

STÖFFLERITE, $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$ 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, named in honor of Dieter Stöffler [4]. These findings provide insights into shock conditions and impact processes on Mars, and also inform the study of deep Earth systems. We identified and named stöfflerite based on its occurrence in the 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 present the occurrence of stöfflerite in Tissint, and discuss its origin and significance.

Occurrence, Chemistry, and Crystallography: Tissint is an olivine-phyric shergottite with scattered shock melt pockets and veins. Stöfflerite occurs as aggregates adjacent to a shock melt pocket (Fig. 1). The melt pocket is $\sim 50 \times 340 \mu\text{m}^2$ in size in the plane of a thin section, contains bridgmanite, wüstite, xieite, stishovite and zagamiite, and is surrounded by augite, pigeonite, maskelynite, ahrensite, ringwoodite and olivine.

Stöfflerite occurs as nanocrystals, $<50 \text{ nm}$ in size (Fig. 1), which are electron beam sensitive and also too small for EBSD analysis. Its crystal structure, based on analysis of SXRD data, has the tetragonal $I4/m$ hollandite-type structure with unit cell parameters: $a = 9.22(2) \text{ \AA}$, $c = 2.71(1) \text{ \AA}$, $V = 230(2) \text{ \AA}^3$, $Z = 2$, yielding a calculated density of 3.87 g/cm^3 . The mean chemical composition of stöfflerite by EPMA shows an empirical formula of $(\text{Ca}_{0.60}\text{Na}_{0.35}\text{K}_{0.01})(\text{Si}_{2.42}\text{Al}_{1.55}\text{Fe}_{0.04}\text{Mg}_{0.01})\text{O}_8$, which is same to the composition of nearby maskelynite (An62).

Origin and Significance: Stöfflerite is natural $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$ -hollandite. This high-pressure polymorph of anorthite is isotopic with lingunite ($\text{NaAlSi}_3\text{O}_8$ -hollandite) and liebermannite (KAlSi_3O_8 -hollandite). 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.

In Tissint, olivine is often transformed to ringwoodite or ahrensite in the vicinity of melt veins or pockets, and in immediate contact melt to bridgmanite plus wüstite [3]. In such regions, chromite is transformed to xieite or chenmingite [5]. Plagioclase is transformed to maskelynite in the host rock, whereas in the surrounding of melt pockets it is transformed to tissintite [2] or stöfflerite [this study].

Given its composition and location in contact with the melt pocket, stöfflerite is likely formed at high P-T via solid-state transformation of maskelynite, with higher T or cooling rate slower than for maskelynite outside melt pockets key to its formation. Stöfflerite is denser than tissintite. They do not occur in same melt pockets. Given the crystal sizes, stöfflerite might have formed next to melt pockets with cooling rates faster than for tissintite-bearing melt pockets. The sequence diaplectic glass (maskelynite) \rightarrow stöfflerite \rightarrow zagamiite + stishovite was observed in shergottites NWA 856 and Zagami, indicating that the peak shock pressures for these meteorites are 20-22 GPa [4,6]. Stöfflerite in Tissint probably formed under similar conditions.

References: [1] Ma C. (2018) *Am. Mineral.*, 103, 1521–1522. [2] Ma C. et al. (2015) *EPSL*, 422, 194–205. [3] Ma C. et al. (2016) *GCA*, 184, 240–256. [4] Tschauer O. et al. (2021) *Am. Mineral.*, 106, 650–655. [5] Ma C. et al. (2019) *Am. Mineral.*, 104, 1521–1525. [6] Ma C. et al. (2024) *Minerals*, 14(1), 18.

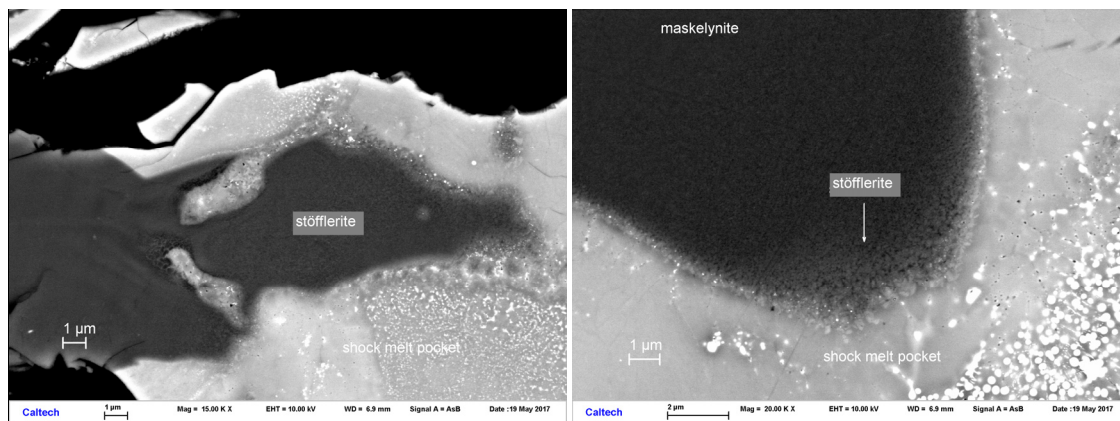


Fig. 1. BSE images revealing stöfflerite adjacent to a shock melt pocket in the Tissint shergottite.