Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 210 (2017) 228–246

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Martian low-temperature alteration materials in shock-melt pockets in Tissint: Constraints on their preservation in shergottite meteorites

C.R. Kuchka [a,1], C.D.K. Herd [a,*], E.L. Walton [a,b], Y. Guan [c], Y. Liu [c,d]

[a] *University of Alberta, Department of Earth and Atmospheric Sciences, Edmonton, AB T6G 2E3, Canada*
[b] *MacEwan University, Department of Physical Sciences, Edmonton, AB T5J 4S2, Canada*
[c] *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA*
[d] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA*

Received 24 June 2016; accepted in revised form 28 April 2017; available online 8 May 2017

Abstract

We apply an array of *in situ* analytical techniques, including electron and Raman microscopy, electron and ion probe microanalysis, and laser ablation mass spectrometry to the Tissint martian meteorite in order to find and elucidate a geochemical signature characteristic of low-temperature alteration at or near the martian surface. Tissint contains abundant shock-produced quench-crystallized melt pockets containing water in concentrations ranging from 73 to 1730 ppm; water content is positively correlated with Cl content. The isotopic composition of hydrogen in the shock-produced glass ranges from $\delta D = 2559$ to 4422‰. Water is derived from two distinct hydrogen reservoirs: the martian near-surface (>500‰) and the martian mantle (−100‰). In one shock melt pocket comprising texturally homogeneous vesiculated glass, the concentration of H in the shock melt decreases while simultaneously becoming enriched in D, attributable to the preferential loss of H over D to the vesicle while the pocket was still molten. While igneous sulfides are pyrrhotite in composition ($Fe_{0.88\text{-}0.90}S$), the iron to sulfur ratios of spherules in shock melt pockets are elevated, up to $Fe_{1.70}S$, which we attribute to shock-oxidation of igneous pyrrhotite and the formation of hematite at high temperature. The D- and Cl-enrichment, and higher oxidation of the pockets (as indicated by hematite) support a scenario in which alteration products formed within fractures or void spaces within the rock; the signature of these alteration products is preserved within shock melt (now glass) which formed upon collapse of these fractures and voids during impact shock. Thermal modeling of Tissint shock melt pockets using the HEAT program demonstrates that the shock melt pockets with the greatest potential to preserve a signature of aqueous alteration are small, isolated from other regions of shock melt, vesicle-free, and glassy.

Keywords: Martian meteorites; Alteration; Shock; Water; Chlorine; Hydrogen Isotopes

1. INTRODUCTION

Tissint, a recent martian meteorite fall from Morocco, has received much attention in the literature with respect to possible martian low-temperature (i.e., secondary) alteration products reported in its first description (Chennaoui Aoudjehane et al., 2012) and also its shock metamorphic history (Baziotis et al., 2013; Walton et al., 2014). The short terrestrial residence time of Tissint (approximately three months) in a hot desert environment means that recovered stones are in near-pristine condition, which implies that any secondary alteration products present in the meteorite are likely martian, not terrestrial. Tissint is also of interest

---

[*] Corresponding author.
E-mail address: herd@ualberta.ca (C.D.K. Herd).

[1] Current address: University of Manitoba, Department of Geological Sciences, Winnipeg, Manitoba R3T 2N2, Canada.

http://dx.doi.org/10.1016/j.gca.2017.04.037

because of its strongly shocked nature, containing numerous "black, glassy" shock melt pockets (Chennaoui Aoudjehane et al., 2012) which themselves variably contain high-pressure polymorphs (e.g., Walton et al., 2014). These shock melt pockets, as well as veins formed during shock by friction-induced melting, cross-cut what is otherwise a fairly typical olivine-phyric shergottite (Chennaoui Aoudjehane et al., 2012).

Recent studies assessing whether the signature of low-temperature alteration is preserved within Tissint have yielded contradictory results – primarily because no discrete, pre-terrestrial alteration products have been identified (e.g., Chennaoui Aoudjehane et al., 2012). Instead, the geochemistry of shock-generated glass is indicative of low-temperature alteration at or near the martian surface: trace element patterns demonstrate that shock melt glass is enriched in light rare earth elements (LREE) with a positive cerium anomaly which may be explained by oxidation to Ce^{4+} (Chennaoui Aoudjehane et al., 2012). Chennaoui Aoudjehane et al. (2012) proposed a scenario in which the Tissint basaltic host rock is emplaced in a surface flow or shallow sill; subsequent low-temperature alteration (particularly of phosphates, carriers for REE) results in secondary minerals within cracks and fractures. These secondary minerals are preferentially melted (and subsequently quenched to glass) during the impact event that ejects the rock into space; as such, only their geochemical signature now remains. Conversely, Barrat et al. (2014) characterized the bulk Tissint and shock-produced glass for major, minor, and trace elements, finding no LREE enrichment or positive cerium anomaly. To explain these contradictory findings, Barrat et al. (2014) suggested that the Tissint samples studied by Chennaoui Aoudjehane et al. (2012) experienced minor terrestrial weathering and thus the glass had been contaminated. They argue that even with favorable fall and collection conditions such as a short pre-collection residence in a hot desert (several months to a few years), meteorites may be susceptible to significant chemical alteration by terrestrial processes (Barrat et al., 1999; Crozaz and Wadhwa, 2001; Crozaz et al., 2003). In contrast, Chen et al. (2015) found unambiguous evidence for volatiles (H_2O, CO_2, F and Cl) within impact-melt pockets in Tissint, with correlations in concentrations and isotopic compositions, and evidence for minimal, if any, terrestrial contamination. A linear correlation between water content and deuterium enrichment (Chen et al., 2015) indicates mixing between the water-poor, D-poor igneous rock and a surface volatile component with a composition similar to that measured in martian surface rocks and atmosphere (e.g., Webster et al., 2013; Villanueva et al., 2015). Further evidence for the incorporation of a near-surface, secondary alteration component into Tissint comes from Cl isotopes: shock melt glass-rich fractions yield $\delta^{37}Cl$ values which are heavier and distinct from the igneous and bulk fractions, consistent with incorporation of a ^{37}Cl-enriched component which results from interaction of surface volatiles with martian crust (Williams et al., 2016). While the association of surface/atmospheric volatiles with impact melt pockets supports the scenario of preferential collapse of secondary alteration-bearing fractures and voids put forward by Chennaoui Aoudjehane et al. (2012), LREE-enrichment in impact-melt pockets was sought but not found by Chen et al. (2015). Thus it appears that Tissint preserves evidence of near-surface alteration in the form of some geochemical signatures (e.g., volatiles, D isotopic composition), but not others (e.g., LREE). Furthermore, only some shergottites preserve evidence for a near surface component within shock melt glass, in the form of minor or trace elements or isotopic compositions (e.g. Schrader et al., 2016; Williams et al., 2016).

The apparent disparity between studies of Tissint, and between Tissint and other shergottites, likely arises from several factors, which include: a high degree of heterogeneity in the abundance and distribution of pre-terrestrial components within the meteorites; differences in the number and distribution of impact-melt pockets; and the nature of the shock process itself. Shock melts are caused by heterogeneous deformation and heating during shock compression, and may form by frictional heating along shear bands, collapse of pore space or shock wave collisions (Sharp and DeCarli, 2006). It is well understood that shock metamorphism is a viable mechanism for implanting gases into meteorites (e.g., Treiman et al., 2000), and it has been demonstrated that the quenched or quench-crystallized shock melt in shergottite meteorites is the specific host of the martian atmosphere component (Walton et al., 2007; Chennaoui Aoudjehane et al., 2012). A possible mechanism for incorporating martian alteration products is similar to that for gas implantation – that is, the secondary alteration materials or regolith were already present in voids or fractures in the target material. Therefore, if any martian secondary alteration products are extant within these meteorites, they will likely be associated with shock-generated melt glass. Current observations, which indicate a small amount of hydrous, secondary alteration material, support this inference (Chennaoui Aoudjehane et al., 2012; Chen et al., 2015; Schrader et al., 2016; Williams et al., 2016).

The purpose of this study is to examine the mineralogy, glass and mineral compositions, and the volatile contents of Tissint shock melt pockets in order to elucidate the nature of the secondary alteration component within shock-produced glass. High-pressure polymorphs in Tissint shock-melt pockets and veins provide insights into their pressure-temperature-time variability. We use our results to elucidate the mechanism for trapping martian volatiles within shock melt pockets and the effect of post-shock conditions on the preservation potential of this material. Our results have implications for targeting other volatile-bearing shock melt pockets in Tissint, as well as in other shergottites.

2. SAMPLES AND METHODS

2.1. Tissint

Tissint is classified as a depleted picritic olivine-phyric shergottite, based on bulk trace element composition (Irving et al., 2012) and texture, and is composed of olivine phenocrysts set in a groundmass of pyroxene and shock-