Evidence in Tissint for recent subsurface water on Mars

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Abstract

We report unambiguous chemical evidence for subsurface water activity in the martian crust at <600 Ma based on the data from Tissint, a fresh martian meteorite fall with minimal terrestrial weathering. The impact-melt pockets in Tissint contain abundant volatiles (H_2O , CO_2 , F, and Cl), and their concentrations are positively correlated with each other. Higher H_2O concentrations also accompany higher deuterium contents. These correlations suggest mixing between two volatile sources. The first source is H_2O in the precursor basalt inherited from martian magma. Magmatic H_2O in the basalt had low deuterium concentration and was likely stored in the nominally anhydrous minerals. This source contributed little CO_2 or halogens to the impact melts. The second source is inferred to be aqueous-alteration products introduced to the basalt by water activity after the basalt erupted. These alteration materials contributed more volatiles to the impact melts than the magmatic source, and had high deuterium abundance, reflecting isotope equilibrium with recent martian atmosphere. The water activities occurred beneath the martian surface after ~600 Ma (crystallization age), but before ~1 Ma (ejection age). The chemical and isotopic signatures of the alteration products in Tissint resemble previously known martian samples associated with old water activities on Mars, which can be traced back to ~4.2 billion years ago (e.g., the mudstone at Gale Crater). This similarity in chemistry and the wide age-span indicate that such water activities were common on Mars throughout its history, which had the potential to form habitable environment. However, the rarity of the volatile-rich zone in Tissint may suggest that recent subsurface-water activities on Mars were limited.

Keywords: Mars, Amazonian, water activity, Tissint meteorite, impact melt

1. Introduction

Plenty of mineralogical and morphological evidence supports the presence of abundant surface and subsurface liquid water on Mars at times >3.6 Ga (e.g., Bibring et al., 2006). At present, the surface of Mars is cold and dry, and water is only stable as ice in the polar regions. However, hydrogen may be bound in surface or subsurface materials at middle to low latitudes (e.g., Bell, 2008; Feldman et al., 2004). As such, it was suggested that after the surface became dry at about 3.6 Ga ago, some water was stored beneath the surface and might form habitable environment (Michalski et al., 2013). However, there are few reports for subsurface liquid water activity on Mars since 3.6 Ga. The seasonal Recurring Slope Lineae (RSL) may be caused by fluid flow, although its exact mechanism is still under debate (McEwen et al., 2011; Ojha et al., 2013).

There has been putative evidence reported in young martian rocks for recent subsurface liquid water, but the chemical signatures of the inferred water sources, particularly their hydrogen isotope compositions, do not completely substantiate this claim. One line of evidence is for evaporates and clay minerals found in veins in three nakhlites (Governador Valadares, Lafayette, and Nakhla), which are inferred to be formed by infiltration of hydrothermal fluids liberated by impact (Bridges and Schwenzer, 2012; Gooding et al., 1991; Treiman et al., 1993); however, the age of the alteration products may be ~ 670 Ma or older (Swindle et al., 2000). Noble gas data of the alteration products show martian atmospheric signatures (Swindle et al., 2000), but the hydrogen isotopes of the alteration products show signs of possible terrestrial contamination (Hallis et al., 2012a). Additional reports of carbonate and sulfate in shergottite EETA 79001 (Gooding et al., 1988, 1990) also indicate water activity, but their martian origin is yet to be verified. A second line of evidence comes from Secondary Ion Mass Spectrometry

(SIMS) measurements of volatile concentrations and hydrogen isotopes in different phases in martian meteorites. Boctor et al. (2003) suggested two hydrogen sources on Mars with contrasting hydrogen isotope compositions. One source is thought to be magmatic water with low δD values, probably a primordial water signature from the martian mantle. The other source is martian surface water and related materials that have exchanged hydrogen isotopes with the martian atmosphere, and hence, have high δD values. However, it is not fully understood how the high δD values in martian meteorites can be related to water activity. Also, the low δD signature from martian mantle and terrestrial contributions can be difficult to distinguish. A recent study of three shergottites (EETA79001, LAR06319, and Y-980459) indicated a water source with 1000-2000 ‰ in δD values, which was interpreted as crustal water or ground-ice in sediments on Mars (Usui et al., 2015). The age-span of this water source is bracketed by the crystallization and ejection ages of the three meteorites (472-0.7 Ma). Interaction between martian rocks and ground water was also evoked by Hu et al. (2014), based on zonation of water concentration and hydrogen isotopes in melt inclusions in olivines in shergottite GRV020090. This interaction occurred after the rock crystallized at 196 Ma (Jiang and Hsu, 2012), and the duration of the alteration is estimated to be from a few hundred to a few hundred thousand years based upon diffusion simulations (Hu et al. 2014). However, the δD value of the ground water is inferred to be ~6000 ‰, in contrast to those by Usui et al. (2015).

The variations among the literature may be due to indigenous heterogeneities of water activities on Mars, terrestrial weathering, or laboratory contamination, in some cases. In search of fresh and less-contaminated, constrained chemical signatures of volatile sources on Mars, we have analyzed the impact melts and maskelynites in the Tissint meteorite, the most recent martian meteorite fall with negligible terrestrial weathering. We report the abundances of

volatile (H_2O , CO_2 , F, Cl, S) and trace elements (Ba, Y, Hf, Nb, and rare earth elements), and hydrogen and carbon isotopes. These data are compared with previous studies and Mars exploration missions and provide new constraints on the evolution of martian water and other volatiles.

2. Sample and methods

The Tissint meteorite is a witnessed fall in Morocco that occurred on July 19, 2011 (Chennaoui Aoudjehane et al., 2012). It is an olivine-phyric shergottite with a depleted trace-element pattern (Balta et al., 2015; Chennaoui Aoudjehane et al., 2012), displaying porphyritic basaltic textures without any signs of martian weathering, as has been observed in nakhlites (e.g., Gooding et al., 1991). It has a crystallization age of ~600 Ma (Brennecka et al., 2014) and a cosmic-ray exposure age of ~1 Ma (Chennaoui Aoudjehane et al., 2012). This meteorite is highly shocked (e.g., Baziotis et al., 2013; Ma et al., 2015) and contains glassy impact melts up to ~1 mm in size, ideal for identifying chemical signatures at micrometer-scale using microbeam analytical techniques. Our sample is a 10 g piece with ~95% coverage of fusion crust, which was recovered within a few weeks after the observed fall. We investigated two polished sections (UT-1-4 and UT-1-6) mounted in epoxy (EpoThinTM, Buehler).

Impact melts and maskelynites in the Tissint meteorites were analyzed using scanning electron microscopy (SEM, ZEISS 1550VP), electron probe micro-analysis (EPMA, JEOL JXA-8200), and Secondary Ion Mass Spectrometry (SIMS). The regions of interest were first inspected under a petrographic microscope and SEM to obtain information on the texture and phase compositions. Volatile concentrations and hydrogen and carbon isotopes were then analyzed using SIMS. The major-element compositions of each SIMS spot were analyzed

afterwards using EPMA. The analytical conditions for EPMA were 15 kV acceleration voltage, 10 nA electron beam current, and 5- μ m beam diameter. For each element, counting times were 20 s on peak and 10 s on the background.

Abundances of H (reported as H₂O), C (reported as CO₂), F, Cl, S, and trace elements, and H and C isotopes were analyzed with a Cameca IMS 7f-GEO using natural and synthetic glasses as standards. We generally followed previous SIMS analytical procedures (supplementary materials), with efforts particularly aimed to reduce the hydrogen background and to minimize terrestrial contamination. Before SIMS analysis, carbon coating on the samples was removed by gentle polishing, and the samples were cleaned and stored under vacuum at room temperature for a few days. Then, the samples were coated with Au and placed in the high-vacuum (1×10^{-8} torr) storage chamber in the SIMS instrument for 2-3 days before analysis. In order to improve the vacuum conditions in the sample chamber and reduce the hydrogen background during analysis, the instrument was baked for at least 12 hours before analysis, and a liquid-N₂ cold trap was used during analysis. The vacuum pressure in the sample chamber during analysis was $4 \times 10^{-10} - 2 \times 10^{-9}$ torr.

Seven ion species, $^{12}\text{C}^-$, $^{16}\text{O}^1\text{H}^-$, $^{18}\text{O}^-$, $^{19}\text{F}^-$, $^{30}\text{Si}^-$, $^{32}\text{S}^-$, and $^{35}\text{Cl}^-$, were analyzed with a Cs⁺ primary-ion beam, using 2-5 nA beam current and a 15- μ m beam diameter. Sample charging was compensated by an electron gun. A mass-resolving power (MRP) of ~5000 was used to separate $^{16}\text{O}^1\text{H}^-$ from $^{17}\text{O}^-$. Ion images of $^{16}\text{O}^1\text{H}^-$ were examined to avoid contamination signals from cracks or holes. Each analysis position was pre-sputtered by the primary beam rastering over a 25 $\times$ 25 μ m area for 1-2 minutes. The secondary-ion $^{18}\text{O}^-$ was then automatically centered and mass-calibrated. During analysis, the raster size of the primary-ion beam was reduced to 10 $\times$ 10 μ m; a field aperture of 100 μ m was used; and an electric gate allowed the secondary ions

from the center 8×8 μm area to be collected. Each analysis position was analyzed for 20 cycles. In each counting cycle, the counting time was 2 s for $^{12}\text{C}^-$, and 1 second for the others. The $^{18}\text{O}^-$ counting rate was $6\times 10^5 - 1\times 10^6$ cps on silicate glasses. A dry olivine standard (GRR1017 with <1 ppm H_2O) was used to monitor the H_2O background during calibration. The $^{16}\text{O}^{1}\text{H}^-/^{18}\text{O}^-$ value on GRR1017 ranged from 5×10^{-4} to 2×10^{-3} , corresponding to 3-10 ppm H_2O background. This background has been subtracted from the standard data.

Hydrogen and carbon isotopes were analyzed in separate sessions using slightly different analytical settings. For hydrogen isotope analysis, an MRP of 800 is sufficient and there was no significant $^1\text{H}^{2-}$ contribution to $^2\text{H}^-$. For carbon isotopes, an MRP of 3000 was used to separate $^{13}\text{C}^-$ from $^{12}\text{C}^{1}\text{H}^-$. Ion images of $^1\text{H}^-$ and $^{12}\text{C}^-$ were examined to avoid spots of anomalously high intensity that likely reflects contamination. After pre-sputtering, the centering of the secondary ion beam and mass calibration for $^1\text{H}^-$ and $^{12}\text{C}^-$ were manually performed. Each spot was analyzed by 30-100 cycles depending on the counting rate. In each counting cycle, $^1\text{H}^-$ was counted for 1 s, $^2\text{H}^-$ for 10 s, $^{12}\text{C}^-$ for 1 s, and $^{13}\text{C}^-$ for 20 s. The instrument fractionation factors for the $^1\text{H}^-/^2\text{H}^-$ ratio were 0.91 and 0.95 in two separated analysis sessions. The $^{12}\text{C}^-/^{13}\text{C}^-$ values are reported without correction for the instrument fractionation (standard-less), due to the lack of suitable standard. Since all carbon isotope analyses were performed on one impact melt region in one session, the relative differences in the $\delta^{13}\text{C}$ values are meaningful. The δD values are

calculated as $\delta\text{D} = \left(\frac{(\text{D}/\text{H})_{\text{sample}}}{(\text{D}/\text{H})_{\text{reference}}} - 1 \right) * 1000 \text{ ‰}$, where $(\text{D}/\text{H})_{\text{reference}}$ is 1.5576×10^{-4} for the

Vienna Standard Mean Ocean Water. The $\delta^{13}\text{C}$ values are calculated as

$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}} - 1 \right) * 1000 \text{ ‰}$, where $(^{13}\text{C}/^{12}\text{C})_{\text{reference}}$ is 1.12372×10^{-2} for the Vienna

Pee Dee Belemnite.

Eighteen trace elements (Ba, Y, Hf, Nb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were analyzed using the energy-filtering technique (supplementary materials). Positive ions of ^{30}Si and the above trace elements were generated by an O^- primary ion beam of 20 nA and 10 μm in diameter. Each analysis position was pre-sputtered by the primary ion beam rastering over a 10 $\times$ 10 μm area for 2 minutes. The secondary ion beam and the peak position of $^{30}\text{Si}^+$ were then automatically centered. During analyses, the primary ion beam rastered the center 10 $\times$ 10 μm area, and secondary ions from this area were counted without electronic gating. In each counting cycle, the counting time was 1 s for ^{30}Si , and 2-10 s for the trace-element ions. Each analysis position was analyzed for 5 cycles. Two glass standards from the National Institute of Standards and Technology (NBS610 and NBS612, supplementary materials) were used as trace-elements standards. Uncertainties at 2σ relative are 10 % or less for Ba, Y, and Dy, 10-40 % for Nb, La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, and Yb, 40-50 % for Tm and Lu, and 100-150 % for Eu and Hf.

After SIMS analysis, each SIMS spot was examined with SEM, and the major-element compositions near each spot were analyzed with the EPMA. Analytical uncertainties (2σ) for the major elements are about 0.7 wt.% for SiO_2 , 0.3 wt.% for Al_2O_3 , FeO , MgO , and P_2O_5 , 0.1 wt.% for TiO_2 , MnO , CaO , Na_2O , and Cr_2O_3 , and 0.02 wt.% for K_2O and S. Analytical uncertainties (2σ) are about 10 % relative for the volatile concentrations, 50-100 ‰ for δD values, and 25 ‰ for $\delta^{13}\text{C}$ (without considering the unknown amount of instrument fractionation). The background levels for CO_2 , H_2O , F, Cl, and S are estimated using the lowest concentrations measured in maskelynites near the impact melts in Tissint, which varied slightly for different samples and SIMS sessions. On average, the background levels are 7 ppm for CO_2 , 50 ppm for H_2O , 1 ppm for F, and 0.2 ppm for Cl and S.

Terrestrial contamination, including terrestrial weathering and laboratory contamination, is a major concern for volatile investigations of samples mounted in epoxy and prepared using water. Terrestrial weathering is negligible in our Tissint sample because of the short residence time (a few weeks) in the dry Moroccan desert. Some researchers have been very cautious and prepared samples without water; nevertheless suspicious contamination signatures may still appear (Usui et al., 2012). We took several precautions to avoid the artifacts of sample contamination during laboratory preparation. First, the contaminants from sample preparation are often concentrated in micro-cracks or cavities, and manifested in very high concentrations of H₂O, carbon, or Cl coupled with relatively low δD values. Thus, $^1H^-$, $^{16}O^1H^-$, and $^{12}C^-$ ion images were used to avoid hot spots of hydrogen and carbon. Second, the surface layer exposed to sample preparation was removed by pre-sputtering. Third, every SIMS spot was examined with SEM after SIMS analysis, and the ones with cracks, holes, or possible contaminating minerals, sometimes emerging beneath the original surface, were excluded. Some of these problematic spots yielded abnormally high ^{12}C counts but not for the other volatiles, indicating pure residual carbon coating. Some spots yielded both high $^{12}C^-$ and $^{16}O^1H^-$ counts, probably reflecting a contaminant different from the carbon coating. None of these spots yielded abnormally high signals for F, Cl, or S. In addition to sample contamination, SIMS analysis on a mixture of glass and fine crystals, all common textures in the impact melts in martian meteorites, might be affected by unknown matrix effects that bring uncertainties to data reduction and interpretation. Most of the impact-melt pockets in this study are large and glassy, ideal for micro-beam analysis. There are a few SIMS spots covering a mixture of glass and fine crystals as tabulated in Supplementary Table 1a. They are consistent with the data obtained from the

glassy regions, indicating that the matrix effect of the mixture is small. We included these data points in the discussion.

3. Results

The major-element compositions of most glassy regions in the impact-melt pockets plot within the whole-rock composition range reported previously (Figs 1a and 1b, Chennaoui Aoudjehane et al., 2012). These regions contain abundant sulfide droplets. Some regions in the melt pockets show large contributions of feldspar components (e.g., >7 wt.% Al_2O_3) and contain less sulfide droplets.

The glassy regions in the impact-melt pockets in Tissint contain 8-173 ppm CO_2 , 179-2388 ppm H_2O , 2-87 ppm F, 1-93 ppm Cl, and 3-4783 ppm S (Fig 2, Supplementary Table 1a). All these concentrations are higher than the estimated backgrounds. One data point (sample# 1-11, Supplementary Table 1a) yielded anomaly high CO_2 concentration (585 ppm). This spot is on a bubble that was initially beneath the polished surface and was excavated by the primary ion beam. Since this bubble was probably completely sealed in the impact glass (no visible cracks), contamination in the bubble is unlikely. There is no anomaly in the other volatile concentrations. To be conservative, we excluded this data point and only discuss the other high CO_2 concentrations (up to 173 ppm CO_2). Some SIMS spots contain sulfide droplets and are tabulated in the Supplementary Table 1a. These data points do not show anomalous S concentrations (1104-4529 ppm) compared to the other clean and glassy spots (3-4783 ppm). Only one data point near a series of sulfide droplets (sample# 10-3) yielded 11,761 ppm S, which is clearly a strong signal from the sulfides. This data point is excluded from the discussion. The volatiles are not correlated with major-element concentrations (Figs 1c and 1d, Supplementary

Table 1a and 2a), but form positive correlations between each other (Fig 2). The δD values vary from 45 ‰ to 4867 ‰, and are negatively correlated with $1/H_2O$ (Fig 3).

The most abundant volatiles were observed in a unique bubbly zone (Fig 4). It is a 100- μm -wide belt on the polished surface, sandwiched by two glassy regions of impact melts. It contains many small bubbles ($<10 \mu m$ in diameter), but no big bubbles ($>100 \mu m$ in diameter) as found in other impact melts in Tissint (e.g., Chennaoui Aoudjehane et al., 2012). The small bubbles can be clearly distinguished from sulfide droplets under transmitted light as they are transparent in the center, while the sulfide droplets are not. Also, some bubbles are exposed on the polished surface. Compared to the adjacent impact-melt regions, H_2O is about four times higher in this bubbly zone, and CO_2 is about seven times higher. It also displays enriched D and ^{13}C signals; δD values are higher than the adjacent regions by ~ 1000 ‰, while $\delta^{13}C$ by ~ 40 ‰. Despite all these anomalous volatile signatures, the trace-element concentrations in the bubbly zone are similar to the other impact melts and whole-rock data of Tissint reported by previous studies (Fig 5). We did not observe the enrichment of La, Ce, and Pr in the impact melts reported by Chennaoui Aoudjehane et al. (2012), similar to Barrat et al. (2014) and Balta et al. (2015).

Maskelynites in Tissint yielded very-low volatile concentrations: 7-20 ppm CO_2 , 33-339 ppm H_2O , 1-2 ppm F, 0.2-15 ppm Cl, and 0.1-8.1 ppm S (Supplementary Table 1b). Most of the maskelynite data are at the lower-end of the ranges and are assumed to be background values, to be conservative. Values of δD for maskelynite show a bimodal distribution; most of the data have low δD values (from -222 to 296 ‰), while three data points have elevated values (1171-2970 ‰). These three points are close to suspected phosphate minerals within maskelynite

(Supplementary Materials), and the δD values may have been affected by the phosphates, which can have different hydrogen isotope composition than maskelynites in the same rock (e.g., Boctor et al., 2003). One of the three points also has elevated H_2O , Cl, and S concentrations that may be contributed by the phosphate nearby. After excluding these three outliers and the background values, it was decided that maskelynites contain less than 111 ppm H_2O , with δD values of -222 to +296 ‰, and no F, Cl, or S.

4. Discussion

4.1. Mixing of two end-members

A negative correlation between δD and $1/H_2O$ (Fig. 3) is consistent with a mixing between two end-members: a volatile-rich end-member with high H_2O and δD values, and a volatile-poor end-member with low H_2O and δD values. This is not consistent with a dehydration trend, which would be a concaved downward in Figure 3 (Hauri et al., 2002), nor consistent with a terrestrial contamination trend, which would point toward terrestrial δD (close to 0 or slightly negative) and high H_2O concentrations (low $1/H_2O$). In the following discussion, we first estimate the contribution of each end-member to the impact melts, and then evaluate their possible sources.

A linear regression (the black line in Fig. 3) suggests that the volatile-rich end-member has a δD value of 4600 ± 600 ‰ (the intercept with the δD -axis). Among the different impact melts in Tissint, the bubbly zone is closest to the volatile-rich end-member, because it has the most abundant volatiles and highest δD and $\delta^{13}C$ values. On the other end, the volatile-poor end-member has 200 ± 40 ppm H_2O (the intercept with $\delta D = 0$ ‰). This H_2O concentration depends

on the assumed δD value of the volatile-poor end-member. If the actual δD value is 500 ‰, the H_2O concentration would be 220 ± 40 ppm.

The proportions of the two end-members in the impact melts can be estimated by a binary mixing calculation along the regression line. We assume that the volatile-rich end-member has 2 wt.% H_2O with 4600 ‰ in δD , 0.5 wt.% CO_2 , and 750 ppm Cl (Point A in Figs. 2a and 2b). We assume that the volatile-poor end-member has 200 ppm H_2O with 0 ‰ in δD , 15 ppm CO_2 , and 10 ppm Cl (Point B in Figs. 2a and 2b). These assumptions are based on the data from Tissint and literature data from other martian samples. The details are discussed in Sections 4.2 and 4.3. The model results suggest that at maximum level (in the bubbly zone), the volatile-rich end-member contributed ≤ 10 wt.% of the impact melts. For the other major and minor elements in the volatile-rich end-member, their abundances would be diluted by a factor of 10 or more, and then mixed with the volatile-poor end-member. If the volatile-rich end-member contained more than 2 wt.% H_2O , its proportion in the impact melts would be even less, and the dilution factor for other elements would be even larger. Such a dilution effect would hinder the identification of other chemical signatures in this end-member, such as major-element compositions and oxygen fugacity.

4.2. Source for the volatile-rich end-member

The δD value for the volatile-rich end-member (4600 ± 600 ‰) indicates that the source exchanged hydrogen isotopes with recent martian atmosphere. This value is consistent with the water released from the Yellowknife Bay mudstone at low temperatures (100-500 °C), but higher than the water released from the mudstone at high temperatures (600-900 °C, Mahaffy et al., 2015). The high-temperature water source is interpreted to be the structural hydroxyl in the

smectite in this mudstone, while the low-temperature water source may include later absorbed water (Mahaffy et al. 2015). This value (4600 ± 600 ‰) is slightly lower than the surface water source inferred by Hu et al. (2014), but higher than those reported by Usui et al. (2015). It is possible that the martian surface contains heterogeneous water reservoirs due to temporal or spatial evolution of water on Mars. Additionally, magmas with low D/H values could also contribute to the heterogeneities observed in other martian meteorites.

Previously suggested sources include the martian atmosphere (Bogard and Johnson, 1983), soils (Rao et al., 1999), ground-water or ice (Hu et al., 2014; Usui et al., 2015), or aqueous-alteration products, as observed in nakhlites (Treiman et al., 1995). Bogard and Johnson (1983) suggested direct implantation of martian atmosphere (noble gases, N₂, and CO₂) into meteorites. Later, Bogard and Garrison (1998) championed a slightly different scenario, where martian meteorites (Allan Hills 84001 and nakhlites) could have acquired martian water with dissolved noble gases. For the volatile-rich end-member in Tissint, the martian atmosphere cannot be the sole contributor because of the high abundances of H₂O, F, and Cl relative to CO₂, which are opposite to the current atmosphere compositions (Mahaffy et al., 2013).

Alternatively, Rao et al. (1999) suggested that regolith was melted and injected into meteorites during impact, based on the presence of abundant sulfides and elevated S, Ca, Al, and Na in impact melts. There are multiple lines of evidence arguing against this source in Tissint. First, the impact melts did not show the enrichment of Ca, Al, or Na compared to the whole-rock composition. In particular, the bubbly zone with the most abundant volatiles and most enriched D and ¹³C isotopes does not show any anomaly in major-element compositions. Second, the impact melts have high concentrations of S and abundant sulfide droplets in some regions. However, S concentrations cannot be explained by mixing with martian regolith, because the

S/Cl values are much higher (> 25 , Fig 2d) than those of the martian surface materials and the alteration veins in nakhlites (Changela and Bridges, 2011; Gooding et al., 1991; Leshin et al., 2013; Ming et al., 2014; Treiman et al., 1993; supplementary materials); this suggests that sulfide in the precursor basalt was a major sulfur source to the impact melts. Hence, the high S concentration and abundant sulfide droplets in the impact melts do not reflect a martian regolith component. Furthermore, the impact melts do not show enrichment of light REEs (Balta et al., 2015; Barrat et al., 2014; Fig 5), a feature often interpreted as from martian regolith. More broadly, it has been suggested that injection of molten soil into rock within the milli-seconds of impact is difficult (Shaw and Walton, 2013).

A third suggestion involves ground water or ice (Hu et al., 2014; Usui et al., 2015). Hu et al. (2014) proposed a ground-water source with ~ 6000 ‰ δD , and Usui et al. (2015) proposed a ground-water or ice source with 1000-2000 ‰ δD . Both are different from the 4600 ± 600 ‰ δD source in Tissint. Also, the ground water or ice by Usui et al. (2015) was inferred to contain low Cl concentration, contrary to the positive correlation between H_2O and Cl in Tissint. Therefore, a ground-water or ice source is unlikely as the source of the volatile-rich end-member in Tissint.

We suggest that the source for the volatile-rich end-member is, instead, the solid altered materials formed by ground water or ice along grain boundaries, vesicles, or cracks in the precursor rock. The bubbly zone, with the most abundant volatiles and high δD and $\delta^{13}C$ values, has similar major-element compositions to the surrounding impact melts and the bulk Tissint, a feature observed previously for nakhlites (iso-chemical weathering; Ming et al., 2008; Treiman et al., 1993). This feature indicates a small water-rock ratio, such that the whole system did not

undergo extensive leaching and was closed or nearly closed for the major elements, but was open for the addition of volatiles (Ming et al., 2008).

The positive correlations among H₂O, F, Cl, and CO₂ suggest the water may have precipitated halogen salts and carbonate. The relatively high $\delta^{13}\text{C}$ values of the bubbly zone, together with the high δD values and high volatile concentrations, indicate an indigenous martian carbon source in the bubbly zone. The standard-less value of 22 ‰ $\delta^{13}\text{C}$ of the bubbly zone is consistent with the carbon component released from whole-rock Tissint at 1100 °C (Chennaoui Aoudjehane et al., 2012), and is also consistent with the high-temperature carbon component released from martian surface materials measured by Curiosity (up to 20 ‰ $\delta^{13}\text{C}$, Leshin et al., 2013). It is lower than the current martian atmosphere value of 46 ‰ (Mahaffy et al., 2013). However, the above comparisons are not rigorous, because of the unknown instrumental-fractionation factor.

The actual volatile concentrations in the alteration products in Tissint cannot be inferred directly from the data, because of the unknown amount of dilution during impact melting and mixing. Instead, comparisons are made for the volatile ratios of different samples assuming that the volatiles are not significantly fractionated during the formation of the impact melts. The presence of bubbles in the impact melts (not limited to the bubbly zone) could cause volatile fractionation because they partition differently between gas and silicate melts, but their behavior is not fully understood. Nonetheless, the data suggest this effect is small. The linear correlation between H₂O and Cl argues against degassing (or in-gassing) because H₂O would be lost more readily than Cl. Furthermore, H₂O concentrations and δD values do not display significant dehydration effects (i.e., the most mobile species was not lost by degassing during impact).

Also, the time scale for the impact-melt formation is exceptionally short for diffusion (Shaw and Walton 2013). Therefore, we infer that the volatile ratios in the impact melts were not significantly changed from the ratios in the precursor alteration products.

Here, we compare the volatile ratios in the bubbly zone, which best represent the volatile-rich end-member, to the other known martian surface-volatile reservoirs. Aqueous-alteration products have been reported in nakhlites (e.g., Treiman et al., 1993), and volatile concentrations in the surface rocks on Mars have been directly measured (Leshin et al., 2013; Ming et al., 2014; supplementary materials). The $\text{H}_2\text{O}/\text{CO}_2$ values of the bubbly zone (4-18) overlap with that of the mudstone at Yellowknife Bay (Ming et al., 2014), but are slightly higher than that in the aeolian fines at Rocknest (Leshin et al., 2013, Fig 2a). The $\text{H}_2\text{O}/\text{Cl}$ value (25-35) is also similar to that of the mudstone at Yellowknife Bay, but slightly higher than that in the other martian surface materials (Fig 2b). The alteration veins in nakhlites have a broad range of $\text{H}_2\text{O}/\text{Cl}$ values from 20 to 700 (Changela and Bridges, 2011; Gooding et al., 1991; Treiman et al., 1993), which brackets the values of the bubbly zone in Tissint. The broad range of $\text{H}_2\text{O}/\text{Cl}$ is because the H_2O concentrations in the alteration veins were not accurately determined but inferred by the difference from 100% total oxide concentrations. In summary, the $\text{H}_2\text{O}/\text{CO}_2$ and $\text{H}_2\text{O}/\text{Cl}$ values in the volatile-rich source in Tissint are best matched by those in the mudstone at Yellowknife Bay, while the alteration products in nakhlites and martian surface materials also contain similar amount of volatiles with slightly different ratios.

The formation of the alteration products in Tissint can be broadly bracketed to be in the late Amazonian, between its crystallization age of ~600 Ma (Brennecka et al., 2014) and its cosmic-ray exposure age of ~1 Ma (Chennaoui Aoudjehane et al., 2012). Moreover, the young cosmic-ray exposure age of Tissint suggests that the rock resided at least a few meters below the

martian surface before the impact launch (Warren, 1994). Combined, the alteration products recorded in Tissint are associated with subsurface water activity in the late Amazonian. Such water activities have been suggested by Hu et al. (2014) and Usui et al. (2015). The high concentrations of CO₂, F, and Cl in the alteration products suggest that the water dissolved significant amounts of halogen salts and carbonates (i.e., saline or brine water), which is similar to the inferred water activities responsible for the alteration products in the nakhlites (Treiman et al., 1993). The rarity of such a bubbly zone in Tissint implies the water activity was limited (local and transient). Given the late-Amazonian water activity in Tissint, the ~670 Ma or older alteration products in nakhlites (Swindle et al., 2000), and the ~3 Ga mudstone at Yellowknife Bay (Grant et al., 2014), *saline or brine water activities beneath the martian surface may have persisted from early history to the present day.*

4.3. Volatile-poor end-member and its source

The low δD value in the volatile-poor end-member in Tissint is consistent with the inferred hydrogen-isotope composition of the martian mantle (Boctor et al., 2003; Hallis et al., 2012b; Leshin et al., 1996; Usui et al., 2012); this indicates that the source is the precursor basalt that inherited the hydrogen-isotope signature from the martian mantle. The inference on the water content of this end-member depends on the corresponding δD value. Assuming a δD value of 0 ‰, water content of this end-member is 200 ± 40 ppm (Fig 3).

The source for the volatile-poor end-member is the pre-impact, non-altered portion of the basalt, and is most likely the nominally anhydrous minerals (NAMs, i.e., olivine, pyroxene, and plagioclase) in the original basalt, because there is no report of hydrous minerals (apatite in particular) in Tissint (Balta et al., 2015). It is well known that NAMs on Earth can store up to a few hundred ppm of H₂O as OH (e.g., Bell and Rossman, 1992). However, analysis for H₂O in

NAMs in martian meteorites is limited, and the data vary from 0 to ~1000 ppm (Boctor et al., 2003; McCubbin et al., 2014; Usui et al., 2015). The volatile-poor end-member inferred from the impact melts could serve as a proxy for the H₂O in bulk sample (mainly NAMs) before impact (detail in section 4.4), which in turn could be an indicator of the magmatic-water content. Such an approach is independent and complementary to the other magmatic-water proxies, such as melt inclusions and hydrous phases (amphiboles and apatites; Boyce et al., 2014; Greenwood et al., 2008; Pernet-Fisher et al., 2014).

4.4. Water in the nominally anhydrous minerals

The scatter in the correlation between δD and $1/H_2O$ is non-negligible (Fig 3), reflecting that each melt pocket represents melting and mixing of different amounts of host minerals (olivine, pyroxene and plagioclase). Thus, the two end-member mixing scenario (volatile-rich and volatile-poor) is in fact a four end-member mixing scenario (volatile-rich, olivine, pyroxene, and plagioclase). For a better assessment of pre-impact H₂O contents in NAMs, we conducted a 2-step calculation, assuming that the alteration products in different impact melts have the same H₂O concentration and δD value. We have estimated the H₂O stored in the Tissint NAMs using a two-step model. First, for each impact-melt pocket that has more than one data point of δD , a straight line was fitted to its δD - $1/H_2O$ trend, with a fixed intercept at δD axis (4600 ‰). The NAM H₂O concentrations for each pocket were inferred by extrapolating the fit to $\delta D = 0$ ‰ (Fig 6a). Second, the inferred NAM H₂O concentrations were plotted against the major-element concentrations of the corresponding impact melts to display the approximate mixing trends (Figs 6b, c, and d).

In detail, the intercepts from different pockets to the δD -axis vary from 4500 to 5500 ‰, which is consistent with the hydrogen-isotope compositions of martian surface materials (Leshin et al., 2013). We further refined the model by fixing the intercepts at 4600 ‰ δD (Fig 6a) to fulfill the assumption that all alteration products share the same δD value and to be consistent with the linear regression of the whole data set (Fig 3). With this fixation, the NAM H₂O concentrations decrease slightly. The NAM H₂O contents also depend on the assumed NAM δD values. Using $\delta D = 500$ ‰ instead of 0 ‰, the NAM H₂O contents would increase by 10%. Using $\delta D = -500$ ‰, the NAM H₂O contents would decrease by 8%. Regardless of these different model parameters, the mixing trends shown in Fig 6 are similar.

The modeling results show that different impact melts contained different contributions from olivine, pyroxene, and plagioclase (Fig. 6). The SiO₂ concentration in the impact melts distinguishes the olivine component (~37 wt.% SiO₂) from pyroxene and plagioclase (~53 wt.% SiO₂), while the Al₂O₃ concentration, labelled near each data point, further distinguishes plagioclase (Al₂O₃ up to 27 wt.%) from pyroxene (low Al₂O₃ close to 4 wt.%). For the impact melts with low Al₂O₃ concentrations (~4 wt%), the NAM H₂O and SiO₂ concentrations form a positive correlation, demonstrating the mixing between olivine and pyroxene. Extrapolating this trend to the pyroxene and olivine compositions suggests 500-600 ppm H₂O in pyroxene and 0 ppm H₂O in olivine. For the impact melts with high Al₂O₃ concentrations (>7 wt%), NAM H₂O and SiO₂ concentrations form a negative correlation, demonstrating the contribution from plagioclase. Extrapolating the negative trend to the plagioclase composition suggests 0-100 ppm H₂O in plagioclase. Similar features can be observed for FeO and Al₂O₃ (Fig 6c and 6d) and other major components, but not for P₂O₅ (Fig 6e).

The estimated 0-100 ppm H₂O in plagioclases is consistent with the data in the maskelynites measured in this study (Supplementary Table 1b), suggesting that the maskelynites did not gain much H₂O during the impact. Literature data on olivines and pyroxenes are limited and scattered. Boctor et al. (2003) reported up to 88 ppm H₂O in olivines and 3360 ppm H₂O in pyroxenes in shergottites and chassignite (EETA 79001, ALHA 77005, Shergotty, Zagami, Chassigny). The model H₂O concentrations in this study fall within literature data range.

The correlation in Figure 6 also argues against terrestrial contamination or impact degassing, because these processes would affect the H₂O concentrations and hydrogen isotopes regardless of the major-element compositions of the impact melts. Lastly, the NAM H₂O content does not correlate with P₂O₅ concentrations, consistent with the absence of hydrous apatite in Tissint.

5. Conclusion

The impact-melt pockets in Tissint contain abundant volatiles that are positively correlated: 8-173 ppm CO₂, 179-2388 ppm H₂O, 2-87 ppm F, 1-93 ppm Cl, and 3-4783 ppm S. The δ D values vary from 45 ‰ to 4867 ‰, and are also positively correlated with H₂O concentrations. These data suggest mixing during impact between two martian volatile sources: magmatic volatiles and aqueous alteration products. The magmatic volatiles are stored in the nominally anhydrous minerals in Tissint, with an average of 200 ppm H₂O. The inferred alteration products have H₂O/CO₂ and H₂O/Cl values similar to the other martian materials associated with ancient aqueous activities on Mars. The aqueous alteration occurred after the crystallization of Tissint at ~600 Ma. Combined, these data suggest common water activities on

469 Mars during its entire history, but at a smaller scale for younger, late Amazonian rocks, on the
470 basis of the low water-rock ratios.

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Reference

1. Balta JB, Sanborn M, Udry A, Wadhwa M, McSween HY (2015) Petrology and trace element geochemistry of Tissint, the newest shergottite fall. *Meteorit. Planet. Sci.* 50, 63-85.
2. Barrat JA, Jambon A, Ferriere L, Bollinger C, Langlade JA, Liorzou C, Boudouma O, Fialin M (2014) No martian soil component in shergottite meteorites. *Geochim. Cosmochim. Acta* 125, 23-33.
3. Baziotis IP, Liu Y, DeCarli PS, Melosh HJ, McSween HY, Bodnar RJ, Taylor LA (2013) The Tissint martian meteorite as evidence for the largest impact excavation. *Nature Communications*, doi:10.1038/ncomms2414.
4. Bell DR, Rossman GR (1992) Water in Earth's mantle: The role of nominally anhydrous minerals. *Science* 255, 1391-1397.
5. Bell J (2008) *The Martian Surface, Composition, Mineralogy, and Physical Properties*. Cambridge University Press, New York.
6. Bibring J-P, Langevin Y, Mustard JF, et al. (2006) Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. *Science* 312, 400, doi:10.1126/science.1122659.
7. Bogard DD, Johnson P (1983) Martian gases in an Antarctic meteorite? *Science* 221, 651-654.
8. Bogard DD, Garrison DH (1998) Relative abundances of argon, krypton, and xenon in the Martian atmosphere as measured in Martian meteorites. *Geochim. Cosmochim. Acta* 62, 1829-1835.
9. Boctor NZ, Alexander CMO'D, Wang J, Hauri E (2003) The sources of water in Martian meteorites: clues from hydrogen isotopes. *Geochim. Cosmochim. Acta* 67, 3971-3989.
10. Boyce JW, Tomlinson SM, McCubbin FM, Greenwood JP, Treiman AH (2014) The lunar apatite paradox. *Scienceexpress*, doi:10.1126/science.1250398.
11. Brennecka GA, Borg LE, Wadhwa M (2014) Insights into the Martian mantle: The age and isotopics of the meteorite fall Tissint. *Meteorit. Planet. Sci.* 49, 412-418.
12. Bridges JC, Schwenzer SP (2012) The nakhlite hydrothermal brine on Mars. *Earth Planet. Sci. Lett.* 359-360, 117-123, doi:10.1016/j.epsl.2012.09.044.
13. Changela HG, Bridges JC (2011) Alteration assemblages in the nakhlites: Variation with depth on Mars. *Meteorit. Planet. Sci.* 45, 1847-1867.
14. Chennaoui Aoudjehane H, Avice G, Barrat JA et al. (2012) Tissint martian meteorite: A fresh look at the interior, surface, and atmosphere of Mars. *Science* 338, 785-788.
15. Feldman WC, Prettyman TH, Maurice S, Plaut JJ, Bish DL, et al. (2004) Global distribution of near-surface hydrogen on Mars. *J. Geophys. Res.* 109, doi:10.1029/2003JE002160.
16. Gooding JL, Wentworth SJ, Zolensky ME (1988) Calcium carbonate and sulfate of possible extraterrestrial origin in the EETA 79001 meteorite. *Geochim. Cosmochim. Acta* 52, 909-915.
17. Gooding JL, Aggrey KE, Muenow DW (1990) Volatile compounds in shergottites and nakhlite meteorites. *Meteorit. Planet. Sci.* 25, 281-289.

18. Gooding JL, Wentworth SJ, Zolensky ME (1991) Aqueous alteration of the Nakhla meteorite. *Meteorit. Planet. Sci.* 26, 135-143.
19. Grant JA, Wilson SA, Mangold N, Calef III F, Grotzinger JP (2014) The timing of alluvial activity in Gale crater, Mars. *Geophys. Res. Lett.* 41, 1142-1148, doi:10.1002/2013GL058909.
20. Greenwood JP, Itoh S, Sakamoto N, Vicenzi EP, Yurimoto H (2008) Hydrogen isotope evidence for loss of water from Mars through time. *Geophys. Res. Lett.* 35, L05203, doi:10.1029/2007GL032721.
21. Hallis LJ, Taylor GJ, Nagashima K, Huss GR, Needham AW, Grady MM, Franchi IA (2012a) Hydrogen isotope analyses of alteration phases in the nakhlite martian meteorites. *Geochim. Cosmochim. Acta* 97, 105-119.
22. Hallis LJ, Taylor GJ, Nagashima K, Huss GR (2012b) Magmatic water in the martian meteorite Nakhla. *Earth Planet. Sci. Lett.* 359-360, 84-92.
23. Hauri E (2002) SIMS analysis of volatiles in silicate glasses, 2: Isotopes and abundances in Hawaiian melt inclusions. *Chem. Geol.* 183, 115-141.
24. Hu S, Lin Y, Zhang J, Hao J, Feng L, Xu L, Yang W, Yang J (2014) NanoSIMS analyses of apatite and melt inclusions in the GRV 020090 Martian meteorite: Hydrogen isotope evidence for recent past underground hydrothermal activity on Mars. *Geochim. Cosmochim. Acta* 140, 321-333.
25. Jiang Y, Hsu W (2012) Petrogenesis of Grove Mountains 020090: An enriched “lherzolitic” shergottite. *Meteorit. Planet. Sci.* 47, 1419-1435, doi:10.1111/j.1945-5100.2012.01404.x.
26. Leshin LA, Epstein S, Stolper EM (1996) Hydrogen isotope geochemistry of SNC meteorites. *Geochim. Cosmochim. Acta* 60, 2635-2650.
27. Leshin LA, Mahaffy PR, Webster CR et al. (2013) Volatile, isotope, and organic analysis of martian fines with the Mars Curiosity rover. *Science* 341, doi:10.1126/science.1238937.
28. Ma C, Tschauner O, Beckett JR, Liu Y, Rossman GR, Zhuravlev K, Prakapenka V, Dera P, Taylor LA (2015) Tissintite, $(\text{Ca}, \text{Na}, [\text{J}])\text{AlSi}_2\text{O}_6$, a highly-defective, shock-induced, high-pressure clinopyroxene in the Tissint martian meteorite. *Earth Planet. Sci. Lett.* doi:10.1016/j.epsl.2015.03.057
29. Mahaffy PR, Webster CR, Atreya SK et al. (2013) Abundance and Isotopic Composition of Gases in the Martian Atmosphere from the Curiosity Rover. *Science* 341, 263-266.
30. Mahaffy PR, Webster CR, Stern JC et al. (2015) The imprint of atmospheric evolution in the D/H of Hesperian clay minerals on Mars. *Science* 347, 412-414.
31. McEwen AS, Ojha L, Dundas CM, et al. (2011) Seasonal flows on warm martian slopes. *Science* 333, 740, doi:10.1126/science.1204816.
32. Michalski JR, Cuadros J, Niles PB, Parnell J, Rogers AD, Wright SP (2013) Groundwater activity on Mars and implications for a deep biosphere. *Nature Geoscience*, 6, 133-138, doi:10.1038/ngeo1706.
33. Ming DW, Morris RV, Clark BC (2008) Aqueous alteration on Mars. In *The Martian Surface: Composition, Mineralogy, and Physical Properties* (JF Bell III, ed.), Cambridge University Press.

34. Ming DW, Archer Jr. PD, Glavin DP, et al. (2014) Volatile and organic compositions of sedimentary rocks in Yellowknife Bay, Gale Crater, Mars. *Science* 343, doi:10.1126/science.1245267.
35. Ojha L, Wray JJ, Murchie SL, McEwen AS, Wolff MJ, Karunatillake S (2013) Spectral constraints on the formation mechanism of recurring slope lineae. *Geophys. Res. Lett.* 40, 5621-5626, doi:10.1002/2013GL057893.
36. Pernet-Fisher JF, Howarth GH, Liu Y, Chen Y, Taylor LA (2014) Estimating the lunar mantle water budget from phosphates: Complications associated with silicate-liquid-immiscibility. *Geochim. Cosmochim. Acta* 144, 326-341, doi:10.1016/j.gca.2014.09.004.
37. Rao MN, Borg LE, McKay DS, Wentworth SJ (1999) Martian soil component in impact glasses in a martian meteorite. *Geophys. Res. Lett.* 26, 3265-3268.
38. Shaw CSJ, Walton E (2013) Thermal modeling of shock melts in martian meteorites: implications for preserving martian atmospheric signatures and crystallization of high-pressure minerals from shock melts. *Meteorit. Planet. Sci.* 48, 758-770.
39. Swindle TD, Treiman AH, Lindstrom DJ, Burkland MK, Cohen BA, Grier JA, Li B, Olson EK (2000) Noble gases in iddingsite from the Lafayette meteorite: Evidence for liquid water on Mars in the last few hundred million years. *Meteorit. Planet. Sci.* 35, 107-115, doi:10.1111/j.1945-5100.2000.tb01978.x.
40. Treiman AH, Barrett RA, Gooding JL (1993) Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite. *Meteorit. Planet. Sci.* 28, 86-97.
41. Usui T, Alexander CM O'D, Wang J, Simon J, Jones JH (2012) Origin of water and mantle-crust interactions on Mars inferred from hydrogen isotopes and volatile element abundances of olivine-hosted melt inclusions of primitive shergottites. *Earth Planet. Sci. Lett.* 357-358, 119-129.
42. Usui T, Alexander CM O'D, Wang J, Simon JI, Jones JH (2015) Meteoritic evidence for a previously unrecognized hydrogen reservoir on Mars. *Earth Planet. Sci. Lett.* 410, 140-151.
43. Warren PH (1994) Lunar and martian meteorite delivery services. *Icarus* 111, 338-363.

Figure captions

Figure 1. Major-element and volatile concentrations of the impact melts in Tissint. **a** and **b**: The major-element composition of the impact melts can be explained by mixing of olivine, pyroxene, and plagioclase in the precursor basalt. The bubbly zone that has the most abundant volatiles does not show an anomaly in major-element composition. **c** and **d**: H₂O and SiO₂, and H₂O and P₂O₅ concentrations are not correlated.

Figure 2. Volatiles in the impact melts in Tissint and comparison to other martian materials (plotted in fields, references in the supplementary materials). Concentrations of H₂O, CO₂, Cl, and F are positively correlated. The black solid lines represent calculated mixing trends between two volatile end-members, and each dot on the line marks a 10 % mixing interval.

Figure 3. Negative correlation between δD and $1/H_2O$, consistent with mixing between two H₂O end-members. Point A represents the volatile-rich end-member, with a δD value of 4600 ± 600 ‰ (the intercept with the δD -axis). Point B represents the volatile-poor end-member, with 200 ± 40 ppm H₂O (the intercept with $\delta D = 0$ ‰). The effects of terrestrial contamination and dehydration are schematically shown, and there are no indications of these effects. The fitting line is $\delta D = -900,000/H_2O + 4600$, where H₂O is in ppm, with $R^2 = 0.61$. The deviation from this trend is discussed in Section 4.4. The hydrogen-isotope data for the mudstone are from Mahaffy et al. (2015).

Figure 4. The most volatile-rich region in the impact melts in Tissint (the bubbly zone). **a**: Back-scattered electron (BSE) and transmitted-light images showing the bubbly zone between

the two dashed lines. The black rectangle box indicates the area of the transmitted light image. This zone has higher δD and $\delta^{13}C$ values than the adjacent regions. **b & c:** This zone also has high H_2O and CO_2 concentrations.

Figure 5. Concentrations of CI-chondrite normalized trace-element concentrations in the bubbly impact-melt zone, and comparison to other impact melts and whole-rock data of Tissint. The whole-rock data are from Chennaoui Aoudjehane et al. (2012) and Balta et al. (2015).

Figure 6. Water in the nominally anhydrous minerals in Tissint. **a:** For each impact melt, extrapolating the $\delta D - 1/H_2O$ trend to $\delta D = 0$ ‰ to infer the NAM H_2O content. **b, c and d:** The inferred NAM H_2O content correlates with SiO_2 , FeO , and Al_2O_3 concentrations of the impact melts, suggesting 400-500 ppm H_2O in pyroxene, 0-100 ppm H_2O in plagioclase, and dry olivine. In sub-figures **b** and **c**, the number labelled near each symbol indicates the Al_2O_3 concentration of each impact melt. In sub-figure **d**, the number near each symbol indicates the corresponding SiO_2 concentration. **e:** the highest H_2O content is not related to high P_2O_5 .

Figure1

Figures

Figure2

Figure3

Figure4

Figure5

Figure 6