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Experimental Constraints on the Crystallization of Silica Phases in Silicic Magmas

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ABSTRACT

Low-pressure silica polymorphs, e.g. quartz (*Qtz*), tridymite (*Trd*), and cristobalite (*Crs*), are common in silicic magmas, but the conditions of their formation are still unclear. The stability fields of these polymorphs have been determined in the SiO₂, SiO₂-H₂O, and haplogranite systems, but these simple systems are not directly applicable to silica polymorph crystallization in natural silicic magmas. The present study compiles an experimental database of new and previously-published data documenting the crystallization of silica phases in natural silicic magmas and simple synthetic systems. Silica polymorphs are identified using Raman spectroscopy and their pressure-temperature domains of occurrence and chemical compositions are determined at pressures between 0.1 and 200 MPa, temperatures between 685 to 1200 °C, and under H₂O-saturated and H₂O-undersaturated conditions.

Qtz is the stable silica polymorph at pressures higher than 25-30 MPa, temperatures between ~700 and 950 °C, and occurs for a narrow range of melt SiO₂ contents (~79-81 wt%). Constraints on *Qtz* stability derived from simple systems are mutually compatible with, and thus applicable to natural compositions. This is consistent with *Qtz* compositions being close to 'pure' SiO₂, both in experiments and nature. In volcanic systems, *Qtz* crystallization may occur in magmatic reservoirs and deep volcanic conduits.

Trd did not crystallize in the experiments conducted as part of this study despite several experiments having been performed in the *Trd* stability field. This is consistent with results from the literature which show that *Trd* crystallization is kinetically inhibited in particular relative to *Crs*. Natural *Trd* have compositions deviating substantially from 'pure' SiO₂, so that stability limits determined in simple systems should not be applied directly to natural cases.

Crs was encountered at pressures below 20-30 MPa (or H₂O contents < ~1.5 wt%), from subsolidus (~800 °C) to near-liquidus (up to 1040 °C), and coexisting with melts having a large range of SiO₂ contents (70-81 wt%). The *Crs* stability field is much larger in natural magmas compared to pure SiO₂ systems. *Crs* is a metastable phase stabilized by components (Al, Na, K; about 3 wt%) present in the silicic melt. In volcanic systems, *Crs* crystallization may thus be restricted to subsurface manifestations such as lava domes.

Key words: silica polymorph; silicic magma; crystallization; metastability; eruptive dynamics

INTRODUCTION

Volcanic products with bulk SiO₂ contents higher than about 60 wt% (i.e. from andesites to rhyolites) often contain low-pressure silica polymorphs, such as *Qtz*, *Crs*, and *Trd*. After the report of *Crs* occurrence at Soufriere Hills, Montserrat (Baxter et al., 1999), there was warranted concern that the respiratory toxicity of *Crs* could cause a significant and previously unrecognized volcanic hazard. Yet, the studies that followed have largely concluded that impure volcanic *Crs* is not as bioreactive as pure *Crs*, and that the difficulty of dispersing significant volumes of pure SiO₂ does not in fact increase risk of pulmonary disease (e.g. Horwell et al., 2012; Damby et al., 2016; Natrass et al., 2017). Despite this, crystalline silica

may still play a major role in volcanic dome explosivity, by conceivably modifying magma viscosity and permeability and thus exacerbating the potential for explosive activity (e.g. [Horwell et al., 2013](#); [Boudon et al., 2015](#); [Kushnir et al., 2016](#)). Critically, the conditions for crystalline silica formation in magmas remain poorly constrained, to the detriment of our ability to assess risks associated to dome-related eruptions.

Occurrence and origin of silica polymorphs in volcanic products

Silica polymorphs are commonly encountered in all magmatic series. In this study, we focus on calc-alkaline magmas that feed active volcanoes at convergent plate margins, mainly because of the importance of the generated volcanic risks. *Qtz* is common in volcanic pyroclasts, such as those from the 1997 andesite at Soufriere Hills, Montserrat ([Devine et al., 1998](#)), the 1991 dacite at Mount Pinatubo, Philippines ([Rutherford & Devine, 1996](#)), the 1991-1995 dacite at Unzen, Japan ([Nakada & Motomura, 1999](#)), and the rhyolitic tuffs at Toba ([Chesner, 1998](#)), to name a few representative examples. *Crs* has been reported in numerous andesitic to rhyolitic dome products, including those at Montagne Pelée, Martinique ([Martel et al., 2000](#); [Boudon et al., 2015](#)), Merapi, Indonesia ([Damby et al., 2013](#); [Kushnir et al., 2016](#)), and the 2011-2012 rhyolitic lava flow at Cordón Caulle, Chile ([Schipper et al., 2015](#)). *Qtz* and *Crs* may coexist, for example in obsidian domes, including the Inyo domes, California ([Swanson et al., 1989](#)) and Chañten, Chile ([Horwell et al., 2010](#)). *Trd* has been more rarely reported, but has been found in dacites from Montagne Pelée ([Westercamp, 1975](#)) and Mount Saint Helens, USA ([Pevear et al., 1982](#); [Blundy & Cashman, 2001](#); [Pallister et al., 2008](#)), where it coexists with *Qtz* and *Crs*. From observations of natural samples, *Crs* is common in silicic lava domes and flows, *Qtz* is often present in pyroclasts from explosive eruptions, and *Trd* is rare.

In volcanic samples, silica polymorphs show different habits, which have been attributed to different mechanisms of formation. *Qtz* and *Trd* commonly appear as prismatic crystals ([Fig. 1A-B](#)), suggesting primary formation from a melt. *Crs* in volcanic samples commonly shows several habits (e.g. [Ivanova et al., 2018](#)). Firstly, *Crs* can appear as prismatic crystals ([Fig. 1D](#)), suggesting a primary phase grown from a melt ([Martel, 2012](#); [Schipper et al., 2015](#); [Kushnir et al., 2016](#)). Secondly, *Crs* can show ‘fish-scale’ cracking textures, with crystals mostly confined to the pore space ([Fig. 1C](#)), which have been interpreted to form by vapor-phase deposition ([Baxter et al., 1999](#); [de Hoog et al., 2005](#); [Reich et al., 2009](#); [Horwell et al.,](#)

2013, Schipper et al., 2017, 2020). Thirdly, *Crs* can show ‘feather’ textures, characterized by a multitude of indistinguishable crystals (Fig. 1C), which have been attributed to devitrification of volcanic glass (Horwell et al., 2013). The two latter types of *Crs* may account for the high *Crs* amounts (several tens of wt%) in lava or dome samples (Schipper et al., 2015). This short overview emphasizes the large diversity of *Crs* textures and origins in volcanic products, implying different effects on dome explosivity. Indeed, vapour-phase *Crs* can occlude pores to reduce permeability, whereas melt-grown *Crs* affects bulk viscosity; both have the potential to increase magma explosivity, but represent very different formation mechanisms.

Stability of silica polymorphs

Under ambient pressure (P), the stable silica phase in the pure SiO_2 system are: α -*Qtz* at temperatures (T) from 0 to 573 °C, β -*Qtz* from 573 to 870 °C, *Trd* from 870 to 1470 °C, and *Crs* from 1470 to 1705 °C (Heaney, 1994 and references therein; Fig. 2A). Increasing P leads to the disappearance of *Trd* at ~300 MPa and then of *Crs* at ~600 MPa, in favour of β -*Qtz*, itself replaced by coesite and stishovite at higher P (e.g. Swamy et al., 1994). Stable polymorphs appearing on the liquidus of a pure SiO_2 melt are *Crs* below ~600 MPa and β -*Qtz* above this P (Boettcher, 1984; Heaney, 1994; Swamy et al., 1994; Fig. 2A). Upon addition of H_2O , liquidus T are significantly reduced. When P is increased under H_2O -saturated conditions, *Crs*, *Trd* and β -*Qtz* appear successively as the stable polymorphs on the liquidus of the SiO_2 - H_2O system (Tuttle & England, 1955; Tuttle & Bowen, 1958; Boettcher, 1984; Fig. 2A). *Crs* is stable below ~30 MPa, *Trd* between 30 and ~150 MPa and β -*Qtz* above ~150 MPa. H_2O does not influence the P - T location of the *Qtz*-*Trd* boundary (Tuttle & England, 1955; Tuttle & Bowen, 1958).

In more complex synthetic silicic systems such as the haplogranite ($\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 - SiO_2 - H_2O) system, the three polymorphs *Crs*, *Trd* and β -*Qtz* can crystallize as stable phases at constrained liquidus T and melt compositions (Tuttle & Bowen, 1958). The main stable polymorph on the SiO_2 -rich ternary liquidus surface under dry/ambient P conditions and at $P \leq 25$ -30 MPa in H_2O -saturated systems, is *Trd*. In these systems, *Crs* and β -*Qtz* are respectively confined to the high T / high SiO_2 corner and low T near-minimum region of the ternary system (Fig. 2B). Upon increasing P under H_2O -saturated conditions, liquidus T

markedly decrease and both *Crs* and *Trd* are progressively replaced by β -*Qtz*. *Trd* is totally eliminated from the liquidus surface between 100 and 150 MPa (Fig. 2B), consistent with the *P-T* location of the *Qtz-Trd* inversion in the SiO₂-H₂O system (Fig. 2A), and β -*Qtz* becomes the sole silica polymorph on the H₂O-saturated liquidus up to at least 1000 MPa (Tuttle & Bowen, 1958; Luth et al., 1964).

Chemistry of the silica polymorphs

In simple systems, silica polymorphs are implicitly assumed to have compositions near pure SiO₂ (no solid solution) which implies that, in principle, their stability fields extend unchanged in natural magmas. However, the validity of this proposition depends on how close to 100 wt% SiO₂ the compositions of silica polymorphs are in both experiments and nature. *Qtz* seems to fulfil this condition, although we note that phase compositions were not determined by electron microprobe in early studies (e.g. Tuttle & Bowen, 1958). In contrast, experimentally grown *Trd* and *Crs* incorporate high concentrations of ‘impurities’ i.e. cations other than Si (Holmquist, 1961; Roy & Roy, 1964; Dapiaggi et al., 2015). This is consistent with *Crs* in volcanic products having > 1 wt% Al₂O₃ (up to ~3 wt%) and significant alkali (especially Na₂O) contents (Pallister et al., 2008; Horwell et al., 2012; Schipper et al., 2015, 2020; Ivanova et al., 2018), whereas *Qtz* generally hosts < 1 wt% Al₂O₃ (Pallister et al., 2008; Horwell et al., 2012; Breiter et al., 2012). For *Trd*, the available data (Pallister et al., 2008) indicate the presence of Al₂O₃ and Na₂O in smaller concentrations than in *Crs* but in greater concentrations compared to *Qtz*. It appears that both *Trd* and *Crs* deviate substantially from 100 wt% SiO₂, so that stabilities of *Trd* and *Crs* determined in simple systems (where they are assumed to be pure SiO₂) cannot be applied directly to natural magmas. Conditions of *Trd* and *Crs* crystallization thus remain to be investigated in complex systems using appropriate methods (e.g. Raman spectroscopy) for the identification of silica polymorphs in experimental charges.

Scope of the study

Based on phase equilibrium results in simple systems (i.e. SiO₂, SiO₂-H₂O, haplogranite), silica polymorphs expected to crystallize under common *P-T* volcanic conditions ($P < 200$ MPa and $700 < T < 1100$ °C) would be *Qtz* and *Trd* (Fig. 2). *Crs* would be expected to be

totally absent given the ‘low’ T range above. Yet, in natural products, *Qtz* and *Crs* are commonly observed whereas *Trd* is rare. To explain this contrast between experimental and natural observations, the basic thesis developed in this paper is that simple systems provide only a simplified framework for the crystallization of silica phases.

In this study, an experimental database documenting the crystallization of silica phases in natural silicic magmas and simple synthetic systems is detailed. To do this, we have compiled previously published data, as well as conducted a suite of experiments. The data constrain the P - T domains of occurrence of silica polymorphs (identified using Raman spectroscopy) and their chemical compositions. Mechanisms of crystallization are discussed and the importance of kinetic factors is emphasized. Results provide a framework to use silica polymorphs as indicators of eruptive processes and conditions in volcanic systems.

EXPERIMENTAL AND ANALYTICAL METHODS

Samples and experimental conditions

We use data from seven series of crystallization experiments. These natural and synthetic series have starting melt compositions ≥ 70 wt% SiO_2 , and are dominated by four components: quartz, albite, anorthite and orthoclase. Their compositions are reported in [Tab. 1](#).

The series reported in the literature include bulk rhyolitic magmas from Cordón Caulle (CC; [Castro et al., 2013](#) and J.M. Castro, pers. comm.) and Chaíten (CHAI; [Castro & Dingwell, 2009](#)), both volcanoes from Chile. The low bulk SiO_2 (~70 wt%) of the CC rhyolite distinguishes this sample from the others that contain 75-77 wt% SiO_2 . Rhyolitic glasses from Montagne Pelée, Martinique (PEL; [Martel & Poussineau, 2007](#); [Martel, 2012](#)) and Soufriere Hills, Montserrat (SH2; [Martel & Schmidt, 2003](#)) are representative of interstitial melts in equilibrium with phenocrysts in the two respective bulk andesitic magmas ([Martel et al., 1998](#); [1999](#); [Barclay et al., 1998](#)). Simple synthetic systems include one haplogranite (HPG; Si, Al, Na, K). The HPG system simulates near cotectic silica-feldspar crystallization from evolved liquids enriched in K_2O . The SiO_2 content of the HPG (76.7 wt%, [Devineau et al., 2020](#)) is similar to natural rhyolites. We also include results in the haplogranite system ([Tuttle](#)

& Bowen, 1958), in particular the data on the ternary minima (hereafter noted HPG_m to distinguish it from the HPG composition).

The new experiments concern 3 experiments to complete the PEL series at $P < 50$ MPa and $900 < T < 1000$ °C, as well as 43 experiments starting with one haplotonalite (HTN; Si, Al, Na, Ca). The HTN system models the behaviour of low-K₂O silicic liquids crystallizing plagioclase before *Qtz* and K-feldspar, a common case in orogenic intermediate magmas (e.g. Martel et al., 1999; Scaillet & Evans, 1999; Pichavant et al., 2018). It contains 76.7 wt% SiO₂, a content identical to HPG, and 13 wt% normative anorthite, similar to those of PEL and SH2.

A total of 126, including 46 new, experimental charges from these seven series have been used and the nature of the crystalline silica phase, when present, has been systematically determined by Raman spectroscopy. The experimental and analytical methods for the new experiments are detailed in SM1; the methods employed for the other series are available in the literature (for references see Tab. 1). The P - T conditions and melt H₂O contents for all experiments are summarized in Tab. 2. Most charges are products of crystallization of a crystal-free melt under constant P - T conditions, but two result from isothermal instantaneous decompression of an initially crystal-free melt (D5 and D6, both for PEL composition) followed by crystallization at a constant final P . About half of the samples were initially saturated with H₂O. Among the other half, most residual glasses are H₂O saturated.

Raman spectroscopy

The presence of crystalline silica was first checked by scanning electron microscopy (SEM; Merlin Compact Zeiss, ISTO, Orléans, France), in all but HPG_m experimental charges. The nature of the silica phase was determined in 35 experimental charges by Raman spectroscopy, using either a Renishaw InVia spectrometer at a wavelength of 514 nm and a maximum power of 100 mW (BRGM-ISTO, Orléans, France) or a Horiba-Yvon Labram-HR Raman microscope operating in conjunction with a solid-state laser at a wavelength of 532 nm and maximum power of 200 mW (Mainz University, Mainz, Germany). Two samples were analyzed using a SEM-coupled Raman spectrometer that allows Raman imaging. Coupled SEM observations and Raman imaging were performed on a Zeiss-WITec RISE microscope combining a ZEISS Gemini SEM 300 LV-FE-SEM to a WITec confocal Raman imaging system (WITec, Ulm, Germany) (Wille et al., 2018). The RISE confocal Raman imaging

system is equipped with a UHTS300 spectrometer, a Zeiss 100x vacuum objective (Numerical Aperture 0.75) mounted inside the SEM chamber, using a 532 nm laser radiation wavelength. Coupled SEM-EDS (energy-dispersive spectrometer) and Raman imaging were performed on non-coated samples at HV = 15 kV under nitrogen pressure of 20 Pa (Cergy Paris University, Neuville/Oise, France). Raman spectra of selected samples are shown in [Fig 3](#).

Chemical analyses

The experimental and natural samples were examined using a scanning electron microscope (MIRA3 TESCAN at ISTO), in order to identify silica crystals favourable for chemical analysis using an electron microprobe (EMP; Cameca SX Five at ISTO). Alkalis were analysed first to minimize their migration under the electron beam. The EMP conditions were set to an acceleration voltage of 15 kV, a beam current of 6 nA, and peak/background counting times of 10/5 s for all elements. Under these conditions, the detection limits are of the order of 900 ppm for Si and K, about 400 ppm for Al, Na, and Ca, and of 1200-2000 ppm for Fe and Ti. The analytical errors on major elements were calculated at ~1% (relative) for SiO₂, Al₂O₃ and CaO, and 5% for Na₂O. [Schipper et al. \(2020\)](#) reported Na migration under the electron beam during cristobalite analyses, as such, we have tested the effect of defocusing the beam under the above conditions. We did not observe differences in Na content between the focused (spot size of 1 μm) and defocused (10x10 μm) beam. This suggests that by analysing Na first, using a low current (e.g. 6 nA), and low peak/background counting times (e.g. 10/5 s), we may reasonably prevent sodium loss during analysis of crystalline silica.

RESULTS

The new haplotonalite (HTN) series

In the new HTN series, plagioclase and *Qtz* were the only mineral phases to crystallize at 200 MPa ([SM2A](#)). Plagioclase is the liquidus phase from about 900 °C under H₂O saturation (~7.0

wt% H₂O) to ~1200 °C under strongly H₂O-undersaturated conditions (0-1 wt% H₂O in the melt). It is followed by *Qtz* in the crystallization sequence and the *Qtz*-plagioclase cotectic runs more or less parallel to the liquidus, being shifted by about 100 °C towards lower *T* for a given melt H₂O content (SM2B).

The melt composition ranges from 76.7 to 77.2 wt% SiO₂ for charges close to the liquidus (SM3, vs. 76.7 wt% SiO₂ in the starting glass; Tab. 1). The SiO₂ content of the melt increases with progressive crystallization, reaching 79.9 to 81.4 wt% along the *Qtz*-plagioclase cotectic (SM3). The near-liquidus plagioclase has a composition of ~An₄₈ (SM2B and SM3). On the cotectic curve, *Qtz* coexists with about 20 vol% of ~An₃₀ plagioclase (SM2B).

Liquidus relations and phases

The H₂O-saturated liquidus relations for the investigated compositions are illustrated in Fig. 4A. For PEL, SH2, CHAI, and CC, the data enable liquidus curves to be constructed at different *P*. Liquidus curves for the three 75-77 wt% SiO₂ rhyolites run close to each other, from 800-850 °C at 200 MPa to ~950-1000 °C at 50 MPa. A marked shift towards higher liquidus *T* is observed at *P* < 50 MPa for the PEL composition (e.g. ~1075 °C at 25 MPa, see also Hammer & Rutherford, 2002; Castro & Dingwell, 2009; Martel, 2012). In contrast, the liquidus *T* of the 70 wt% SiO₂ CC rhyolite lies above 925 °C at 200 MPa and between 950 and 975 °C at 50 MPa (Castro et al., 2013), distinctly higher than the range for the three 75-77 wt% SiO₂ rhyolites at 200 MPa. The CC liquidus is also much steeper than the PEL, SH2, and CHAI curves. HPG has a liquidus *T* of ~720 °C at 200 MPa (Devineau et al., 2020), i.e. lower by > 100 °C than liquidus *T* for the other series and consistent with its composition close to the 200 MPa haplogranite minimum (HPG_m). For the HTN series, the 200 MPa H₂O-saturated liquidus *T* is ~875 °C (SM2B).

Liquidus phases for the natural rhyolites are either feldspar, pyroxene or Fe-Ti oxides (Martel et al., 1999; Castro & Dingwell, 2009; Martel & Schmidt, 2003; Martel, 2012; Castro et al., 2013). None of the rhyolites investigated here has a silica polymorph on the liquidus. The two simple synthetic compositions both have feldspar on their liquidus: plagioclase for HTN (SM2B) and K-feldspar for HPG (Devineau et al., 2020).

Silica polymorphs

Quartz. Experiments where *Qtz* saturation is reported are compiled in [Tab. 2](#). *Qtz* largely dominates our experimental database and mostly appears as <50 μm prismatic crystals ([Fig. 5A](#); [SM2A](#)). The *Qtz* saturation curves are shown in [Fig. 4B](#) for the different starting compositions. At 200 MPa under H_2O -saturated conditions, *Qtz* saturates at ~ 780 $^\circ\text{C}$ in HTN ([SM2B](#)). Under the same conditions in HPG, *Qtz* crystallizes at ~ 690 $^\circ\text{C}$ ([Devineau et al., 2020](#)). In the H_2O -saturated haplogranite ternary minimum (HPG_m), *Qtz* crystallizes at 685 $^\circ\text{C}$ at 200 MPa, 720 $^\circ\text{C}$ at 100 MPa, and 770 $^\circ\text{C}$ at 50 MPa ([Tuttle & Bowen, 1958](#); [Fig. 2](#)). It is worth recalling that the ternary minimum defines the conditions of co-saturation of a silica phase with an alkali feldspar on the liquidus. Thus, under H_2O -saturated conditions for a given P in the haplogranite system, the saturation T of *Qtz* (or another silica polymorph) cannot be lower than the ternary minimum T . For PEL, SH2 and CHAI, no *Qtz* saturation data are available at 200 MPa. Under H_2O -saturated conditions, the *Qtz* saturation curve in PEL extends from 800-850 $^\circ\text{C}$ at 100 MPa to 925 $^\circ\text{C}$ at 50 MPa ([Martel, 2012](#); [Fig. 4B](#)). In CHAI, the *Qtz* saturation curve extends from ~ 775 $^\circ\text{C}$ at 100 MPa to 800-825 $^\circ\text{C}$ at 50 MPa ([Castro & Dingwell, 2009](#); [Fig. 4B](#)). In CC, *Qtz* did not saturate under the experimental conditions investigated ([Castro et al., 2013](#)).

The 200 MPa experiments on HTN and HPG constrain the effect of H_2O on silica polymorph formation. *Qtz* is the only silica polymorph that crystallized in the H_2O -undersaturated charges ([Tab. 2](#)), thus lowering the melt H_2O content has no influence on the nature of the SiO_2 phase in the investigated P - T range. Yet, *Qtz* saturation is progressively shifted toward higher T for a given P . For HTN, *Qtz* saturation occurs at ~ 1050 $^\circ\text{C}$ for 0-1 wt% H_2O (vs. ~ 780 $^\circ\text{C}$ for 7 wt% H_2O ; [SM2B](#)). For HPG, *Qtz* saturates at 750 $^\circ\text{C}$ for 5.0 wt% H_2O), as opposed to 690 $^\circ\text{C}$ for 6.2 wt% H_2O ([Devineau et al., 2020](#)).

Tridymite. None of the natural or experimental compositions investigated in this study crystallized *Trd*.

Cristobalite. The experimental charges that contain *Crs* are reported in [Tab. 2](#). *Crs* mostly appears as <10 μm prismatic crystals ([Fig. 3B](#), [5B](#)), in agreement with primary crystallization from the melt. Yet, in charges with large amounts of excess H_2O vapour (several wt% above solubility), the prismatic crystals coexist with larger ‘fish-scale’ patches ([Fig. 5C](#)). Interestingly, ‘fish-scale’ *Crs* was not observed in the absence of prismatic crystals. Co-crystallization of *Qtz* and *Crs* was observed in one experimental charge, constraining the *Qtz*-

Crs boundary at around 925 °C and 25 MPa in the PEL composition (Fig. 4C). *Qtz* in that charge appears as ~50 µm spongy patches likely reflecting disequilibrium textures. *Crs* is found between 850 °C and 1040 °C and restricted to H₂O-saturated *P* below 30 MPa (Fig. 4C). There are small differences in *Crs* occurrence between the rhyolites: *Crs* crystallizes between 25 and 50 MPa in SH2 (at 860 °C), between 10 and 25 MPa in PEL (at 850 °C), and between 3 and 20 MPa in CC (at 860-900 °C). *Crs* also crystallizes in PEL between 25 and 30-40 MPa at 1040 °C, i.e. near the liquidus (Fig. 4A), although its identification in the 25 MPa charge could not be confirmed by Raman spectroscopy due to the small size of the crystals.

Composition of the silica polymorphs

New electron microprobe analyses of experimental and natural *Qtz* and *Crs* have been reported in Tab. 3. In the simple HPG system (run 33-4c from Devineau et al., 2020), *Qtz* is almost pure SiO₂, showing only about 0.2 wt% of other components, mainly Al₂O₃ (0.12 ± 0.08 wt%), which is consistent with the <0.1 wt% impurities in *Qtz* of the natural samples of Soufrière of Guadeloupe. Yet, the HTN system and the PEL rhyolite both show up to 0.9 wt% impurities including about 0.6 wt% Al₂O₃, which likely reflect analyses of crystals smaller than the microprobe beam size and which are therefore contaminated by glass. In contrast, *Crs* crystallized in the PEL composition contains about 3 wt% of components other than SiO₂, mainly Al₂O₃ (2 wt%) and alkalis (1 wt%), in agreement with the *Crs* compositions in its natural volcanic counterpart. *Trd* was not observed in the experiments of this study, but analyses of natural *Trd* from Bezymianny 2017 lava flows show about 1.3 wt% impurities consisting of ~1 wt% Al₂O₃ and 0.3 wt% Na₂O (V.O. Davydova, pers. comm.), confirming impurity contents in *Trd* between those in *Qtz* and *Crs*.

Melt compositions

The melt compositions are given in SM3 for HTN and in SM4 for the new PEL experiments and new analyses of CC and CHAI samples. For the other series, the glass compositions are given in the literature (see Tab. 2 for references). SiO₂ concentrations of low *P* (≤ 100 MPa) H₂O-saturated melts are plotted as a function of either H₂O content or *P* in Fig. 6. A distinction is drawn between charges with *Qtz*, with *Crs*, and without silica phase. The data

define conditions of *Qtz* saturation in the melt when either H₂O content or *P* is varied from ~100 MPa down to ~20 MPa. The resulting saturation curve has a negative slope and extends from ~78-79 wt% SiO₂ at ~4 wt% H₂O to ~79-80 wt% SiO₂ at ~1.5 wt% H₂O. The *Crs*-bearing charges are confined to below ~2 wt% H₂O (or below ~25 MPa). Remarkably, *Crs* crystallizes over a large range of glass SiO₂ contents, from 72 to 81 wt%, i.e. from within the region saturated with respect to either *Qtz* or *Trd* to the silica-undersaturated region. *Crs* is often the sole silica phase present as in PEL (~76.5 wt% SiO₂) and in CC (72-73 wt% SiO₂). As a subliquidus phase, *Crs* crystallizes in melts from ~77 to ~81 wt% SiO₂. The horizontal *Qtz*-*Crs* boundary (Fig. 6) emphasizes that the transition from a *Qtz*- to a *Crs*-bearing assemblage is not controlled by the SiO₂ content of the melt.

DISCUSSION

The applicability of silica phase crystallization in simple systems to that in natural magmas

Quartz. In our database limited to *P* up to 200 MPa and *T* > 680 °C, *Qtz* saturation in the rhyolite experiments is observed in a relatively narrow *P* range: from 25 to 100 MPa under H₂O-saturated conditions. In the HPG and HTN systems, *Qtz* is present at 200 MPa (Tab. 2; Fig. 4B). Previous studies on haplogranitic melts have reported *Qtz* crystallization up to 800-1000 MPa (Luth et al., 1964; Holtz et al., 2001) and in excess of ~1000 MPa in natural silicic melts (e.g. Stern & Wyllie, 1981; Conrad et al., 1988; Prouteau & Scaillet, 2003). Concerning *T*, *Qtz* saturation is observed between 750 and 925 °C in the studied rhyolites, extending to between 690 and 1050 °C in the HPG and HTN systems. Previous studies of the haplogranite system have reported *Qtz* to be present from approximately 650 °C (Luth et al., 1964) to 1200 °C (Holtz et al., 2001), thus encompassing (and even expanding) the volcanic *T* range considered here. For natural magmas, maximum *T* of 900-950 °C have been found previously for *Qtz* crystallization in a rhyolite (Conrad et al., 1988) and a dacite (Prouteau & Scaillet, 2003), overlapping with the *T* range found for the rhyolites contained in the present database (Tab. 2). *Qtz* has been reported to crystallize at higher *T* (up to 1100-1200 °C) at 0.1 MPa in several natural and synthetic rhyolites (Brugger et al., 2003). However, the identification of the silica phase as *Qtz* was not confirmed by unequivocal methods such as Raman

spectroscopy in most of these studies (e.g. Conrad et al., 1988; Brugger et al., 2003). Overall, what emerges is the wide range of P - T conditions appropriate for Qtz crystallization in silicic melts. Most importantly, the Qtz saturation conditions deduced from simple systems are consistent with those from natural compositions (Fig. 4B). There is also general agreement between SiO_2 melt compositions at Qtz saturation for the three natural rhyolites and for the haplogranite system. In comparison, for the HTN composition, Qtz saturation occurs for melt SiO_2 concentrations higher by ~1 wt% than in the other charges (Fig. 6), consistent with the respective positions of eutectics in the Qtz -albite and Qtz -anorthite systems (Tuttle & Bowen, 1958; Stewart, 1967; Boettcher et al., 1984). Thus, the location of the Qtz saturation curve in Fig. 6 is weakly dependent on the melt composition. Therefore, for the prediction of Qtz occurrences, experimental results in simple systems are appropriate and applicable to natural magmas. This conclusion is consistent with the observation that Qtz chemistries are close to pure SiO_2 , both in experiments and nature (Tab. 3 and see above).

Tridymite. The lack of Trd in our experiments is attributed primarily to P - T conditions being mostly outside the Trd stability field. For example, at 200 MPa, the HTN charge at 1000 °C (the hottest where Qtz saturation is reported, SM2B; 1000_1.0, Tab. 2) is ~250 °C lower than the temperature of the Qtz - Trd inversion at this P (Fig. 2A). Also, in natural rhyolites, Trd should form in SiO_2 -saturated melts at $T > 870$ °C, in agreement with the minimum T needed for Trd to crystallize as the stable polymorph (Fig. 2A). For example, the CC charge at 900 °C and 3 MPa (Puy#3, Tab. 2) and the PEL charges at 1040 °C, 25 and 10 MPa (VM250 and VM100, respectively, Tab. 2) have melt SiO_2 contents far from the saturation curve shown in Fig. 6, thus explaining why they did not crystallize Trd . Among the SiO_2 -saturated experiments above 870 °C, the PEL charge at 925 °C and 50 MPa (925PEL50, Tab. 2) is very close to the Qtz - Trd boundary but still within the Qtz stability field for this P (Fig. 2A). The only charge that meets the SiO_2 -saturation and T conditions to crystallize stable Trd , i.e. the PEL charge at 925 °C and 25 MPa (925PEL25, Tab. 2), does not contain Trd . In simple systems, Trd was present only in some SiO_2 -alkali systems at 0.1 MPa (Hirschmann et al., 2008), and upon melting of a Qtz -anorthite mixture at 1040 °C, 100 MPa and under H_2O -saturated conditions (Stewart, 1967), which is a rare case of Trd being present at $P > 0.1$ MPa. Thus, to date, Trd has not been experimentally crystallized from haplogranitic melts nor from natural silicic magma compositions; from this point of view, the PEL charge 925PEL25 (Tab. 2) is no exception. Although Trd was apparently ‘encountered in some experiments’ (Tuttle & Bowen, 1958, p. 28), its quasi absence in the volcanologically relevant near-minimum region

of the haplogranite system can be understood by noting that experimental data are available either at 0.1 MPa (where crystallization of near-minimum melts is nearly impossible; Schairer, 1950; Schairer & Bowen, 1935; 1947a; 1955; 1956) or at 50 MPa under H₂O-saturated conditions (where the liquidus phase is *Qtz*; Tuttle & Bowen, 1958). We conclude that experimental constraints on conditions of *Trd* crystallization in simple systems remain theoretical only and are still absent in natural magmas.

Cristobalite. The appearance of *Crs* is restricted to the rhyolite experiments (Tab. 2; Fig. 4C), which suggests that the conditions for *Crs* crystallization from hydrated simple melts were not met in the studied range of conditions. In simple systems, however, *Crs* readily crystallizes in binary SiO₂-alkali (Kracek et al., 1937) and in ternary systems such as Na₂O-Al₂O₃-SiO₂ and K₂O-Al₂O₃-SiO₂ (Schairer & Bowen, 1947a; 1955; 1956), occurring both above and below 1470 °C (the *Crs-Trd* inversion *T* at 0.1 MPa; Fig. 2A), that is to say, as a stable and a metastable phase. *Crs* has been grown at high *T* (1200-1600 °C) and 0.1 MPa from highly silicic (> 80-90 wt% SiO₂) haplogranitic compositions (Schairer, 1950; Schairer & Bowen, 1935; 1955; 1956). Therefore, the *Crs*-bearing charges in our database have counterparts in simple systems, but at *T* (> 1000 °C) and melt compositions (very SiO₂-rich and H₂O-free) remote from natural conditions. For natural silicic magmas, no other *Crs*-bearing charges than those listed in Tab. 2 apparently exist in the literature. Chemistries of *Crs* crystallized in the haplogranite system are unknown but *Crs* in the PEL rhyolite shows significant amounts of Al₂O₃, Na₂O and K₂O (Tab. 3), indicating deviation from pure SiO₂. We conclude that experimental constraints in simple systems are difficult to use to predict *Crs* occurrence in nature and that results in natural silicic magmas need more study to understand the significance of *Crs* in the experiments.

Stable versus metastable crystallization of the silica phases

There are three charges in which *Qtz* occurs outside of its theoretical stability field. The first case is the 925 °C, 25 MPa charge (925PEL25, Tab. 2) where *Qtz*, coexisting with *Crs*, is present above its theoretical stability limit (see Roy & Roy, 1964; Venezia et al., 2001 for similar cases). The *Qtz* in this charge displays a ‘spongy’ texture that likely suggests disequilibrium crystallization. The two other cases are the H₂O-poor 850 °C PEL experiments at ≤ 10 MPa where *Qtz* failed to crystallize and *Crs* is present (Tab. 2; Fig. 4C). Yet, apart from these exceptions, the experimental phase compositions are chemically homogeneous and

follow consistent trends (e.g. melt SiO₂ content at silica saturation as a function of P ; Fig. 6), generally suggesting near-equilibrium in *Qtz*-bearing charges.

Primary *Crs* grown from the melt was found from 850 to 1040 °C, that is to say in a T range more than 400 °C cooler than the lower stability limit for *Crs* at 0.1 MPa (1470 °C; Fig. 2A). This is consistent with findings in many silicate systems where *Crs* may crystallize and persist metastably for long periods of time at T within the stability range of *Trd* (e.g. Schairer & Bowen, 1947b). *Crs* also crystallized instead of *Qtz* in the two 850 °C PEL experiments at and below 10 MPa (Tab. 2; Fig. 4C). *Crs* is found for a large range of glass SiO₂ content, from 72 to 81 wt%. *Crs* coexists in some CC and PEL charges with melts having SiO₂ contents several wt% lower than SiO₂ saturation (Fig. 6). Thus, the appearance of *Crs* is not controlled by the SiO₂ content of the melt, which makes *Crs* an unreliable indicator of SiO₂ saturation, unlike *Qtz* (Fig. 6). The fact that, in our database, *Crs* occurrences are restricted to the low P region (Fig. 4C) suggests that the appearance of *Crs* is favoured when reaction rates become more sluggish as melt H₂O content decreases and viscosity increases. *Crs* is indeed ubiquitous for H₂O contents below about 1.5 wt% (Fig. 6), although not present in H₂O-undersaturated charges (e.g. absent in the 200-MPa HTN charge at 1200 °C with a melt H₂O content of 1.1 wt%; 1200_1.0, Tab. 2), suggesting that H₂O saturation is a prerequisite for *Crs* appearance. Also, the *Crs*-bearing PEL charge that is at H₂O saturation and contains no excess H₂O vapour (VM100, Tab. 2; Fig. 3B), indicates that a vapor phase in excess is not necessary for *Crs* crystallization from the melt. Yet, when the amount of free vapour H₂O is high enough, the primary prismatic *Crs* coexists with ‘fish-scale’ *Crs* mineralized from the vapour phase in gas bubbles (e.g. PEL charges D5, Tab. 2; Fig. 5C). Chemistries of experimental *Crs* (Tab. 2) indicate significant deviations from the pure SiO₂ composition expected for a stable *Crs*. We conclude that (1) the T range of *Crs* occurrences, (2) the possible SiO₂-undersaturated nature of the coexisting melts and (3) the *Crs* compositions deviating from pure SiO₂, all suggest a mechanism of metastable crystallization for *Crs*.

Influence of reaction kinetics and melt composition on the silica phase crystallization

In simple systems, *Qtz* has a simple and dense structure, whereas *Crs* and *Trd* have more open structures. As such, the solid-state transformation from *Crs* to *Qtz* is energetically unfavourable because it involves a ‘reconstructive’ transformation, with the breaking up and reforming of the Si-O framework that demands high activation energy (e.g. Deer et al., 2004;

Lakshtanov et al., 2007). Inversions (e.g. transformations from *Qtz* to *Trd* and *Trd* to *Crs*) are also difficult because they are kinetically inhibited (Holmquist, 1961; Roy & Roy, 1964; Dapiaggi et al., 2015 and references therein). Crystallization of silica phases from amorphous materials (e.g. melts) can be either thermodynamically/kinetically inhibited or produce metastable assemblages. For example, neither *Trd* nor *Qtz* could be crystallized in and near the binary join albite-silica at 0.1 MPa, and *Crs* formed instead (Schaier & Bowen, 1947a; 1956). In the same way, in and near the binary join leucite-silica at 0.1 MPa, *Trd* did not appear and *Crs* formed (Schaier & Bowen, 1947a; b; 1955). In the simple systems above, however, these kinetic difficulties have been overcome, leading to equilibrium data on stabilities of the different silica polymorphs (Fig. 2). However, there is no requirement that equilibrium is established in volcanic systems (e.g. Pichavant et al., 2007). Therefore, the use of equilibrium results should be questioned.

In our experiments on rhyolitic melts, the charge (925PEL25, Tab. 2) that co-crystallized *Qtz* and *Crs* in the stability field of *Trd*, suggests that *Trd* crystallization was kinetically inhibited relative to *Qtz* and *Crs*. This situation has been encountered previously. For instance, *Crs* persists in the *Trd* domain to at least 150 °C lower than the stable *Trd-Crs* inversion (1470 °C) at 0.1 MPa and in the presence of NaAlSi₃O₈ and CaAl₂SiO₄ melts. Conversely, in presence of KAlSi₃O₈ melt, the *Trd* stability domain extends up to 1500 °C in the *Crs* domain (Roy & Roy, 1964). In binary alkali oxide-silica melts at 0.1 MPa, *Qtz* did not form whereas *Crs* was stabilized in the sodic composition and both *Trd* and *Crs* coexisted in the potassic composition at 800 °C (Venezia et al., 2001). It is worth pointing out that in the volcanologically relevant albite-silica and leucite-silica systems, *Trd* appeared as soon as ternary peralkaline (molar alkali concentration, either Na₂O or K₂O, > Al₂O₃ concentration) compositions were crystallized instead of the binary (Schaier & Bowen, 1947a; 1955; 1956). This demonstrates that, in addition to reaction kinetics, melt composition has an effect on the mechanism of *Trd* crystallization. In the ternary system anorthite-leucite-silica at 0.1 MPa, *Crs* also formed instead of *Trd* for compositions in the *Trd* stability field and persisted for ‘more than a month’ (Schaier & Bowen, 1947b), which provides an indication of the minimum timescales needed for the transformation of a *Crs* (metastable) to a *Trd* (stable) assemblage in this system.

In compositionally complex systems, the studies attempting to constrain the mutual relations between the different polymorphs agree that melt chemistry plays an important role in favouring one silica polymorph over the other. In general, the presence of *Crs* at ‘low’ *T*

outside its stability domain is attributed to the stabilizing influence of Na, K and Al in its crystal structure (Roy & Roy, 1964; Chao & Lu, 2002; Dappiagi et al., 2015; Liang et al., 2017; Schipper et al., 2020). In-situ investigations show that *Qtz*-alkali oxide mixtures reacted in the *Trd* stability field first crystallize *Crs* in greater proportions for the sodic than the potassic system. *Trd* then crystallizes second with an expanded cell volume and progressively replaces early *Crs* (Dappiagi et al., 2015). The contrasted stabilizing influences of alkali, i.e. Na stabilizing more *Crs* and K more *Trd*, can be understood in terms of the respective size of the stabilizing ion and of the cell in the structure of the silica polymorph (Holmquist, 1961; Venezia et al., 2001; Dappiagi et al., 2015). This chemical model, although very qualitative, is consistent with the stabilization of *Crs* in our experiments (Tab. 3), since the investigated rhyolites are sodic and contain relatively little K₂O and/or normative orthoclase (KAlSi₃O₈; Tab. 1). Therefore, the combination of low H₂O contents (high viscosity) and melts with ‘impurities’, such as natural rhyolitic melts, likely creates favourable conditions for the crystallization of metastable *Crs*. However, the stabilizing mechanism is complex and catalytic processes involving elements not substituted in the structure have been identified (e.g. V; Bruhn & Fischer, 2001).

Volcanological implications

The results from this study reveal a fundamental difference between occurrences of silica polymorphs in silicic magmas. *Qtz* is an indicator of near-equilibrium crystallization processes at various depths in volcanic plumbing systems, whereas *Crs* and *Trd* only record shallow crystallization processes in subsurface volcanic conduits and domes. Below, this difference is elaborated further and illustrated by natural examples.

All rhyolitic compositions investigated in this study lack a silica phase on their liquidus (Fig. 4A-B). This can be explained by the rhyolites having bulk SiO₂ concentrations (70-77 wt%; Tab. 1) lower than required for silica saturation at ≤ 100 MPa (Fig. 6). Other SiO₂-rich rhyolitic magmas, equilibrated at low *P* (e.g. Novarupta, 77.5 wt% SiO₂), show similar behaviour with plagioclase and Fe-Ti oxides as liquidus phases (Coombs & Gardner, 2001). In contrast, one of the synthetic compositions (78 wt% SiO₂) investigated by Brugger et al. (2003) has a silica phase (apparently *Qtz*, although not confirmed) on the liquidus at 0.1 MPa, a case which seems exceptional. Although rare on the liquidus, *Qtz* is a systematic sub-liquidus phase in the rhyolitic compositions investigated (Fig. 4B) and in examples from the

literature (Coombs & Gardner, 2001; Brugger et al., 2003), implying that *Qtz* can crystallize as a stable phenocryst in rhyolitic magmas for a wide range of *P-T* conditions and thus be used to record the pre-eruptive conditions in silicic magma storage zones (e.g. Breiter et al., 2012). This conclusion also applies in the case of less silicic intermediate arc magmas since *Qtz* is a late phase in experimental crystallization sequences of andesites to dacites (e.g. Barclay et al., 1998; Holtz et al., 2005; Scaillet & Evans, 1999). However, in such intermediate magma compositions, an advanced crystallization of the magma is necessary for *Qtz* to reach saturation in the residual melt.

In addition to constraining pre-eruptive conditions in magma storage zones, *Qtz* occurrences are useful indicators of melt evolution and *P-T* conditions during syn-eruptive magma ascent and degassing. Our experimental results show that *Qtz* saturation at $P \leq 100$ MPa requires silica-rich residual melts/groundmasses (~80 wt% SiO₂ recalculated on a volatile-free basis; Fig. 6). As a first illustration, the 1530 AD sub-Plinian eruption of La Soufrière of Guadeloupe produced pumices with *Qtz* microlites/microphenocrysts (Fig. 1A). Since *Qtz* is absent as a phenocryst in this magma (Pichavant et al., 2018), it likely crystallized during magma ascent from a residual melt having 79.2-80.2 wt% SiO₂ and 1.8-3.2 wt% H₂O (Pichavant et al., 2018) corresponding to *P* of 25-75 MPa (using the H₂O solubility model of Newman & Lowenstern, 2002). At 25-75 MPa and ~825 °C (the coldest pre-eruptive *T*; Pichavant et al., 2018), and for the residual glass SiO₂ and H₂O contents, *Qtz* is expected to crystallize (Figs 4B, 6), in agreement with the natural samples. A second example concerns the P1 and P2 Plinian eruptions of Montagne Pelée in La Martinique, which yielded silica-phase-free pumices hosting residual glasses with 73.4-76.7 wt% SiO₂ and 1.8-2.5 wt% H₂O (Martel & Poussineau, 2007), which corresponds to a *P* of 25-50 MPa (Newman & Lowenstern, 2002). Although at 25-50 MPa and 875 °C (pre-eruptive *T*, Martel et al., 1998), *Qtz* would be expected to crystallize (i.e. below the PEL curve in Fig. 4B), plotting the SiO₂ and H₂O contents of the residual glasses in Fig. 6 suggests that they are far away from *Qtz* saturation in the PEL experiments, and thus cannot crystallize *Qtz*. A third example concerns the 1902 and 1929 pyroclastic flows and surges at Montagne Pelée, which produced *Crs*-bearing clasts, showing both primary ('prismatic') and vapour-deposited ('fish-scale') crystals (Boudon et al., 2015; Fig. 1C-D). These occurred in residual glasses having 76.9 to 80.1 wt% SiO₂ and less than 1 wt% H₂O (Martel & Poussineau, 2007) and the glass H₂O contents suggest a *P* range below 10 MPa for a magma *T* of ~875 °C (Martel et al., 1998). Both, the *P-T* range and the glass SiO₂ and H₂O composition meet the conditions of *Crs* crystallization in

the PEL experiments (Fig. 4C, 6), which is confirmed by the natural samples. These three examples highlight that experimentally-determined constraints on silica phase saturation combined with natural sample data on P - T crystallization conditions and residual glass SiO_2 and H_2O contents may provide a useful framework for interpreting conduit crystallization processes and predicting silica phase occurrences in natural samples.

Overall, *Qtz* occurs at depths of magmatic reservoirs and volcanic conduits (i.e. > 25-30 MPa), whereas *Crs* typically crystallizes at shallower, subsurface conditions, such as in a lava dome, provided that the residence time is long enough to nucleate and grow the silica phase. For *Crs*, this residence time is ≥ 2 days (Mollard et al., 2012) and is confirmed by the run durations of the charges containing *Crs* (Tab. 2). In lava domes, extensive degassing- and cooling-induced crystallization of feldspar microlites drives the matrix towards increasing melt SiO_2 contents and vapour excess, which both foster conditions conducive to *Crs* formation. These conditions produce primary ‘prismatic’ crystals grown from the melt and ‘fish-scale’ crystals deposited from the vapour phase, respectively. If the magma resides long enough, ‘feathery’ *Crs* formation by glass devitrification can also occur. Concurrent microlite and *Crs* crystallization may generate gas overpressures capable of overcoming the strength of the magma, contributing to the mechanism proposed for the triggering of high-energy surges such as those of 1902 at Montagne Pelée (Martel, 2012).

The experiments suggest that two silica polymorphs do not coexist at equilibrium for given P - T conditions, so that in volcanic products, the presence of more than one silica polymorph may indicate distinct conditions of crystallization. For example, the rhyolitic pumices erupted during the Plinian event of May 2008 at Chañten contain 0.6-2.3 wt% *Qtz* (and traces of *Crs*), whereas the domes that followed the Plinian event contain 1.5-2.0 wt% *Qtz* and 14-19 wt% *Crs* (Horwell et al., 2010). Such a difference between proportions of *Qtz* and *Crs* in pyroclasts is quite systematic, with *Qtz* barely exceeding a few vol% (e.g. Luhr & Melson, 1996; Barclay et al., 1998; Damby et al., 2013) and *Crs* reaching up to 30 vol% in some dome samples (e.g. Baxter et al., 1999; Boudon et al., 2015; Kushnir et al., 2016). Our results suggest that *Qtz* could have crystallized at depth in the volcanic conduit during magma ascent, thus explaining its presence in both the Plinian and the dome samples. Fragmentation of the Plinian magma likely occurred at a P higher than the stability P of *Crs*, whereas the magma residing in dome

crystallized *Crs* in significant amounts, so that both silica polymorphs eventually coexisted in the dome samples.

From theoretical constraints (Fig. 2A), *Trd* should crystallize from SiO₂-saturated melts at low *P* (H₂O-poor) and hot conditions. Using the haplogranite system as a model, *Trd* would appear for ~80 wt% SiO₂ melts at < 25 MPa or < 1.5 wt% H₂O in the melt (Fig. 6) and above ~900 °C. These conditions are rarely encountered in arc volcanic systems, where an elevated SiO₂ concentration of the residual melt requires extensive magma crystallization at *T* < 900 °C for initially H₂O-rich magmas (Martel et al., 1999; Scaillet & Evans, 1999; Pichavant et al., 2018). Yet, one notable example of crystallization under the above conditions is provided by the dacites of the 1980-1986 dome of Mount Saint Helens. In these rocks, *Trd* is interpreted to replace *Qtz* as the silica saturating phase in the groundmass when *P* decreased below 11 MPa upon magma ascent, for a *T* estimated at ~900 °C (Blundy & Cashman, 2001). Another reason for the *Trd* rarity is that its crystallization is kinetically inhibited relative to *Crs* and *Qtz* (see section above). As an illustration, some andesite samples from the dome-related 2017 pyroclastic flows of Bezymianny, Kamchatka, contain *Crs* as the sole crystalline silica phase whereas others only contain *Trd* (Fig. 1B; Tab. 3). All samples have residual glasses with similar rhyolitic compositions (77-78 wt% SiO₂; V.O. Davydova, pers. comm.). Therefore, the growth environment was chemically the same for the two polymorphs and an influence of the type of stabilizing cations (i.e. Na versus K; see section above) is unlikely. One possible explanation is that the *Crs*-bearing and *Trd*-bearing samples resided for different durations and/or at different *T* in the dome before being erupted. Samples with either a longer residence time or a higher *T* could have transformed to the stable *Trd*-bearing assemblage whereas, in those with a shorter residence time or a lower *T* in the dome, the early metastable *Crs*-bearing assemblage persisted. This hypothesis, which remains to be tested further, stresses the potential of using *Crs* and *Trd* to constrain crystallization kinetics in lava domes.

CONCLUSIONS

From our compiled database that includes published and new experimental results, covering both synthetic and natural high-SiO₂ melts, we conclude that:

- Quartz (1) has near end-member composition in both experiments and nature, so that its stability limit determined in simple systems (e.g. SiO₂, SiO₂-H₂O, haplogranite) is applicable to natural silicic magmas; (2) occurs for a narrow range of melt SiO₂ content and is a reliable indicator of melt SiO₂ saturation; (3) is a stable phase in natural silicic magmas; and (4) is a useful indicator of relatively deep-seated crystallization processes, from magma storage zones to volcanic conduits.
- Cristobalite (1) crystallization is strongly enhanced in natural magmas compared to pure systems; (2) from experimental rhyolitic melts readily incorporates impurities (Al and alkalis), in agreement with natural magmatic *Crs* chemistries; (3) crystallizes in melts with a large range of SiO₂ content and is thus not a reliable indicator of silica saturation; (4) is a metastable phase in natural silicic magmas; and (5) preferentially forms at low-*P* (< 25 MPa) conditions typical of lava domes.
- Tridymite (1) was not observed in the investigated range of *P-T*-composition conditions, despite having experimental data from within its theoretical stability field; (2) has chemistries that deviate substantially from ‘pure’ SiO₂, so that its stability limit determined in simple systems should not be applied directly to natural cases; and (3) crystallization is kinetically inhibited relative to *Crs*, but there is agreement that *Trd* should form in SiO₂-saturated melts at > 900 °C and low *P*, such as in lava domes.

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Figure Caption

Figure 1. SEM pictures of silica phases in natural volcanic products. (A) ‘Prismatic’ *Qtz* in a pumice clast from the 1530 eruption of La Soufrière, Guadeloupe, F.W.I. (SG7B-1 sample in Pichavant et al., 2018); (B) ‘Prismatic’ *Trd* in a vesicular clast from the 2017 pyroclastic flows of Bezymianny, Kamchatka, Russia (VK18-5h-6 sample; V.O. Davydova, pers. comm.); (C) ‘Fish-scale’ and ‘feathery’ *Crs* in a dense clast from the 1902 August 30th surge of Montagne Pelée, Martinique, F.W.I. (MT36V15 sample in Martel & Poussineau, 2007), and (D) ‘Prismatic’ *Crs* in the 1902 dome of Montagne Pelée (MT34M sample in Martel & Poussineau, 2007). The black areas are pores and the white crystals are either orthopyroxenes or Fe-Ti oxides.

Figure 2. Stability of silica polymorphs in simple systems. (A) Pressure-temperature liquidus phase relations for three systems: pure SiO_2 (black solid and dashed lines; modified from Heaney, 1994), $\text{SiO}_2\text{-H}_2\text{O}$ (green solid and dashed lines; modified from Tuttle & Bowen, 1958), and haplogranite- H_2O (minimum compositions; red solid and dashed lines from Tuttle & Bowen, 1958, and Luth, 1976). For the $\text{SiO}_2\text{-H}_2\text{O}$ and haplogranite- H_2O systems, only H_2O -saturated relationships are considered. Stability domains for the different silica polymorphs in the three systems are labelled using the same color coding. (B) $\text{SiO}_2\text{-albite (Ab)-orthoclase (Or)}$ ternary diagram illustrating the change from *Trd* to *Qtz* as the stable silica polymorph on the liquidus in the haplogranite system at 0.1 and 100 MPa (Tuttle & Bowen, 1958); **m** represents minimum compositions; *Qtz*: quartz, *Crs*: cristobalite, *Trd*: tridymite.

Figure 3. Raman spectra characterizing crystalline silica using SEM-coupled Raman spectroscopy (‘RISE’ technique) in (A) HTN_950HTN1 and (B) PEL_VM100 (sample numbers as referred in Tab. 2). *Qtz*: quartz, *Crs*, cristobalite, *Fsp*: feldspath.

Figure 4. Silica polymorphs in natural rhyolitic melts and analogues (Tab. 1 for compositional details). (A) liquidus phase relations, (B) quartz saturation, and (C) quartz-cristobalite boundary. PEL (Montagne Pelée) in dark blue; SH2 (Soufriere Hills) in pink; CHAI (Chaïten) in brown; CC (Cordón Caulle) in light blue; HPG (haplogranite) in orange; HTN (haplotonalite) in green. The subscript numbers attached to the labels in (A) give the SiO_2 wt% content of the melts, as reported in Tab. 1.

Figure 5. SEM pictures of silica phases in the rhyolitic PEL series. (A) ‘Prismatic’ *Qtz* in charge LPE750, (B) ‘Prismatic’ *Crs* in charge 925PEL25, and (C) ‘Prismatic’ and ‘fish-scale’ *Crs* coexisting in charge D5. Details on the run conditions are given in Tab. 2. The black areas

are pores and the white crystals are either orthopyroxenes or Fe-Ti oxides. All images are at x1000 magnification.

Figure 6. Melt SiO₂ contents (wt%, recalculated anhydrous) as a function of H₂O content (wt%). For the PEL (dark blue), SH2 (pink), and CC (light blue) compositions, the data are from low pressure ($P \leq 100$ MPa) H₂O-saturated experiments (Tab. 2). For the HTN (green) composition, the data are from the 200 MPa H₂O-undersaturated experiments (Tab. 2). The haplogranite (HPG_m) data (red) are from Tuttle & Bowen (1958) and Luth (1976). Point labels are experimental temperatures. *Qtz*: quartz, *Crs*: cristobalite, *Trd*: tridymite. The lines represent the silica phase saturation or boundary from a silica phase to another (dashed line where not precisely constrained) for the different compositions. Note that for HPG_m (red), the silica polymorph is *Qtz* above and *Trd* below 20-30 MPa (Schairer, 1950; Tuttle & Bowen, 1958; Fig. 2A), with an uncertain melt SiO₂ content at *Trd* saturation at 0.1 MPa (Schairer & Bowen, 1935; Schairer, 1950; Luth, 1976). The colored areas refer to glass compositions in natural samples, such as the *Qtz*-bearing pumice of the 1530 AD eruption of Soufrière of Guadeloupe (Pichavant et al., 2018), the silica-phase-free pumice of P1 and P2 Plinian fallout of Montagne Pelée, and the *Crs*-bearing dome products from the 1902 and 1929 domes and associated pyroclastic flows of Montagne Pelée (Martel & Poussineau, 2007).

Table 1. Origin and composition of the studied samples.

Table 2. Experimental conditions and characterization of the silica polymorphs.

Table 3. Selected analyses of natural and experimental silica polymorphs.

SM1. Experimental and analytical methods for the new experiments.

SM2. HTN series : phase relations.

SM3. HTN series: glass and plagioclase compositions.

SM4. New glass analyses.