

DISCOVERY OF A NEW HIGH-PRESSURE SILICATE PHASE, $(\text{Fe,Mg,Cr,Ti,Ca},\square)_2(\text{Si,Al})\text{O}_4$ WITH A TETRAGONAL SPINELLOID STRUCTURE, IN A SHOCK MELT POCKET FROM THE TISSINT MARTIAN METEORITE. Chi Ma^{1,*}, Oliver Tschauner², John R. Beckett¹; ¹Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA; ²Department of Geoscience, University of Nevada, Las Vegas, NV 89154, USA; *chi@gps.caltech.edu.

Introduction: The Tissint Martian meteorite 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 [1]. Plagioclase is transformed to maskelynite or even melted and partially crystallized to tissintite [2]. Chromite is transformed to xieite or chenmingite [3]. These responses to shock conditions on Mars provide clues to the nature of ejection events for Martian meteorites and to local shock conditions. Where new-to-science high-pressure phases are discovered, meteoritic occurrences can also inform the study of deep Earth systems at high pressures and temperatures.

During an ongoing nanomineralogy investigation of the Tissint shergottite, we discovered the new high-pressure minerals ahrensite [1], tissintite [2] and chenmingite [3]. Here, we describe a new high-pressure, Fe-rich, Cr-,Ti-bearing silicate in Tissint, $(\text{Fe,Mg,Cr,Ti,Ca},\square)_2(\text{Si,Al})\text{O}_4$ with a tetragonal $I4_1/amd$ spinelloid structure. It occurs on an aggregate of xieite grains in a shock melt pocket (Figs. 1-2). We characterized its composition, structure and petrography using a high-resolution scanning electron microscope (SEM), electron back-scatter diffraction (EBSD), and low-voltage (10 kV) electron probe microanalysis (EPMA). We also attempted synchrotron X-ray diffraction (SXR) but were unable to acquire structural information on the new phase. For the purposes of this abstract, we refer to this material as “phase Spd-II” in deference to the magnesian “phase Spd” [with a formula of $(\text{Mg,Fe,Si},\square)_2\text{SiO}_4$] observed by [4] in Tenham.

Occurrence, chemistry, and crystallography: In Tissint, phase Spd-II occurs as euhedral crystals bounding an aggregate of xieite grains within a shock melt pocket (Fig. 2). The melt pocket is about $120 \times 160 \mu\text{m}^2$ in the plane of the thin section. The xieite grains formed after chromite in the melt pocket (note residual chromite in Fig. 2); the high-pressure phases ringwoodite, ahrensite, bridgmanite and wüstite are also found in or adjacent to this melt pocket, which is surrounded by olivine and pyroxene. Overall, the host rock consists mainly of pyroxene (mostly zoned pigeonite), ‘maskelynite’ (An58-69), and olivine (typically ~Fo₇₀ but ranging from Fo₄₀ to Fo₈₀), with minor ilmenite and chromite and trace pyrrhotite, magnetite, and merrillite [e.g., 1,2]. Melt pockets and veins are scattered throughout the meteorite.

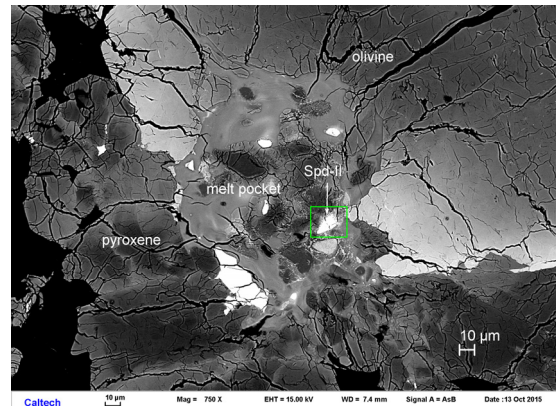


Fig. 1. Backscatter electron (BSE) image showing a Tissint melt pocket and surrounding phases. Rectangle outlines region shown in Fig. 2.

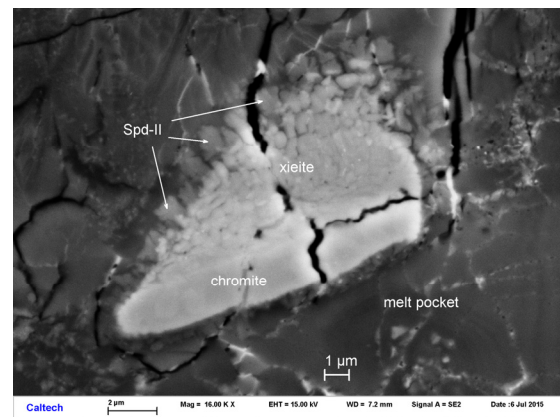


Fig. 2. Enlarged BSE image showing phase Spd-II on an aggregate of xieite grains, within the melt pocket.

Phase Spd-II occurs as lath-shaped crystals, $\sim 0.2 - 1.0 \mu\text{m}$ in size, extending from a xieite substrate into the melt region. Its composition (Table 1) gives rise to an empirical formula based on 7 oxygen *apfu* of $(\text{Fe}_{1.63}\text{Mg}_{1.12}\text{Ti}_{0.13}\text{Ca}_{0.11}\text{Mn}_{0.02}\text{Na}_{0.01})(\text{Si}_{1.64}\text{Cr}_{0.21}\text{Al}_{0.17}\text{P}_{0.01})\text{O}_7$ with a corresponding general formula of $(\text{Fe,Mg,Ti,Ca})_3(\text{Si,Cr,Al})_2\text{O}_7$ [i.e., one third molecule of $\frac{1}{2}\text{FeCr}_2\text{O}_4 + \frac{1}{2}\text{Fe}_2\text{TiO}_4$ plus two thirds molecule of $(\text{Fe,Mg})_2\text{SiO}_4$ plus one molecule of $(\text{Mg,Fe,Ca})\text{SiO}_3$]. EBSD (Fig. 3) reveals that this silicate has a tetragonal $I4_1/amd$ spinelloid structure (the pattern was indexed using $a = 5.92\text{\AA}$ and $c = 8.34\text{\AA}$ from [4], yielding mean angular deviations $< 0.63^\circ$), similar to that of the phase Spd discovered in Tenham

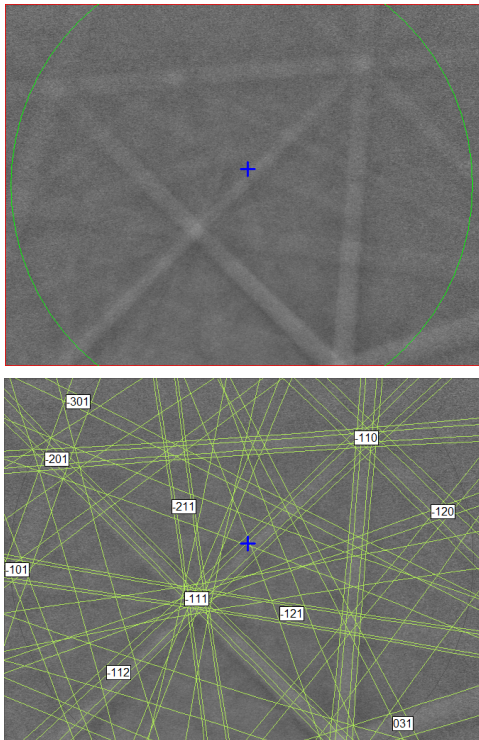


Fig. 4. (top) EBSD pattern of one crystal of Spd-II; (bottom) the pattern indexed with the tetragonal spinel-oid structure using crystallographic parameters from [4]. The blue cross indicates the center-point of the pattern

Table 1. EPMA data for Fe-rich silicate Spd-II.

Constituent wt%	Spd-II n=5	SD
SiO ₂	32.54	0.50
FeO	38.81	1.15
MgO	14.92	1.31
Cr ₂ O ₃	5.25	0.29
TiO ₂	3.48	0.63
Al ₂ O ₃	2.79	0.10
CaO	1.96	0.66
MnO	0.58	0.12
Na ₂ O	0.15	0.02
P ₂ O ₅	0.14	0.07
Total	100.62	

by [4]. This implies that the structural formula should be based on 4 oxygens *pfu*, which leads to an empirical formula of $(\text{Fe}_{0.93}\text{Mg}_{0.64}\text{Cr}_{0.12}\text{Ti}_{0.08}\text{Ca}_{0.06}\text{Al}_{0.02}\text{Na}_{0.01}\text{Mn}_{0.01}\square_{0.13})_{\Sigma 2.00}(\text{Si}_{0.93}\text{Al}_{0.07})_{\Sigma 1.00}\text{O}_4$ for Spd-II with a general formula of $(\text{Fe,Mg,Cr,Ti,Ca},\square)_2(\text{Si,Al})\text{O}_4$, where vacancies occupy about 13% of the Fe-dominant octedral site and Si

is restricted to the tetrahedral site. Note in Fig. 2, that Spd-II occurs on xieite but not on the residual chromite, even though both surfaces would have been exposed to similar melts and pressure(P)-temperature (T) conditions. This preferred nucleation may reflect a crystallographic orientation effect. Associated xieite in Fig. 2 has an empirical formula of $(\text{Fe}_{0.87}\text{Mg}_{0.10}\text{Mn}_{0.03})(\text{Cr}_{0.72}\text{Fe}^{2+}_{0.50}\text{Ti}^{4+}_{0.47}\text{Al}_{0.20}\text{Fe}^{3+}_{0.12})\text{O}_4$, close to a 50:50 mixture of FeCr_2O_4 and Fe_2TiO_4 with minor MgAl_2O_4 and Fe_3O_4 components. Residual chromite in Fig. 2 has an empirical formula of $(\text{Fe}_{0.87}\text{Mg}_{0.13})(\text{Cr}_{1.63}\text{Al}_{0.27}\text{Fe}^{3+}_{0.10})\text{O}_4$.

Origin and significance: Phase Spd-II in Tissint is a shock-induced, high P – high T, vacancy-stabilized silicate spinel with a tetragonal metric, structurally similar to the vacancy-stabilized silicate Spd in Tenham [4]. As with Spd, Spd-II is a new-to-science material. Its composition, in the form of $(\text{Fe,Mg,Ti,Ca})_3(\text{Si,Cr,Al})_2\text{O}_7$, can be derived from a mixture of olivine $(\text{Fe,Mg})_2\text{SiO}_4$ plus chromite-ulvöspinel-spinel, $\text{FeCr}_2\text{O}_4\text{-Fe}_2\text{TiO}_4\text{-MgAl}_2\text{O}_4$, plus pyroxene $(\text{Mg,Fe,Ca})\text{SiO}_3$ in various proportions with likely trace plagioclase $(\text{Ca,Na})(\text{Si,Al})_4\text{O}_8$.

In the melt pocket that contains phase Spd-II, like other melt pockets in Tissint, xieite and ringwoodite, formed through solid state transformation of chromite and olivine, respectively [1,3]. Bridgmanite and wüstite, which are also found in this melt pocket, formed from the decomposition of olivine [1]. Textures in the region containing phase Spd-II (Fig. 2) suggest that this phase nucleated on xieite but grew through crystallization from the melt, possibly taking advantage of a xieite/chromite dissolution region.

Formation of the above phases occurred at high P and T during the Tissint impact event on Mars. For example, the formation of xieite requires P in excess of ~20 GPa [5] and the presence of bridgmanite implies a peak P of at least 23-25 GPa with T on the order of 2200-2400 K [6]. If Spd-II formed after xieite, nucleation and growth may have been during cooling so that peak P-T conditions are maxima for its formation. The stability of Spd and Spd-II for typical bulk compositions in the Earth’s mantle is unknown but their possible occurrence should be taken into account, especially if one is considering the distribution of Cr.

References: [1] Ma C. et al. (2016) *Geochimica et Cosmochimica Acta* 184:240–256. [2] Ma C. et al. (2015). *Earth and Planetary Science Letters* 422:194–205. [3] Ma C. et al. (2018) LPSC 49th, Abs. #1564. [4] Ma C. et al. (2018) LPSC 49th, Abs. #1566. [5] Chen M. et al. (2003) *Proceedings of the National Academy of Science* 100:14651-14654. [6] Tschauner O. et al. (2014) *Science* 346:1100-1102.