DISCOVERY OF STÖFFLERITE, $(Ca,Na)(Si,Al)_4O_8$ IN HOLLANDITE STRUCTURE, A SHOCK-INDUCED, HIGH-PRESSURE MINERAL IN THE TISSINT MARTIAN METEORITE.

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Introduction: With advanced electron-beam and synchrotron techniques, more than ten new high-pressure minerals and phases have been discovered in shocked Martian meteorites since 2013 [e.g., 1-3], including stöfflerite (IMA 2017-062) – a high-pressure polymorph of anorthite [4]. These findings provide insights into shock conditions and impact processes on Mars, and also inform the study of deep Earth systems at high pressures and temperatures. We identified and named stöfflerite based on its occurrence in the Northwest Africa (NWA) 856 shergottite [4]. During a nanomineralogy investigation of the Tissint shergottite, we also found stöfflerite, with other recently-discovered high-pressure minerals, tissintite [2], ahrensite [3], and chenmingite [5]. Here, we report the occurrence of stöfflerite from Tissint, and discuss its origin and significance. We characterized its petrography, composition, structure using a field-emission scanning electron microscope, low-voltage (10 kV) electron probe microanalysis (EPMA), and synchrotron X-ray diffraction (SXRD).

Stöfflerite is natural $(Ca,Na)(Si,Al)_4O_8$-hollandite. This high pressure polymorph of anorthite is isotypic with lingunite ($NaAlSi_3O_8$-hollandite) and liebermannite ($KAlSi_3O_8$-hollandite) [6] and crystallizes in space group *I*4*/m*. Prior to our full structural characterization and approval as a mineral from a shock melt pocket in NWA 856 [4], observation of $(Ca,Na)(Si,Al)_4O_8$-hollandite was reported by [7] via transmission electron microscopy and by [8] via Raman-spectroscopy in the Zagami shergottite, and by [9,10] from the Manicouagan impact structure, Canada, based on electron backscatter diffraction (EBSD) and Raman analyses. $CaAl_2Si_2O_8$-hollandite was synthesized from a laser-heating experiment on anorthite at > 14 GPa [11].

Occurrence, chemistry, and crystallography: Stöfflerite occurs as aggregates in or adjacent to a shock melt pocket in Tissint (Figs. 1-3). The melt pocket is ~ 50 × 340 μm^2 in size in the plane of the thin section, contains bridgmanite, wüstite, xieite, stishovite and zagamiite, and is surrounded by augite, pigeonite, maskelynite, ahrensite, ringwoodite and olivine. Overall, the host rock consists mainly of pyroxene (mostly zoned clinopyroxene), maskelynite (An_{58-69}), and olivine (typically ~Fo_{70}, ranging from Fo_{35} to Fo_{81}), with minor merrillite and chromite and trace sparse pyrrhotite, magnetite, and ilmenite [e.g.,

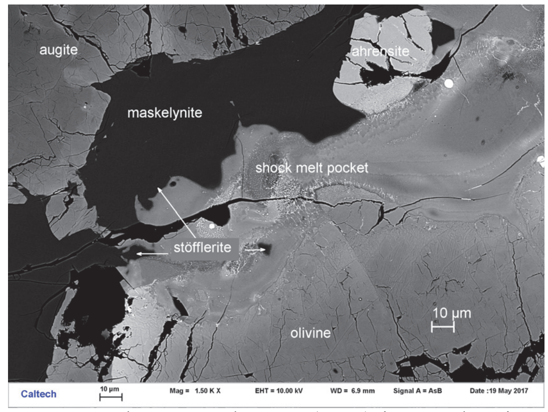

Fig. 1. Back-scatter electron (BSE) image showing stöfflerite in or adjacent to a shock melt pocket in Tissint section UT1.

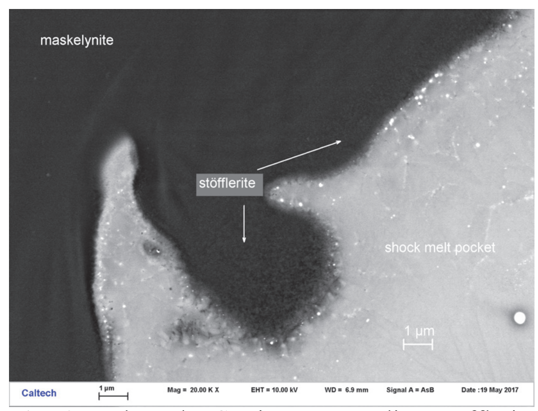

Fig. 2. Enlarged BSE image revealing stöfflerite adjacent to the shock melt pocket.

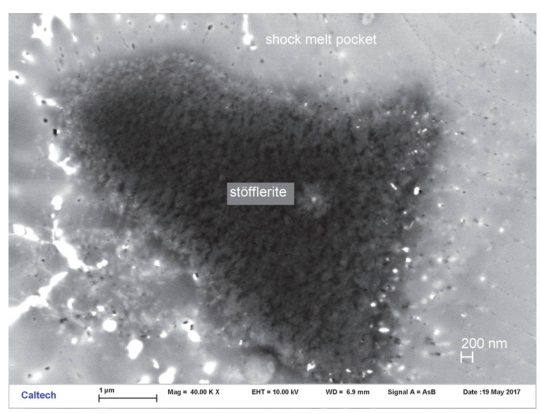

Fig. 3. Enlarged BSE image showing stöfflerite within the shock melt pocket.

2,3]. Melt pockets and veins are scattered throughout the meteorite.

Stöfflerite occurs as nano-crystals, <50 nm in size, (Figs. 2-3), which are electron beam sensitive and also too small for EBSD analysis. Its crystal structure, based on analysis of SXRD data, is the tetragonal $I4/m$ hollandite-type structure with unit cell parameters: a = 9.22(2) Å, c = 2.71(1) Å, V = 230(1) Å^3, Z = 2, yielding a calculated density of 3.94 g/cm^3. The mean chemical composition of stöfflerite by EPMA (Table 1) yields an empirical formula (for 8 O atoms *pfu*) of $(Ca_{0.60}Na_{0.35}K_{0.01})(Si_{2.42}Al_{1.55}Fe_{0.04}Mg_{0.01})O_8$, which is same to the composition of nearby maskelynite (An_{62}).

Zagamiite, $(Ca,Na)(Al,Fe,Mg,)_2(Si,Al,\square)_4O_{11}$ with a $P6_3/mmc$ hexagonal structure [12, 13], was identified by SXRD in this stöfflerite-bearing melt pocket along with stishovite, occurring as fine-grained prismatic crystals, crystallized from a melt of Ca-rich plagioclase and minor clinopyroxene.

Tissintite, $(Ca,Na,\square_{1/4})AlSi_2O_6$, is another high-pressure polymorph of Ca-rich plagioclase, discovered in a number of shock melt pockets from Tissint [2]. However, tissintite was not identified in this stöfflerite-bearing shock melt pocket; stöfflerite was not observed in tissintite-bearing shock melt pockets. Tissintite is more common than stöfflerite in Tissint. Crystal sizes of tissintite are up to 3 µm in diameter (Fig. 4), much larger than those of stöfflerite. Tissintite is not electron beam sensitive, giving rise to decent EBSD patterns.

Origin and significance: Stöfflerite and tissintite are the only high-pressure polymorphs of Ca-rich plagioclase reported from nature, here formed by shock metamorphism during the impact event(s) on Mars that led to the excavation and ejection of Tissint off the red planet.

Tissint is a highly-shocked, olivine-phyric shergottite. Olivine is often transformed to ringwoodite or ahrensite and, in melt veins or pockets, even to bridgmanite plus wüstite [3]. Chromite is transformed to xieite or chenmingite [5]. The overall chemistry of stöfflerite, tissintite and maskelynite suggests plagioclase as precursor. Plagioclase is transformed to maskelynite in the host rock or melted and partially crystallized to tissintite [2] or stöfflerite [this study] in melt pockets. These responses to shock conditions on Mars provide clues to the nature of ejection events for Martian meteorites and to local shock conditions.

Table 1. EPMA data for stöfflerite in Tissint.

Constituent (wt%)	stöfflerite (n=12)	S.D.
SiO_2	53.02	0.90
Al_2O_3	28.92	0.49
CaO	12.32	0.46
Na_2O	3.93	0.20
FeO	1.14	0.20
K_2O	0.13	0.03
MgO	0.14	0.02
TiO_2	0.06	0.05
Total	99.65	

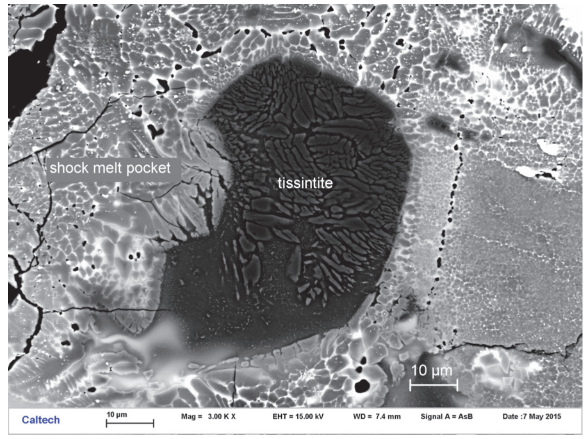

Fig. 4. BSE image showing tissintite – a high-pressure clinopyroxene with plagioclase composition (An_{62}), in a different Tissint shock melt pocket.

Given their composition and location in the midst of melt pockets, both stöfflerite and tissintite apparently formed at high P-T, perhaps via maskelynite melt or solid-state transformation of maskelynite, with higher T or cooling rates slower than for maskelynite outside melt pockets that is key to their formation. Stöfflerite is denser than tissintite. Given the crystal sizes, stöfflerite might have formed in melt pockets with cooling rates faster than for tissintite-bearing melt pockets.

The sequence diaplectic glass (maskelynite) → stöfflerite → zagamiite + stishovite was observed in shergottites NWA 856 and Zagami, indicating that the peak shock pressures for these meteorites are 20-22 GPa [4]. Stöfflerite in Tissint probably formed under similar conditions.

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