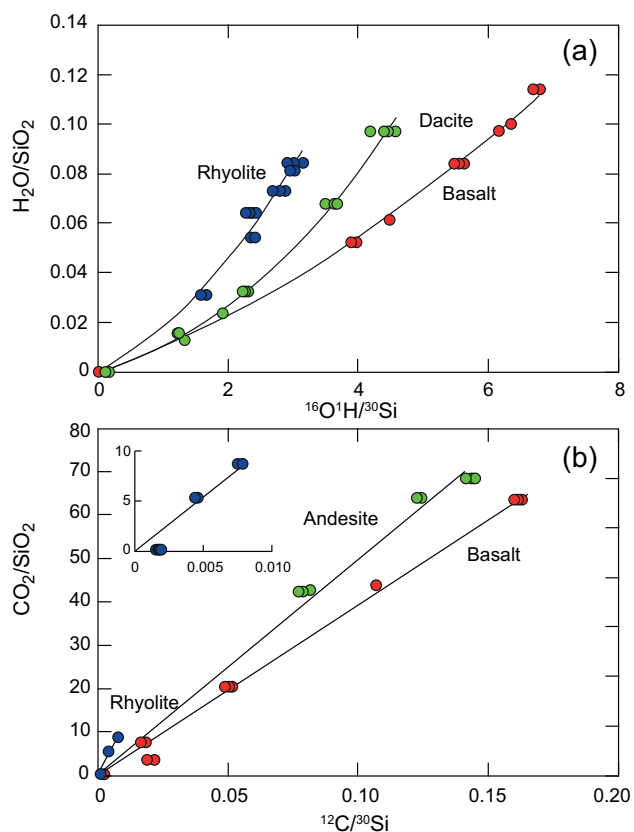


Fig. 3. Examples of SIMS standard calibration curves for (a) H_2O and (b) CO_2 . The standards are listed in Appendix A. Sample H_2O and CO_2 values were determined by extrapolating between the standard curves, using renormalized silica contents, as described in the text.

15–680 ppm. The andesitic set was synthesized especially for this study in Clermont-Ferrand using a Santorini andesite (Appendix B). These glasses defined three calibration lines with slopes increasing as a function of melt polymerization (Fig. 3b). The best-fit calibration curves were linear,

$$\left(\frac{\text{CO}_2}{\text{SiO}_2}\right) = C \left(\frac{^{12}\text{C}}{^{30}\text{Si}}\right)$$

where the slope C is a function of SiO_2 content. The matrix effect for CO_2 was then corrected by linear extrapolation between neighbouring curves, as for H_2O .

The H_2O and CO_2 contents of all analysed MIs fall within the calibration range of the standards. Uncertainties (relative percentage on the mean) on H_2O and CO_2 abundances owing to SIMS counting statistics are $<3\%$ and $<5\%$ (rarely up to 10%) respectively, and the detection limits are 0.01 wt % and 50 ppm, respectively (Supplementary Data Appendix 1; supplementary data are available for downloading at <http://www.petrology.oxfordjournals.org>). Uncertainties on the H_2O and CO_2 calibration curves are about $\pm 5\%$.

For S, Cl and F, the SIMS data were calibrated using electron microprobe analyses of a subset of MIs ranging from basaltic to rhyolitic in composition (Fig. 4).

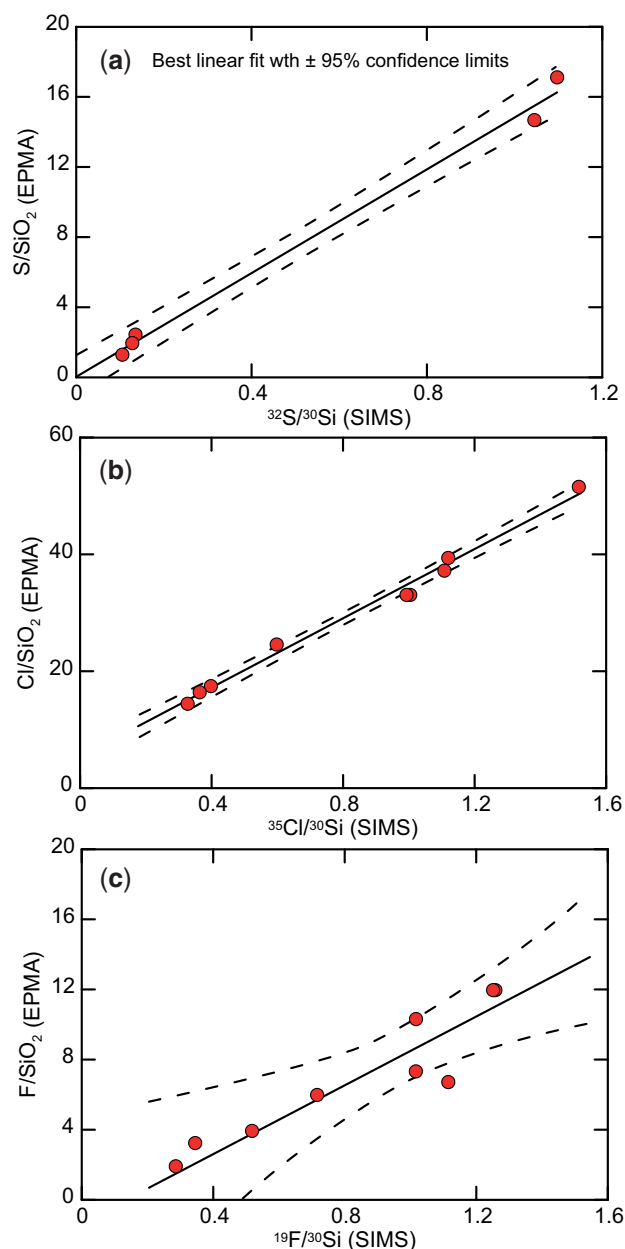


Fig. 4. Examples of calibration curves for SIMS analyses of S, Cl and F using electron microprobe analysis (EPMA) of the same melt inclusions. The continuous lines are linear best fits to the data, and the dashed lines are the 95% confidence limits on the fits.

A separate calibration was used for each SIMS sample batch. The electron microprobe analyses of S, Cl and F were carried out following the technique of Moune *et al.* (2007), with a 40 nA sample current, 10 μm beam diameter, and counting times of 200 – 400 s. To minimize volatile loss during analysis, the beam was blanked regularly with the Faraday cup and counts were collected at 20 s intervals by 10 iterations for Cl and S, and 20 iterations for F. As S speciation can be significantly affected by oxidation state (Moretti & Ottonello, 2005; Métrich *et al.*, 2008), the S peak position was checked

before each analysis to improve measurement accuracy. The electron microprobe analyses were calibrated on three international standards: Vg2 (S, 1400 ppm), Alvin (S, 993 ppm) and KE12 (Cl, 3300 ppm; F, 4500 ppm). Uncertainties (relative percentage on the mean) on S, Cl and F abundances owing to SIMS counting statistics are <5%, and most are 1–2% (Supplementary Data Appendix 1). Uncertainties on calibration curves for S, Cl and F are about $\pm 5\%$, $\pm 8\%$ and $\pm 12\%$, respectively.

The D/H ratios of 27 representative MIs were analyzed in sample batch 4 by SIMS using the IMS 1280 system with the same primary beam as for H₂O and CO₂. Negative secondary ions H and D were measured at a mass resolution of 1500, without energy offset and a 30 eV energy slit, in monocollection mode by ion counting for D and on FC for H. A 10 μm \times 10 μm raster was used for 80 s to pre-sputter through the gold coat. Each analysis consisted of between 15 and 20 scans, with counting times per scan of 4 s and 30 s for H and D respectively. The D/H ratio calibrations were done using two sets of standard glasses of basaltic and andesitic composition (Metrich & Deloule, 2014). No systematic matrix effect was observed as a function of either SiO₂ or H₂O content, so the same correction was applied to all of the measured compositions, with a calibration error of <8%.

Shrinkage bubbles in six representative MIs in doubly polished crystal wafers were analysed using a Renishaw InVia Raman spectrometer at the Laboratoire Magmas et Volcans, Clermont-Ferrand, to determine whether CO₂ was present at levels above the detection limit. If CO₂ partly partitioned into bubbles during cooling, then the amount present must be 'added back' into the MIs for estimation of the original melt value (e.g. Neave *et al.*, 2014). The spectrometer was equipped with a Peltier cooled charge-coupled device (CCD) detector and a microscope in confocal setting. The samples were excited by a 532 nm wavelength laser source. The source output power was 1 W for all analyses, and the power on the samples was 30 mW. The counting time was 30 s (three cycles of 10 s). A grating of 2400 grooves per mm was used.

RESULTS

The results are summarized in Table 3, and are given in full in Supplementary Data Appendix 1.

Melt inclusion textures

The 138 glassy MIs selected for study have maximum diameters of 30–270 μm and minimum diameters of 20–170 μm (Fig. 2); 93 are hosted by plagioclase, 32 by olivine, and 13 by pyroxene. A sixth of the MIs contain no shrinkage bubble; most of the others contain a single bubble of diameter 1–55 μm , but some contain multiple bubbles nucleated on the inclusion margins. The majority of bubbles account for <5 vol. % of the MIs, with a few up to 12 vol. %, as typical of shrinkage bubbles.

Only two MIs from plinian units have bubble fractions in excess of that expected from shrinkage (Middle Pumice, 16 vol. %; Minoan, 28 vol. %; Supplementary Data Appendix 1); however, these could in part be artefacts of underestimation of MI volume.

Major elements of melt inclusions and minerals

The olivine crystals containing MIs are weakly zoned, and range in composition from Fo₇₃ to Fo₈₆; the weak zoning implies relatively simple MI entrapment histories in the olivines. A range of olivine composition is observed in each olivine-bearing sample, except in M12, where the Fo content is uniformly high (Fo_{85–86}). All compositions of olivine-hosted MIs were corrected for post-entrapment crystallization using a melt–olivine equilibrium constant $K_D = (\text{FeO}/\text{MgO})_{\text{ol}}/(\text{FeO}/\text{MgO})_{\text{melt}}$ of 0.31 (Toplis, 2005); the extent of post-entrapment crystallization is less than 10% in all cases. Clinopyroxene and orthopyroxene hosts have compositions of Wo_{43–46} En_{37–39} Fs_{16–19} and Wo₃ En_{55–57} Fs_{39–42}, respectively. Plagioclase hosts have compositions from An₃₇ to An₉₄; most are zoned, apart from those from the Vourvoulos eruption (An_{47–49}). Because K_D values in the pyroxene–melt and plagioclase–melt systems are not well constrained, we did not correct the compositions of MIs trapped in pyroxenes and plagioclase.

Major element compositions of the MIs are plotted in Fig. 5. The melts range from basaltic to rhyolitic, with a gap at intermediate compositions (SiO₂ from 57 to 63 wt %). The gap is a sampling artefact of our dataset, not a real feature of Santorini melts. For example, MIs in mafic components of Lower Pumice 2 [analysed by Gertisser *et al.* (2009), but not us] have compositions lying within the gap. Overall, our analysed MIs from 46 to 57 wt % SiO₂ are hosted by olivine (Fo_{73–86}), cpx or calcic plagioclase (An_{79–95}), and those from 63 to 75 wt % SiO₂ are hosted by plagioclase (An_{33–60}), cpx or opx.

The MIs from each of the mafic interplinian units (M6e, M7c, M8-MSF, M10-FS3, M10-Y/B6, M12) exhibit significant ranges of composition; in M6e and M10-FS3 the plagioclase-hosted MIs are slightly more evolved than those hosted by olivines in the same sample, but in M7c and M8-MSF, there is no difference. The silicic MIs are, on the other hand, compositionally more uniform in terms of major elements. Taken together, the MIs define a trend in which MgO, FeO, CaO and TiO₂ decrease, and K₂O and Na₂O increase, with increasing SiO₂ (Table 3). This is similar to the trends of Santorini whole-rock data (Fig. 5), which have been successfully modelled by fractional crystallization with minor crustal assimilation (Mann, 1983; Huijsmans & Barton, 1989; Druitt *et al.*, 1999). Vectors of fractional crystallization, based on phase equilibria experiments performed on Santorini basalt at 400 MPa pressure (Andújar *et al.*, 2015), reproduce the MI trends (Fig. 5). Superimposition of MI and whole-rock data in Fig. 5 shows that the MI compositions are representative of typical Santorini magmas.

Table 3: Melt inclusion analyses and calculated parameters

Sample	Crystal	MI	Host crystal (wt %)		Melt inclusion (recalculated dry) (wt %)										MI volatiles and H isotopes						Pressure (MPa)*				Temperature (°C)†					
			Phase	Mg#	An	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O (wt %)	CO ₂ (ppm)	S (ppm)	Cl (ppm)	F (ppm)	δD (‰)	VoiCalc	Papale	SolEx	Ol-melt Putirka	Pl-melt Putirka	Ol-melt Putirka	Pl-melt Lange			
<i>Kamenit, AD 726</i>																														
PKB3	1		plag	50	70.6	0.42	15.29	3.63	0.11	0.72	2.47	4.37	2.36	4.69	139			3243	697			148						903	895	
PKB3	2		plag	52	69.2	0.96	15.13	4.05	0.13	0.79	2.62	4.85	2.30	5.20	41			3467	709			159						900	873	
PKB3	3		plag	49	69.8	0.55	15.23	3.50	0.17	0.80	2.74	4.84	2.38	4.18	72			3031	615			113						922	920	
PKB3	4		plag	49	70.1	0.43	15.19	3.59	0.13	0.71	2.55	4.90	2.39	4.06				3263	635											
PKB3	5		plag	51	70.0	0.56	14.81	3.58	0.15	0.75	2.58	5.25	2.35	4.23	75			3031	718			113						919	928	
<i>Minoan, Phase 1</i>																														
S82-28	1-0	a	cpx	69	73.0	0.35	15.15	1.97	0.00	0.12	1.10	4.10	4.26	4.26	130	59		4019	764			139								
S82-28	1-3	a	cpx	69	72.6	0.39	15.00	2.28	0.00	0.16	1.44	4.89	3.29	4.50	118	86		3688	807			149								
S82-28	1-18	a	cpx	71	73.5	0.35	14.76	1.97	0.00	0.18	1.20	4.69	3.35	4.35	114	79		3956	794			141								
S82-28	1-18	b	cpx	70	74.6	0.29	14.37	1.31	0.00	0.09	1.01	4.37	3.98	4.31	139	75		3830	746			143								
S82-30	5-54	a	cpx	69	73.8	0.36	14.73	1.55	0.00	0.17	1.28	4.72	3.38	4.23	69	62		3921	733			128								
S82-30	5-54	b	cpx	70	73.5	0.39	14.84	1.48	0.00	0.13	1.51	4.84	3.28	4.18	107	73		3806	746			132								
S82-30	2-20	a	cpx	67	74.8	0.36	14.25	1.30	0.00	0.11	1.13	4.61	3.48	4.73	100†							157								
S82-30	4-20	a	cpx	68	73.0	0.30	14.72	2.20	0.00	0.24	1.37	4.72	3.50	4.52	152	74		3641	802			155								
S82-30	5-43	a	cpx	66	74.0	0.32	14.35	2.06	0.00	0.20	1.23	4.52	3.34	4.39	135	69		3986	743			146								
S82-30	1-30	a	opx	59	73.0	0.32	14.50	2.52	0.00	0.15	1.27	4.79	3.43	4.38	122	82		3820	760			143								
S82-30	1-39	a	opx	57	74.0	0.31	14.21	2.35	0.00	0.08	1.48	4.52	3.08	4.13	98	64		3568	725			128								
S82-30	3-3	a	opx	58	74.3	0.32	13.67	2.41	0.00	0.12	1.27	4.53	3.37	4.38	99	84		3962	771			140								
S82-30	3-46	a	opx	59	73.1	0.32	14.18	2.79	0.00	0.25	1.35	4.53	3.51	4.14	106	78		3545	764			130								
S82-30	1-16	b	plag	42	73.1	0.41	14.58	2.32	0.00	0.30	1.43	4.17	3.64	5.02	126	100		4573	765			173								
S82-30	1-38	a	plag	44	73.2	0.38	14.19	2.44	0.00	0.36	1.51	4.44	3.44	4.61	136	94		3653	771			157								
S82-30	1-41	a	plag	40	74.6	0.30	13.82	2.05	0.00	0.30	1.28	4.23	3.44	4.69	152	78		3429	743			160								
S82-30	1-49	a	plag	42	74.3	0.32	13.76	1.86	0.00	0.20	1.41	4.66	3.52	4.71	132	79		3604	736			159								
S82-30	1-64	a	plag	42	73.8	0.30	14.31	1.88	0.00	0.28	1.34	4.50	3.56	4.38	149	90		3164	708			147								
S82-30	2-8	a	plag	37	73.7	0.30	13.93	2.26	0.00	0.36	1.24	4.40	3.81	4.45	198	83		3535	722			156								
S82-30	2-10	a	plag	41	73.5	0.35	14.16	2.33	0.00	0.31	1.39	4.23	3.77	4.33	130	58		4320	823			142								
S82-30	4-2	a	plag	42	74.3	0.32	13.97	1.81	0.00	0.33	1.31	4.49	3.43	4.56	151	64		3059	684			155								
S82-30	4-2	b	plag	38	74.4	0.25	14.06	1.73	0.00	0.28	1.27	4.62	3.39	4.67	98	56		3322	714			151								
S82-30	4-13	a	plag	41	73.7	0.27	14.23	1.88	0.00	0.29	1.46	4.66	3.50	4.68	116	43		3514	710			156								
S82-30	4-22	a	plag	34	75.4	0.22	13.43	1.70	0.00	0.23	1.31	4.25	3.45	4.68	84	85		3747	752			147								
S82-30	3-9	a	plag	41	73.7	0.28	14.04	1.92	0.00	0.32	1.50	4.87	3.37	4.25	109	77		3252	666			136								
S82-30	1	1	plag	49	73.6	0.37	14.28	2.14	0.07	0.32	1.49	4.39	3.32	6.85	80	86		3879	826			253								
S82-30	2	1	plag	43	73.8	0.30	14.13	2.08	0.16	0.29	1.45	4.27	3.54	5.17	73	58		3604	799			171								
S82-30	2a	1	plag		74‡										4.33	100‡						147								
S82-30	3a	1	plag		74‡										4.53	100‡						156								
S82-30	5a	1	plag		74‡										4.34	100‡						147								
S82-30	6a	1	plag		74‡										4.45	100‡						147								
S82-30	7a	1	plag		74‡										4.34	100‡						147								
S82-30	8a	1	plag		74‡										6.71	100‡						238								
S82-30	9a	1	plag		74‡										6.16	100‡						219								
S8234a¶	2	1	plag	45	72.5	0.86	14.12	2.85	0.08	0.43	1.68	3.97	3.55	5.38	26	129		4773	806			176								
S8234a¶	4	1	plag	37	75.1	0.25	13.60	1.87	0.07	0.27	1.26	4.02	3.57	6.55	56	48		3479	756			231								
<i>Minoan, Phase 2</i>																														
S82-34b	1	1	plag	46	73.5	0.32	14.19	2.05	0.11	0.29	1.46	4.58	3.50	6.06	21	61		3519	787			206								
S82-34b	3	1	plag	42	73.9	0.29	14.08	1.94	0.02	0.28	1.41	4.60	3.48	4.33	24	56		3332	753			125								

(continued)

Table 3: (Continued)

Sample	Crystal	MI	Host crystal (wt %)		Melt inclusion (recalculated dry) (wt %)										MI volatiles and H isotopes										Pressure (MPa)*				Temperature (°C)†	
			Phase	Mg#	An	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O (wt %)	CO ₂ (ppm)	S (ppm)	Cl (ppm)	F (ppm)	δD (‰)	VoiCalc	Papale	SolEx	Ol-melt Putirka	Ol-melt Putirka	Pl-melt Putirka	Pl-melt Lange			
S82-34b	4	1	plag	42	74.4	0.32	13.92	1.97	0.01	0.27	1.30	4.43	3.38	4.52	19	43	3002	752	132	124						846	929			
S82-34b	6	1	plag	43	73.9	0.31	14.16	2.04	0.08	0.30	1.38	4.37	3.49	4.67	30	59	3467	789	141	136						848	917			
<i>Minoan, Phase 3</i>																														
R2	1	2	plag	43	73.4	0.28	14.25	2.25	0.02	0.33	1.47	4.57	3.42	4.22	17	41	3495	702	120	108						864	945			
R2	3	1	plag	42	73.7	0.34	14.30	2.08	0.10	0.31	1.39	4.36	3.44	4.17	28	60	3575	759	119	109						860	945			
<i>Minoan, Phase 4</i>																														
S82-2	1-1	a	plag	42	73.4	0.35	14.48	2.23	0.00	0.35	1.45	4.37	3.35	4.82	100‡	70	3803	708	160	157						850	905			
S82-2	1-49	a	plag	39	73.8	0.27	13.90	2.24	0.00	0.27	1.33	4.80	3.42	4.41	129	56	3329	694	145	135						848	929			
S82-2	1-49	b	plag	33	74.6	0.27	13.88	1.82	0.00	0.25	1.36	4.33	3.46	4.49	100‡	47	3304	696	142	138						837	899			
S82-2	1-75	a	plag	42	74.4	0.25	14.00	1.97	0.00	0.29	1.29	4.45	3.35	4.46	113	64	3286	682	145	137						848	933			
S82-2	1-75	b	plag	42	74.7	0.30	13.92	1.81	0.00	0.26	1.40	4.14	3.46	4.38	64	64	3392	697	133	127						850	925			
S82-2	1-66	a	plag	43	73.7	0.32	13.98	2.24	0.00	0.36	1.46	4.43	3.49	5.81	127	64	3635	707	209	230						824	854			
S82-2	1-24	a	plag	42	73.6	0.37	13.99	2.34	0.00	0.35	1.41	4.38	3.58	4.46	96	65	3671	728	143	134						852	924			
S82-11	2-63	a	plag	42	73.6	0.36	14.01	2.11	0.00	0.30	1.40	4.83	3.36	4.18	118	71	3478	600	134	123						861	949			
S82-11	3-10	a	plag	42	73.4	0.29	14.63	1.98	0.00	0.28	1.47	4.50	3.49	4.33	140	70	3515	661	145	139						862	937			
S82-11	3-10	b	plag	40	73.5	0.33	14.36	1.82	0.00	0.35	1.53	4.69	3.45	4.77	87	67	3331	643	156	154						850	902			
S82-11	3-16	a	plag	41	73.6	0.33	14.21	2.20	0.00	0.24	1.36	4.59	3.52	4.12	147	65	3220	632	136	127						859	950			
S82-11	3-16	b	plag	42	73.3	0.30	14.53	2.23	0.00	0.35	1.40	4.32	3.51	4.21	65	65	3211	626	127	118						862	942			
S82-11	3-19	a	plag	38	74.1	0.35	14.31	1.86	0.00	0.25	1.32	4.25	3.54	4.09	123	67	3099	612	130	124						854	942			
S82-11	3-50	a	plag	42	73.7	0.29	14.04	1.82	0.00	0.27	1.43	4.90	3.51	4.40	163	72	3280	668	151	144						856	936			
S82-11	3-61	a	plag	41	73.5	0.37	14.05	1.89	0.00	0.35	1.52	4.85	3.48	4.15	152	90	3266	636	139	131						864	942			
S82-11	1-23	a	plag	39	74.0	0.30	13.89	2.16	0.00	0.29	1.30	4.70	3.41	4.14	161	71	3043	634	138	129						853	942			
S82-11	2-34	a	plag	40	73.9	0.31	13.90	2.02	0.00	0.29	1.41	4.57	3.57	4.03	156	77	3180	600	133	124						858	945			
S82-11	2-34	b	plag	38	74.7	0.30	14.01	1.79	0.00	0.26	1.40	4.10	3.43	4.74	135	72	3528	732	160	161						839	894			
S82-11	3-7	a	plag	39	74.5	0.26	13.66	1.88	0.00	0.27	1.23	4.70	3.46	4.57	126	72	3232	713	150	144						837	921			
S82-11	2-30	a	plag	41	73.4	0.36	14.31	2.00	0.00	0.30	1.48	4.68	3.43	4.84	164	99	3906	610	171	170						849	903			
S82-11	3-57	a	plag	42	73.6	0.31	14.12	2.25	0.00	0.30	1.43	4.41	3.57	4.75	165	87	3597	740	167	162						847	909			
S12-10	2	1	plag	40	74.6	0.23	14.00	1.80	0.03	0.24	1.32	4.40	3.38	4.90	100	45	3039	752	162	162						835	900			
<i>M 12</i>																														
Vaggeli	2	1	oliv	85	57.3	0.88	18.27	5.61	0.15	4.71	8.31	3.40	1.32	3.30	253	656	770	303	101	101						1065				
Vaggeli	3	1	oliv	85	50.7	0.68	19.81	7.28	0.13	6.16	12.76	2.19	0.26	3.10	193	1273	573	159	71	71						1087				
Vaggeli	4	1	oliv	85	51.6	0.83	19.61	6.91	0.03	5.80	12.16	2.46	0.61	3.20	190	1138	586	105	75	75						1080				
Vaggeli	6	1	oliv	86	53.8	0.67	18.80	6.56	0.13	5.82	10.98	2.23	0.98	3.30	232	1157	496	116	89	89						1082				
<i>Cape Riva, Phase 1</i>																														
S09-39	1	1	plag	40	71.2	0.50	14.90	3.11	0.07	0.41	1.66	5.04	3.00	4.70	145	76	2466	747	151	151						867	909			
S09-39	2	1	plag												3.35	222	103	3303	961	106	106									
S09-39	3	1	plag												5.15	130	105	3078	912	173	173									
S09-39	3	2	plag												3.32	155	91	3295	958	99	99									
S09-39	4	1	plag												131	82	3166	935	99	99										
S09-39	5	1	plag	52	68.1	0.86	14.39	4.79	0.29	1.17	2.83	4.68	2.66	3.69	385	385	2646	1075	-79	-79						940	951			
<i>MT0a-6Y/B</i>																														
S12-37	1	1	oliv	82	52.0	0.99	17.81	8.76	0.45	6.03	10.61	2.70	0.54	2.66	800	733	668	155	104	104						230	1103			
S12-37	1	2	oliv	83	52.7	1.04	17.56	8.60	0.20	6.30	9.92	2.90	0.64	3.10	645	1075	711	175	117	117						230	1108			
S12-37	1	3	oliv	82	50.8	0.91	18.63	8.67	0.14	6.63	10.99	2.76	0.43	2.71	483	736	735	151	76	76						175	1120			
S12-37	2	1	oliv	77	52.8	0.98	17.79	9.79	0.15	5.40	9.39	3.00	0.63	2.46	950	99	149	41	119	119						255	1103			
S12-37	5	1	oliv	78	54.5	1.35	16.53	9.41	0.12	5.08	8.43	3.54	0.88	2.91	480	556	957	222	105	105						1098				

(continued)

Table 3: (Continued)

Sample	Crystal	MI	Host crystal (wt %)		Melt inclusion (recalculated dry) (wt %)										MI volatiles and H isotopes						Pressure (MPa)*				Temperature (°C)†	
			Phase	Mg#	An	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O (wt %)	CO ₂ (ppm)	S (ppm)	Cl (ppm)	F (ppm)	δD (‰)	VoiCalc	Papale	SolEx	Ol-melt Putirka	Pl-melt Putirka	Pl-melt Lange
S12-37	5	2	oliv	78	51.9	0.99	16.95	10.73	0.21	5.82	9.77	2.94	0.57	2.49	80	379	903	202		41	80		1113			
S12-37	6	1	oliv	78	53.6	1.23	16.11	10.52	0.22	5.47	8.71	3.26	0.73	2.71	123	426	922	251	-51	53	184		1105			
S12-37	8	1	oliv	78	54.0	1.18	16.17	9.80	0.18	5.22	9.48	2.97	0.78	2.57	1190	481	870	277					1095			
MT10a-FS3																										
S12-43	1	1	oliv	78	52.9	1.26	17.17	9.37	0.23	5.41	9.70	3.48	0.42	1.60	32	467	938	283	-90	23	33		1114			
S12-43	2	1	oliv	73	55.7	1.36	16.05	9.73	0.17	3.94	7.87	4.06	1.02	3.28	161	863	1546	344	-84	78			1056			
S12-43	3	1	oliv	79	53.0	1.10	16.79	9.88	0.25	5.48	9.68	3.29	0.44	1.17	199	483	677	222		20	60		1125			
S12-43	4	1	oliv	79	53.3	1.08	17.58	9.02	0.13	5.11	9.79	3.45	0.43	1.75	37	452	945	262	-109	26			1101			
S12-43	5	1	oliv	73	55.9	1.29	16.35	9.59	0.16	4.10	7.89	3.55	0.99	3.23	157	853	1527	345		74			1060			
S12-43	6	1	oliv	77	50.7	1.00	17.35	11.14	0.34	5.48	10.35	2.94	0.59	1.65	512	785	746	277	-72	45	135		1118			
S12-43	7	1	oliv	82	48.2	0.82	18.75	10.33	0.28	6.80	11.89	2.53	0.29	1.48	801	712	158		-71	42	190		1146			
S12-43	11	1	plag	78	57.8	1.32	16.75	8.57	0.00	2.86	7.09	4.12	1.36	3.21	267	793	1570	307	-62	91			1064	1060		
S12-43	12	1	plag	83	57.2	1.11	17.11	8.75	0.26	3.06	7.33	3.92	1.18	3.24	291	727	1562	322	-38	91			1071	1090		
S12-43	13	1	plag	91	54.4	1.03	16.74	9.94	0.12	5.27	8.23	3.52	0.67	2.50	152	894	1910	431	-61	51			1103	1189		
MT10a-BP																										
S12-41	3	1	plag	53	64.5	0.78	16.18	6.02	0.08	0.98	3.8	5.02	2.27	2.71	79	247	3309	780		54			1005	1028		
Vourvoulos																										
S12-67	1	1	plag	47	68.5	0.62	14.22	5.43	0.20	0.63	2.73	4.84	2.79	3.56	95	130	3595	594		82			931	956		
S12-67	2	1	plag	48	69.3	0.51	14.81	5.16	0.16	0.61	2.65	4.07	2.78	3.59	69	117	3670	605		81			932	942		
S12-67	3	1	plag	47	68.6	0.42	14.93	4.83	0.17	0.56	2.98	4.83	2.72	3.30	79	111	3383	578		73			947	961		
S12-67	5	1	plag	47	69.0	0.64	14.57	4.85	0.19	0.51	2.44	4.98	2.84	3.47	50	106	3442	598		73			929	968		
S12-67	6	1	plag	46	69.0	0.50	14.61	4.74	0.17	0.54	2.68	4.85	2.88	3.43	59	112	3501	576		74			933	956		
S12-67	7	1	plag	47	69.4	0.59	14.45	4.92	0.16	0.53	2.43	4.70	2.82	3.31	71	110	3416	611		71			931	970		
S12-67	7	2	plag	47	69.0	0.51	14.47	4.95	0.17	0.55	2.53	4.95	2.88	3.06	143	106	3352	594		76			941	993		
M8, Main Scoria Fall																										
S12-68	4	1	plag	94	52.3	0.85	16.65	9.30	0.19	6.72	11.29	2.40	0.27	2.59	113	570	629	234		50	95		1120	1167		
S12-68	5	1	oliv	74	53.9	1.18	14.99	12.12	0.24	5.40	8.45	2.85	0.82	2.75	185	446	805	216		60			1112			
S12-68	6	1	oliv	82	50.0	0.75	18.01	9.59	0.12	6.87	11.92	2.47	0.24	2.78	63	783	618	113		49	90		1125			
S12-68	7	1	oliv	75	53.2	1.32	15.83	11.45	0.25	5.74	8.49	3.20	0.52	2.78	71	733	859	294		49			1120			
S12-68	8	1	oliv	77	52.2	1.45	16.01	11.39	0.20	5.98	8.69	3.42	0.63	2.84	102	925	923	192		54	105		1123			
Middle Pumice, Phase 1																										
S12-59	1	1	oliv	76	52.9	1.31	18.04	8.86	0.11	4.41	10.57	3.13	0.72	4.25		1017	958	210		108	200		1039			
S12-59	3	1	oliv	81	51.3	0.94	18.31	8.46	0.09	5.92	12.12	2.60	0.28	3.95	150	1017	718	128	-80	98	180		1077			
S12-59	4	1	plag	46	68.8	0.56	15.57	3.90	0.19	0.66	2.68	4.56	3.09	5.01	78	108	2647	654		155			897	875		
MT7a																										
S12-46	1	1	plag	47	67.6	0.61	15.65	4.52	0.07	0.59	2.93	4.93	3.07	2.31	197	120	2630	595	-88	65			978	1039		
S12-46	2	1	plag	50	66.6	0.74	15.80	4.71	0.11	0.73	3.45	5.00	2.90	3.49	160	135	2503	559		97			961	960		
S12-46	4	1	plag	50	66.9	0.85	15.39	4.82	0.10	0.72	3.41	4.93	2.86	2.32	172	135	2601	580		61			991	1036		
MT7c																										
S12-44	1	1	plag	92	50.2	0.83	20.01	8.14	0.16	4.30	13.87	2.34	0.17	2.51	181	856	650	105	-82	32			1133	1185		
S12-44	2	1	plag	92	54.0	0.90	14.85	8.78	0.19	7.12	11.21	2.56	0.50	1.80	115	839	636	329								
S12-44	3	1	oliv	85	49.9	0.77	17.57	8.73	0.16	7.72	12.37	2.33	0.45	1.87	227	827	661	122		35	85		1157			
S12-44	5	1	oliv	84	50.1	0.82	18.58	8.59	0.16	7.01	11.69	2.69	0.35	1.81	355	831	644	125	-63	37	115		1143			
S12-44	6	1	oliv	86	49.0	0.71	19.49	7.59	0.16	7.41	12.94	2.52	0.21	1.94	196	765	662	116		34	80		1142			
S12-44	7	1	oliv	81	56.2	1.25	15.84	8.38	0.11	5.45	8.08	3.35	1.29	2.12	211	283	834	266	-79	53			1117			

(continued)

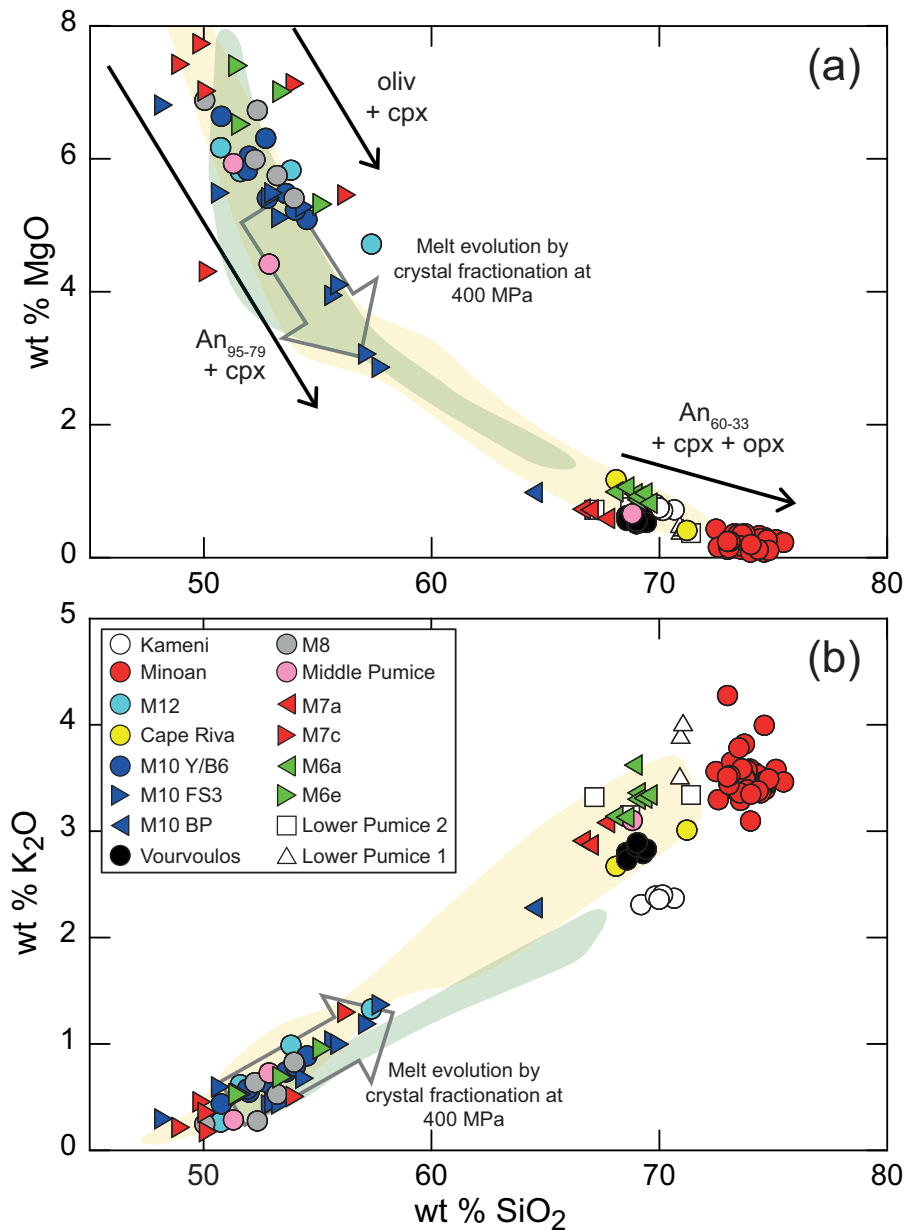


Fig. 5. Silica variation diagrams for (a) MgO and (b) K₂O of the MIs analysed in this study. Compositional fields of whole-rocks from cycle 2 (yellow) and cycle 3-Kameni (green) are shown for comparison. The large arrows show the melt evolution vectors of fractional crystallization of Santorini basaltic melt in experiments at 400 MPa from [Andújar *et al.* \(2015\)](#).

K₂O increases approximately linearly with increasing SiO₂ (Fig. 5b). Potassium behaves incompatibly in almost all but the oldest (>550 ka) Santorini magmas ([Mann, 1983](#); [Huijsmans *et al.*, 1988](#); [Huijsmans & Barton, 1989](#); [Druitt *et al.*, 1999](#); [Gertisser *et al.*, 2009](#)). This is because K feldspar is absent as a phenocryst phase. We therefore use K₂O as a proxy for degree of fractional crystallization, but caution that this is approximate because modelling of Santorini magmas requires ~10% of crustal contamination to explain the contents of incompatible elements such as K in more evolved compositions ([Barton *et al.*, 1983](#); [Druitt *et al.*, 1999](#)). Another complication is that the content of K (and other incompatible elements such as Th, Rb, Nb and Zr)

decreases with time at Santorini ([Huijsmans *et al.*, 1988](#); [Fabbro *et al.*, 2013](#)). Hence in Fig. 5b Lower Pumice 1, Lower Pumice 2, M6a, M7a and Middle Pumice have higher K₂O than Vourvoulos, M10BP and Cape Riva, whereas Kameni melts have the lowest K₂O of all at a given SiO₂ content. The different liquid lines of descent are in detail only approximately cogenetic.

Sulphur and halogens

The S, Cl and F contents of the MI suites are shown in Fig. 6 as functions of K₂O. Sulphur contents are up to 1200 ppm in basaltic compositions; they decrease rapidly in a nonlinear fashion to ~100 ppm in silicic compositions (Fig. 6a). This range is typical of arc magmas

(Wallace, 2005). The different MI lineages also show decreasing S with increasing K₂O; M10 Y/B6 shows the steepest depletion trend, and M12 the shallowest. The overall trend for S resembles those published previously by Michaud *et al.* (2000), Gertisser *et al.* (2009) and Vaggelli *et al.* (2009).

Chlorine contents range from ~500 ppm in basaltic MIs to 2500–6000 ppm in silicic ones, with an overall trend that is almost flat at the mafic end, but that steepens with increasing K₂O (Fig. 6b). At the mafic end of the spectrum, MIs from interplinian units M6e, M8-MSF, M7c and M12 form gently sloping arrays parallel to the overall trend. The highest Cl values are from the silicic plinian units (Lower Pumice and Minoan).

The F contents of the MIs range from <100 to 400 ppm in the mafic part of the spectrum, and from 600 to 1000 ppm in the silicic part (Fig. 6c). Overall the analyses form a linear trend with considerable scatter, in part owing to the large analytical error on this element. Arrays of MIs from single units scatter too much for distinct trends to be recognized. Indeed, MIs from single units plot with a range of F/K ratios. The highest F contents are found in MIs from the silicic plinian units.

H₂O contents

The variation of H₂O contents is plotted in Fig. 7a versus K₂O; the data scatter considerably. That this scatter is real is shown by MIs from the Vourvoulos plinian eruption, which are large and very homogeneous. Seven of these inclusions give H₂O of 3.39 ± 0.17 (1 σ) wt %, which agrees with the uncertainty ($\pm 5\%$) on the H₂O values based on SIMS data calibration.

Water contents in the mafic MIs range from 1.1 to 4.3 wt %, and those in silicic MIs from 2.2 to 6.9 wt % (Table 3). In the five units that yield both bubble-bearing and bubble-free MIs, the range of H₂O content is essentially independent of whether a bubble is present or not (Table 3), showing that little H₂O was partitioned into the shrinkage bubble upon quench. Moreover, in four units in which both olivine-hosted and plagioclase-hosted MIs were analysed, there is no obvious difference in MI H₂O contents between the two hosts (Fig. 8a). Only in interplinian unit M10 FS3 are there olivine-hosted MIs with H₂O significantly lower than the plagioclase-hosted MIs, but this is because the H₂O content of MIs in this unit is positively correlated with K₂O content, and those olivine-hosted inclusions with the lowest H₂O are particularly poor in K₂O. When MIs with the same K₂O are compared in unit M10 FS3, H₂O content is independent of mineral host (Table 3).

MIs from single units form subhorizontal arrays in Fig. 7a, with H₂O content increasing only very slightly with increasing K₂O. This is particularly clear for MIs from units M7c, Middle Pumice, M8-MSF and M12. It is also evident from vectors linking closely related pairs of mafic and silicic units such as M6e to M6a and M7c to M7a. MIs of M10-FS3 with <1 wt % K₂O fall on a steeper positive trend that passes through the origin of the

H₂O–K₂O plot, whereas those with >1 wt % K₂O define a horizontal trend (Fig. 7a).

MIs from the plinian units exhibit a broad range of H₂O contents over a small range of K₂O. H₂O in the 62 MIs analysed from Minoan rhyodacitic pumice ranges from 4.0 to 6.9 wt % (Table 3). MIs in the cores (An_{50±7}; Druitt *et al.*, 2012) of plagioclase crystals in these pumices contain 4.6–6.9 wt % H₂O, whereas those in the rims (An_{43±3}) contain 4.0–5.0 wt % H₂O. MIs in pyroxenes in the same pumices contain 4.1–4.7 wt % H₂O. The total range of H₂O contents in Minoan MIs agrees well with the data of Cottrell *et al.* (1999) (3.5–6.5 wt %) and Cadoux *et al.* (2014) (4.0–5.8 wt %). Two MIs in a volumetrically minor andesitic component in the Minoan (microphenocryst-rich andesitic pumice; Druitt, 2014) contain 5.4 and 6.6 wt % H₂O.

In general, MIs from the plinian units contain more (>3.5 wt %) H₂O than the interplinian ones (<3.5 wt %). This is true of mafic as well as silicic compositions; the two mafic MIs from the Middle Pumice plinian unit are richer in H₂O than those from all the mafic interplinian MIs. However, there are two exceptions. First, MIs of the Vourvoulos plinian eruption plot at the limit, and slightly on the interplinian side, and this is consistent with Vourvoulos being the thinnest (and probably least voluminous) of the plinian units recognized by Druitt *et al.* (1999). Second, MIs from the AD 726 explosive eruption of Kameni Volcano have H₂O contents more typical of plinian MIs. The ratio Cl/H₂O in all the MIs is <0.15 and increases with SiO₂ content (Fig. 9).

CO₂ contents

The data for CO₂ are plotted against H₂O in Fig. 7b. Concentrations of CO₂ in the MIs range from <50 ppm (the detection limit) to 1200 ppm. Contents in most of the mafic MIs are <230 ppm; only olivines of unit M10 FS3 and M10 Y/B6 contain MIs with higher CO₂. The M10 FS3 and M10 Y/B6 data form parallel, vertical, trends at different H₂O contents. All silicic MIs contain <150 ppm CO₂. No relationship is observed in MIs from Minoan pumice between CO₂ content and position in the crystal or in different mineral phases.

As for H₂O, there is no significant difference between the CO₂ contents of bubble-bearing and bubble-free MIs (Fig. 8b). Bubbles in the MIs are empty and lack any CO₂ liquid phase visible under high magnification. The CO₂ contents of shrinkage bubbles from two olivine-hosted mafic MIs (sample M12) and four plagioclase-hosted silicic MIs (samples S12-67 and PKB) were found to lie below the detection limit of our micro-Raman spectrometer; the Fermi couplet typical of molecular CO₂ (~1285 and ~1385 cm⁻¹) was absent in all six bubbles studied.

D/H isotopic ratios

Hydrogen isotopic ratios of 27 representative MIs (12 olivine-hosted; 15 plagioclase-hosted) with compositions ranging from basaltic to silicic, range from

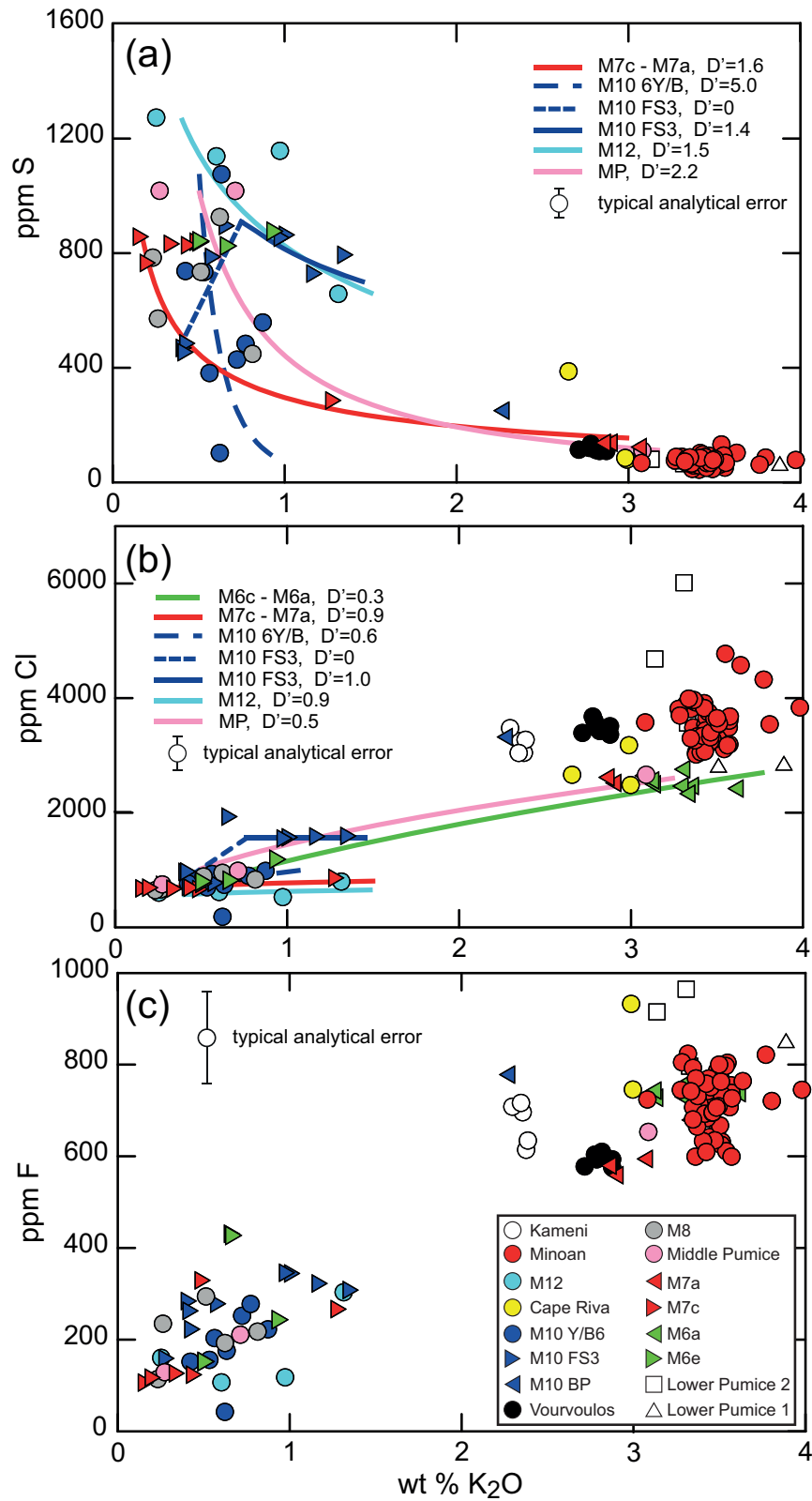


Fig. 6. Variations of (a) S, (b) Cl and (c) F contents with K_2O . Lines show models of crystallization-modified Rayleigh distillation of several of the different melt inclusion series, as explained in the text and in Table 4.

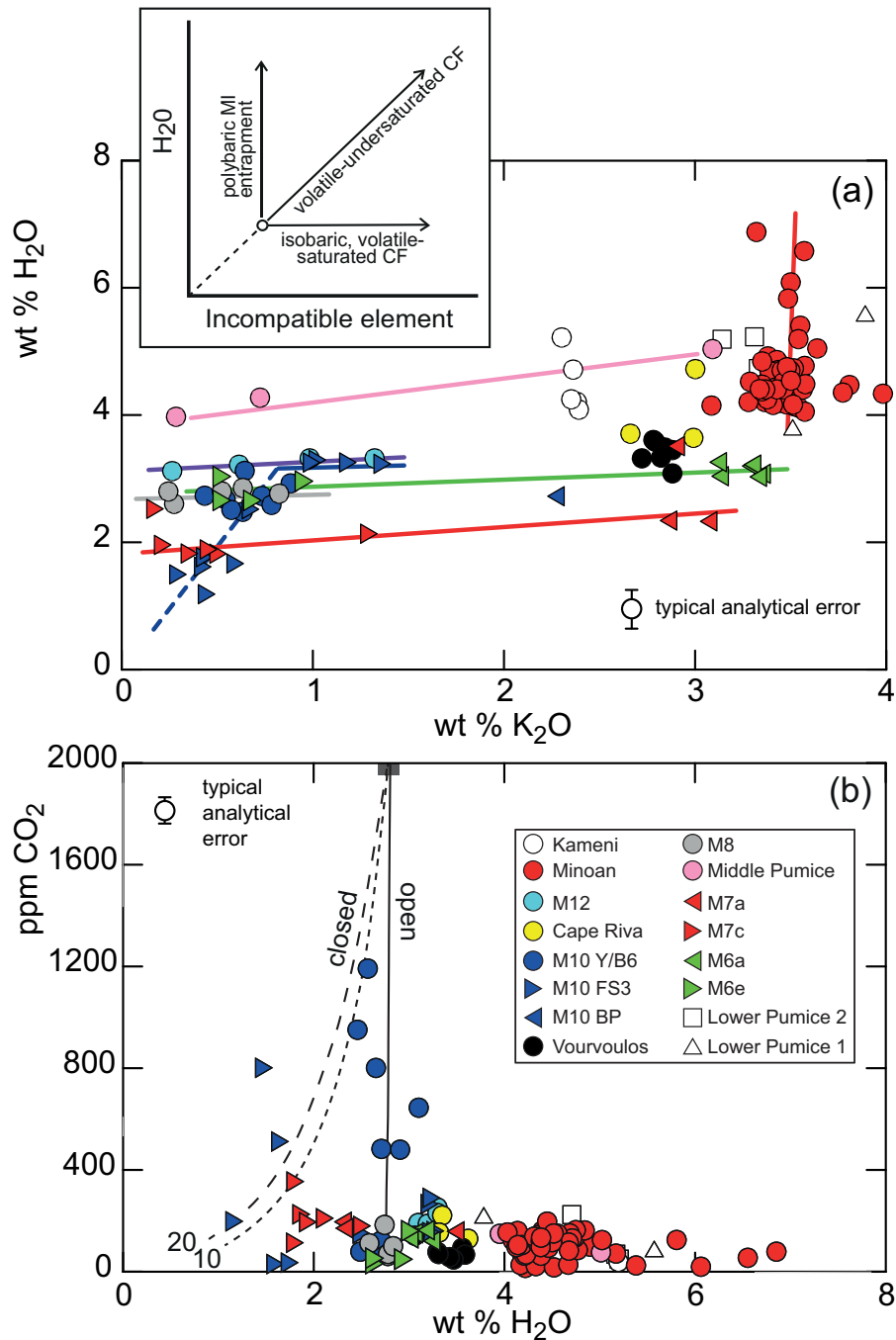


Fig. 7. (a) Variation of melt H₂O vs K₂O. K₂O is an incompatible component in Santorini magmas. The coloured lines show the trends (fitted by eye) of each of the following related samples: mafic to silicic MIs from the Middle Pumice, M6e to M6a, and M7c to M7a series; compositionally diverse mafic MIs from M10, M8-MSF and M12; compositionally uniform MI from the Minoan. Different theoretical trends on such a plot are shown in the inset (CF, crystal fractionation). Most of the trends are essentially flat, showing that H₂O behaves compatibly (volatile-saturation) during differentiation (in fact, the trends are gently inclined because wt % H₂O solubility increases with increasing SiO₂ content). There is one exception: MIs from unit M10 FS3 with <1 wt % K₂O lie on a trend of volatile-undersaturation for H₂O, whereas those with >1 wt % K₂O lie on a trend of volatile-saturation. MIs from the Minoan eruption exhibit a range of H₂O contents at approximately constant K₂O, and this is interpreted as due to polybaric entrapment. (b) CO₂ vs H₂O for the MIs. The black lines show model degassing trends under open and closed (10% gas and 20% gas) conditions, calculated using VolatileCalc (Newman & Lowenstern, 2002) for a 1050°C basaltic melt with 2.8 wt % H₂O and 2000 ppm CO₂.

$\delta D = -37$ to -104% , with no evident correlation with either SiO₂ or H₂O contents (Fig. 10). MIs from sample M10 FS3, which contain a range of H₂O contents in both olivine and plagioclase hosts, show no significant variation of δD with H₂O. Overall the δD values are

similar to those of eight Santorini whole-rocks analysed by [Druitt et al. \(1999\)](#) (-54 to -81%); they also lie between the value of mid-ocean ridge basalt (MORB; $-80 \pm 10\%$) and the estimated value of slab fluids (-34%) ([Shaw et al., 2008](#)).

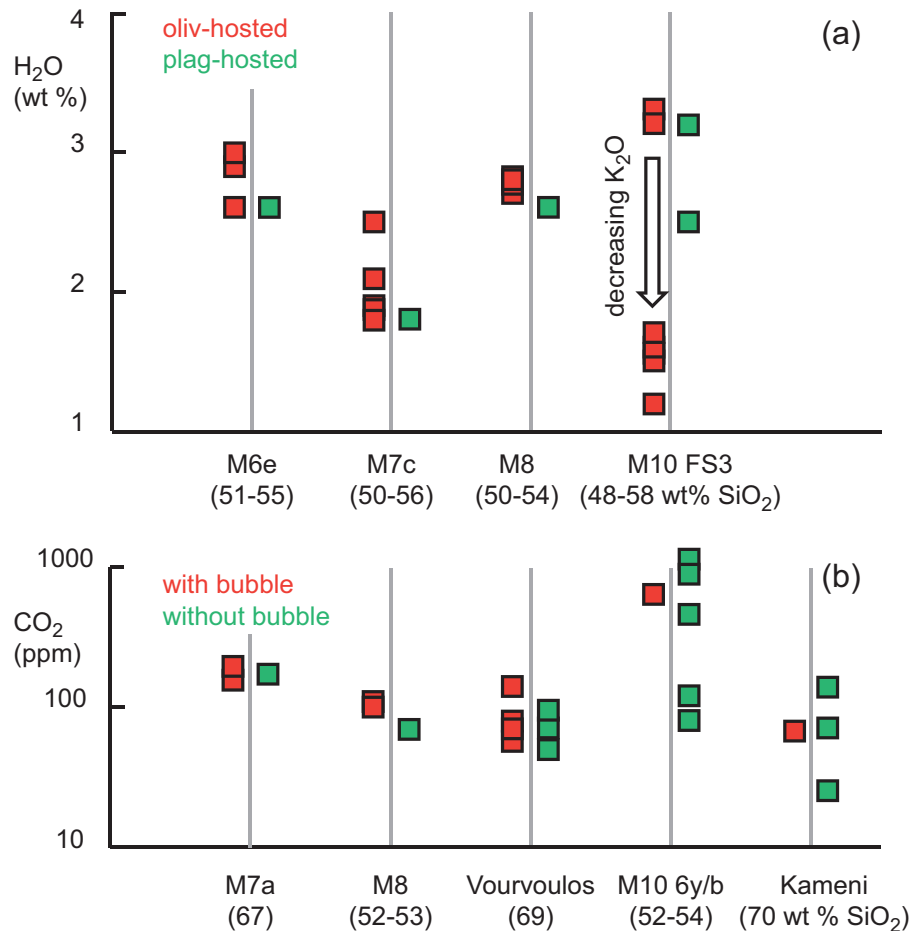


Fig. 8. (a) H₂O contents of melt inclusions (MIs) from four samples, showing that there are no systematic differences in H₂O between MIs hosted by olivine and those hosted by plagioclase. Indeed, the contents in olivine-hosted MIs are if anything a little higher than those in plagioclase. This suggests that the olivine-hosted MIs retain most of their original magmatic H₂O. The large spread of H₂O contents in sample M10 FS3 is related to increasing degree of melt evolution. (b) CO₂ contents of MIs in five samples, showing that there are no systematic differences in CO₂ between those MIs that contain shrinkage bubbles and those that do not. This strongly suggests that CO₂ has not been sequestered from the melt into the bubble during quench. The numbers in parentheses are the silica contents of the MIs.

CALCULATED INTENSIVE PARAMETERS

Entrapment temperatures

Entrapment temperatures for the MIs were calculated using three thermometers: the Putirka (2008) formulation for olivine–melt [his equation (22)] and the Putirka [2008; equation (24a)] and Lange *et al.* (2009) formulations for plagioclase–melt. In each case, we computed the temperatures from major element compositions of the MIs and their host mineral phases, along with SIMS-derived H₂O contents. When plotted as a function of K₂O (Fig. 11), the olivine–melt and Putirka plagioclase–melt temperatures form a coherent trend, showing that they are mutually consistent. Almost all the temperatures from Lange *et al.* (2009) are higher (average +20°C, and as high as +85°C) than those from Putirka (2008) (inset, Fig. 11).

The calculated temperatures for interplinian MIs decrease from ~1150°C to ~950°C with decreasing K₂O content. Silicic MIs from the plinian units yield systematically lower temperatures (down to 800°C) than the

interplinian silicic MIs, owing to their higher H₂O contents. Our only two mafic MIs from a plinian unit (Middle Pumice) give lower temperatures than most mafic interplinians, again owing to their higher H₂O contents. Overall the temperatures agree with those obtained previously for Santorini from coexisting Fe–Ti oxides, MI rehomogenization, and phase equilibrium experiments (Cottrell *et al.*, 1999; Druitt *et al.*, 1999; Michaud *et al.*, 2000; Cadoux *et al.*, 2014; Druitt, 2014), although values for intermediate compositions are 50–100°C higher than previous estimates (Fig. 11). The plagioclase–melt temperatures of Lange *et al.* (2009), being slightly higher than those of Putirka (2008), are less consistent with the temperatures from other methods. We therefore use the Putirka temperatures in calculating volatile saturation pressures.

Volatil saturation pressures

Calculation of H₂O + CO₂ saturation pressures requires use of solubility models calibrated within the range of our

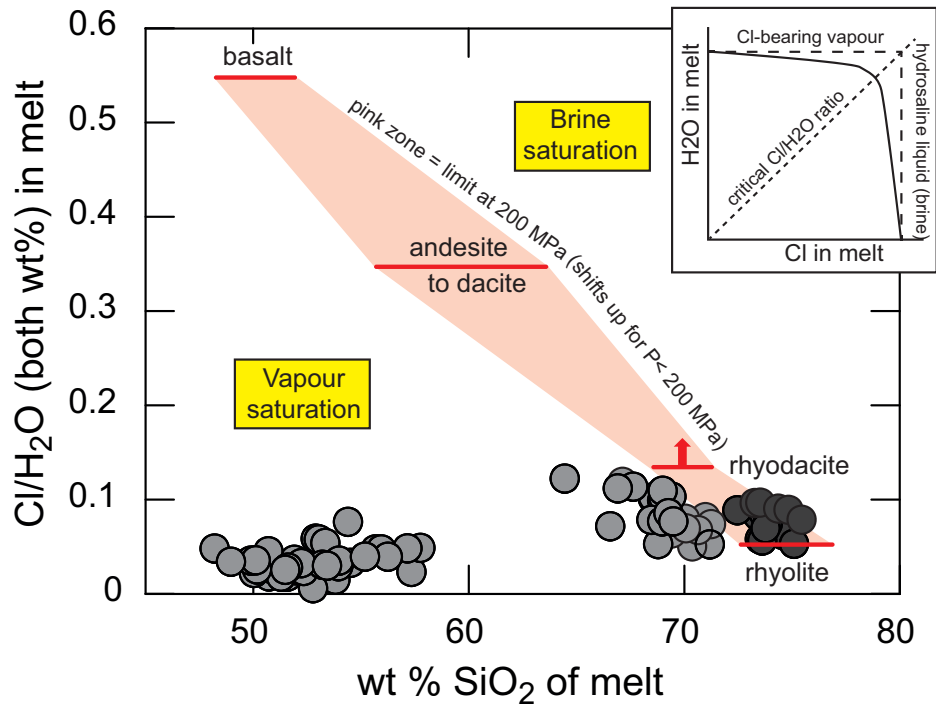


Fig. 9. Cl/H₂O ratios for the melt inclusions as a function of SiO₂ content. The red bars (within the pink field) are experimentally determined values separating vapour-saturated from brine-saturated eruption fields at 200 MPa; from Webster (2004). Lowering the pressure shifts these values upwards. Melt inclusions from the Minoan eruption are shown in dark grey.

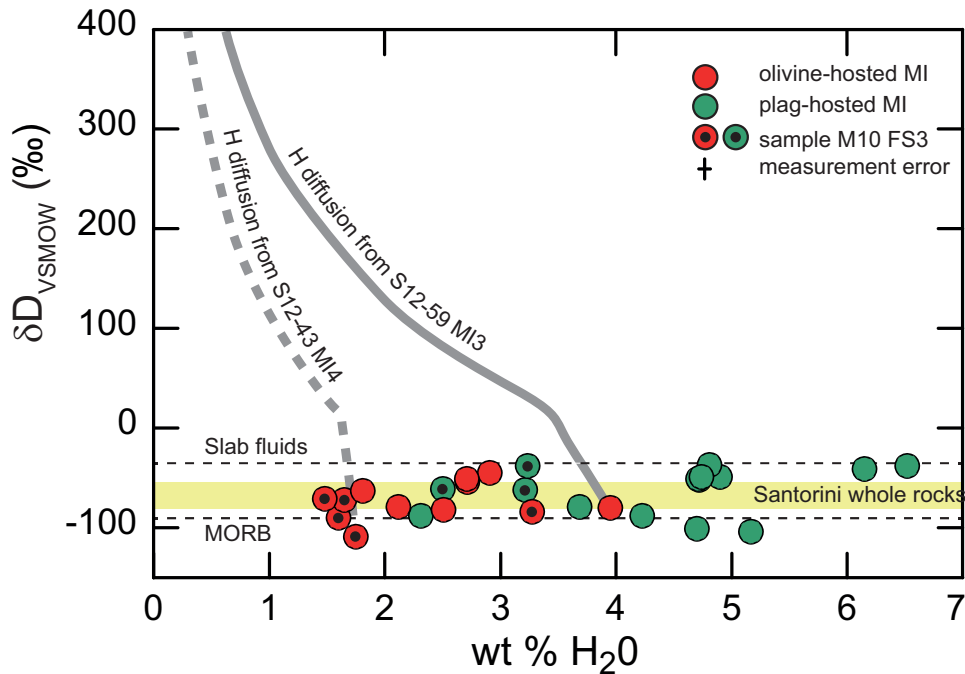


Fig. 10. Variation of δD vs H₂O content for 27 melt inclusions (MIs). The δD values agree with those of Santorini whole-rocks (yellow field; Druitt *et al.*, 1999), and lie within a narrow range of values between those of MORB and slab fluids (Shaw *et al.*, 2008). The grey lines are models of δD -H₂O evolution owing to hydrogen diffusion for two representative inclusions (continuous line: S12-59 MI 3, 3.95 wt % H₂O, -80‰ δD , 1077°C, 48 μ m MI radius, 300 μ m host olivine radius; dotted line: S12-43 MI 4, 1.75 wt % H₂O, -109‰ δD , 1101°C, 32 μ m MI radius, 300 μ m host olivine radius). The model used was that of Bucholz *et al.* (2013); this shows that none of the olivine-hosted MIs have lost significant H₂O by this mechanism. Symbols with dots are MIs from unit M10 FS3; all MIs from this unit (either olivine-hosted or plagioclase-hosted) lie in the same δD range, showing that none of the olivine-hosted MIs, which have particularly low H₂O contents, have lost significant amounts of H₂O by hydrogen diffusion; the low H₂O contents are therefore interpreted to be original.

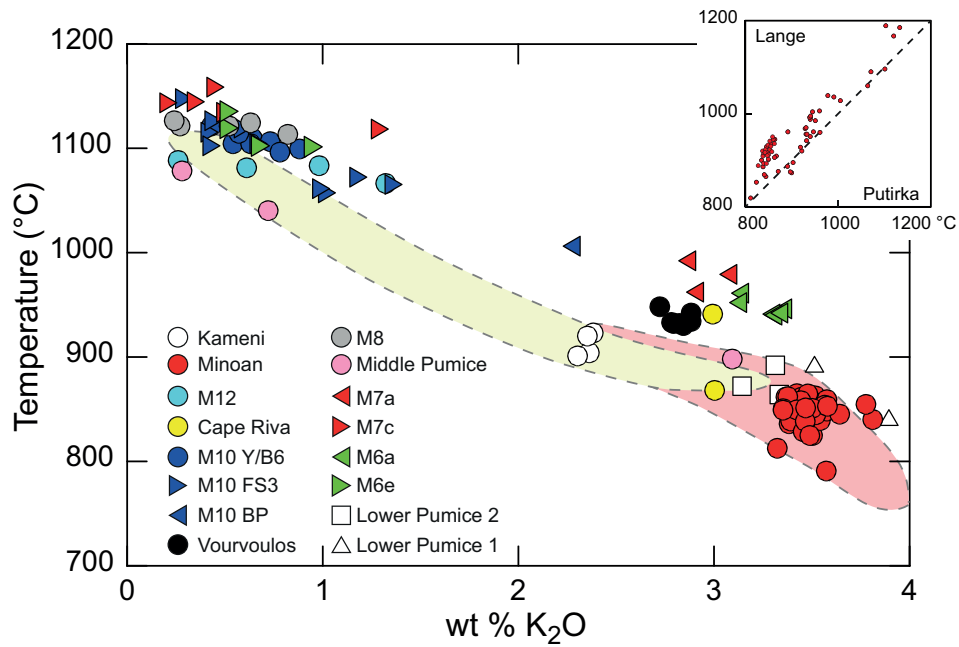


Fig. 11. Variation of melt inclusion equilibration temperature, derived from olivine–melt and plagioclase–melt equilibria. For olivine–melt we used equation (22) of Putirka (2008). For plagioclase–melt we used equation (24a) of Putirka (2008). The plagioclase–melt model of Lange *et al.* (2009) gives slightly higher temperatures than that of Putirka (see inset). The results are compared with previously published temperature estimates: melt inclusion rehomogenization temperatures of Michaud *et al.* (2000) (yellow field), and Fe–Ti oxide temperatures of Cadoux *et al.* (2014) and Druitt (2014) (pink field).

MI data. Four main appropriate models exist, as reviewed by Moore (2008). Dixon *et al.* (1995) and Dixon (1997) developed a regular solution model for the solubility of H₂O and CO₂ in basaltic melts, ranging from tholeiite to nephelinite in composition. The melt composition was accounted for by a compositional parameter Π , which in the melts used for the CO₂ calibration in their model ranges from 0.5 (tholeiitic) to 2.2 (highly alkaline). The model VolatileCalc (Newman & Lowenstern, 2002) is based on pure species solubility data and linear mixing of H₂O and CO₂. The program has a model for rhyolite and a model for basalt that is based on the Dixon (1997) formulation, valid for melts with <52 wt % SiO₂. The basaltic model assumes a linear correlation between SiO₂ content and parameter Π of Dixon (1997). The SolEx program of Witham *et al.* (2012) for basaltic melts also uses the Dixon (1997) formulation, but with the full parameter Π , and it also incorporates partition laws for S and Cl. SolEx is applicable only to basalts (≤ 53 wt % SiO₂). The most complete model is that of Papale (1999), modified by Papale *et al.* (2006), which uses a multivariate regression of a large dataset of published H₂O, CO₂ and H₂O + CO₂ solubility data in melts ranging from basalt to rhyolite in composition.

Moore (2008) compared the results of the VolatileCalc and Papale models against recent experimental data and reached the following conclusions: (1) VolatileCalc (basalt) overestimates saturation pressure P_{sat} in some calcic and calc-alkaline basalts, whereas these can be underestimated by Papale; (2) Papale satisfactorily recovers P_{sat} for a calc-alkaline andesite (57 wt % SiO₂) and a dacite (66 wt % SiO₂) at 200–400 MPa,

whereas VolatileCalc does not; (3) both VolatileCalc (rhyolite) and Papale recover P_{sat} for metaluminous rhyolite to $\pm 10\%$ relative. Witham *et al.* (2012) showed that the Dixon model can overestimate P_{sat} , particularly at >300 MPa, and that Papale can underestimate it, in agreement with Moore (2008).

Basaltic (<53 wt % SiO₂) MIs in our dataset have Π values of -0.8 to $+0.6$, which lie outside the Dixon (1997) CO₂ calibration used by both VolatileCalc and SolEx, and this is in accord with the calc-alkaline nature of Santorini melts. On the other hand, the andesite and dacite modelled well by the Papale model (Moore, 2008) are both very similar compositionally to Santorini melts. Similarly, Santorini rhyolitic melts are metaluminous to very slightly peraluminous, and hence lie within the calibration of VolatileCalc (rhyolite). The total compositional range of our MIs overlaps completely the spread of melt data used by Papale *et al.* (2006) to calibrate their model.

We apply the following approach to our MI data: (1) P_{sat} for basaltic MIs are estimated using the SolEx formulation of the Dixon model (maximum P_{sat} estimate) and using the Papale model (minimum P_{sat} estimate); (2) P_{sat} values for mafic andesitic MIs are estimated using the Papale model (minimum P_{sat} estimate); (3) P_{sat} for silicic andesitic, dacitic and rhyodacitic MIs are estimated using the Papale model; (4) P_{sat} for rhyolitic MIs are estimated using VolatileCalc (rhyolite) and the Papale model. The resulting H₂O + CO₂ pressures are shown in Fig. 12. Precisions on the pressures, owing to analytical errors in H₂O and CO₂ and to uncertainties in the temperatures, are about ± 10 MPa.

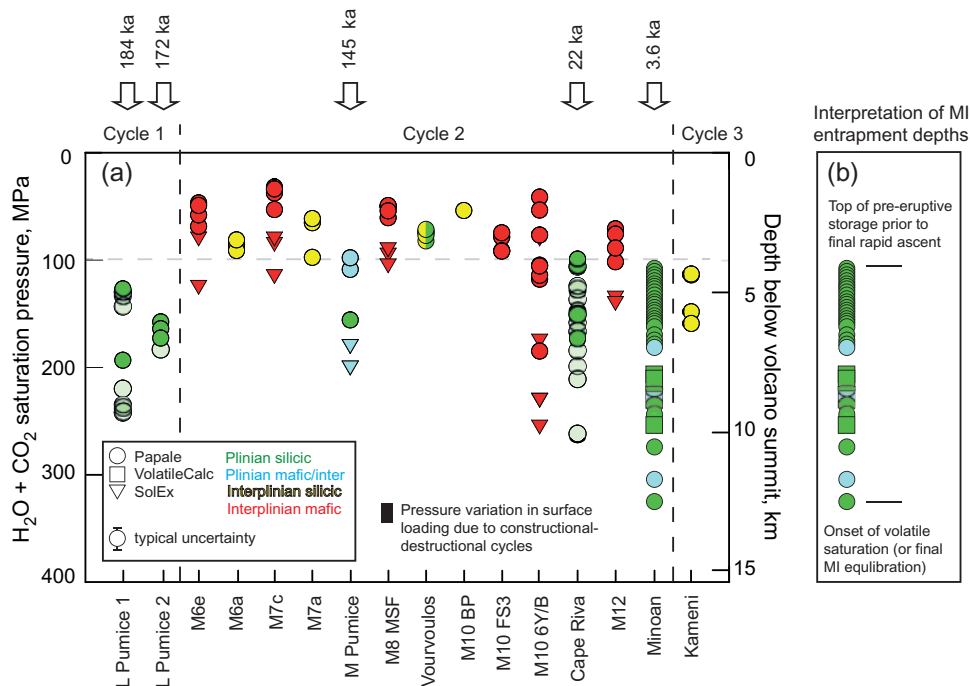


Fig. 12. (a) $\text{H}_2\text{O} + \text{CO}_2$ saturation pressures for the melt inclusion suites as a function of time. (See the text for justification of the different solubility models used.) Given the evidence for volatile saturation presented here, the pressures are interpreted as total pressures and are converted into depths using the mean density of the upper crust beneath Santorini (2640 kg m^{-3} ; Konstantinou, 2010). The depth is that below the summit of the volcano at that time, and the surface edifice load has varied by $\sim 750 \text{ m}$ (18 MPa) between pre-plinian and interplinian states. Volatile-undersaturated MIs from unit M10 FS3 are not shown. Filled symbols are from this study; pale green symbols are data from Cadoux *et al.* (2014), as described in the text. The effect of high Cl contents in silicic melts could be to increase the saturation pressures based on $\text{H}_2\text{O} + \text{CO}_2$ by a factor of as much as ~ 1.2 . (b) Our interpretation of the MI entrapment depth ranges, using the Minoan data as an example.

We include in Fig. 12 a series of 27 MIs analysed by Cadoux *et al.* (2014) for H_2O , but not CO_2 . By reanalysing three of their MIs using our standards and calibration technique, we confirmed that the two H_2O datasets are comparable; the H_2O contents obtained by us are close to those obtained by Cadoux *et al.* (2014), despite slightly different calibration procedures (S09-62f-10 MI 1 5-27 and 5-40, S09-62f-10 MI 2 4-74 and 4-96, and S09-17 c-1 MI 1 2-45 and 2-00, the first value being Cadoux *et al.*'s wt % H_2O , and the second being ours). However, because Cadoux *et al.* selected their MIs prior to analysis in two dimensions, not three dimensions, H_2O leakage through fractures or surface-connected melt tubes cannot be excluded. We therefore include only their MIs with H_2O contents higher than our minimum value, on the reasoning that their higher H_2O values are likely to be original.

The pressures plotted in Fig. 12 assume that total pressure equals the sum of the partial pressures of H_2O and CO_2 . However, the presence of dissolved S and halogens could increase the actual p_{sat} for given values of $p_{\text{H}_2\text{O}}$ and p_{CO_2} , through $p_{\text{sat}} = p_{\text{H}_2\text{O}} + p_{\text{CO}_2} + p_{\text{S}} + p_{\text{Cl}} + p_{\text{F}}$. Another way of looking at this is that the presence of S, Cl and F decreases the solubilities of H_2O and CO_2 , for a given value of p_{sat} . The effect of dissolved S on estimation of p_{sat} in basaltic melts has been discussed by Lesne *et al.* (2014). They showed that S contents typical of our

MIs ($< 1300 \text{ ppm}$) will increase the estimated p_{sat} by no more than $\sim 20 \text{ MPa}$ at redox conditions typical of Santorini magmas (QFM–NNO; Gertisser *et al.*, 2009; Cadoux *et al.*, 2014; Druitt, 2014; Andújar *et al.*, 2015). This effect can therefore be neglected. The effect of Cl on H_2O solubility has been studied extensively at 200 MPa (Webster, 2004). Experiments show that H_2O solubility is unaffected by $< 10,000 \text{ ppm}$ Cl in basaltic, andesitic and latitic melts (Webster *et al.*, 1999; Botcharnikov *et al.*, 2007; Stelling *et al.*, 2008). Rhyolitic melts can, however, exhibit greater sensitivity within the range of pressures of interest. For example, H_2O solubility in a haplogranite melt at 200 MPa can be reduced significantly by Cl contents of $> 2000 \text{ ppm}$. However, such Fe-free compositions may not be applicable to natural silicic melts (Cadoux *et al.*, 2014). Botcharnikov *et al.* (2004) have studied H–O–Cl–S solubility in a natural rhyodacitic melt, and the H_2O melt contents listed in their Table 3, although imprecise, suggest a drop in H_2O solubility of $\sim 10\%$ (relative) as melt Cl content increases from 0 to 6000 ppm (the highest content of our MIs). Indeed, this would be consistent with the conclusion of Cadoux *et al.* (2014), based on their phase equilibria study of magmas from the four largest plinian eruptions, that Santorini silicic melts are saturated in H_2O –Cl-rich fluid, but slightly undersaturated with respect to pure H_2O . The effect of high Cl in our silicic melts would therefore be equivalent

to increasing saturation pressure based solely on $\text{H}_2\text{O} + \text{CO}_2$ by an amount equivalent to $\sim 10\%$ (relative) of H_2O , that is to say by a factor of about 1.2. The solubility of H_2O in rhyolitic melts is independent of F content up to 6 wt % of dissolved F (Webster, 1990); the effect of ≤ 1000 ppm in our MIs is therefore negligible in this respect.

INTERPRETATION OF THE VOLATILE DATA

Entrapment and post-entrapment modification of MI compositions

Use of MI volatile contents in estimating entrapment depths requires that the MIs record equilibrium melt compositions. Entrapment of the boundary layer at a crystal–melt interface can potentially result in concentrations of slower-diffusing elements in MIs that are higher than equilibrium far-field melt values (Faure & Schiano, 2005). However, most of our MIs are larger than $40\ \mu\text{m}$, suggesting minimal boundary layer effects (Lu *et al.*, 1995). Moreover, experiments and modelling of MI entrapment and diffusive re-equilibration show that H_2O (also K_2O) diffuses sufficiently fast that values in MIs should record equilibrium values. The measured concentrations of slower-diffusing S, Cl, F and CO_2 could, however, somewhat overestimate equilibrium values.

Volatiles can be lost from MIs following entrapment by leakage along crystal fractures or by diffusion through 3D melt networks connected to the crystal surface (Anderson *et al.*, 1989; Wallace, 2005; Liu *et al.*, 2007; Humphreys *et al.*, 2008). We exclude loss of significant H_2O and CO_2 by these processes, because all of the MIs selected were ellipsoidal, isolated, and lacked textural evidence for crystal fracturing.

Melt inclusions within olivine can also lose H_2O by hydrogen diffusion through the host crystal during syn-eruptive decompression and post-eruptive cooling on timescales as short as a few hours (Hauri, 2002; Chen *et al.*, 2011, 2013; Gaetani *et al.*, 2012). MIs in bombs can lose more water than those in lapilli and ash from the same eruption, because the bombs take longer to cool (Lloyd *et al.*, 2013); however, even MIs in lapilli and ash can lose H_2O on the timescale of an eruption (Le Voyer *et al.*, 2014). Loss of H_2O from our olivine-hosted MIs by H diffusion during, or after, eruption is believed to be unimportant, for the following reasons. First, the olivine-hosted MIs were all extracted from lapilli-sized (0.5–1 cm radius) fallout tephra, which would have cooled within a few minutes in the atmosphere (Thomas & Sparks, 1992). Second, the olivine-hosted MIs have similar H_2O contents to plagioclase-hosted MIs with the same K_2O content from the same sample (Fig. 8a). Third, the MIs lack the heavy magnetite ‘dusting’ indicative of significant H_2O loss (Danyushevsky *et al.*, 2002), and there is no correlation between MI H_2O content and size (Chen *et al.*, 2011). Fourth, δD values of a representative subset of MIs lie within a narrow range

of values that is similar to that of Santorini whole-rock samples (Druitt *et al.*, 1999), and that lies between the values of mantle and slab-derived fluids (Shaw *et al.*, 2008). δD is very sensitive to H_2O loss by hydrogen diffusion, as H diffuses faster than D, thereby resulting in a large increase in δD (Hauri, 2002; Gaetani *et al.*, 2012; Bucholz *et al.*, 2013). In Fig. 10 we show two curves for δD increase as a function of H_2O loss using the H diffusion model of Bucholz *et al.* (2013). The narrow range of observed MIs δD values rules out syn-eruptive loss of H_2O by H diffusion in excess of about 0.2 wt %. Even the lowest MI H_2O contents observed (< 2 wt %; units M7c and M10 FS3) cannot be attributed to H diffusion, as their δD values are no higher (and if anything are a little lower) than those of MIs richer in H_2O from the same units.

Pressure changes in MIs during ascent and cooling can cause partitioning of CO_2 from melt into bubbles (Anderson & Brown, 1993; Bucholz *et al.*, 2013; Hartley *et al.*, 2014). CO_2 contents of bubbles in six representative MIs of mafic to silicic composition are below the detection limit of our Raman spectrometer. Assuming a detection limit CO_2 density of $\sim 0.04\ \text{g cm}^{-3}$ as used by Neave *et al.* (2014), and ‘adding back’ the bubble CO_2 in the same way as those researchers, the original CO_2 contents of our MIs could be underestimated by as much as 20–4500 (average 615) ppm. The lack of detection by Raman spectrometry therefore places only weak limits on any CO_2 sequestration into bubbles. More convincing evidence that CO_2 sequestration was minimal is the lack of any systematic differences in CO_2 contents between MIs containing bubbles and those lacking them in the same sample (Fig. 8b). This is consistent with most bubbles being shrinkage bubbles formed rapidly upon sample quench. Although we cannot exclude some CO_2 loss to bubbles, the effect appears not to have been large.

We conclude that our MIs (1) have near-equilibrium H_2O contents, (2) have not (in olivine) been significantly modified syn- or post-eruptively by the H diffusion mechanism, and (3) have lost minimal CO_2 to retraction bubbles. They therefore provide meaningful information about MI entrapment conditions and pre-eruptive magma storage in the crust.

Behaviour of volatiles in Santorini magmas

The data provide evidence for entrapment of many MIs under volatile-saturated conditions, as typical of arc magmas (Scaillet *et al.*, 2003; Wallace, 2005). H_2O dissolved in the MIs increases only very slightly with increasing K_2O , and much less than expected from incompatibility (Fig. 7a). This is particularly clear in the case of some of the mafic MI series, which exhibit almost constant H_2O over a range of K_2O contents (Fig. 7a). There are very few occurrence of hydrous crystalline phases in < 550 ka Santorini magmas, amphibole occurring only sparsely in some magmatic components of the Lower Pumice 2 and Minoan eruptions (Cottrell

et al., 1999; Gertisser *et al.*, 2009; Druitt, 2014); so it follows that H₂O must partition into an H₂O-rich fluid phase during melt crystallization and MI entrapment.

This conclusion holds even if Santorini magmas experience 'cryptic' amphibole fractionation. Many arc volcanic suites show differentiation trends that are consistent with amphibole fractionation, even if they lack modal amphibole at low pressures (Davidson *et al.*, 2007; Smith, 2014). Increasing La/Yb and decreasing Dy/Yb ratios (chondrite-normalized) with increasing SiO₂ at Santorini suggest that amphibole may indeed be a fractionating phase at depth (Gertisser *et al.*, 2009), it being stable in Santorini basalt at melt H₂O contents of >4 wt % and temperatures of <1000°C (Andújar *et al.*, 2015). However, amphibole would have a minimal effect on melt H₂O content during crystallization, because it contains only ~2.5 wt % H₂O (Cottrell *et al.*, 1999; Gertisser *et al.*, 2009). Let us suppose that a parental basalt with 2 wt % H₂O fractionates by 80% crystallization to a silicic residual melt under H₂O-undersaturated conditions. Simple mass balance shows that the H₂O content of the residual melt would be 10 wt % in the case of an entirely anhydrous crystal assemblage, and 8 wt % if amphibole made up a fifth of the crystals. Even if half the crystals were amphibole, the residual melt would still contain 5 wt % H₂O, so the H₂O content of amphibole is too low to buffer melt H₂O at an approximately constant value during crystallization. The H₂O contents in Fig. 7a remain approximately constant because H₂O was extracted by an exsolved fluid phase during crystallization under a limited range of pressures (see below). These observations support the previous findings of Cadoux *et al.* (2014) that plinian silicic melts at Santorini coexisted with an H₂O-rich fluid phase prior to eruption.

The only melts that may have been volatile-undersaturated are those of basaltic interplinian M10 FS3. MIs of this unit with <1 wt % K₂O fall on a positive trend that passes through the origin on the H₂O–K₂O plot, whereas MIs with >1 wt % K₂O fall on a flat trend (Fig. 7a). The least evolved MIs of this sample cannot have lost H₂O by intracrystalline H diffusion, as their δD values are the same as those of all other MIs (Fig. 10). We infer that these melts were volatile-undersaturated up to about 1 wt % K₂O.

On the plot of CO₂ vs H₂O (Fig. 7b), the subvertical trend defined by series M10 Y/B6 can be modelled by open-system degassing from a melt with 2–3 wt % H₂O and ≥1200 ppm CO₂ (we have assumed ~2000 ppm). Two MIs of series M10 FS3 also have elevated CO₂, and define a similarly steep trend. However, volatile undersaturation of M10 FS3 MIs with <1 wt % K₂O would rule out degassing. One possibility is that these steep CO₂–H₂O trends are due to mixing of shallow-derived, CO₂-poor melt and deeper-derived CO₂-rich melt, as observed in other violent strombolian eruptions such as Vesuvius 1944 (Marianelli *et al.*, 1999) and Parícutin 1943–1952 (Pioli *et al.*, 2008). A further possibility is that they are due to the fluxing of CO₂ from a deeper, non-

degassed magma. Further work is required to understand the behaviour of CO₂ in our samples.

Volatile-saturated crystallization of Santorini melts will result in the exsolution of a free vapour phase. The amount of H₂O and CO₂ exsolved as a function of residual melt fraction can be crudely estimated using measured K₂O, H₂O and CO₂ contents of initial and derivative melts. The procedure is described fully in Table 4, in which we estimate the exsolved vapour contents of residual melts of several of the MI suites. It should be noted that, owing to concomitant crustal assimilation, K₂O contents at Santorini underestimate F by 15–20% (Druitt *et al.*, 1999), so that the values of F are probably slightly too low. The results in Table 4 show that, were crystal fractionation and vapour exsolution to take place under perfectly closed conditions, the H₂O + CO₂ bubble fractions at 100–200 MPa storage pressures would be 50–90 vol. % in andesitic residual melt and >90 vol. % in dacitic–rhyodacitic residual melt. Of course, retention of such large volume fractions of gas would not be possible. Escape of vapour from residual melt would be inevitable above the bubble percolation threshold of >30 vol. % (Rust & Cashman, 2011), thereby limiting melt bubble contents to less than this value. Moreover, buoyancy-driven melt–vapour segregation would also take place, particularly in mafic, less viscous, melts. Crystallization in the shallow crust must take place under essentially open-system conditions, with the vapour leaving the melt and either reacting with surrounding rocks, segregating into subsurface gas pockets, and/or escaping to the surface. This is consistent with the data trend for MI series M10 Y/B6 in Fig. 7b.

The observed variations of S and Cl are also consistent with MI entrapment under open-system, volatile-saturated conditions. S decreases markedly with fractionation whereas Cl increases. Mafic to intermediate MIs from some units (e.g. M7c and M8-MSF) form flat-lying arrays on the Cl–K₂O plot, in a manner similar to H₂O (Fig. 6b). The only S-bearing crystalline phase in Santorini magmas is pyrrhotite, which occurs very sparingly in magmas of all compositions. However, although the S content of this phase is 37 wt % (Gertisser *et al.*, 2009), its abundance in the bulk crystal assemblage (<<0.1 vol %, equivalent to <<370 ppm bulk S) is far too low to drive down S along the observed liquid line of descent. Similarly, apatite, which contains 0.3–1 wt % Cl (Cadoux *et al.*, 2015), is far too sparse in the bulk mineral assemblage (<0.1 vol %, equivalent to <10 ppm bulk Cl) to explain the observed Cl liquid line of descent. The variations of S and Cl must therefore be largely controlled by extraction of S and Cl by a free vapour phase, and the removal of that vapour by bubble transfer. The possibility of a free S–Cl-bearing vapour phase has been raised in previous studies of Santorini MIs (Michaud *et al.*, 2000; Gertisser *et al.*, 2009).

Evolution of S and Cl during open-system, volatile-saturated crystallization can be modelled by a modified Rayleigh distillation law (Villemant *et al.*, 2008). In such a system there is competition between crystallization,

Table 4: Volatile-saturated crystallization of selected melt inclusion suites

	[SiO ₂] _i (wt %)	[K ₂ O] _i (wt %)	[H ₂ O] _i (wt %)	[CO ₂] _i (ppm)	[SiO ₂] _f (wt %)	[K ₂ O] _f (wt %)	[H ₂ O] _f (wt %)	[CO ₂] _f (ppm)	<i>T</i> (°C)	1 - <i>F</i>	<i>X</i> (200 MPa)	<i>X</i> (100 MPa)	<i>k</i>	<i>D'</i> S	<i>D</i> S	<i>D'</i> Cl	<i>D</i> Cl
M6c-a	51.6	0.5	2.6	162	68.4	3.1	3.2	122	951	0.84	90	95	39	—	—	0.3	12
M7c-a	50.2	0.2	2.5	180	66.6	2.9	3.5	135	978	0.94	97	98	41	1.6	66	0.9	37
M10 6Y/B	52.7	0.5	3.1	800	54.5	0.8	2.5	80	1095	0.38	67	80	23	5	120	0.6	14
M10 FS3 (<1% K ₂ O)	53.0	0.4	1.2	199	55.9	0.9	3.2	157	1103	0.51	0	0	∞	0	0	0	0
M10 FS3 (>1% K ₂ O)	55.9	0.9	3.2	157	57.5	1.3	3.2	270	1064	0.28	50	66	31	1.4	45	1	32
M12	50.7	0.5	3.1	193	57.3	1.3	3.3	253	1065	0.62	79	89	33	1.5	52	0.9	31
MP	52.0	0.5	4.1	150	68.8	3.1	5.0	78	897	0.84	93	97	25	2.2	58	0.5	13

Volatile-saturated fractional crystallization transforms a unit mass of melt into a mixture of residual melt (mass fraction n_m), solid (n_s) and vapour (n_v), such that $n_m + n_s + n_v = 1$. The mass fraction of residual melt is $F = n_m$, and the ratio of solid to vapour is $k = n_s/n_v$. The table gives the initial (i) and final (f) dissolved concentrations of SiO₂, K₂O, H₂O and CO₂ observed in several series of melt inclusions assumed to be related by fractional crystallization. Species concentrations are denoted in square brackets. In all cases, except those inclusions of the M10 FS3 series with < 1 wt % K₂O, fractional crystallization took place under vapour-saturated conditions, as described in the text. F for each series is calculated using the initial and final K₂O contents of the melt, $F = [K_2O]_i/[K_2O]_f$. The mass fraction of H₂O + CO₂ vapour exsolved between the initial and final states is $n_v = [H_2O + CO_2]_i - F[H_2O + CO_2]_f$. The ratio of solid to vapour is then given by $k = (1 - F - n_v)/n_v$. The volume fraction of exsolved vapour within the residual melt is given by $X_v = (n_{H_2O}/\rho_{H_2O} + n_{CO_2}/\rho_{CO_2})/(n_m/\rho_m + n_{H_2O}/\rho_{H_2O} + n_{CO_2}/\rho_{CO_2})$, where the vapour densities ρ_{H_2O} and ρ_{CO_2} are calculated using the ideal gas law. It should be noted that, owing to concomitant crustal assimilation, K₂O contents at Santorini underestimate F by 15–20% (Druitt *et al.*, 1999). D' is an apparent (crystallization-modified) distribution coefficient for S and Cl and is modelled on Fig. 6; D is the real distribution coefficient, given by $D = D'/(k + 1)$ (Villemant *et al.*, 2008).

which causes enrichment in S and Cl, and degassing, which causes depletion. If $D_i = C_i^v/C_i^m$ is the vapour (v)–melt (m) distribution coefficient of volatile species i of concentration C_i , then the Rayleigh equation for the system is $C_i^m = C_{i,0}^m F^{(D' - 1)}$, where D' is an apparent distribution coefficient modified by concomitant crystallization. If k is the ratio of mass of crystals to mass of exsolved vapour, then the apparent distribution coefficient D' is given by $D' = D/(k + 1)$ (Villemant *et al.*, 2008). In Fig. 6a and b we have modelled S and Cl for the different MIs lineages (see figure legend for details). Evolution from basaltic to andesitic compositions can be successfully modelled using D' values of 1.4–5.0 for S and 0.3–1.0 for Cl. These can be converted to real D values using estimates of k from Table 4. The resulting values of D (45–120 for S; 12–37 for Cl) are in the range of experimentally measured values for basaltic to andesitic melts (e.g. Scaillet & Pichavant, 2005; Witham *et al.*, 2012). The success of these models for the evolution of andesite to rhyodacite is less clear. For S, a constant value of D' describes the observed variations across the entire compositional spectrum, from basalt to rhyolite. For Cl, however, dacitic to rhyodacitic melts may be too Cl-rich to be successfully modelled in such a simple manner. For example, whereas the models for Middle Pumice and for M6c–M6a reproduce the most silicic MIs, that for series M7c–M7a does not. More rigorous modelling of Cl variations from intermediate to silicic compositions may need to take into account (1) variations of D_{Cl} with melt and/or vapour composition, and/or (2) enrichment of silicic melts in Cl by processes other than fractional crystallization (e.g. incorporation of seawater; Wallace, 2005).

S and Cl in melt inclusions of sample M10 FS3 containing <1 wt % K₂O both behave incompatibly

($D' = D = 0$; Table 4), reinforcing the interpretation that these melts were volatile-undersaturated.

We conclude that most Santorini melts ranging from basaltic to rhyolitic in composition coexisted with a free COHSCI vapour phase at the time of MI entrapment. Typical basaltic melts at Santorini contained up to 2–4 wt % H₂O, at least 1200 ppm CO₂, 1200 ppm S, 500 ppm Cl and 100 ppm F (Figs 6 and 7); this is consistent with recent phase equilibria studies that inferred 3–5 wt % H₂O for the ~340 ka Balos basalt (Andújar *et al.*, 2015). Some basaltic melts with lower H₂O contents (1–2 wt %) appear to have been volatile-undersaturated.

Presence of a hypersaline phase in silicic melts

By comparing the experimental solubility relationships for Cl-bearing silicic melts with their MI data, Cadoux *et al.* (2014) postulated that some Santorini silicic melts are saturated not only with an H₂O-rich vapour, but probably also with a hydrosaline liquid (brine). Our extended dataset now allows us to address this same question for the entire range of melt compositions at the volcano.

The solubility behaviour of H₂O–Cl-bearing silicate melts has been reviewed by Webster (2004). In a volatile-saturated system, exsolution of a vapour phase is favoured at low Cl/H₂O melt ratios, whereas higher ratios favour exsolution of a Cl-rich hydrosaline liquid (brine). The critical Cl/H₂O ratios have been determined experimentally at 200 MPa for melts of a wide range of compositions, including basaltic (critical Cl/H₂O ratio 0.55), andesitic and latitic (0.35), and rhyolitic (topaz-bearing rhyolite and haplogranite) (0.05). The solubility data of Botcharnikov *et al.* (2004) constrain the critical ratio for rhyodacitic melt to be at least 0.13. The critical ratios increase with decreasing pressure. In Fig. 9 the

Cl/H₂O ratios of our MIs are compared with these published values. The mafic melts, and most silicic melts, fall beneath the brine saturation field at 200 MPa. It should be noted that decreasing the pressure to <200 MPa would raise the limit of brine saturation, and so reinforce this conclusion. However, the rhyolitic melts of the Minoan eruption lie at the limit of brine saturation at 200 MPa. This supports the conclusion of Cadoux *et al.* (2015) that the Minoan eruption may have discharged a melt containing a H₂O–Cl-rich liquid phase, as well as a vapour phase. Melts of the present-day Kameni magmas appear not to be saturated in brine at ≤200 MPa.

MAGMA STORAGE AND EXTRACTION

Based on (1) the isolated, leakage-free nature of the MIs, (2) the absence of evidence for syn-eruptive or post-eruptive loss of H₂O or CO₂, and (3) the evidence for vapour saturation (with the exception of the least evolved MIs of M10 FS3), saturation pressures from MI H₂O + CO₂ contents can be recalculated as depths assuming a lithostatic stress field and a geophysically determined mean density of the upper crust (~2640 kg m⁻³; Konstantinou, 2010) (Fig. 12a). The lithostatic assumption is justified because non-lithostatic stress components in the upper crust, as reflected in earthquake stress releases, are typically a few MPa (Oth, 2013), and magma excess pressures necessary for reservoir fracturing and dyke propagation to the surface do not exceed ~10 MPa (Gudmundsson, 2012). Both contributions are comparable in magnitude with the error on our pressure estimates (±10 MPa; ±0.4 km), and can be neglected.

All of our MIs record entrapment in the topmost 10 km or so of the crust (Fig. 12a). There are two possible explanations for this (Plank *et al.*, 2013). One is that Santorini melts become volatile saturated at depths of <10 km, so that ascent under undersaturated conditions from deeper levels leads to resorption of any existing crystals, and only crystals and MIs formed at <10 km are preserved. The other is that crystal growth occurs throughout the crust, but that deep-derived crystals remain long enough above ~10 km for volatiles and H isotopes in early formed MIs to re-equilibrate. Crystal growth and MI entrapment in the upper ~10 km is envisaged to be driven by a combination of volatile-saturated decompression and cooling as melts rise through progressively lower-pressure and cooler environments.

We interpret the observed range of MI entrapment depths for each eruption (Fig. 12a) in the following way. The deepest observed depth corresponds either to the onset of volatile-saturated crystal growth or to the last level of MI re-equilibration. This is, of course, a minimum estimate owing to possible sampling bias. The shallowest depth corresponds to that at which the ascending magma last paused prior to rapid final ascent and eruption (Fig. 12b).

Plinian eruptions

Depths given by the four large silicic plinian eruptions (Lower Pumice 1, Lower Pumice 2, Cape Riva, Minoan) are all ≥4 km (≥100 MPa), and span a range of values. They include the best-estimate pre-eruptive depth of ~8 km (~200 MPa) for these same four eruptions based on phase equilibria experiments (Cadoux *et al.*, 2014) (Table 1), but extend to lower and higher values. The lower values are interpreted to be real, because of our rigorous MI textural selection criteria. If we include the MIs from Cadoux *et al.* (2014), as described above, then MIs from the two Lower Pumice eruptions of cycle 1 yield 4.8–8.9 km (125–230 MPa), Cape Riva 3.9–10.4 km (100–270 MPa), and the Minoan 4.2–12.3 km (100–320 MPa), all using the Papale *et al.* (2006) solubility law. Pressures or depths from MIs in Lower Pumice 2 (150–180 MPa; 5.8–6.9 km) are significantly lower than those calculated from Al-in-hornblende barometry (Gertisser *et al.*, 2009; Table 1), as also observed by Cadoux *et al.* (2014). Use of VolatileCalc in the Minoan case (the only truly rhyolitic MIs) yields depths up to 9.6 km (250 MPa), lower than Papale. MIs from a high-Ba microphenocryst-rich andesitic pumice from the Minoan (Druitt *et al.*, 2014) yield a depth range similar to that of MIs in the main, rhyodacitic pumice. A silicic MI from the Middle Pumice eruption gives 6.0 km (155 MPa), and two associated mafic MIs from inmixed, basalt-derived olivines in the same pumices give ~4–8 km (100–200 MPa), depending on the solubility law used. Only MIs of the Vourvoulos eruption, the smallest plinian event recognized by Druitt *et al.* (1999), yield depths of less than ~4 km. It should be recalled that pressures and depths based on H₂O + CO₂ solubility may be underestimated by up to 10–20% in the most Cl-rich of silicic MIs.

Our MIs from the four main plinian units therefore record MI entrapment over large pressure intervals (ΔP , up to 220 MPa). This has also been reported from large silicic eruptions at other volcanoes. For example, the 760 ka, >600 km³ Bishop Tuff eruption sampled melts trapped over a pressure interval of $\Delta P \approx 160$ MPa, the 26.5 ka, ~530 km³ Oruanui eruption over $\Delta P \approx 100$ MPa, and the 160 ka, >60 km³ Kos Plateau Tuff eruption over $\Delta P \approx 100$ MPa (Wallace *et al.*, 1995; Liu *et al.*, 2005; Bachmann *et al.*, 2009). There are two possible interpretations for this. Either (1) magmas were extracted simultaneously during eruption from a wide range of storage pressures, or (2) some of the magma was transferred from deep to shallow levels shortly prior to eruption, with some of the MIs retaining a memory of higher pressures.

Constraints from the Minoan eruption

Constraints on these explanations are provided by the Minoan eruption, for which we have analysed the most MIs from a single unit, and for which we have an approximate dense-rock equivalent (DRE) volume estimate (30–80 km³; Pyle, 1990; Sigurdsson *et al.*, 1990; Johnston *et al.*, 2014). It should be recalled that all but

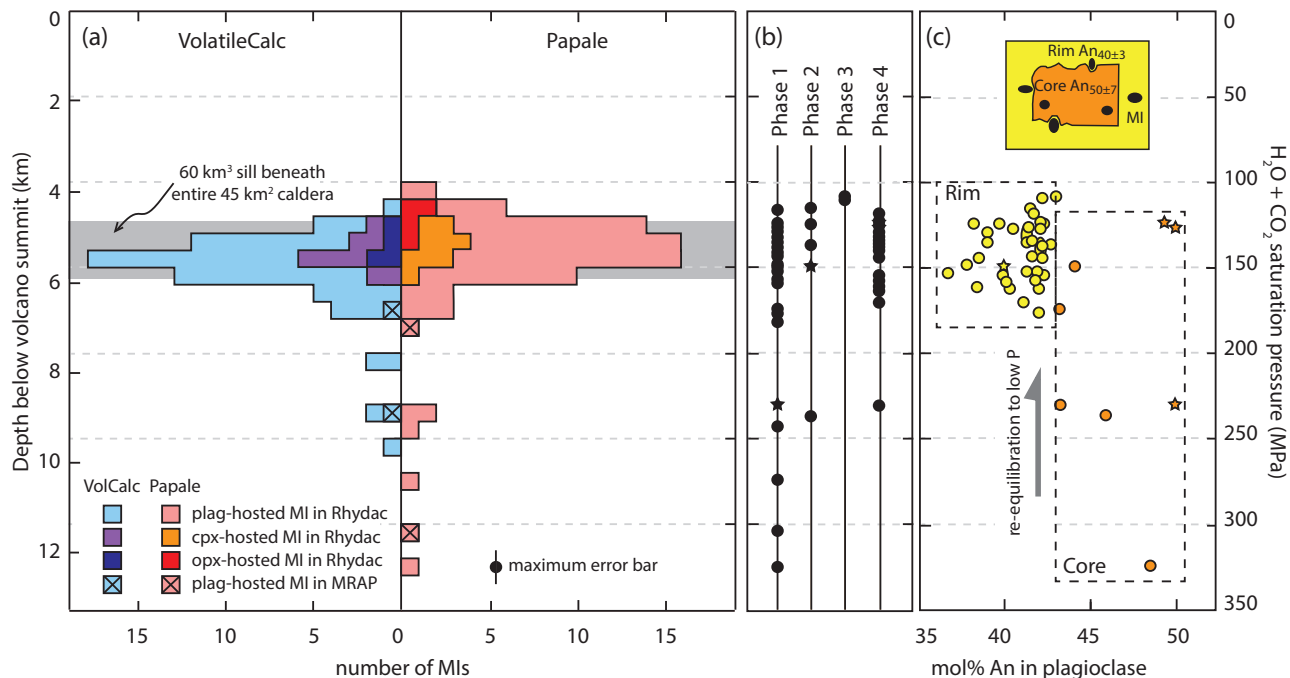


Fig. 13. (a) Histograms of $H_2O + CO_2$ saturation pressures calculated using melt inclusions from the Minoan eruption. All but two of the MI come from the main Minoan rhyodacitic pumice; the other two are from a minor andesitic component (MRAP, microphenocryst-rich andesitic pumice; [Druitt, 2014](#)). The pressures are recalculated using two solubility models relevant to silicic melts: VolatileCalc ([Newman & Lowenstern, 2002](#)) and the model of [Papale et al. \(2006\)](#). (b) Distribution of MI saturation pressures between the eruptive phases. (c) Plot of saturation pressure vs An content of the host plagioclase, distinguishing MIs in the cores of the plagioclase phenocrysts from those in the rims. The stars are data from [Cadoux et al. \(2014\)](#), which are comparable with those of this study.

two of our Minoan MIs come from the main ($\gg 99\%$), rhyodacitic magmatic component of the eruption ([Druitt, 2014](#)). The MI-derived pressure–depth data are plotted in [Fig. 13](#), from which we make the following observations. First, the majority of plagioclase-hosted MIs, and all pyroxene-hosted MIs, derive from an upper layer no more than 2 km thick (from 4 to 6 km depth), with a ‘tail’ of plagioclase-hosted MIs recording depths between 6 and 10–12 km. Two MIs from the volumetrically minor andesitic component also record depths beneath the main layer. Second, the entire range of depths is recorded in MIs from eruptive phase 1, as well as (to varying degrees) in those from subsequent phases ([Fig. 13b](#)).

If the whole depth interval records purely syn-eruptive extraction, then the Minoan reservoir must either have had the form of an upward-flaring funnel, with a wide top at 4–6 km and a narrow root extending to 10–12 km, or the magma must have been stored as a plexus of interconnected melt lenses within a mush body several kilometres thick (e.g. [Cashman & Giordano, 2014](#)). In either of these cases, the early erupted magma (phase 1) would be expected to have come from the shallowest levels, and the last-erupted magma (phase 4) from the deepest levels. However, the entire depth range is recorded in MIs from the first phase, which is not consistent with top-down extraction.

[Cottrell et al. \(1999\)](#) used phase equilibria constraints to argue for late-stage ascent of Minoan melt from deeper to shallower crustal levels. Plagioclase crystals

in the magma have cores of $An_{50 \pm 7}$ mantled by rims of $An_{40 \pm 3}$ ([Cottrell et al., 1999](#); [Druitt et al., 2012](#)). [Cottrell et al.](#) measured MI H_2O contents of 3.5–6.2 wt % in the cores, and inferred (but did not measure) 2.5–3.0 wt % in the rims. Our new dataset now includes many MIs from plagioclase rims, and these contain 4.0–5.0 wt % H_2O ([Fig. 13c](#)). They are contained within deep resorption embayments in the cores and surrounded by thin shells of rim plagioclase, visible only on high-resolution BSE images. MIs in the cores have higher contents of H_2O (4.6–6.9 wt %; [Fig. 13c](#)). The data therefore support the hypothesis of [Cottrell et al.](#), but refine the source depths.

We infer that the plagioclase cores derive from at least 10–12 km depth, and were transported by ascending silicic melt to a shallow magma chamber (4–6 km) where they were overgrown by the rims. Some core MIs with lower H_2O probably partly re-equilibrated upon arriving in the chamber. MIs in opx and cpx were either trapped by pyroxene growth in the chamber, or were carried from depth and re-equilibrated upon arrival.

[Druitt et al. \(2012\)](#) used Mg-in-plagioclase diffusion chronometry to show that this last event of melt (plus plagioclase cores) transfer from depth occurred within a few decades to a few months of the eruption. Whereas [Cottrell et al. \(1999\)](#) interpreted it as involving the entire Minoan magma volume, [Druitt et al. \(2012\)](#) argued that it may have involved only the most recent batch of a series of deeper inputs during prolonged assembly of the shallow chamber.

This interpretation may explain two other features of the Minoan eruption. First, the rhyodacitic magma is extremely homogeneous, both compositionally and thermally (Fe–Ti oxide temperatures), irrespective of eruptive phase, which implies a late-stage homogenization event (Druitt *et al.*, 2012; Druitt, 2014). Second, the full range of MI entrapment depths from 4 to 10–12 km is recorded by MIs of the first eruptive phase. Because Santorini melts are volatile-saturated at shallow crustal pressures, ascent of silicic melt from 10–12 km to 4–6 km might have resulted in vesiculation. A simple calculation based on the exsolution of 2 wt % H₂O (from 6.5 to 4.5 wt %), a final storage pressure of 130 MPa and the ideal gas law suggests that the melt could have arrived in the shallow chamber with ~20 vol. % more bubbles than it started with. This bubbly melt might then have risen buoyantly as a plume to the top of the chamber, causing (1) mixing and homogenization of the chamber contents prior to eruption, and (2) extraction of both deep-derived and shallow-derived MIs during the first eruptive phase.

The MI data, combined with the compositional and thermal homogeneity of the Minoan rhyodacite, show that the magma was stored immediately prior to eruption in a single, sill-shaped chamber <2 km thick, the top of which was situated ~4 km beneath the volcano. Assuming that the chamber underlay the entire 45 km² caldera (Johnston *et al.*, 2014), then the DRE volume of the eruption of 30–80 km³ gives caldera collapse heights from 0.7 to 1.8 km, suggesting that much, if not all, of the chamber was extracted during the eruption.

Interplinian eruptions

The cycle 2 interplinian eruptions

MI entrapment depths for the cycle 2 interplinian mafic magmas (excluding those of the volatile-undersaturated MIs of M10 FS3, for which total pressures cannot be calculated) range from 1 to 10 km (<50 to 250 MPa) (Fig. 12). This shows that, although these magmas saturated as deep as 10 km, they stalled at very high crustal levels (1–3 km) prior to final ascent and eruption.

Three silicic interplinian eruptions of cycle 2 give saturation depths of ~4 km, and pre-eruptive storage depths of 2–3 km (50–100 MPa), both much shallower than the corresponding depths for plinian eruptions of the same cycle [the Vourvoulos eruption, one of the smallest of the plinian eruptions identified by Druitt *et al.* (1999), plots with the interplinians]. The differences could be an artefact due to the extra lithostatic load exerted by intracaldera edifices. Intracaldera edifices grow progressively during interplinian periods, are highest prior to plinian eruptions, and are destroyed by caldera collapse prior to the onset of the subsequent interplinian. Associated height changes can reach ~750 m, from edifices up to 350 m above sea level (e.g. 67–54 ka Skaros edifice) to caldera floors 300–400 m below sea level (e.g. present-day caldera), corresponding to changes in lithostatic loading of ±9 MPa (Fig. 12a). Given that lithostatic pressure is measured from

the top of the volcano, storage pressures during interplinian periods (deep caldera and small intracaldera edifices) might be expected to be slightly lower than those prior to plinian eruptions (high edifices partly or entirely filling calderas) for a given chamber depth below a fixed surface datum (e.g. present-day sea level). However, this ±9 MPa lithostatic effect does not seem to be able to account for the observed differences (Fig. 12a). We therefore conclude that the differences between pre-plinian and interplinian depths are real.

One possible explanation is that the cycle 2 interplinian silicic melts had inherently lower H₂O contents than the plinian silicic melts, allowing them to ascend higher in the crust before reaching saturation. Another possibility relates to the existence of surface edifices. In addition to increasing vertical stresses in the shallow crust, pre-plinian edifices can increase horizontal compressive stresses, thereby inhibiting dyke ascent (Pinel & Jaupart, 2003). This effect might cause ascending silicic melts to pond deeper prior to plinian eruptions than during the interplinian periods that follow caldera collapse and consequent release of the edifice-generated horizontal stresses.

The (cycle 3) AD 726 Kameni eruption

Melt inclusions from the AD 726 explosive eruption of Kameni Volcano imply a saturation depth of at least ~6 km and pre-eruptive storage depth of ~4 km (Fig. 12a), which is in good agreement with the storage depth estimation of Barton & Huijsmans (1986) using clinopyroxene–plagioclase equilibria for Kameni magmas in general (Table 1). The eruption was of much smaller magnitude than the interplinian eruptions of cycle 2 sampled in this study, because its fallout is not observed outside the caldera. The AD 726 magma was stored deeper than those of the cycle 2 interplinian silicic eruptions, near the top of the (presumably now largely crystallized) Minoan chamber. However, Kameni magma is not residual Minoan magma, because it is lower in incompatible trace elements and represents a new batch from depth following the Minoan eruption (Huijsmans *et al.*, 1988). One possibility is that the Minoan eruption, one of Santorini's largest, resulted in (or was triggered by) modifications of the stress field beneath the volcano that were large enough to cause a change in the ponding level of silicic magma during the subsequent and current interplinian period.

We note that the AD 726 storage depth (~4 km) is similar to depths of Mogi pressure sources calculated for surface uplift of the 2011–2012 unrest period: ~4 km [global positioning system (GPS) data; Newman *et al.*, 2012], 4.4 +1.1/–1.0 km [InSAR (interferometric synthetic aperture radar) data; Parks *et al.*, 2012], 3.3 km (GPS data; Papoutsis *et al.*, 2012), 6.5 km (InSAR data; Papoutsis *et al.*, 2012) and 3.5–3.8 km (joint GPS and InSAR data; Foumelis *et al.*, 2013). This reinforces published evidence that the uplift in 2011–2012 was due to shallow magmatic intrusion (Parks *et al.*, 2012, 2015; Rizzo *et al.*, 2015).

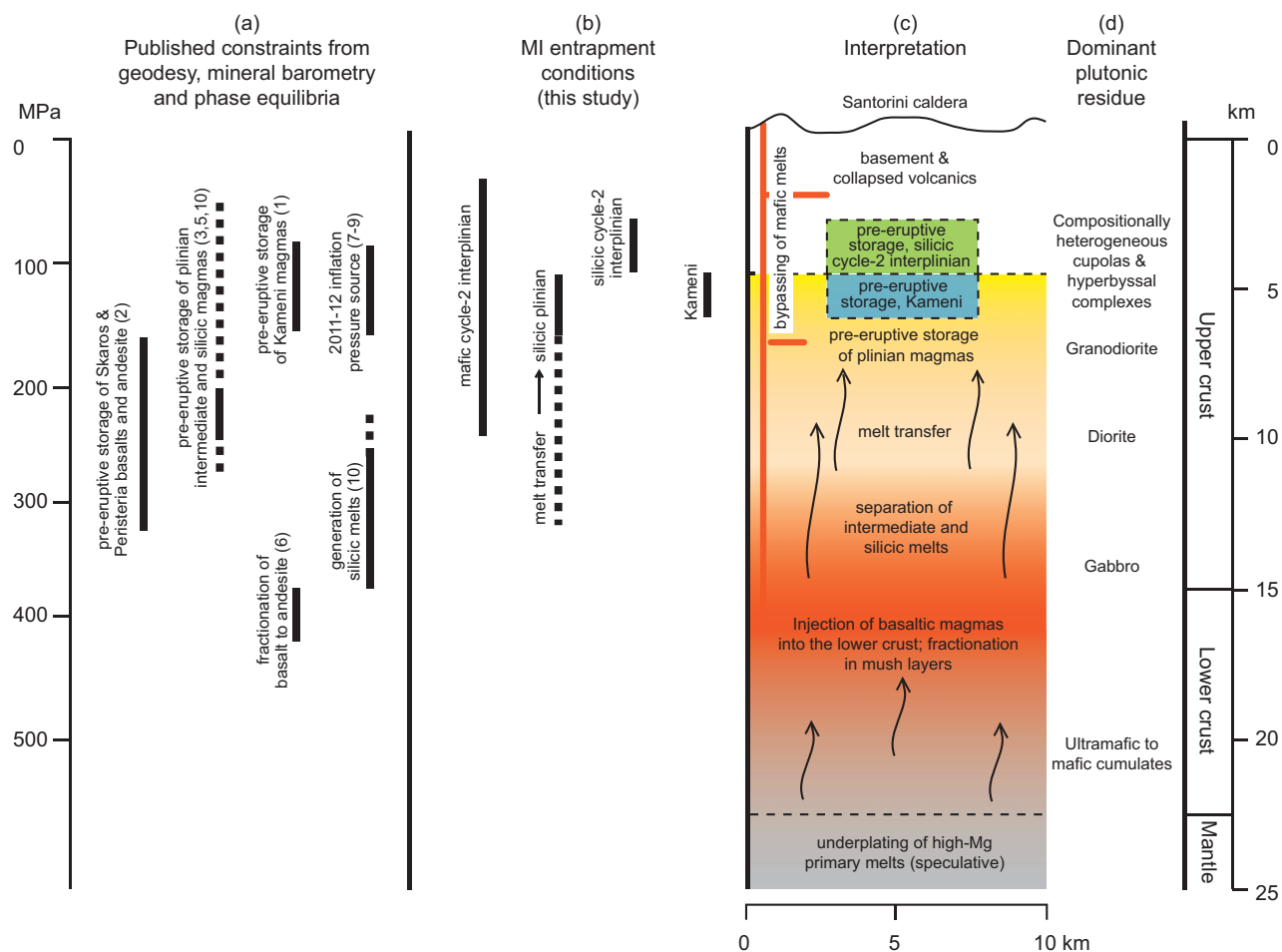


Fig. 14. Constraints on magma pressures–depths from (a) previously published studies (numbers are references in Table 1) and (b) the melt inclusion entrapment data from this study. The constraints are combined in the form of (c) a schematic model of the Santorini plumbing system. (d) Lithologies inferred to form the present-day plutonic complex beneath the caldera.

PLUMBING SYSTEM ARCHITECTURE AT SANTORINI

Our results, combined with those of other recent studies, allow us to place quantitative constraints on the depths of magma storage and extraction beneath Santorini. They are presented in the form of a one-dimensional, time-integrated petrological image of the plumbing system (Fig. 14).

The present-day crustal column beneath the caldera is the product of more than half a million years of magmatism. *Druitt et al. (1999)* estimated that 300–600 km³ of magma has passed through the crust beneath the caldera, implying that much of the 25 km thick crust has been replaced by variably solid to mushy plutonic residues. We envisage a crustal magmatic system similar to that postulated by *Annen et al. (2006)*. The system is driven by repeated underplating and injection of the lower crust by basalt, which fractionates in ultramafic to gabbroic mush bodies to more evolved residual melts, accompanied by crustal assimilation. Gravitational compaction of crystal mush layers expels residual melts, which ascend by porous flow to higher structural levels. Percolating melts equilibrate chemically with

progressively cooler host environments, leading to continued fractionation and production of more evolved compositions until the melts segregate into dykes and ascend too rapidly for equilibrium to be maintained (*Solano et al., 2012*). These melts inject into the upper crust, where they either accumulate as eruptible lenses or crystallize as plutons (*Annen, 2009; Gelman et al., 2013; Menand et al., 2015*).

Primary mantle-derived melts at Santorini have up to 9–12 wt % MgO (*Nichols, 1978*), at least several wt % H₂O (*Andújar et al., 2015; this study*), and a range of trace element and isotopic signatures owing to varying degrees of contamination by subduction fluids and sediment-derived melts (*Huijsmans et al., 1988; Francalanci et al., 2005; Bailey et al., 2009; Vaggelli et al., 2009*). Fractionation of these primary melts generates residual melts ranging from basaltic through intermediate to silicic. Three lines of evidence place constraints on the levels at which residual melts separate from their parent mushes. First, typical andesitic melts can be explained as residual melts produced by fractionation of basalt with ~50 wt % SiO₂ and 4–6 wt % H₂O near the base of the upper crust (~15 km;

~400 MPa) (Andújar *et al.*, 2015). Second, silicic melts can be explained by fractionation of andesite in the 8–15 km depth range (200–400 MPa; Andujar *et al.*, in preparation). Third, melt inclusions from the cores of plagioclase crystals in Minoan pumices record ascent of silicic melt batches from depths as great as 10–12 km (present study). These observations suggest that intermediate to silicic melts separate from their parent mushes in the depth interval from 8 to ≥ 15 km, then rise rapidly through the upper crust. Nodules of gabbro and diorite brought to the surface by erupting magmas may be samples of cumulates from which evolved interstitial melts have been removed (Druitt *et al.*, 1999). Most residual melts travel through the upper <10 km of the crust volatile-saturated (Fig. 12), resulting in crystal growth, MI entrapment, vesiculation and outgassing.

During the repose periods that precede plinian eruptions basalt accumulates at depth, generating large volumes of evolved melts by fractional crystallization, crustal assimilation, and defrosting of extant, mushy plutons. Successive melt batches then ascend, via a series of high-flux transfer events, into the upper crust on geologically short timescales (Druitt *et al.*, 2012; Fabbro *et al.*, 2013), where they amalgamate to form sill-shaped reservoirs of crystal-poor magma in the 4–8 km depth range, perhaps under the influence of horizontal stresses induced by intracaldera edifices. The origin of these melt transfer events is not understood, but they may result from high, transient mantle input rates (Fabbro *et al.*, 2013), tectonic forcings (Feuillet, 2013), or spontaneous, gravitationally driven reorganizations of mush layers (Christopher *et al.*, 2015). The magma chamber of the 30–80 km³ Minoan eruption was a single lens of well-stirred melt, between 0.7 and 2 km in thickness (Fig. 13), that had a late-stage growth spurt within a decade of its eruption (Druitt *et al.*, 2012). The >10 km³ magma reservoir of the 22 ka Cape Riva plinian eruption was situated in a similar depth range (Fig. 12), and was assembled in less than ~3000 years (Fabbro *et al.*, 2013). Caldera collapse during plinian eruptions probably empties most of these magma layers, any residue then crystallizing following eruption-induced decompression.

During interplinian periods of cycle 2, evolved melts accumulated pre-eruptively in small, superficial (1–3 km deep) reservoirs above the main plinian storage levels, perhaps in compositionally heterogeneous cupolas and hyperbyssal complexes. The AD 726 eruption of Kameni Volcano was fed from a small body of dacitic magma situated near the top of the largely crystallized remains of the Minoan magma chamber.

CONCLUSIONS

We have analysed the H₂O contents of 138 plagioclase-, olivine- and pyroxene-hosted melt inclusions (MIs), along with CO₂, S, Cl, F and δD in various subsets, from eruptions of the last 200 kyr at Santorini caldera. The aim was to constrain magma storage/extraction depths

associated with plinian eruptions, as well as those associated with smaller eruptions that characterize interplinian periods. The sampling focused mainly on the products of explosive cycle 2. The main conclusions are as follows.

1. Mafic MIs contain 1–4 wt % H₂O and up to 1200 ppm CO₂; silicic MIs contain 2–7 wt % H₂O and up to 150 ppm CO₂. The high Cl contents (<6000 ppm) and low to moderate S contents (<1500 ppm) of the MIs relative to arc magmas elsewhere are in agreement with the findings of previous studies.
2. The MIs selected for analysis were isolated in olivine, plagioclase or pyroxene phenocrysts, with no textural evidence for leakage. A subset of 27 MIs in olivine and plagioclase has δD values ranging from –37 to –104‰, encompassing mantle to slab values, with no evidence for H₂O loss from olivine-hosted MIs by hydrogen diffusion. There is no systematic difference in CO₂ contents between bubble-bearing MIs and bubble-free MIs within given units, suggesting little sequestration of CO₂ into bubbles. Raman analysis of selected MIs also revealed no detectable CO₂ in bubbles.
3. Santorini parental basalts contain 2–4 wt % H₂O, ≥ 1200 ppm CO₂, 1200 ppm S, 500 ppm Cl and 100 ppm F. Most MIs, from mafic to silicic, were saturated with a free COHSCI vapour phase at upper crustal pressures, as shown by the compatible behaviours of H₂O, S and Cl in melt inclusions suites. However, some basaltic MIs have lower H₂O contents (1–2 wt %), and may have been volatile-undersaturated when trapped. The Minoan magma probably contained an H₂O–Cl-rich hypersaline liquid phase.
4. The leak-free nature of the MIs and the evidence for volatile saturation allow calculation of H₂O + CO₂ saturation pressures using suitably calibrated solubility models, and conversion to depths using a geophysically determined mean density for the upper crust. Saturation pressures of some particularly Cl-rich MIs may be underestimated by 10–20%. Most MIs record entrapment at depths of <10 km, and so provide no information on processes at greater depths.
5. Melt inclusions from plinian eruptions record melt extraction from >100 MPa (>4 km), and over depth intervals of several kilometres. A large dataset of MIs from the rhyodacitic magma of the Minoan eruption shows that MIs trapped in cpx, opx, and the An_{40 ± 3} rims of plagioclases record pre-eruptive storage within an upper crustal magma layer ≤ 2 km in thickness, from 100 to 160 MPa (4–6 km depth). MIs in the An_{50 ± 7} plagioclase cores, however, record storage at higher pressures, up to 320 MPa (10–12 km). The large depth range recorded by MIs in the Minoan eruption is attributed to late-stage transfer of silicic melt (+ antecrystic plagioclase cores) from the middle crust to a shallow magma chamber, from which the magma was finally erupted. This late-stage replenishment event has been previously constrained by diffusion chronometry as having taken

place less than about ~10 years prior to the eruption. The plagioclase cores were carried from depth in the ascending melt, then overgrown by the rims in the shallow chamber.

6. The Minoan silicic melt may have vesiculated while decompressing from 320 to 100–160 MPa. Injection into the shallow chamber as a buoyant, bubbly plume may have caused mixing and homogenization, explaining (a) the compositional and thermal homogeneity of the Minoan magma, and (b) the wide range of pressures recorded by MIs in plagioclases of the first eruptive phase.
7. Silicic magmas of cycle 2 interplinian periods were stored pre-eruptively in reservoirs situated above the pre-plinian storage levels, possibly in cupolas and hyperbyssal complexes.
8. The depth of the small magma body that fed the AD 726 eruption of Kameni Volcano (~4 km) was similar to those estimated for the pressure source during the 2011–2012 unrest period, lending support to a magmatic origin for the unrest. It lay near the top of the largely crystallized remains of the Minoan magma chamber.
9. Mantle-derived basalt injects into the lower crust below Santorini, where it fractionates in bodies of hot crystal mush. Residual melts of intermediate to silicic composition separate from their parent mushes in the 8 to >15 km depth interval, then ascend through the upper crust, where they either crystallize or accumulate in reservoirs of eruptible, crystal-poor magma. Most residual melts travel through the upper ~10 km of the crust volatile-saturated, leading to crystal growth, MI entrapment, vesiculation and outgassing.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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APPENDIX A: H₂O AND CO₂ GLASS STANDARDS USED IN SIMS ANALYSIS

Basaltic standard	H ₂ O (wt %)	CO ₂ (ppm)	Andesitic standard	CO ₂ (ppm)	Dacitic standard	H ₂ O (wt %)	Rhyolitic standard	H ₂ O (wt %)	CO ₂ (ppm)
M34	5.70 ± 0.13	375 ± 30	MP18.1	2618 ± 302	Dac 0	0	Rhy 0	0	
M35	4.20 ± 0.12	1019 ± 81	MP20.1	2639 ± 106	Dac 212	2.12	Rhy 242	2.42	
M40	3.07 ± 0.12	2183 ± 178	MP20.3	4288 ± 58	Dac 445	4.45	Rhy 424	4.24	
M43	2.62 ± 0.11	3172 ± 265	MP23.2	3639 ± 226	Dac 636	6.36	Rhy 638	6.38	
M48	0.77 ± 0.11	176 ± 15	MP23.3	4225 ± 120			BT2 628-5	6.57 ± 0.18	14 ± 3
M49	1.25 ± 0.10	140	MP24.1	3948 ± 182			BT2 628-6	5.69 ± 0.06	411 ± 22
M50	2.43 ± 0.10	35					BT2 628-7	4.98 ± 0.11	676 ± 44
M66	0.66 ± 0.10	3856							
M1 roman	3.50 ± 0.10								
M2 roman	4.93 ± 0.10								
M3 roman	4.77 ± 0.10								
M5 roman	5.05 ± 0.10								
N72	0	0							

M34, M35, M40, M43, M48–M50, M66, M1, M2, M3, M5 and N72 are international basaltic glass standards. MP 18.1, 20.1, 20.3, 23.2, 23.3 and 24.1 are doped andesitic glasses fabricated by the authors at Clermont-Ferrand (see Appendix B). Dac 0, 212, 445 and 636 are doped dacitic glasses fabricated from Pinatubo pumice; H₂O determined by Karl Fischer titration (Scaillet & Evans, 1999). Rhy 0, 242, 424 and 638 are doped rhyolitic glasses fabricated from Pinatubo pumice; H₂O determined by Karl Fischer titration (Scaillet & Evans, 1999). BT2 628-5, 628-6 and 628-7 are doped rhyolitic glasses fabricated from Bishop Tuff pumice; H₂O and CO₂ determined by Fourier transform infrared spectrometry (Cadoux *et al.*, 2014).

APPENDIX B: PREPARATION OF THE ANDESITIC STANDARDS ‘MP’ FOR CO₂

The andesitic CO₂ standards ‘MP’ (Table B1) were synthesized for this study using pumice from the Middle Pumice eruption. Clasts were crushed, and the powder was heated in a vertical furnace at 1400°C in air for 2 h in a Pt crucible. The resulting dark glass was then crushed to a fine powder, which was mixed with appropriate proportions of CaCO₃ powder; 50 mg of the mixture was then arc-welded into 4 mm diameter Au₈₀Pd₂₀ capsules. Each capsule was submerged in acetone for at least 15 min, and was weighed before and after to check for possible leaks.

The syntheses were performed in a 3/4 inch piston-cylinder apparatus at the Laboratoire Magmas et Volcans (Clermont-Ferrand). The piston-cylinder furnace comprised two Pyrex tubes (inside and outside the graphite furnace), MgO spacers, and a graphite furnace. To reduce H and C diffusion inside the capsule, finely powdered Fe₂O₃ was packed between the capsule and the internal Pyrex tube. Temperatures were measured using W₅Re₉₅ thermocouples and controlled to ±2°C. All experiments were carried out at 1.0 GPa, 1300°C and CO₂-undersaturated conditions to ensure the production of bubble-free glasses. For each experiment, the assembly was first pressurized to 300 MPa, then heated to 650°C, and left at 650°C for several minutes, before ramping simultaneously to the final pressure–temperature conditions. Each experiment lasted 3 h, and the samples were quenched approximately isobarically to below the glass transition temperature in about 8 s. The absence of crystals, bubbles or oxides in the resulting glasses was checked optically and on BSE images; chemical

Table B1: Composition of MP glass standards

	Mean (<i>n</i> = 60)	1σ
SiO ₂	62.83	0.34
TiO ₂	0.99	0.06
Al ₂ O ₃	15.91	0.22
FeO	5.80	0.18
MnO	0.17	0.03
MgO	1.97	0.08
CaO	4.53	0.20
Na ₂ O	4.29	0.16
K ₂ O	2.27	0.11
P ₂ O ₅	0.25	0.10
Total	99.02	0.47

homogeneity of the glasses was checked by electron microprobe analysis (Table B1).

The CO₂ concentrations of experimental glasses were measured by micro-Fourier transform infrared spectrometry at the Laboratoire Magmas et Volcans in Clermont-Ferrand. Spectra were collected using a Vertex 70 Bruker spectrometer with a KBr beam splitter, MCT-A detector coupled to a Hyperion microscope equipped with 15 × objective and condenser. Spectra were measured through a CaF₂ plate. They were integrated between 700 and 7500 cm⁻¹ with a resolution of 4 cm⁻¹ and up to 300 scans. The entire system was continuously purged with dry air.

Glass fragments were doubly polished to a 0.25 μm corundum disk finish with thicknesses ranging from 80 to 150 μm. The samples were cleaned in acetone and ethanol, and no residues on sample surfaces were observed. A 100 μm diameter area was examined using a microscope to avoid any bubbles and surface imperfections. Dissolved CO₂ was measured from the intensities of the absorption bands at 1515 and 2350 cm⁻¹. These bands correspond respectively to antisymmetric

stretching vibration of distorted carbonate groups and molecular CO₂ (e.g. [Fine & Stolper, 1986](#); [Dixon *et al.*, 1995](#)). The concentrations of total CO₂ were obtained by adding the concentrations of each carbon species. These were determined, for each band, using the Beer–Lambert law (e.g. [Fine & Stolper, 1986](#)). For baseline corrections, we subtracted the spectrum of a CO₂-free sample of the same glass. Sample thicknesses were measured using a micrometer and compared with measurements obtained by optical microscope in reflected light mode. Densities of the glasses were calcu-

lated using the model of [Lange & Carmichael \(1987\)](#). The molar absorptivity coefficient for the 1515 cm⁻¹ band, which depends strongly on glass composition, was estimated as 261 l mol⁻¹ cm⁻¹ using the Na/(Na + Ca) value following [Dixon & Pan \(1995\)](#). This method is more applicable to basaltic compositions, but the obtained value is in agreement with that used by [King *et al.* \(2002\)](#) for andesitic compositions. For the 2350 cm⁻¹ band, we used a coefficient value of 945 l mol⁻¹ cm⁻¹ determined for Na–Al–Si–O glasses ([Fine & Stolper, 1986](#)) and used for andesitic compositions ([King *et al.*, 2002](#)).