

Revision 1

Making Tissintite: Mimicking Meteorites in the Multi - Anvil

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Abstract

Tissintite is a shock-induced Ca-rich isomorph of jadeite observed in several meteorite samples, such as the martian shergottite Tissint. It has been suggested to form within a “Goldilocks Zone,” indicating a potential to provide strict constraints on peak pressure and temperature conditions experienced during impact. Here we present the first laboratory synthesis of tissintite, which was synthesized using a large volume multi-anvil apparatus at conditions ranging from 6 – 8.5 GPa and 1000 – 1350 °C. For these experiments, we utilized a novel heating protocol in which we reached impact-relevant temperatures within 1 s and in doing so approximated the temperature-time conditions in a post-shock melt. We have established that heating for impact-relevant time scales is not sufficient to completely transform crystalline labradorite to tissintite at these pressures. Our findings suggest that tissintite forms from amorphous plagioclase during decompression.

Introduction

The study of high-pressure, high-temperature phases in meteorite samples gives us insight into the impact processes that shape the evolution of planetary surfaces. High-pressure, high-temperature minerals observed within meteorites act as snap shots of the P-T conditions experienced by the rocks during the impact events that produced them (Chen et al., 1996; Ohtani

26 et al., 2004; Xie et al., 2006; Sharp and DeCarli, 2006; Gillet et al., 2007; Fritz et al., 2017).
27 However, using these phases as index minerals to determine impact conditions is dependent upon
28 the availability of experimentally derived P-T stability field data, which do not exist for many
29 newly discovered minerals observed in meteorites, such as tissintite.

30 Tissintite is reported as a non-stoichiometric clinopyroxene (CPX), $(\text{Ca},\text{Na},\square)\text{AlSi}_2\text{O}_6$, with a
31 calcium-rich plagioclase or labradorite ($\sim\text{An}_{65}$) composition and a jadeite-type structure. It was
32 first observed in the Martian shergottite, Tissint (Ma *et al.*, 2014), and has since proven to be
33 prevalent in shocked samples, including other shergottite meteorites (Herd et al., 2017), a eucrite
34 meteorite (Pang, et al, 2016) and a possible terrestrial occurrence in shock-generated melts from
35 the Manicouagan crater (Boonsue and Spray, 2017). It occurs as sub-micron sized crystalline
36 aggregates within maskelynite grains that are entrained in or adjacent to shock-generated melts
37 with no other co-existing crystalline phases detected by Raman Spectroscopy (Ma et al., 2015).
38 Tissintite is proposed to contain approximately 25% vacancies at the M2 site, the highest
39 concentration ever reported for either natural or synthetic CPX; however, a refined crystal
40 structure confirming these structural defects has not been determined (Ma et al., 2015). Tissintite
41 has been suggested to form within a so-called “*Goldilocks Zone*” where pressure, temperature,
42 time and composition (P-T-t-X) are just right to facilitate growth of the phase, thus suggesting its
43 great potential to provide strict constraints on the P – T path followed during an impact event
44 (Ma et al., 2015). Previous to this study, tissintite had never before been synthesized, and little
45 was known about the controls on its formation during an impact event.

46 There are several path-dependent variables that could influence the formation of tissintite
47 during an impact event, including pressure, temperature, and time, as well as non-path-dependent
48 variable such as composition, and crystallinity of the precursor. Some of these have been

49 estimated through observations of natural occurrences by Walton et al. (2014) and Ma et al.
50 (2015). The first reported occurrence of tissintite (Ma et al., 2014) was observed within
51 maskelynite grains of calcic-plagioclase composition while being absent in sodic-plagioclase
52 grains. Tissintite was exclusively found in grains that abut or are entrained in >500 μm shock-
53 generated melt veins or pockets and only within ~ 25 μm of the melt-grain interface. These
54 observations indicate the following requirements for tissintite formation: (1) a calcium-rich
55 plagioclase precursor, and (2) temperatures > 900 $^{\circ}\text{C}$. Additionally, tissintite does not occur with
56 any accompanying crystalline phases in any of the reported occurrences. This is significant, as it
57 suggests these natural occurrences of tissintite may be controlled by kinetic factors rather than
58 pressure or temperature alone as has been suggested for other phase transformations spatially
59 associated with shock melt such as olivine to ringwoodite (Xie et al., 2006).

60 Although the number of studies concerning the behavior of intermediate plagioclase
61 compositions at elevated P-T is limited, we can use studies of the endmembers albite and
62 anorthite to make inferences on how these intermediate compositions may behave. At high
63 pressure and temperature, albite and labradorite have been observed to form jadeite + stishovite
64 at HP-HT with differing crystallization rates where jadeite crystallizes first and is subsequently
65 followed by a crystalline silica phase after >100 s (Kubo et al., 2010). These observations, taken
66 together with tissintite's association with melt veins and pockets (Walton et al., 2014; Ma et al.,
67 2015), suggest that the precursor needs to be at temperature for up to ~ 1 s or longer (Langenhorst
68 and Poirier, 2000, Walton and Shaw, 2013; Walton et al., 2014) for the plagioclase-to-tissintite
69 transformation to occur, but not so long as to form accompanying crystalline phases.
70 Furthermore, it is unclear from natural samples whether the precursor is crystalline plagioclase or
71 if it is maskelynite/amorphous plagioclase. The experiments performed here were designed to

72 approximate and test these conditions. Here we have determined an initial range of formation
73 conditions for tissintite of approximate An_{60} composition, which is relevant to martian basaltic
74 shergottites and eclogites.

75 **Methods**

76 **Synthesis**

77 We performed high-pressure, high-temperature experiments coupled with in situ energy
78 dispersive X-ray diffraction and imaging at the Argonne National Laboratory Advanced Light
79 Source using the large volume multi-anvil press with a D-DIA apparatus available on the 6-BM-
80 B beamline. The possible effects of crystallinity of the precursor were tested by using two
81 different starting materials, a natural crystalline plagioclase feldspar powder of approximate
82 labradorite composition ($An_{59.25}Ab_{39.25}Or_{1.5}$), originating from Chihuahua, Mexico and provided
83 by Byrne et al., (2015), and an amorphous powder with the same composition. The amorphous
84 material was a fused glass synthesized using the natural labradorite powder and heated in a
85 Deltec Furnace to ~ 1500 °C in a sealed Pt capsule for 2 hours and quenched in air. The
86 composition used here is consistent with the average composition of natural tissintite (Ma et al.,
87 2015).

88 Each sample was loaded into a high-pressure cell assembly (Figure 1), with mullite as the
89 pressure medium and a graphite furnace. The pressure and temperature were monitored using a
90 MgO pressure calibrant and a W3%Re – W25%Re alloy thermocouple. The samples were cold
91 compressed at ambient temperature to peak pressure followed by heating. We utilized two
92 different heating protocols: (1) a stepped heating method where the temperature was increased
93 by 200 °C every 60 s, and (2) a spike heating method where the sample was elevated to peak

94 temperature within ~1 s, followed by a rapid quench after 60 s at peak temperature. The spike
95 heating method was meant to loosely mimic the rapid temperature increase and decrease that
96 material would experience when adjacent to melts produced during an impact event. While shock
97 melts can reach up to 2500 °C or higher, this is not necessarily the temperature materials reach
98 when heated through conduction when in contact with melt, thus the target peak temperature
99 range for these experiments was 1200 – 1400 °C, which is comparable to temperatures estimated
100 for materials in contact with shock melts (Langenhorst and Poirier, 2000; Walton et al., 2006;
101 Shaw and Walton, 2013. Ma et al., 2016, Walton et al., 2017).

102 Energy dispersive X-ray diffraction patterns for the sample and the pressure calibrant were
103 collected by solid state Ge detectors. The incident X-ray beam was collimated to 100 x 100 μm
104 for diffraction. Though the spectra from only a single detector are shown in the later figures for
105 simplicity, beamline 6-BM-B is equipped with a 10-element detector array with the individual
106 elements oriented in a circular array. A series of two conical slits then fixes the 2-theta of the
107 diffracted X-ray beam at 6.50° for all ten detector elements. The conditions at which diffraction
108 data were collected for each sample are shown in Figures 2 - 5.

109 **Recovered Sample Analysis**

110 The samples were recovered as dense pellets ~ 2 mm in diameter and ~ 0.5 to 1 mm in
111 thickness. A portion of each was embedded in epoxy, thinly sliced and polished to produce thick
112 sections, ~100 – 200 μm thick. These samples were analyzed using micro-Raman spectroscopy.
113 Raman spectra were collected using a WiTec Alpha 300R confocal imaging system equipped
114 with a 532 nm Nd:YAG laser available in the Center for Planetary Exploration (CPeX) at Stony
115 Brook University. All spectra were collected through a 50x (NA=0.85) objective with a working

116 spot size of 0.76 μm . Each spectrum is an accumulation of 60 scans with an integration time of 1
117 s.

118 **Results and Discussion**

119 The progression of the in situ diffraction patterns for 3 experimental runs denoted as L01,
120 L02, and L03 respectively are shown in Figures 2 – 4. Each run tested 3 different sets of
121 conditions, which, along with the experimental outcomes, are summarized in Table 1. During
122 cold compression, no new phases were observed in both the crystalline and amorphous starting
123 material. The apparent broadening and disappearance of diffraction peaks for the crystalline
124 material during compression shown in Fig. 2 and Fig. 3 is consistent with partial amorphization
125 and/or differential stress distribution (Miyahara et al., 2013). We observed the formation of
126 tissintite only after heating in all three experiments, where the diffraction pattern is consistent
127 with a jadeite-like structure. The formation of tissintite occurred via solid-state reaction as the
128 temperatures tested in all three experiments are below the liquidus for labradorite and no melting
129 was observed. In Figures 2-4, the prominent diffraction peaks associated with each phase are
130 labeled; tissintite is denoted by the prominent double doublet features between 2 and 3
131 angstroms. Representative Raman spectra for each recovered sample are shown in Figure 5 along
132 with a spectrum of natural tissintite for comparison provided by C. Ma (personal
133 correspondence). Raman peak positions for each sample and natural tissintite are shown in Table
134 2.

135 In run L01, where the crystalline starting material was compressed to 8.5 GPa and step
136 heated to 1400 $^{\circ}\text{C}$, tissintite began to crystallize at ~ 1000 $^{\circ}\text{C}$ and the crystalline material was
137 completely converted to tissintite at 1400 $^{\circ}\text{C}$. However, in run L02 where crystalline labradorite
138 was spike heated, we observed remaining crystalline labradorite in both the *in-situ* diffraction

139 patterns and in the Raman spectrum. Figure 5 shows a reflected light image of a labradorite grain
140 within the recovered sample from run L02. In this sample, an apparent “rind” of tissintite that has
141 formed along the edges of the labradorite grain can be seen. In the natural setting, tissintite can
142 form as a rind along the edges of a maskelynite grain that are abutting or entrained in shock melt
143 (Ma et al., 2015). While both occurrences appear similar, the textural contexts are different.
144 Besides the remnant labradorite, no other coexisting crystalline phases were identified in either
145 the diffraction or the spectral data.

146 In addition, we observed the crystallization of tissintite as a function of time during the spike
147 heating of the amorphous material by collecting an average diffraction pattern in 15 sec intervals
148 during the 60 second spike. Tissintite begins to nucleate within the first 15 seconds. While the
149 major tissintite doublet peaks are not apparent in the diffraction pattern for the first 15 sec at
150 temperature (Fig. 3), the limits of the technique make it likely that the peaks are masked by noise
151 at the beginning of nucleation, rendering them indiscernible until after the crystals have grown
152 above a certain size. In similar experiments reported by Kubo et al., (2010), crystallization of a
153 jadeite-like material was observed in labradorite at 12.6 GPa and 930 °C after ~ 10 sec. While
154 our experiments are performed at temperatures closer to a shock event, there could be a lag
155 during spike heating from ambient to peak temperature where the center of the sample does not
156 reach peak temperature for the first 2 – 3 seconds.

157 **Implications**

158 We have found that tissintite readily forms under the following range of conditions; 6 – 8
159 GPa, and 1000 – 1350 °C. While the temperatures are similar to those estimated for materials in
160 contact with shock generated melts in basaltic materials (Langenhorst and Poirier, 2000; Shaw
161 and Walton, 2013), the pressures are low relative to maskelynite formation pressures of ~29 GPa

162 (Stöffler et al., 1986, Fritz et al., 2017). Further, through our novel spike heating protocol we
163 observed that heating at shock-like time scales is not sufficient to convert crystalline labradorite
164 to tissintite. This observation is significant as it clearly indicates that in the natural case, where
165 tissintite is only seen in conjunction with maskelynite (amorphous plagioclase), the crystalline
166 plagioclase had to become amorphous before contact with shock melt to produce tissintite with
167 no coexisting crystalline plagioclase or other phases. This not only gives us an idea of when
168 during the impact event tissintite began to form, but also when maskelynite forms as well. Thus,
169 tissintite likely forms during decompression from an amorphous plagioclase precursor that
170 became amorphous during compression in the same event or became amorphous during a
171 previous impact event.

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262 Table 1. Experimental runs and outcomes.

263 Table 2. Raman shift peak positions for synthetic tissintite (this study) and natural tissintite (Ma
264 et al., 2015).

265 Figure 1. Cross-section view of the standard cell assembly used in these experiments.

266 Figure 2. Formation of tissintite (Ts) from crystalline labradorite (Lb) at 7.5 GPa and >1000°C
267 using stepped heating. The prominent peaks of each phase are labeled.

268 Figure 3. Formation of tissintite (Ts) from crystalline labradorite (Lb) at 8.5 GPa and 1320°C
269 using spike heating. The prominent peaks of each phase are labeled.

270 Figure 4. Formation of tissintite (Ts) from amorphous labradorite at 6 GPa and 1200 °C using
271 spike heating. The prominent peaks of each phase are labeled.

272 Figure 5. Representative spectra for each run compared to data for natural tissintite (Ma et al.,
273 2015). The three major peaks for tissintite are 377, 693, and 1003 cm⁻¹. Synthetic tissintite from
274 this study shows remarkable agreement with natural tissintite, confirming its synthesis.

275 Figure 6. In this reflected light image a light halo of tissintite is evident around a large
276 plagioclase grain within L02. This texture is reminiscent of that observed in natural tissintite
277 samples.

Run No.	Starting Material	Peak Pressure (GPa)	Peak Temperature (°C)	Heating Method	Product
L01	Crystalline	8.2	1400	Step	tissintite
L02	Crystalline	8.5	1320	Spike	tissintite + labradorite
L03	Amorphous	6	1200	Spike	tissintite

L01	L02	L03	Natural tissintite
202	200	203	203
378	377	378	377
432	437	433	417
-	485*	-	-
-	512*	-	-
524	-	517	518
573	-	574	573
698	696	696	693
993	987	990	1003

*Labradorite Peaks











