

COMPOSITIONS OF MAGMATIC AND IMPACT MELT SULFIDES IN TISSINT AND EETA79001: PRECURSORS OF IMMISCIBLE SULFIDE MELT BLEBS IN SHERGOTTITE IMPACT MELTS. D. K. Ross¹ M. N. Rao¹, L. Nyquist², C. Agee³, S. Sutton⁴ ¹Jacobs-ESCG, 2224 Bay Area Blvd., Houston TX, 77058 (daniel.ross@nasa.gov), ²NASA-JSC-ARES, 2101 NASA Parkway, Houston Tx 77059, mailcode KR, ³Institute of Meteoritics and Dept. of Earth and Planetary Sciences, Univ. of New Mexico, Albuquerque, NM, 87131, ⁴Dept. of Geophysical Sciences, University of Chicago, Chicago, IL.

Introduction: Immiscible sulfide melt spherules are locally very abundant in shergottite impact melts. These melts can also contain samples of Martian atmospheric gases [1], and cosmogenic nuclides [2] that are present in impact melt, but not in the host shergottite, indicating some components in the melt resided at the Martian surface. These observations show that some regolith components are, at least locally, present in the impact melts. This view also suggests that one source of the over-abundant sulfur in these impact melts could be sulfates that are major constituents of Martian regolith, and that the sulfates were reduced during shock heating to sulfide. An alternative view is that sulfide spherules in impact melts are produced solely by melting the crystalline sulfide minerals (dominantly pyrrhotite, Fe_{1-x}S) that are present in shergottites [3]. In this abstract we report new analyses of the compositions of sulfide immiscible melt spherules and pyrrhotite in the shergottites Tissint, and EETA79001,507, and we use these data to investigate the possible origins of the immiscible sulfide melt spherules. In particular, we use the metal/S ratios determined in these blebs as potential diagnostic criteria for tracking the source material from which the numerous sulfide blebs were generated by shock in these melts.

Analytical Method: As these sulfide blebs are often $\sim <1\text{-}5$ microns in size, FE-SEM is better suited for studying them, rather than EPMA, because of the nanometer beam size and the ease of carefully siting the spot to be analyzed. Metal/S ratios (atomic) were determined in sulfide blebs (metal usually consisting of only Fe + Ni + Cr within our detection limits, but overwhelmingly dominated by Fe) using the JEOL FE-SEM lab. at NASA-JSC, equipped with an SD-ED x-ray detector.

Results and Discussion: Most blebs yielded spectra showing Fe and S peaks (some with small amounts of Ni, or Cr) showing that the vast majority of blebs are immiscible sulfide melts. However, among numerous sulfide blebs, there are rare spherical blebs yielding Fe, S and O signals suggesting iron sulfate minerals as possible contributing precursors. Note that the modal abundance of the sulfide blebs in some of these impact melt pockets is $> 15\%$, whereas the modal abundance of sulfide (pyrrhotite) in host rocks is typically very low (average $\sim 0.4\%$, ref. 4). It appears difficult to pro-

duce such large concentrations of sulfides in melt pockets by shock-melting the host rock sulfides alone.

Backscattered electron images of sulfide-rich impacts melts are shown in Fig. 1a (Tissint) and Fig. 2a (EETA79001,507). Metal/S ratios were determined in large S-bearing blebs ($> 2\text{ }\mu\text{m}$ size) in impact melt pockets in Tissint and the results are shown in Fig. 1b. Metal/S ratios measured in Tissint vary over a wide range from ~ 0.52 to 1.12 (blue bars). Pyrrhotite metal/S ratios of $0.87\text{-}0.92$ were measured in crystalline igneous sulfide (large angular grains) in Tissint and plotted in Fig. 1 (red bars). The pyrrhotite ratios found here are <1 and are in agreement with M/S of pyrrhotites measured in other shergottites by [4]. Fig. 2b shows the compositions of crystalline sulfides, and immiscible sulfide melt blebs in EETA79001,507. Our data for sulfides in EETA79001,507 show immiscible melts with M/S ratios exceeding 1, and dissimilar to that found in pyrrhotites. Metal/S ratios determined in some sulfide blebs in Tissint, and in EETA79001,507 are >1 and suggest that these sulfide blebs are not direct melts of pyrrhotite.

In EETA79001,507, metal/S ratios were determined in several $\sim 2\text{-}5\text{ }\mu\text{m}$ size blebs in a large impact melt pocket #507 (these blebs show Fe and S but no oxygen signal). We found an average value of 1.08 (range $1.03\text{-}1.12$) for the metal/S ratio in the sulfide blebs. The metal/S ratios found in EETA79001,507 are similar to those found in some locations in Tissint.

Rare sulfide blebs showing Fe and S peaks and oxygen peaks were also detected in both of these meteorites. In two clusters of $\sim 1\text{-}2\text{ }\mu\text{m}$ grains located in different melt pockets in EETA79001,507, we found metal/S ratios of 1.36 and 1.42 . These grains showed an oxygen peak in addition to Fe and S peaks suggesting sulfate as a precursor. Also, we found similar blebs in Tissint showing Fe, S and oxygen signals in the FE-SEM spectra suggestive of sulfate. These oxygen-bearing blebs in Tissint yielded metal/S ratios of 1.5 and 2.3 . There is a small amount of Ni ($\sim 1\text{-}3\%$) in Tissint blebs whereas the Ni content of 507 blebs is close to the detection limit. The oxygen bearing blebs in Tissint and EETA79001,507 are spherical, indicating their origin as immiscible melts, but are distinctive relative to most blebs due to their high oxygen content. Several immiscible sulfide blebs are observed with a range of intermediate compositions between pyrite-like

(metal/S ~ 0.5) and pyrrhotite-like compositions (~ 0.9) as end members.

The wide range of metal/S ratios in immiscible sulfide melts in Tissint argues against an origin simply and solely by direct melting of pyrrhotite grains in the host rock. We doubt that sufficient time for extensive exchange of metal and sulfur between silicate and sulfide impact melts was available to permit production of the wide range of M/S ratios in the sulfide melts. Moreover, the Fe and S abundances in enclosing silicate impact melts have only limited ranges, negating the likelihood of varying chemical potentials between silicate and sulfide impact melts driving the production of the wide range of sulfide impact melt compositions.

In summary, S-bearing blebs in Tissint and EET79001,507 are produced from at least two, and perhaps more precursor materials. Some blebs appear to be direct melts of pyrrhotite precursors, but others with metal/S ratios >1 , and very rarely with oxygen dissolved in them, appear to require precursors with metal/S > 1 . They are likely produced from a ferric sulfate bearing material such as jarosite which abundantly occurs near Meridiani, Mawrth Vallis, etc. on Mars surface [6-7]. We suggest that some impact-melted sulfide droplets in both Tissint and EETA79001,507 were produced by shock-reduction of sulfate, and melting to produce immiscible sulfide melt with metal/S ratios >1 , and other sulfide droplets resulted from direct melting of host-rock crystalline sulfide minerals (pyrrhotite).

References: [1] D.D. Bogard and P. Johnson, *Science*, 221, 651, 1983. [2] M.N.Rao et al. *JGR*, 116, doi: 10.1029/2010JE003764. [3] E. Walton et al. *GCA*, 74, 4829, 2010 [4]. J. P. Lorand et al., *Meteorit. Planet. Sci.* 40, 1257, 2005. [6]. W.H. Farrand et al. *Icarus*, 204, 478, 2009. [7] G. Klingelhofer et al. *Science*, 306, 1740, 2004.

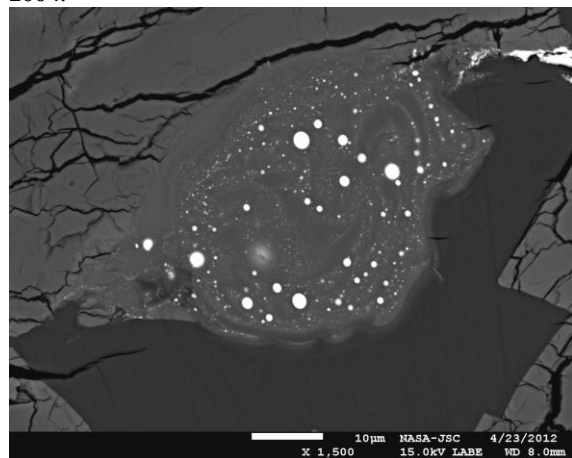


Fig.1a. BSE image of immiscible sulfide droplets in a small impact melt pocket in Tissint.

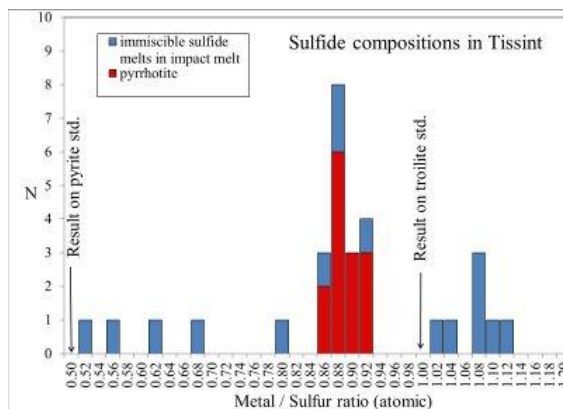


Fig. 1b. Histogram of metal/S ratios in Tissint sulfides.

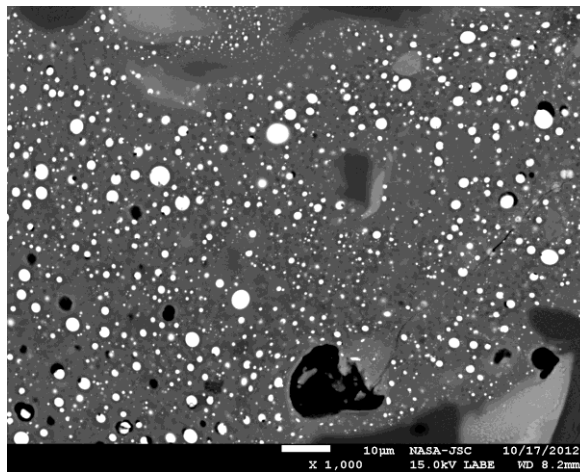


Fig. 2a. BSE image of abundant sulfide droplets in a large melt pocket in EETA79001,507.

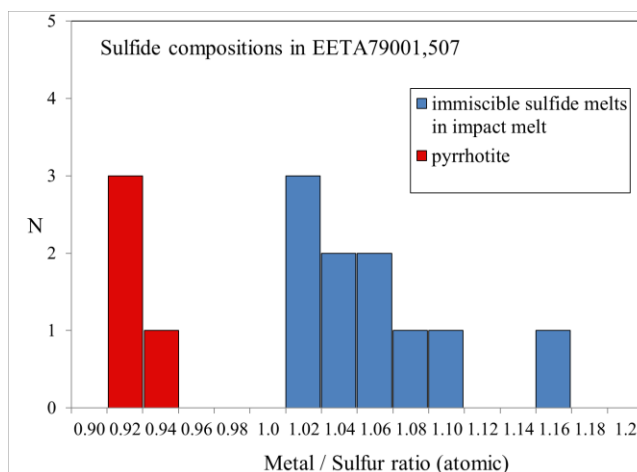


Fig. 2b. Histogram of metal/S ratios in EETA79001 sulfides.