# IN SITU SHOCK VEINS ON EARTH: DONWILHELMSITE, MASKELYNITE, STISHOVITE, STÖFFLERITE, TISSINTITE (AND MORE) FROM THE MANICOUAGAN IMPACT STRUCTURE.

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**Introduction:** Shock veins are a common feature of many meteorite types but they have been only described on Earth from a limited number of locations. To date, in situ shock veins have been documented from three impact structures: Vredefort [1], Manicouagan [2] and Steen River [3]. Ex situ (allochthonous) shock veins have also been described in lithic clasts from suevites in the Ries [4] and Xiuyan [5] impact structures. The terrestrial in situ occurrences provide important constraints on the likely source volumes within the cratering regime; a parameter lost in meteorites and terrestrial ex situ examples. The three terrestrial in situ examples suggest that their shock veins originate from uplifts that were buried at the time of contact and compression and remained so during excavation (i.e., being located below the transient cavity). The uplifts subsequently breached surface during the modification stage. The uppermost surface underwent exfoliation and spall to release nascent meteors, with the remaining material locally retaining in situ shock veins.

Here we present results from shock veins developed in the central uplift of the Manicouagan impact structure of Quebec, Canada. The shock veins occur in anorthositic rocks, which provide a link to lunar materials, given the plagioclase-dominant composition of the Moon's Feldspathic Highlands and associated regolith. Building on previous work [6,7], and using various analytical techniques, we have been able to expand the number of polymorphs and minerals species recognized within the veins and their margins.

**Analytical Techniques:** Analytical field emission scanning electron microscopy was performed with an Hitachi SU70 model with an Oxford Instruments energy dispersive spectrometer (EDS), and a ZEISS 1550VP with EDS and EBSD. Raman spectroscopy utilized a Renishaw InVia model equipped with 514 nm argon and 785 nm solid-state lasers. Quantitative elemental microanalysis was performed using a JEOL JXA-iHP200F field emission electron probe microanalyzer (FE-EPMA). Synchrotron diffraction data were obtained at the GSECARS undulator beamline 13-IDD, Advanced Photo Source, Argonne National Laboratory, U.S.A., using a microfocused beam (3 × 4 $mm^2$) of $\lambda$= 0.4133 Å and a MAR165 CCD area Synchrotron X-ray detector. Sample detector distance and geometric correction factors were determined using GSE-ADA [8] and Dioptas [9]. Diffraction frame integration was conducted with Dioptas software. Diffraction data cover a range down to ~0.69 Å.

**Geologic Setting:** The Manicouagan impact structure was formed at 215 Ma within target rocks of the ~1 Ga Grenville Province [10]. The structure is elliptical in shape with a collapsed rim-to-rim diameter of 85 x 75 km [11]. An impact melt sheet of variable thickness (250 m to 1800 m) covers most of the central island (Île René Levasseur), which is breached by a central uplift comprising metamorphosed anorthositic rocks [12]. Locally, the anorthosites are pervaded by thin (1-5 mm wide) white veins, which contain high pressure-high temperature polymorphs [2], similar to to shock veins developed in many meteorites [13].

**Previous Shock Vein Studies at Manicouagan:** The shock veins are exposed on Mont de Babel and Maskelynite Peak on the central island of Île René Levasseur. They are most commonly observed as clusters of thin (<2.5 mm), milky-white wispy veins that contrast with the more darkly weathered outcrop surface.

| *Polymorph* | *Unit Cell Dimensions $10^{-10}$ m* | *Density g/cm³* |
|---|---|---|
| Triclinic $An_{54}$ (with PDFs) **Labradorite (Manic)** | a = 8.22; b = 12.91; c = 14.20 α = 92.8; β = 115.8 γ = 91 | 2.66 |
| Tetragonal ($Sto_{54}Lin_{46}$) (hollandite-structure) **Stöfflerite (Manic)** | a and b = 9.31; c = 2.72 α and β and γ = 90 | 3.82 |
| ($Sto_{60}Lin_{40}$) **Stöfflerite (NWA 856)** Tschauner et al. 2021 [13] | a and b = 9.255; c = 2.742 α and β and γ = 90 | 3.84 |
| Monoclinic (clinopyroxene structure) **Tissintite (Manic)** | a = 9.45; b = 8.614; c = 5.24 α and γ = 90; β ~107.57 (jadeite) | 3.34 |
| Monoclinic $(Ca,Na,\square)AlSi_2O_6$ **Tissintite (Tissint)** Ma et al. 2015 [14] | a = 9.21; b = 9.09; c = 5.20 α and γ = 90; β = 109.6 | 3.32 |

Table 1. Calculated unit cell dimensions and densities of polymorphs with plagioclase composition from Manicouagan (Manic) compared to stöfflerite from the lunar meteorite NWA 856 [14] and tissintite from the Tissint martian meteorite [15].

Some clusters are dominated by curvilinear veins that display consistent angular relationships with respect to one another [2]. Offset associated with the shock veins is typically <<2 mm, if recognized. Spacing between individual veins ranges from centimeters to meters. Previous work on the Manicouagan shock veins has revealed maskelynite, stishovite and kyanite [2] and distinct tetragonal and monoclinic structures [6,7], the latter two originally being identified via EBSD as (a) a tetragonal phase with plagioclase composition and (b) a jadeite-like (monoclinic) phase (Table 1 & Fig. 1).

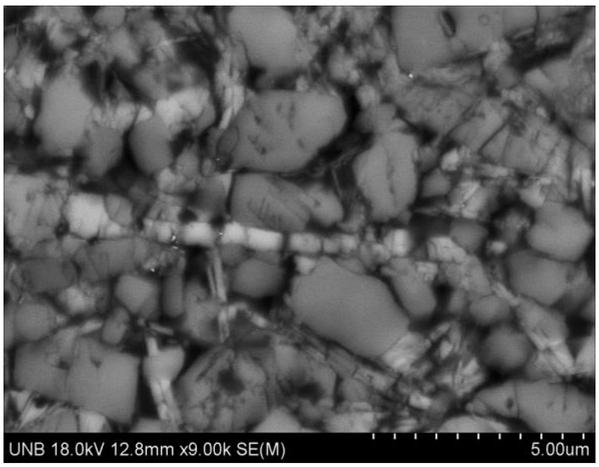

Figure 1. FESEM secondary electron image showing lighter-toned hexagonal phase (donwilhelmsite) and darker-toned monoclinic phase (tissintite).

**New Insights:** Synchrotron diffraction, FE-SEM and FE-EPMA have been deployed to explore the shock veins at Manicouagan in more detail. Several additional high pressure-high temperature phases have been identified (Fig. 1). These include a number of Ca-Al silicates: stöfflerite $(Ca,Na)(Al,Si)_4O_8$ [14], tissintite $(Ca,Na,\square)AlSi_2O_6$ type I [15], donwilhelmsite, ideally $CaAl_4Si_2O_{11}$ [16], and grossular-rich garnet.

Table 2. EPMA data for tissinite and donwilhelmsite from the Manicouagan impact structure.

| Constituent (wt%) | Tissintite (n=6) | Donwilhelmsite (n=6) |
|---|---|---|
| $SiO_2$ | 54.58 | 43.52 |
| $TiO_2$ | 0.07 | 0.08 |
| $Al_2O_3$ | 29.01 | 42.22 |
| CaO | 10.65 | 11.12 |
| $Na_2O$ | 5.48 | 1.00 |
| FeO | 0.27 | 0.37 |
| $K_2O$ | 0.14 | 0.44 |
| MgO | 0.07 | 0.07 |
| Total | 100.27 | 98.82 |

At Manicouagan, tissintite has an empirical formula of $(Ca_{0.39}Na_{0.36}K_{0.01}\square_{0.24})(Al_{0.99}Fe_{0.01})(Si_{1.84}Al_{0.16})O_6$, and donwilhelmsite an empirical formula of $(Ca_{0.75}Na_{0.12}K_{0.04})(Al_{3.12}Si_{2.73}Fe_{0.02}Mg_{0.01})O_{11}$ (Table 2).

**Conclusions:** New analyses obtained from shock veins in the Manicouagan impact structure reveal the presence of stöfflerite, donwilhelmsite, tissintite and grossular in addition to the stishovite, kyanite and maskelynite previously described [2,6,7]. These phases are limited to shock veins and their margins as part of the anorthositic central uplift. Modification stage uplift is estimated to be 8-10 km, with the sample positioned ~11.7 km from ground zero at the time of impact. At this location, and using the methodology of Hopkins and Spray [17], we calculate an initial shock vein melt temperature of 1850 ºC, an attenuated shock front pressure of ~14 GPa and a detached shock wave width of ~4 km. Dwell time (i.e., duration at P >1 GPa) was determined to be 0.745 s. While the stability fields of many of these newer phases remain poorly defined, the calculated conditions define a P-T-t window for the development and preservation of these mineral species.

Manicouagan provides valuable terrestrial context for shock vein formation and the development of stishovite, maskelynite and several Ca-Al silicates that have previously only been described from meteorites.

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