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High pressure, halogen-bearing melt preserved in ultra-high temperature felsic granulites of the Central Maine Terrane, Connecticut (US)

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Abstract

Inclusions of high pressure melts provide crucial information on the fate of crustal rocks in the deep roots of collisional orogens during collision and crustal thickening, often at rather extreme conditions, e.g. temperatures in excess of 1000°C. However, findings of this type are still a relative rarity among case studies of MI in metamorphic rocks. Here we present the results of the experimental and microchemical investigation of nanogranitoids in garnets from the felsic granulites of the Central Maine Terrane (Connecticut, US). Their successful experimental re-homogenization at almost 2 GPa confirms that they originally were trapped portions of deep melts and makes them the first direct evidence of high pressure during peak metamorphism and melting for these felsic granulites. The trapped melt has a hydrous, granitic and peraluminous character typical of crustal melts from metapelites. This melt is higher in mafic components (FeO and MgO) than most of the nanogranitoids investigated so far, likely the result of the extreme melting temperatures – well above 1000°C. This is the first natural evidence of the positive correlation between temperature and mafic character of the melt, a trend previously supported only by experimental evidence. Moreover it poses a severe *caveat* against the common assumption that partial melts from metasediments at depths are always leucogranitic in composition.

NanoSIMS measurement on re-homogenized inclusions show significant amounts of CO_2, Cl and F. Halogens abundance in the melt is considered a proxy for the presence of brines, strongly saline fluids, at depth. Brines are known to shift the melting temperatures of the system toward higher values, and may have been responsible for delaying melt production via biotite dehydration melting until these rocks reached extreme temperatures of more than 1000°C, rather than 800-850°C as commonly observed for these reactions.

Keywords

High pressure granulites, anatexis, nanogranitoids, carbon, halogens, piston cylinder

INTRODUCTION

The investigation of melt inclusions in felsic (Ferrero et al., 2015; Cesare et al., 2015) and mafic (Ferrero et al., 2018a) granulites is the most straightforward approach to the investigation of melting processes in the lower continental crust, directly in their source region. These droplets of anatectic melt are generally partially to totally crystallized, i.e. as nanogranitoids due to the slow cooling of the host rock (Ferrero et al., 2012; Cesare et al., 2015). They contain a cryptocrystalline aggregate of phases consistent with the crystallization of a silicate rich melt (Ferrero et al., 2018b). The expected phases include, but they are not limited to, OH-bearing phases, quartz and feldspar(s) or their metastable polymorphs (Ferrero et al., 2016). Just like fluid and mineral inclusions, melt inclusions in metamorphic rocks are tools for natural scientists to peer into the history of the host rocks, obtain geochemical information on deep processes, and to better constrain P-T-t-X history of the rock (Ferrero and Angel, 2018).

Multiphase inclusions with features consistent with nanogranitoids were reported by Ague and Axler (2015) in garnets from layers of sillimanite-rich rocks hosted in gneisses of the Central Maine Terrane (CMT - Acadian orogeny, NE Connecticut, US). Phase assemblages in the inclusions and microstructures classify them as former droplets of melt trapped during garnet formation at the metamorphic peak, ~1050°C and ≥1 GPa (Axler and Ague, 2015). The host rock has attracted considerable interest in recent years because of its very high T of re-equilibration at relatively low P (including cordierite-spinel assemblages), allowing Ague et al. (2013) to interpret them as the first example of ultrahigh temperature (*UHT*) metamorphic rocks in North America. By definition, *UHT* metamorphism involves T in excess of 900°C achieved along apparent geothermal gradient ≥20°C/Km (Brown, 2006), i.e. mostly in the stability field of sillimanite. *UHT* metamorphism has been to date identified in dozens of localities worldwide, mostly in Precambrian rocks (Kelsey, 2008), although much younger *UHT* rocks, i.e. Miocene in age, have been also recently reported (Pownall et al., 2018). More recent studies of other rocks in the CMT document high-pressure granulite facies metamorphism (~1050 °C, ~1.8 GPa) of silica-undersaturated garnet-spinel-corundum gneisses (Keller and Ague, 2018), as well as UHP metamorphism (Keller and Ague, 2020).

Piston cylinder re-homogenization followed by in situ characterization is a common and well-established approach for nanogranitoids studies to follow in order to (1) prove that they originally were indeed droplets of melt, and (2) characterize geochemistry and fluid content and speciation content of anatectic melt (e.g. Acosta-Vigil et al., 2016; Bartoli et al., 2016; Carvalho et al., 2018; Bartoli et al., 2019). Our detailed experimental and microchemical work confirmed that the CMT multiphase inclusions were originally a hydrous and halogen-rich granitic melt formed at T in excess of 1000°C, the hottest preserved melt so far found in natural metasedimentary protolith. Our approach leads to surprising outcomes with broad significance in terms of melt composition and melting processes in the deepest parts of orogenic root zones, as well as of regional geodynamic evolution.

METHODS

Our study involved the use of a piston cylinder press, back-scattered-electron (BSE) imaging, electron probe analyses (EPMA), energy-dispersive-spectrometry (EDS) elemental mapping and micro-Raman spectroscopy. Several garnet chips with unexposed nanogranitoids of both equant and tubular shape were manually separated from doubly-polished thick sections and used as starting material in re-homogenization experiments. The chips were loaded in a platinum capsule then filled with silica powder, without adding water. The capsules were kept at in a Johannes-type piston-cylinder apparatus at GFZ-Potsdam at variable T and P conditions for up to 24 hours.

The temperature in the capsule was controlled using a Type S thermocouple (Pt-PtRh10) with a ±10 °C uncertainty, while the accuracy of the pressure (*P*) measurement is estimated to be ±0.05 GPa. Quenching of the experimental charge took place at high *P*, and the machine was unloaded only after reaching ambient temperature. In-situ analyses were then performed on capsules mounted in epoxy and polished to expose re-homogenized inclusions (for further details see Bartoli et al. 2013b; Ferrero et al. 2015).

The Field Emission Gun electron microprobe (FEG-EMP) JEOL Hyperprobe JXA-8500F available at the Natural History Museum of Berlin was used to acquire high-resolution BSE images and EDS elemental maps on nanogranitoids and re-homogenized inclusions. The glass resulting from re-homogenization was analyzed using a JEOL JXA-8200 EMP at Potsdam University. Analytical conditions were similar to previous studies of nanogranitoids (Ferrero et al. 2012; 2015) at 15 kV, 3.5 nA and beam diameter of 1 µm to avoid contamination from the surrounding host. Alkali loss correction factors were estimated using haplogranitic standards (Morgan and London, 2005) and are in the range 17-23% relative for Na_2O and 10-13 % relative for K_2O depending on the analytical session.

Fluorine, CO_2, and H_2O analyses were performed via Nano Secondary Ion Mass Spectrometry (NanoSIMS) using the Cameca NanoSIMS 50 operated at the Muséum National d'Histoire Naturelle of Paris following the procedure described in Bartoli et al. (2014) and Créon et al. (2018). Polished capsules with re-homogenized inclusions on the garnet surface were mounted in Indium along with standard glasses, and the inclusions identified through images of $^{28}Si^-$ and $^{56}Fe^{16}O^-$ secondary ions. Pre-sputtering on a 5×5 µm^2 surface area for 2 min preceded each analysis in order to remove gold coating, surface contamination and achieve a steady-state sputtering regime. A 20 pA Cs^+ primary beam was used for data acquisition via rastering of a 3×3 μm^2 surface area. Ions were exclusively collected from the inner 1×1 μm^2 (using the beam blanking mode) to minimize surface contamination. Each analysis comprised 200 cycles with a duration of 1.024 s. Secondary ions of $^{12}C^-$, $^{16}OH^-$ (proxy for H_2O), $^{19}F^-$, $^{28}Si^-$ and $^{56}Fe^{16}O^-$ were recorded simultaneously in multicollection mode, using electron multipliers with a dead time of 44 ns. Mass resolution was set to 5500 to resolve any mass interference on the selected ions. Only analyses with a stable $^{16}OH^-/^{28}Si^-$ ratio were considered in this study. Three glasses of leucogranitic composition and known concentrations of H_2O, varying between ~0.3 and 4.86 wt% were used for calibration (see Supplementary material). For F concentration, we used NIST 610 and 612 standards to determine [F]/[SiO_2] ratios from $^{19}F^-/^{28}Si^-$. Four trachyandesitic standards (STR 9, 10, 11 and 13) were used to correct for carbon measurements (Créon et al., 2018): these are glass fragments of shoshonite lava from the Stromboli volcano that were experimentally doped in carbon and water by Bureau et al. (2003). Analytical uncertainty on each NanoSIMS measurement (based on the Poisson error due to counting statistics) was combined with the uncertainty on the calibration (corresponding to 66% interval of confidence) by quadratic sum to obtain the 66% uncertainty on values reported in Table 3.

Micro-Raman spectroscopy was performed using a HORIBA Jobin Yvon LabRAM HR 800 located at the Institute of Geoscience, University of Potsdam. An air-cooled Nd:YAG laser was used for excitation (λ = 532 nm, laser power on the sample of 2–3 mW) with a grating of 300 lines/mm, slit width and confocal hole set to 100 μm and 200 μm, respectively. The Raman spectra of re-homogenized glass inclusions as well as crystal phases were acquired with a 100× objective in the wavenumber range 100–4000 cm^{-1}, integrating 3 repetitions of 60 s with spectral resolution of 10 cm^{-1}. Raman maps were obtained integrating 2 repetitions of 30 s in 4 spectral windows on each point of the mapped area. Different phases were visualized in the map by color coding of the indexed Raman bands of the phases (cf. O'Brien & Ziemann, 2008).

PETROGRAPHIC FEATURES OF THE STARTING MATERIAL

The host rocks are rusty schists characterized by the assemblage garnet+sillimanite+K-feldspar+plagioclase+quartz+cordierite+biotite (Fig.1a). The sillimanite is commonly found as pseudomorphs after kyanite. Detailed information on sample location and petrographic features are in Axler and Ague (2015). The inclusions occur in the inner part of garnet porphyroblasts with a random distribution indicative of a primary nature, i.e. they formed during growth of the host garnet (Fig. 1b; see also Ferrero et al., 2012). They vary in shape from isometric with diameter ≤10 µm (Fig. 1c) to needles with length ≤100 µm and few µm across (Fig. 1d). The latter type is by far the most common in each cluster, a shape never before observed in such abundance in case studies of nanogranitoid, more commonly isometric (Ferrero et al., 2018b; Cesare et al., 2015). The most elongated inclusions show often cracks of limited extension at the corners, evidence of decrepitation. The detailed microchemical and microstructural investigation of the inclusions performed by Axler and Ague (2015) showed that, before the experimental runs, they contain a rather constant assemblage consisting of quartz, phlogopite, white mica and, very often, a compositionally variable phase (CV phase in Axler and Ague 2015) interpreted as residual glass.

Raman investigation (Fig. 2a) and mapping of isometric inclusions shows that cristobalite is present instead of quartz in some inclusions (Fig. 2b) and coexists with two micas and accessory phases such as apatite and ilmenite (Fig. 2c, d, e), whereas no inclusion show the presence of residual glass. However, the Raman map shows a crystalline phase with main peaks at 292, 430 and 479 cm^{-1}, assigned to a still unidentified and possibly new phase (hence "phase 430") already found and analyzed in nanogranitoids from HP/UHP rocks of the Bohemian Massif, and having composition similar to a granitic glass. Graphite occurs as mineral inclusions in garnet and occasionally as a trapped phase in the inclusions. A prominent feature of the host garnet is the presence of abundant rutile and ilmenite needles dominantly oriented parallel to <111> of garnet. Interestingly, needle-shaped nanogranitoids are oriented in the same directions, and typically contain rutile and /or ilmenite as trapped phases.

RESULTS

Multiple re-homogenization experiments were performed at T=1050°C and variable confining P, in the range 1.0 – 2.0 GPa (details on experimental runs and products are in Table 1; P-T conditions of each experiment are summarized in Fig. 3). The experimental conditions were chosen to be as close as possible to the conditions of formation, estimated to be ≈1040°C based on Zr-in-Rt thermometry on the rutile needles present along with nanogranitoids in the garnet core (Axler and Ague, 2015). The T estimates were calculated assuming 1 GPa as formation P of the host garnet and melt entrapment, thus representing a minimum value (Ague et al., 2013).

Each experiment shows complete re-melting of the inclusions, i.e. no leftovers of the original phases in the nanogranitoids are visible after the heating run, with the exception of clearly trapped accessories such as rutile and ilmenite. The absence of embayments and regular linear walls in the inclusions rules out that garnet dissolved into the melt (Ferrero et al., 2012; Bartoli et al., 2013), as expected in case of significant overheating during the experiments, i.e. the chosen temperature is likely very close to the liquidus of the trapped melt. However, the experiments performed at P <1.7 GPa (numbers 1, 2 in fig. 3) constantly show formation of new garnet, higher in Mg than the original host phase (Figs. 4a,b,c,d) and occasionally small orthopyroxene crystals identified via Raman spectroscopy at P ≤1.2 GPa. Moreover, at 1 GPa most inclusions show extensive evidence of decrepitation (Fig. 4a). The two experiments performed at 1.7 and 2.0 GPa (numbers 3 and 4 respectively, Fig. 3) do show fully re-homogenized glassy inclusions without evidence of decrepitation and/or formation of new phases (Figs. 4e,f,g,h,i).

Melt composition

The glass measured in the inclusions after successful experimental re-homogenization is hydrous, granitic (Fig. 5a,b) and very K-rich (av. K_2O/Na_2O= 3.89, Table 2), with a clear peraluminous (ASI=1.22, Fig. 6c) and alkalic to alkali-calcic character (Fig. 5d). Importantly, such melts are not leucogranitic, as commonly expected for anatectic melts from melting of metasediments: they have indeed a rather high FeO+MgO content (4.05 wt%; 4.27 wt% when recalculated on an anhydrous basis; Table 2). The presence of H_2O in the glass is visible in Raman spectra acquired on re-homogenized nanogranitoids, which show the broad band of water in the region 3200-3800 cm^{-1} (Fig. 6).

The H_2O content of the melt, along with CO_2 and F, was measured in garnets from experiment #3 and #4 using NanoSIMS. One single inclusion shows very low values of all three volatile species, suggesting that it may have lost most of its volatiles possibly as result of decrepitation during quenching (measurement Exp3_MI_1 in Table 3) and thus it is not further considered in the average values calculated below. The volatiles were quantified as 4.40 wt% H_2O, 3072 ppm CO_2 and 3161 ppm F on average (Fig.7a). With the exclusion of the single analysis discussed above, H_2O content in the rest of the dataset is rather consistent (Fig. 7a), whereas the CO_2 and F contents of the melt vary by an order of magnitude (Figure 7a; Table 3) depending on the inclusion (Fig. 7b, c). Interestingly, EMPA measurements on the re-homogenized inclusions show that Cl is also present in remarkable amounts, reaching almost 1 wt%, with average 0.32 wt%, making this melt more enriched in halogens (Cl, F) than any previous anatectic melt so far investigated in nanogranitoids.

DISCUSSION

The present study targets polycrystalline inclusions in garnet form felsic granulites of the Central Maine Terrane. Our results confirm that they are volumes of crystallized melt trapped during garnet growth at the metamorphic peak, as already proposed based on mineralogical and microstructural investigation by Axler and Ague (2015). Raman investigation shows the presence of metastable cristobalite, i.e. formed outside its stability field (see e.g. Hwang et al., 2004). The occurrence of metastable polymorphs in nanogranitoids has been interpreted as direct evidence that the inclusions preserve their original composition, as these phases recrystallize to their most common counterparts (i.e. quartz) when the inclusions decrepitates, i.e. becomes an open system, able to exchange components with the rock matrix via cracks in the host garnet (Ferrero et al., 2016). Such inclusions therefore offer access to unaltered deep melts still preserved in the natural rock which underwent melting at depth (Ferrero and Angel, 2018).

The investigation of CMT nanogranitoids thus provides a detailed portrait of formation conditions, geochemistry, and volatile content of melt from metasediments at crustal depth. The extremely high T at which the melt was produced is rather close to the Bt-out curve according to the melting experiments on metasediments of Auzeanneau et al. (2006). Indeed the peraluminous and granitic nature of the re-homogenized melt, its relatively low amount of H_2O and its occurrence in (peritectic) garnet are all features consistent with melt generated by biotite dehydration melting (LeBreton and Thompson, 1988), with residual biotite still locally visible as mineral inclusions (Fig. 1a). Furthermore, the enrichment in chlorine and fluorine of the trapped melt is likely to influence the stability of the biotite (see discussion in the paragraph "volatiles in high pressure melt").

The composition measured in the re-homogenized inclusions, especially its granitic character and the high K/Na ratio (≈4:1) is consistent with the phase assemblage, which always includes quartz/cristobalite plus two K-bearing phases (muscovite and phlogopite). The phase 430 identified via Raman investigation is likely to be the "phase CV", reported in these inclusions by Axler and Ague (2015) and interpreted as residual glass because of their granitic-like composition: the narrow peaks visible in its Raman spectrum however clearly belongs to a crystalline rather than a glass phase. Moreover, very similar compositions to the one reported by Ague and Axler (2015) were measured in phase 430 from garnet pyroxenites from the Granulitgebirge (Bohemian Massif; unpublished EMP data; Ferrero et al., in preparation), thus making this phase the main Na repository in the targeted nanogranitoids.

A peculiarity of this case study is represented by the shape of the inclusions. Most case studies of nanogranitoids show inclusions with a more or less developed negative crystal shape, the response of host garnet to the need of lowering the surface free energy of the melt-garnet interface and move toward textural equilibration (Ferrero et al., 2012). Instead tubular/acicular shapes in nanogranitoids are not unheard of (Ferrero et al, 2012; Cesare et al., 2015) but they are overall a rarity. CMT nanogranitoids are a rather unique case as the acicular shape, i.e. defined by an extreme elongation/width ratio, characterizes the majority of the inclusions (Fig. 1b,c). So far only the polycrystalline inclusions in the garnet megacrysts of Gore Mountain in the Adirondacks (Darling et al., 1997) show similar features, although in the latter case only ~50% of the inclusions have such shape (Ferrero and Angel, 2018). Further investigations are needed to understand the reasons underlying the dichotomy negative-crystal versus acicular shape in inclusions from different localities.

The original rationale at the base of our work was two-folds: verifying the former melt nature of the inclusions and obtaining the bulk composition of the original melt. The study however generated three most unexpected results: (a) re-homogenization experiments show that this melt formed under high pressure (*HP*) conditions, in contrast with previous studies of these felsic granulites; (b) whereas the melt itself is peraluminous and granitic in composition, rather common features in melts from metasediments, it shows an unexpected high mafic (FeO+MgO) component; (c) in terms of volatiles, the melt contains significant amounts of halogens (Cl, F) besides typical species observed in silicate melts, e.g. H_2O and CO_2.

First evidence of *HP* in the felsic granulites of the Central Maine Terrane

Possibly the most consequential result of our study is that the inclusions re-homogenize completely in equilibrium with the host garnet only at $P \geq 1.7$ GPa, considerably in excess of the minimum of 1.0 GPa as originally expected based on the estimates of Ague et al. (2013) and Axler and Ague (2015). Garnet growth conditions and thus MI entrapment coincide with those of partial melting, as both garnet and melt are products of the same melting reaction (Cesare et al., 2015 and references therein), and are under chemical equilibrium during their formation. Thus, successful re-homogenization experiments on nanogranitoids are a completely independent tool to constrain the PT conditions of garnet formation in presence of melt (Ferrero et al., 2018b). Both *P* and *T* still need to be calculated beforehand using independent methods, e.g. thermodynamic modeling and classic geothermobarometry on the metamorphic assemblage to which the inclusion-bearing garnet belongs, in order to proceed with the experiments. If the calculated formation conditions are correct, (most of) the nanogranitoids should re-melt completely without reacting with the host during the experimental run (see Bartoli et al. 2013a,b; Acosta-Vigil et al., 2016; Ferrero et al., 2015; 2016; 2018b; Borghini et al. 2018). Conversely, textural evidence of melt-garnet disequilibrium as well as decrepitation evidence would indicate the experimental parameters were not representative of the formation conditions. As an example, the critical evaluation of the nanogranitoid microstructures after heating experiments at different P allowed Ferrero et al. (2018b) to bracket the P conditions of melting of the felsic granulites of Orlica–Śnieżnik Dome (OSD; Bohemian Massif) to 2.7 ±0.1 GPa, starting from an initial range of calculated *P* spanning from 1.8 to 3.0 GPa based on previous geothermobarometric and modelling studies.

Our detailed experimental work on the CMT nanogranitoids shows that the nanogranitoids re-melt at T=1050°C. At 1.0 GPa the abundance of decrepitation cracks in the re-melted inclusions is a clear evidence of insufficient confining *P*, which leads to failure of the container (the garnet) due to inclusion overpressurization during the heating run. Moreover, all the experiments at P <1.7 GPa show evidence of chemical disequilibrium between the newly produced glass and the surrounding garnet. This causes melt-garnet interaction, with formation of new phases not present in the inclusions before experimental runs, e.g. orthopyroxene and/or change in composition (Mg-increase) of the garnet around the inclusion. Newly formed, Mg-richer garnet was also reported in nanogranitoids from the OSD felsic granulites after experiments at *P* lower than those of melt formation (Ferrero et al., 2018). Hence the microstructural appearance of the CMT nanogranitoids after reheating show an evolution similar to that reported in Ferrero et al. (2018b), with the Mg-rich garnet disappearing once the confining *P* reaches 1.7 GPa, thus suggesting that both garnet and melt formed at P ≥1.7 GPa.

High mafic content in pristine anatectic melt from metasediments

Granitic melts with geochemistry similar to the CMT nanogranitoids, i.e., high ASI index, rather high normative orthoclase and high FeO+MgO, are reported from experiments on natural metapelitic rocks at 1 GPa and 1025-1075 °C (Patiño-Douce and Johnston, 1991) and in nanogranitoid from metapelitic migmatites which experienced UHT conditions, 950°C and 0.5 GPa, in the Kerala Khondalite Belt, Southern India (Cesare et al., 2009; Ferrero et al., 2012; see table 2 and fig. 8a,b for the whole nanogranitoid and experimental dataset). It may be argued that such a mafic-rich character is the result of contamination between glass and host, as the inclusions are hosted in Fe- and Mg-rich garnet (Axler and Ague, 2015). However, contamination via (even limited) dissolution of garnet during re-heating experiments can be excluded based on microstructural basis, i.e. the inclusions show regular shapes and lack embayments indicative of melt-garnet interaction. Contamination during EMPA analysis can be also ruled out for the inclusions selected for EMPA investigation and reported in Table 2. The size of the re-homogenized inclusions was sufficiently large (>5 µm in diameter) to avoid the excitation volume created by the electron beam (diameter 1 µm) to come in contact with the host. In the few cases where the inclusions were ≤5 µm, garnet contamination was clearly visible as the measured SiO_2 showed a sharp decrease, coupled with FeO increase (Fig. 8a). As microstructural evidence of garnet dissolution was completely absent from these small inclusions, we ascribed this phenomenon to the fact that the excitation volume created by the beam also included a portion of the host. Analyses from inclusions below 4-5 µm were then removed from the dataset (contaminated analyses are given in the supplementary material). Based on such considerations, the high mafic component of the melt preserved in these felsic granulites should be considered a primary feature.

CMT nanogranitoids have a very high average FeO+MgO content when compared with experimental melts from metasedimentary protoliths, i.e. 4.27 wt% in the CMT nanogranitoids versus 0.9-3.9 wt% of the experimental dataset when taken on anhydrous basis, as compiled by Stevens et al. (2007). The database of nanogranitoids and melt inclusions (Bartoli et al., 2016) shows that most of the melt inclusions (for a total of ~600 analyses in 2016) show a FeO+MgO+TiO_2 content in the range 0.25-2.50 wt%, with only ~10% of the whole database having contents 4 - 5 wt%. As CMT nanogranitoids show an average FeO+MgO+TiO_2 =4.63 wt% (Table 2), their mafic component is higher than almost 90% of the anatectic melt inclusions measured so far.

Experimental work on Fe and Mg contents in haplogranitic melts (Johannes and Holtz, 1996) and melting experiments on metasediments (Patiño-Douce and Johnston, 1991; Montel and Vielzeuf, 1997; Droop et al., 2003) show that a granitic melt produced during melting of metasediments can accommodate a progressively higher amount of Fe and Mg as the formation *T* of the melt increases. Such observations, so far rooted exclusively in experimental findings, are now supported by our natural data. This is clearly visible when they are plotted against data available in literature on granitic inclusions from metasediments melted at different *T* (Fig. 7; see also Table 2). Different case studies of nanogranitoids show a positive correlation between melting *T* (corresponding in turn to melt entrapment in the growing host) and FeO+MgO content. Indeed, the melt in the CMT nanogranitoids, which shows the highest FeO+MgO content among all the granitic inclusions, formed at $T \geq 1000$°C, the highest formation *T* identified so far in nanogranitoids from metasediments. Conversely, the melt produced at lower *T*, 700-710°C, shows the lowest FeO+MgO content, in the range 1.34-1.83 wt%.

A variable degree of FeO+MgO enrichment is commonly observed in S-type (anatexis-related) granites (e.g. Stevens et al., 2007; Villaros et al., 2009) and in leucosomes and small granite sheets associated with migmatite bodies with sedimentary protoliths, coupled to increases in A/CNK and decreases in silica content (Taylor and Stevens, 2012).This has been proposed to be the result of selective entrainment in the magma of peritectic garnet, possibly the most common repository of Fe, Mg and Al in metamorphosed crustal rocks, as the melt progressively coalesces at depth and migrates upwards (Stevens et al., 2007). This hypothesis assumes that most pristine anatectic melts from metasediments are leucogranitic and very low in mafic components, a concept so far supported by both experiments (Stevens et al., 2007) and melt inclusions (Bartoli et al., 2016). However, our study proves that anatectic melts can instead show a rather high content of Fe and Mg when produced at *T*>1000°C and, thus, they should be considered to have a pristine, “starting” composition (Ferrero et al., 2012; Bartoli et al., 2016). This observation does not affect the validity of the peritectic phase entrainment hypothesis, which remains a sound explanation for FeO+MgO enrichment in S-type granites. It does however pose a significant caveat for researchers who want to correctly estimate the magnitude of peritectic phase entrainment experienced by the granitic body/leucosome under investigation, warning in particular against overestimating the magnitude of entrainment by assuming a too small FeO+MgO content in the original anatectic melt when the latter is produced at *T* in excess of 950-1000 °C.

Volatiles in high pressure melt

H_2O is necessary to stabilize any silicate melt under crustal conditions, and the quantification of H_2O, as well as of other species such as CO_2 and halogens, partitioned into deep partial melts is of utmost importance for quantifying volatile cycles at depth and how they affect deep melting processes (Bartoli et al., 2014). NanoSIMS analyses on re-homogenized nanogranitoids is a routine approach in nanogranitoid studies (e.g. Acosta-Vigil et al. 2016), and it has shown that nanogranitoids generally preserve their original composition in terms of H_2O (Bartoli et al., 2014) and CO_2 contents (Carvalho et al., 2019). In particular, the loss of H_2O (even as OH) from the inclusion to the matrix surrounding the garnet would shift the liquidus of the trapped melt toward higher T (Johannes and Holtz, 1996). Thus the nanogranitoids would re-homogenize only at *T* significantly higher than those obtained via independent geothermobarometry on the host rocks, which is not the case here: the inclusions re-homogenize indeed at ~1050°C, consistently with the *T* range of Zr-in-Rt thermometers on the rutile needles present in the nanogranitoid-bearing garnets (Axler and Ague, 2015). In this work, the average H_2O value (4.40 wt%) is rather close to that obtained via difference from 100 of the EMP totals after alkali loss correction (4.63 wt%). Both values are consistent with experimental estimates of H_2O content in haplogranitic melts at the PT conditions of interest, as the experimental parameters of the two successful experiments (point 3 and 4 in Fig. 2) are close to the 4 wt% H_2O liquidus curve extrapolated at P >1.0 GPa (Johannes and Holtz, 1996).

The melt also contains significant amounts of CO_2, on average ~ 3000 ppm (0.3 wt%). This CO_2 may be internally produced as result of the devolatilization of hydrous silicates in the presence of graphite (Connolly and Cesare, 1993; Cesare et al., 2005) visible in the CMT felsic granulites as trapped minerals in inclusions and/or as mineral inclusions in garnet and the rock matrix (Axler and Ague 2015). The CO_2 content of the CMT nanogranitoids is higher, on average, than in the nanogranitoids measured in the graphite-bearing metasediments of the Ivrea-Verbano Zone (IVZ; Carvalho et al., 2019), the only other case study so far where CO_2 was measured in situ in re-homogenized nanogranitoids. It is likely that the different depth at which melting occurred played a major role in shaping the CO_2 content of the melt. Experimental studies have shown that CO_2 solubility in melt increases dramatically with increasing P (~500 ppm each 0.1 GPa in experimental studies; Ni and Keppler, 2013), and in fact our results show that CMT nanogranitoids likely formed at significantly greater depth than IVZ nanogranitoids, 1.7-2.0 GPa (this study) vs. 0.8 GPa (Carvalho et al., 2019).

Probably the most striking feature of the CMT melt is the presence of a significant amount of halogens. Chlorine (0.32 wt% average) and F (3161 ppm, or ~0.32 wt%) account together for 0.64 wt% on average of the total melt composition. This is also consistent with the fact that phlogopite crystallized inside the CMT nanogranitoids has been found, in one case, to contain an unusually high amount of F (>1 wt%; Axler and Ague, 2015). Halogens are characteristic of brines, i.e. saline and Cl-rich fluid with low H_2O activity, proposed by some authors to play an important role in the melting processes occurring in a thickened crust at either lower crustal or upper mantle conditions (Aranovich et al., 2014). The Cl content of partial melts can be used as proxy for the presence of brines during melt production at depth (Acosta-Vigil et al., 2016). CMT nanogranitoids contain 0.10-0.98 wt% of Cl, an amount comparable to those reported in experimental melts coexisting with brines, i.e., ranging between ~0.2 and 1.6 wt% (Webster and Mandeville, 2007; Aranovich et al., 2013; Safonov et al., 2014). Experiments show furthermore that brines in a haplogranitic system may cause a significant shift of the minimum melting T toward higher values due to the lowering of the H_2O activity (Aranovich et al., 2013), thus helping to create the conditions for melting to occur at extreme temperatures (>1000°C) as proposed for the CMT felsic granulites, a notion independently supported by both previous PT estimates (Ague et al., 2013; Axler and Ague, 2015) as well as by the complete re-homogenization of the nanogranitoids at 1050°C. Another possibility is that the enrichment in halogens predated the metamorphic peak, i.e. the brines were not present during melting but had infiltrated the felsic granulites during their prograde metamorphic evolution. In this scenario, Cl and F are incorporated in the biotite, and this process extends biotite stability field toward UHT conditions (Martin and Hand, 2015), thus allowing biotite to destabilize at significantly higher *T* than commonly expected.

IMPLICATIONS and CONCLUSIONS

The deep nature of granulite metamorphism and the high thermal flux required to achieve melting favor post-melting re-equilibration and re-crystallization of granulites/migmatites, often obliterating the most direct evidence of the presence of melt, such as leucosomes and melt pseudomorphs (White et al., 2011). For this reason the preserved melt inclusions sheltered in peak peritectic garnet of the CMT felsic granulites are a crucial finding. They indeed provide new data necessary to a more comprehensive portrait of the multiple aspects of melting, melt preservation, and crustal evolution during metamorphism in the deep roots of orogens. In particular:

- HP melts from metasediments are still underrepresented in the nanogranitoid database, as the bulk of the reported case studies of nanogranitoids are from rocks melted at P <1.5 GPa (see lists in Cesare et al., 2015; Bartoli et al., 2016; Acosta-Vigil et al., 2016; Ferrero et al. 2018b). The only two case studies of melts produced at P>1.5 GPa are from significantly greater depths of 2.7 GPa (Ferrero et al. 2015) and >4.5 GPa (Stepanov et al 2016). Along with the recent work on the metasomatic nanogranitoids hosted in the Granulitgebirge pyroxenites (Borghini et al., 2018; 2020), our data are a step toward filling the gap in knowledge on natural partial melts forming at intermediate P (~2.0 GPa). A further important feature of CMT nanogranitoids is the fact that they are richer in mafic components (FeO and MgO) than the majority of nanogranitoid case studies. Their pristine nature thus provides a direct confirmation that the granitic melt from anatexis can accommodate an increasing amount of Fe and Mg with increasing T, an observation rooted until now exclusively in experimental studies. This finding is thus a caveat against assuming that natural pristine anatectic melts are always leucogranitic.

- Our independent experimental results provide the first evidence of HP conditions during the metamorphic peak / melting of the felsic granulites in the Central Maine Terrane, pointing toward melting conditions of ~1050°C and 1.7-2.0 GP. HP metamorphism, rather than purely UHT (Ague et al., 2013), is also supported by the widespread presence of pseudomorphs of sillimanite after kyanite in the matrix (Axler and Ague, 2015). Our findings warrants a reappraisal of the metamorphic peak conditions in the area and finds direct support in other recent studies in nearby localities: HP conditions (1.8 GPa) reported in silica-undersaturated gneisses (Keller and Ague, 2018), whereas other metapelites contain evidence of UHP metamorphism (>5 GPa; Keller and Ague, 2020);
- H_2O, CO_2, Cl and F were measured directly in situ in the HP crustal melt still preserved in its original source rock. H_2O was so far measured in nanogranitoids from rocks equilibrated between ~0.4 GPa and 1.4 GPa (Bartoli et al., 2014; 2016; Acosta-Vigil et al., 2016; Carvalho et al., 2019), whereas CO_2 in situ measurements are only available from the IVZ, equilibrated at 0.8 GPa (Carvalho et al. 2019). Our new measurements extend the existent dataset toward significantly greater depth and provide the foundation of further studies to further clarify how the interplay of protolith, fluid speciation, and PT conditions influence H_2O and carbon budgets

during crustal subduction and thickening. Moreover, to our knowledge our study presents the first data on F measured in situ in anatectic melt inclusions. Previous experimental studies suggest that the presence of a significant amount of Cl such as the one measured in the CMT inclusions may be indicative of the presence of saline fluids, e.g. brine, during melting. This is the first direct natural evidence that brines infiltrating the lower crust as a metasomatic fluid may be an influential factor for the establishment of conditions necessary to produce melt at such extreme temperatures (>1000°C), commonly inferred to be characterized by fluid-absent melting conditions.

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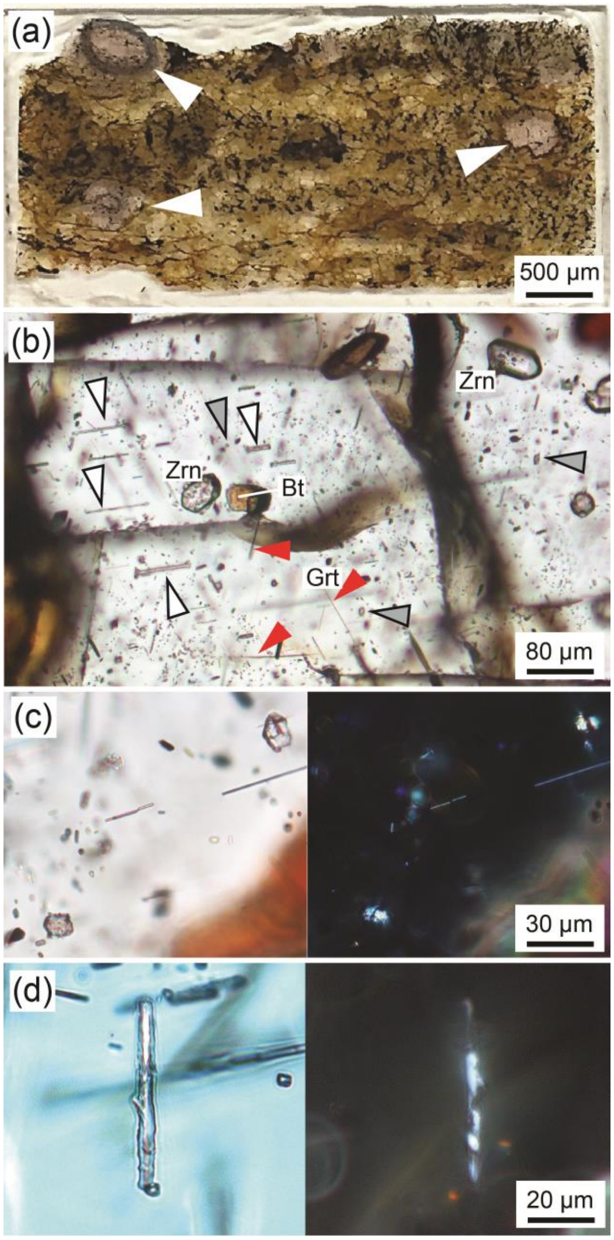

FIGURE 1. A) Microstructural features of inclusions and host rocks. (**a**) Scan of a representative thin section with garnets in a more felsic matrix; the garnet in the upper left corner has a circle made with a black marker. *White arrows:* MI-bearing garnets. (**b**) Cluster of polycrystalline inclusions occurring in the center of the garnet, mineral abbreviations from Whitney and Evans (2010). *White arrows:* needle shaped nanogranitoids. Gray arrows: isometric nanogranitoids, generally smaller than the first inclusion type. *Red arrows:* thin rutile needles. (**c**)

Close up of isometric nanogranitoids (**left**) with multiple birefringent phases visible under crossed polars (**right**). (**d**) Close up of a needle shaped nanogranitoid (**left**), occasionally with the rough outline already described by Axler and Ague (2015), and showing once again several birefringent phases under crossed polars (**right**).

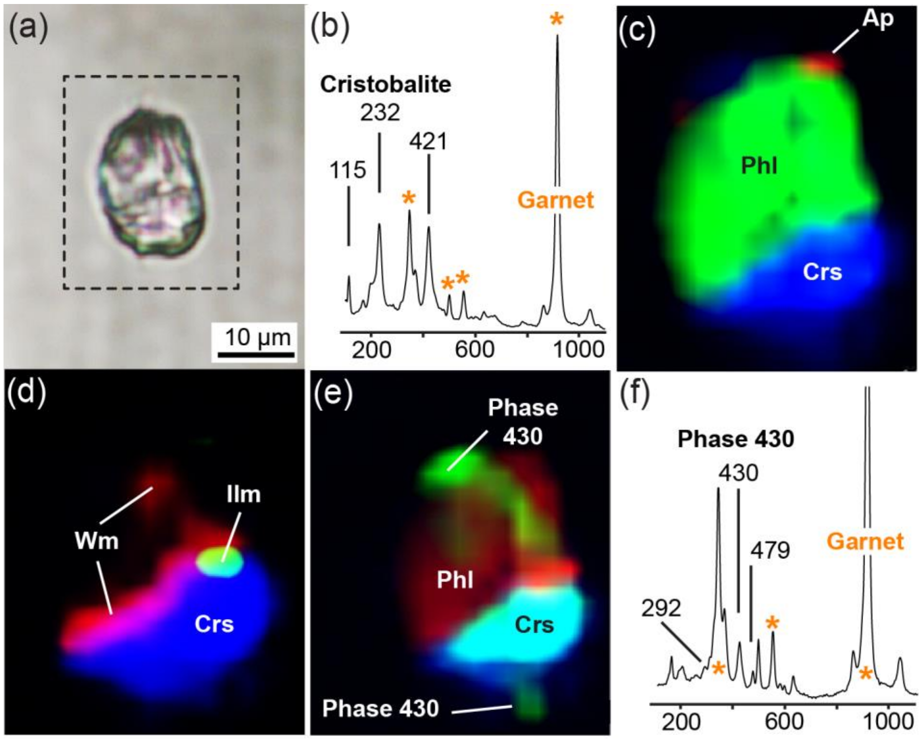

FIGURE 2. Results of MicroRaman investigation of a representative inclusion below the surface (**a**). (**b**) Raman spectrum of cristobalite from the CMT nanogranitoids. (**c**) The map shows the distribution of Raman peak 415 cm^{-1} of cristobalite (blue), 196 cm^{-1} of phlogopite (green) and 963 cm^{-1} of apatite (red). In (**d**) also the distribution of peak 707 of white mica (red) and the 675 cm^{-1} peak of ilmenite (green) are visible. In (e) the distribution of peak 430 cm^{-1} is visible in green, whereas in (f) a representative spectrum of phase 430 is reported.

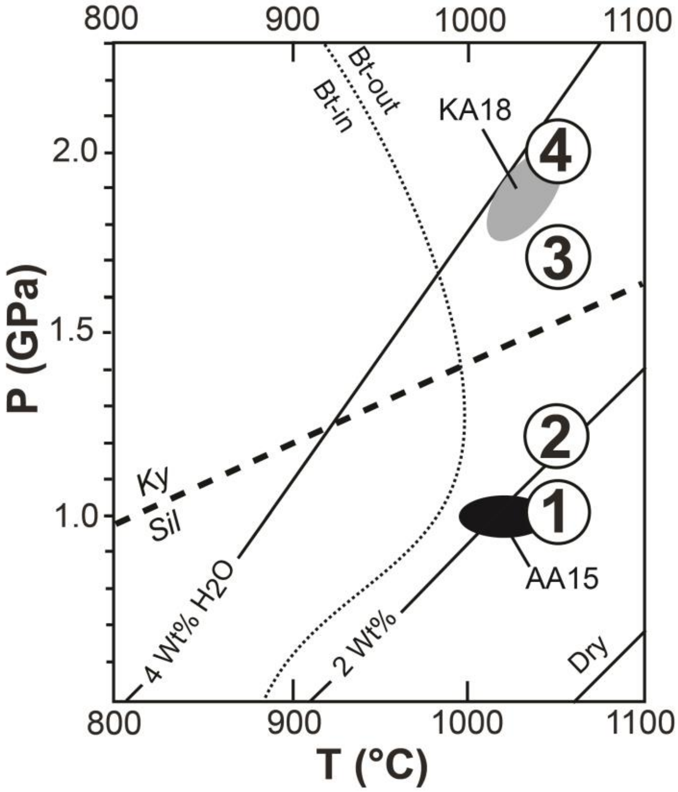

FIGURE 3: Experimental conditions (numbers in circles) versus previous estimates of metamorphic peak equilibration for the host gneisses of the investigated nanogranitoids. Solid lines: liquidus curves for different amount of H_2O according to Johannes and Holtz (1996). AA15: Temperature and minimum P conditions proposed by Axler and Ague (2015) for the felsic granulites investigated in the present study. KA18: HP conditions estimated on garnet-spinel-corundum gneisses of the Central Maine Terrane by Keller and Ague (2018).

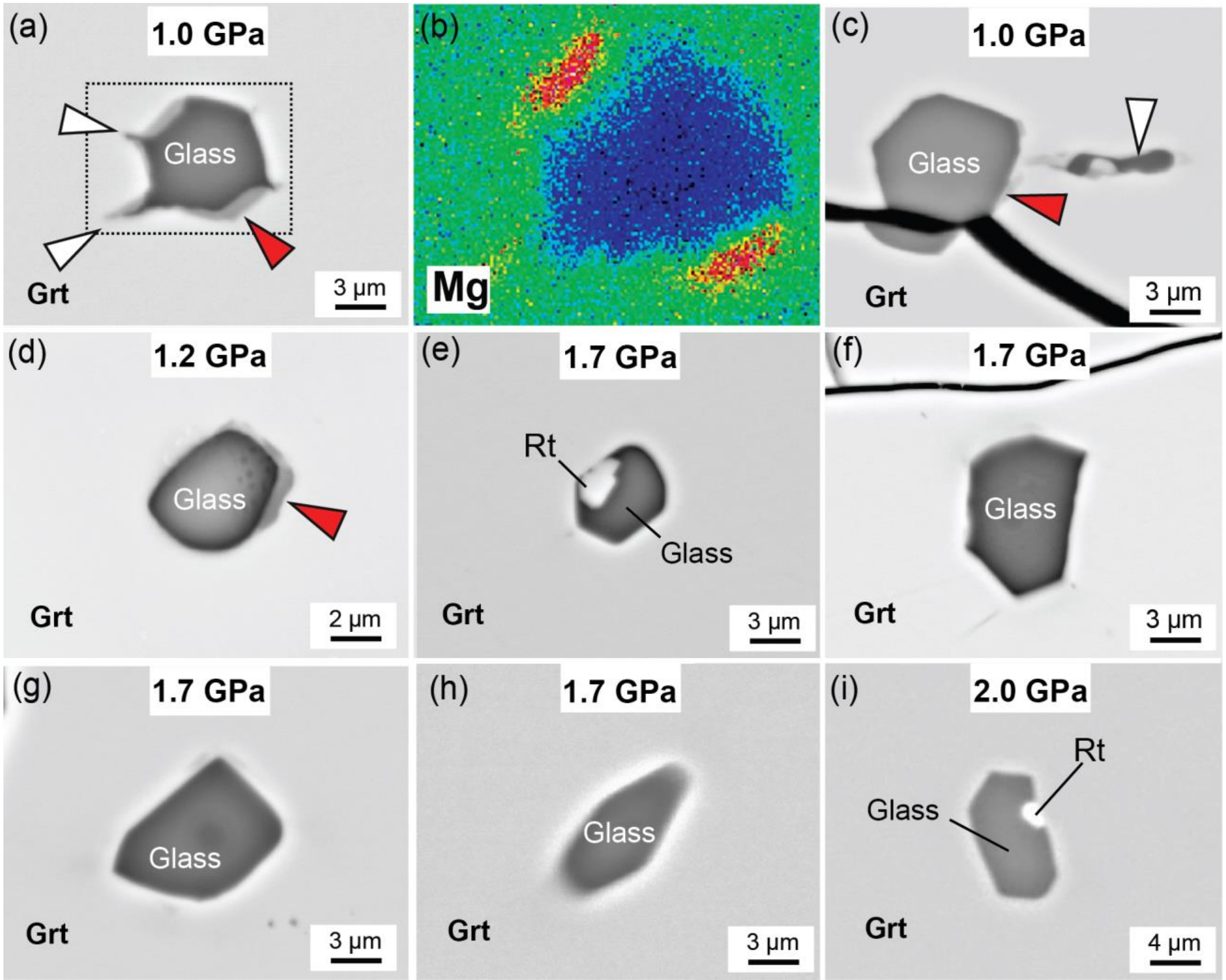

FIGURE 4. BSE images of CMT nanogranitoids after piston cylinder experiments under different confining *P*. *White arrows:* decrepitation cracks. *Red arrows*: new Mg-richer garnet. See text for details on the single images.

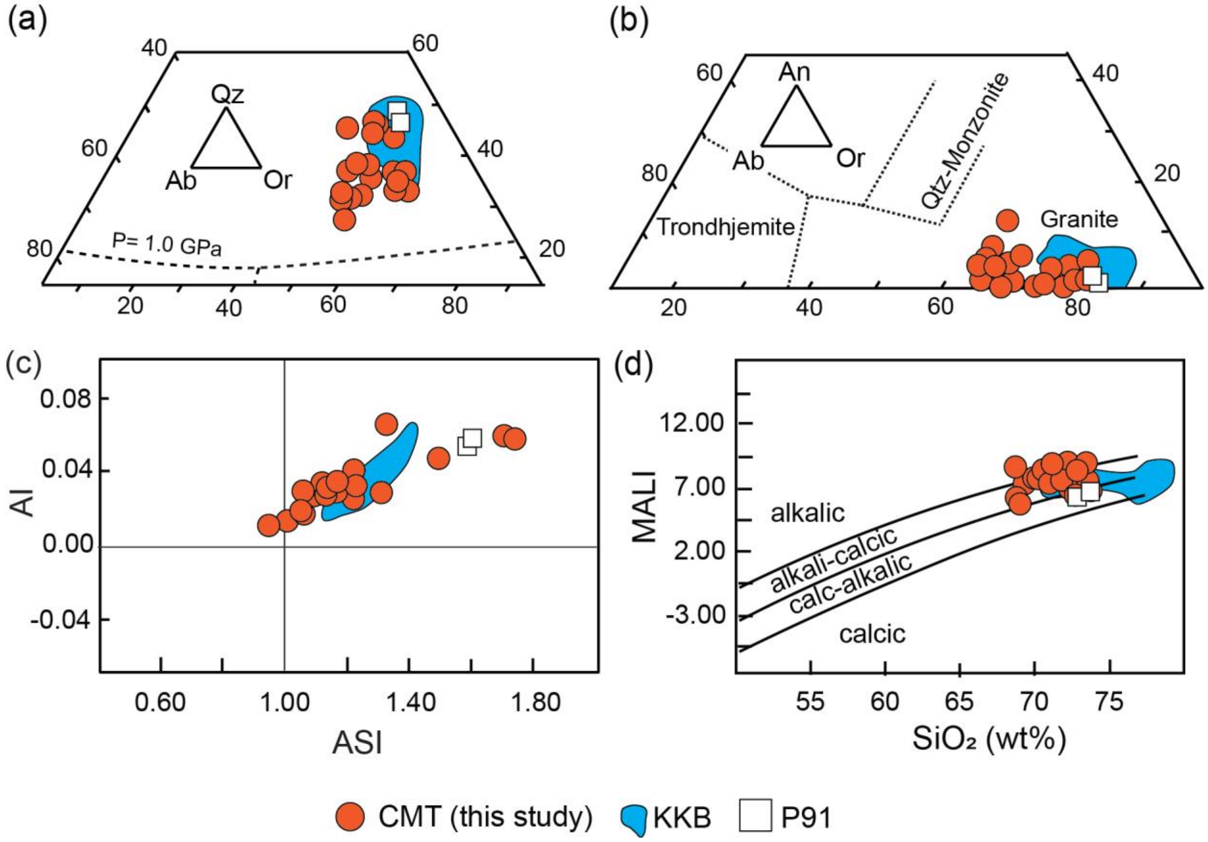

FIGURE 5: composition of re-homogenized nanogranitoids. (**a**) Ab-Or-Qz and (**b**) Ab-Or-An normative diagrams. (**c**) Alumina Saturation Index (ASI)= molar Al/(Ca+Na+K)) versus Alkalinity Index (AI)= molar Al-(Na+K). (**d**) Silica content versus Modified Alkali-Lime Index (MALI)= $Na_2O+K_2O–CaO$. CMT= central Maine Terrane; KKB= UHT nanogranites of the Kerala Khondalite Belt (Ferrero et al., 2012). P91= experimental melts from Patiño-Douce and Johnston (1991). For EMP compositions and *P-T* conditions of formation of the KKB and P91 melts see Table 2.

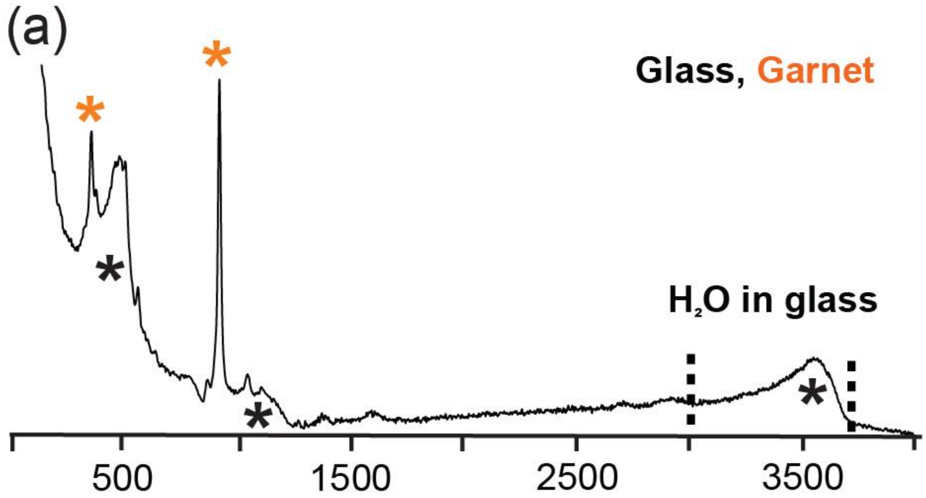

FIGURE 6: Raman spectrum of nanogranitoid re-homogenized to glass.

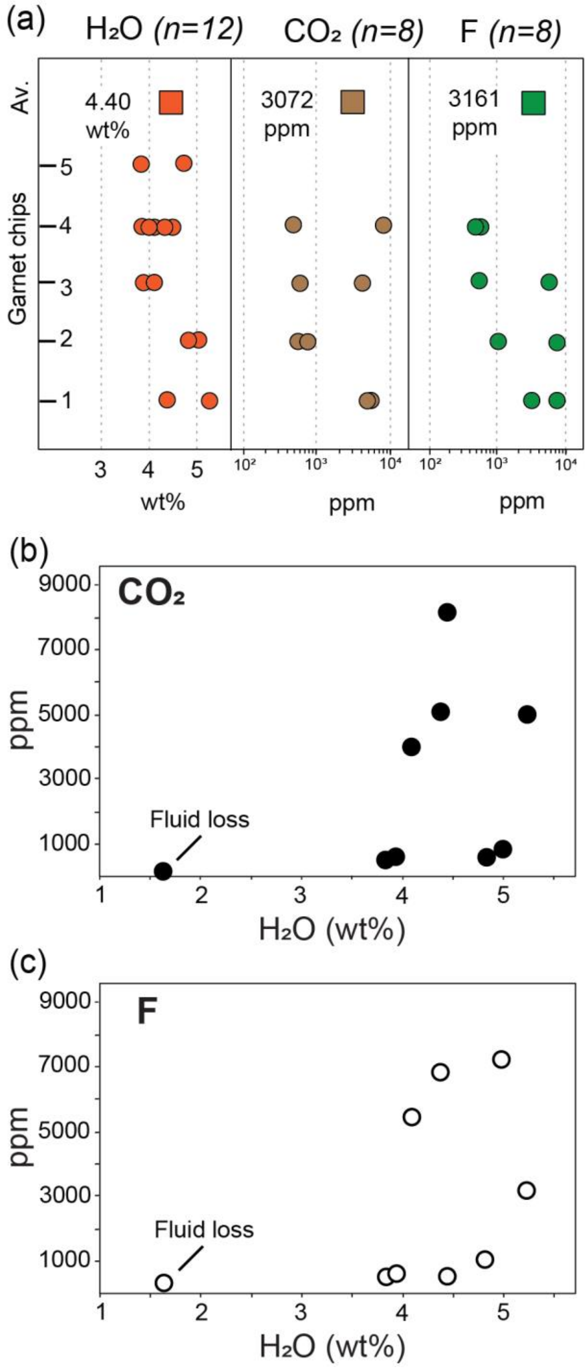

FIGURE 7: NanoSIMS measurements on re-homogenized nanogranitoids. (**a**) Measurements of H_2O, CO_2 and F presented according to the garnet chip in which they were measured. Variation diagrams of (**b**) CO_2 and (c) F with respect to H_2O for each single NanoSIMS analysis, including one inclusion with clear fluid loss (indicated in figure).

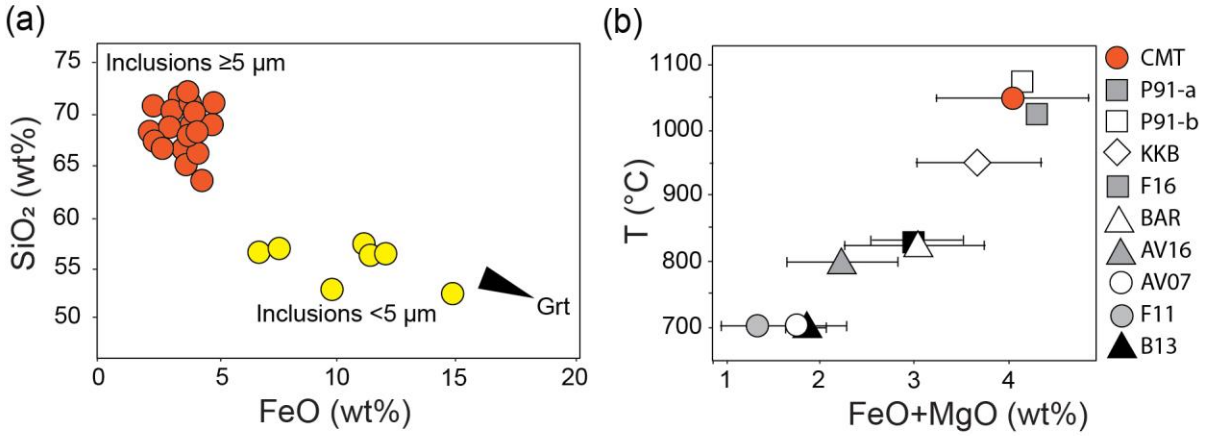

FIGURE 8. High FeO+MgO content in re-homogenized CMT nanogranitoids. (**a**) Comparison between inclusion with diameter ≥5 µm (orange circles) and <5 µm (yellow circles). (**b**) FeO+MgO versus T diagram, comparing nanogranitoids compositions from this study with previous case studies of inclusions in partially melted rocks with metasedimentary protolith (including standard deviations; data from Table 2). For abbreviations see caption Table 2.

Experiment	Figures	T(°C)	P (GPa)	t (h)	Melting	Decrepitation	Melt-host interaction	Full Re-homogenization
1	Fig. 4a,b,c	1050	1.0	≈15	X	X (extensive)	X (new Grt+New Opx)	-
2	Fig. 4d	1050	1.2	24	X	-	X (new Grt)	-
3	Fig. 4e,f,g,h	1050	1.7	24	X	-	-	X
4	Fig. 4i	1050	2.0	24	X	-	-	X

Table 1: Conditions, relevant info and results of piston cylinder experiments.

	Central Maine Terrane																					Experiments		Other Nanogranitoids													
n=19	*21*	*43*	*av.44-4*	*18*	*20*	*21*	22	23	24	7	8	32	35	34	3	6	36	39	21/22	**Aver.**	*Stdv*	P91	P91	KKB		BAR	*Stdv*	F16	*Stdv*	AV16	*Stdv*	AV07	*Stdv*	F11	*Stdv*	B13	*Stdv*
Duration	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*4h*					n=11		n=4		n=4		n=5		n=62		n=15		n=15	
T (°C)	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*			*1025*	*1075*	*950*		*830*		*825*		*800*		*700*		*700*		*700*	
P (Gpa)	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*1.7*	*2.0*	*2.0*	*2.0*	*2.0*	*2.0*	*2.0*			*1.0*	*1.0*	*0.5*		*0.8*		*0.5*		*1.2/1.4*		*0.5*		*0.5*		*0.5*	
Wt%																									*Stdv*												
SiO_2	64.96	68.89	63.61	67.10	69.15	68.22	67.64	66.00	68.32	66.80	67.30	70.97	70.92	68.83	71.07	68.24	71.97	71.91	66.36	**68.33**	(2.34)	70.62	69.44	73.96	(2.63)	73.77	(2.34)	70.78	(3.44)	70.16	(1.29)	71.23	(1.43)	68.95	(1.65)	70.03	(2.28)
TiO_2	0.64	0.36	0.03	0.05	0.91	0.24	0.14	0.14	0.10	0.05	0.16	0.22	0.15	0.13	0.10	0.00	0.33	0.66	0.07	**0.23**	(0.25)	0.65	0.73	0.11	(0.09)	0.09	(0.08)	0.06	(0.05)	0.07	(0.06)	0.10	(0.03)	0.10	(0.12)	0.04	(0.07)
Al_2O_3	12.61	12.50	14.74	12.39	12.96	12.89	13.80	12.42	13.71	12.84	14.03	13.18	14.00	12.06	11.83	13.46	13.23	11.93	13.14	**13.04**	(0.81)	13.4	13.64	12.95	(1.31)	12.90	(1.46)	11.91	(0.68)	14.89	(0.98)	14.44	(0.33)	12.82	(1.14)	11.71	(0.86)
FeO	3.71	4.76	4.43	3.27	3.22	3.53	3.25	4.10	3.08	2.89	2.38	3.53	2.41	3.97	4.75	2.22	3.49	3.47	3.54	**3.47**	(0.74)	3.26	3.04	3.03	(0.69)	2.51	(0.37)	2.39	(0.76)	2.14	(0.59)	1.71	(0.52)	1.32	(0.40)	1.71	(0.21)
MnO	0.11	0.11	0.04	0.02	0.09	0.14	0.02	0.08	0.01	0.00	0.00	0.06	0.09	0.01	0.01	0.00	0.03	0.08	0.07	**0.05**	(0.05)	0.11	0.08	0.04	(0.03)	0.25	(0.17)	0.10	(0.10)	0.46	(0.07)	0.08	(0.05)	0.16	(0.17)	0.17	(0.10)
MgO	0.61	0.58	0.63	1.11	0.38	0.41	0.70	1.01	0.63	0.57	0.30	0.62	0.45	0.56	0.61	0.34	0.52	0.54	1.18	**0.62**	(0.20)	1.04	1.09	0.65	(0.21)	0.53	(0.13)	0.61	(0.07)	0.09	(0.02)	0.05	(0.04)	0.02	(0.03)	0.12	(0.07)
CaO	1.17	0.98	1.68	0.01	0.36	0.14	0.12	0.36	0.03	0.94	0.55	1.09	0.58	0.54	0.60	0.98	0.56	0.84	0.88	**0.65**	(0.45)	0.26	0.28	0.53	(0.20)	0.85	(0.48)	1.04	(0.56)	0.48	(0.13)	0.60	(0.09)	0.68	(0.16)	0.45	(0.13)
Na_2O	1.32	1.28	1.58	1.71	1.28	1.50	1.66	1.17	1.14	1.89	1.68	2.11	2.17	2.29	2.45	3.03	2.68	0.96	1.52	**1.76**	(0.58)	0.79	0.84	1.10	(0.32)	1.94	(0.13)	0.57	(0.45)	2.88	(1.24)	3.63	(0.39)	2.25	(0.35)	2.79	(0.35)
K_2O	6.93	7.00	5.11	6.10	7.23	7.17	4.71	5.23	5.51	6.01	7.41	5.81	6.68	6.18	6.07	6.69	6.51	6.45	6.13	**6.26**	(0.78)	5.98	6.05	6.72	(0.70)	4.86	(0.79)	6.24	(1.10)	3.97	(1.00)	4.97	(0.31)	4.56	(0.83)	4.05	(0.39)
P_2O_5	0.59	0.75	0.28	0.05	0.18	0.15	0.16	0.12	0.07	0.23	0.19	0.17	0.07	0.07	0.00	0.12	0.25	0.20	0.38	**0.21**	(0.19)	0.11	0.06	0.03	(0.05)	0.02	(0.02)	0.28	(0.09)	0.01	(0.01)	0.37	(0.09)	0.16	(0.07)	0.26	(0.23)
Cl	0.07	0.21	0.08	0.86	0.82	0.68	0.95	0.93	0.97	0.01	0.04	0.00	0.01	0.09	0.10	0.10	0.10	0.00	0.01	**0.32**	(0.39)	-	-	-		-		-		-		-		-		-	
Total	92.64	97.21	92.12	91.79	95.76	94.38	92.20	90.62	92.59	96.17	98.00	97.76	97.53	94.64	97.49	99.07	99.57	97.05	93.29	**95.37**		96.22	95.25	99.12		97.73		93.97		95.15		97.16		91.02		91.33	
Q	26	30	27	29	31	29	36	34	37	32	30	31	29	27	27	25	27	37	29	**30**		39	37	37		39		39		35		29		36		36	
C	2	3	4	3	3	3	6	4	6	2	2	2	2	1	0	0	1	2	3	**3**		5	5	3		3		3		5		3		3		3	
Or	41	41	30	36	43	42	28	31	33	37	45	34	39	37	36	41	38	38	36	**37**		35	36	40		29		37		23		29		27		24	
Ab	11	11	13	14	11	13	14	10	10	15	14	18	18	19	21	25	23	8	13	**15**		7	7	9		16		5		24		31		19		24	
An	2	0	7	0	1	0	0	1	0	3	1	4	2	2	3	3	1	3	2	**2**		1	1	2		4		3		2		1		2		1	
Hy	7	10	10	9	6	7	8	10	7	7	5	8	5	8	10	4	7	7	9	**7**		8	7	7		6		6		5		3		3		4	
ASI	1.07	1.09	1.32	1.31	1.22	1.23	1.71	1.51	1.74	1.11	1.16	1.12	1.18	1.05	1.01	0.95	1.06	1.18	1.22	**1.22**		1.63	1.62	1.29		1.29		1.24		1.50		1.16		1.30		1.19	
H_2O by diff	7.36	2.79	7.88	8.21	4.24	5.62	7.80	9.38	7.41	3.83	2.00	2.24	2.47	5.36	2.51	0.93	0.43	2.95	6.72	**4.63**		3.78	4.75	0.88		2.27		6.03		4.85		2.84		8.98		8.67	
Mg#	0.22	0.18	0.20	0.38	0.17	0.16	0.27	0.30	0.27	0.26	0.18	0.24	0.24	0.20	0.19	0.21	0.21	0.21	0.37	**0.23**		0.35	0.38	0.27		0.26		0.30		0.06		0.04		0.03		0.10	
FeO+MgO+Tio$_2$	4.95	5.69	5.08	4.42	4.51	4.17	4.09	5.24	3.80	3.51	2.84	4.36	3.02	4.66	5.46	2.56	4.34	4.67	4.79	**4.30**		4.95	4.86	3.79		3.13		3.05		2.30		1.86		1.44		1.87	
FeO+MgO	4.31	5.34	5.05	4.37	3.60	3.94	3.95	5.11	3.70	3.47	2.67	4.15	2.86	4.53	5.36	2.56	4.01	4.01	4.72	**4.05**		**3.94**	**3.92**	**3.68**		**3.04**		**2.99**		**2.23**		**1.76**		**1.34**		**1.83**	
K_2O/Na_2O	5.24	5.48	3.24	3.57	5.64	4.79	2.84	4.48	4.82	3.18	4.41	2.76	3.07	2.69	2.48	2.21	2.43	6.71	4.04	**3.89**		7.57	7.20	6.09		2.51		11.01		1.38		1.37		2.02		1.45	

Table 2: Geochemistry and PT conditions of formation of re-homogenized melt inclusions from the Central Maine Terrane, high temperature experimental melts from metasediments (P91= Patiño-Douce and Johnston, 1991) and averages of melt inclusion analyses from different case studies of metasediments melted under different conditions. KKB (Kerala Khondalite Belt, Southern India) and BAR (Barun gneiss, Himalaya) are from Ferrero et al., (2012). F16 = Oberpfalz migmatites from Ferrero et al. (2016). AAV16= Jubrique migmatites, Betic Cordillera (S Spain) from Acosta-Vigil et al., (2016). AAV07= Grt+Bt granulitic enclaves of El Hoyazo, Neogene Volcanic Province (S Spain) from Acosta-Vigil et al., (2007). F11= Spl-Crd granulitic enclaves of El Hoyazo from Ferrero et al. (2011). B13= Sierra Alpujata metatexites, Betic Cordillera (S Spain) from Bartoli et al., (2013).

Garnet	Analysis	H_2O (wt.%)	1σ error	CO_2 (ppm)	*1σ error*	F (ppm)	*1σ error*
1	Exp4_M1_1	4.38	*0.05*	5073	*204*	6820	*106*
	Exp4_M4_1	5.24	*0.06*	4979	*201*	3198	*49*
2	Exp4_M2_1	4.83	*0.05*	538	*32*	1033	*15*
	Exp4_M3_1	5.00	*0.05*	790	*34*	7223	*112*
3	Exp3_MI_2	3.93	*0.05*	603	*34*	541	*8*
	Exp3_MI_6	4.09	*0.05*	3983	*164*	5462	*85*
4	Exp3_MI_3	4.46	*0.05*	8109	*339*	535	*8*
	Exp3_MI_1	1.64	*0.07*	113	*38*	79	*2*
	Exp3_tub_1	3.85	*0.05*	504	*32*	479	*7*
	Exp3_1	4.18	*0.17*				
	Exp3_2	4.29	*0.17*				
5	Exp3_3	3.84	*0.17*				
	Exp3_4	4.69	*0.17*				

Table 3. H_2O, CO_2 and F contents in re-homogenized inclusions measured by NanoSIMS.

Supplementary Information

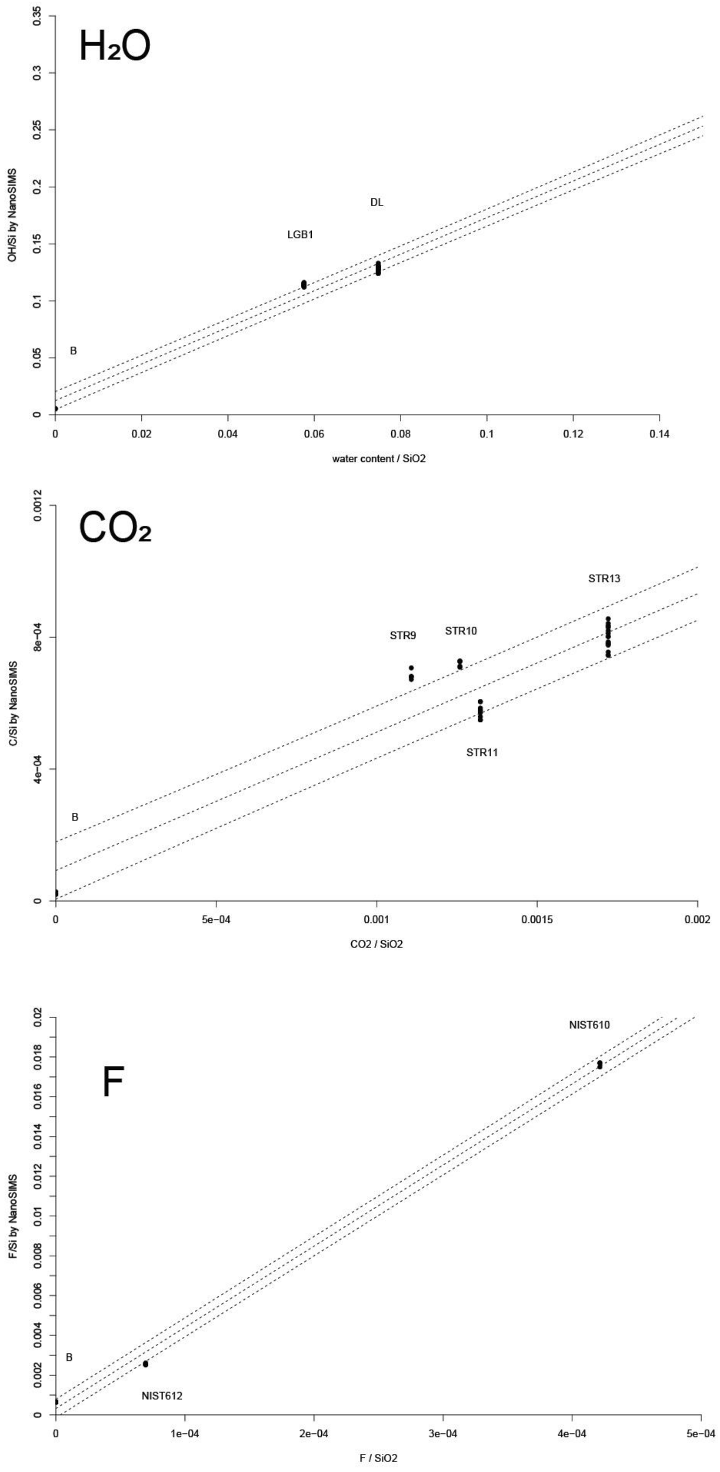

Figure S1. Calibration curves for NanoSIMS measurements.

Analyses	**24**	**36**	**59**	**60**	**61**	**62**	**64**
Duration	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*	*24h*
T (°C)	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*	*1050*
P (GPa)	*1.0*	*1.0*	*1.2*	*1.2*	*1.2*	*1.2*	*1.2*
Wt%							
SiO_2	56.42	57.42	56.95	56.52	52.89	56.33	52.55
TiO_2	0.78	0.00	0.01	0.13	0.00	0.39	0.05
Al_2O_3	14.75	18.67	13.87	16.58	13.89	14.77	15.49
FeO	12.01	11.13	7.45	6.71	9.86	11.41	14.91
MnO	0.11	0.11	0.04	0.02	0.09	0.14	0.08
MgO	1.24	4.67	2.78	3.17	2.94	3.28	4.36
CaO	2.66	0.99	0.86	1.55	1.05	1.34	1.26
Na_2O	3.43	1.08	1.08	1.33	0.89	1.23	0.88
K_2O	3.48	4.20	4.98	5.75	5.03	3.10	3.47
P_2O_5	1.72	0.12	1.78	0.04	0.12	0.16	0.16
Cl	0.07	0.21	0.08	0.86	0.82	0.68	0.93
Total	96.49	98.65	89.74	91.78	86.67	92.00	93.13

Table S1. EMP analyses of inclusions <5 µm in diameter.