FORMATION OF TISSINTITE AND ITS IMPLICATIONS FOR IMPACT STUDIES. M. J. Rucks[1], M. L. Whitaker[1], T. D. Glotch[1], and J. B. Parise[1], [1]Stony Brook University (Melinda.rucks@stonybrook.edu).

**Introduction:** Shock pressures and temperatures induced during impact events often result in the formation of mineral phases with unique properties. Such materials can be used to infer the extent of shock a particular meteorite has experienced. Tissintite is a clinopyroxene with a calcic-plagioclase composition and ~25% structural vacancies at the M2 site ($(Ca,Na,\_)AlSi_2O_6$), and has been interpreted by [1-2] to form within a tight P-T-t-X "Goldilocks Zone". Tissintite was first synthesized by [3-4] using multi-anvil techniques. Here we have expanded upon this previous study and have defined a range of conditions for the formation of tissintite from labradorite $An_{60}$. Thus, the presence of this phase may provide insight into evolution of the impact event that produced it.

**Methods:** We performed high-pressure and temperature experiments coupled with *in-situ* energy dispersive X-ray diffraction measurements at the Argonne National Laboratory Advanced Photon Source using the large volume multi-anvil press with a D-DIA apparatus available on the 6-BM-B beamline. We used both a crystalline and amorphous plagioclase starting material of ~An60 composition. The amorphous material is a fused glass synthesized from the crystalline plagioclase.

Each sample was loaded into a high-pressure cell assembly with fired pyrophyllite as the pressure medium and a graphite furnace and compressed relatively fast (~2 h) to peak pressure. A spike heating protocol was used where temperature was increased to the target temperature within 1 s then rapidly quenched after 5 to 60 s. Our target pressure was ~ 10 GPa. The actual peak pressures and temperatures varied from 9 – 10.4 GPa between experiments due to minor differences within the sample cell assemblies. The samples were spike heated to ~ 1300˚C then rapidly quenched after 60 s apart from one run where an amorphous sample was spike heated for only 5 s. Diffraction patterns of each sample were collected during compression, heating and after decompression.

The samples were recovered as hard pellets. A portion of each was embedded in epoxy, thinly sliced and polished to produce thick sections. These samples were imaged and analyzed using optical microscopy and micro-Raman spectroscopic techniques. Raman spectra of the recovered samples were collected using the WiTec alpha 300R confocal imaging system, equipped with a 532 nm Nd YAG laser available in Center for Planetary Exploration at Stony Brook University.

**Results:** A representative plot of an average run using the crystalline labradorite as the starting material is shown in Figure 1. It shows the progression of diffraction patterns for crystalline starting material during compression to 10.2 GPa followed by 60 s spike heating.

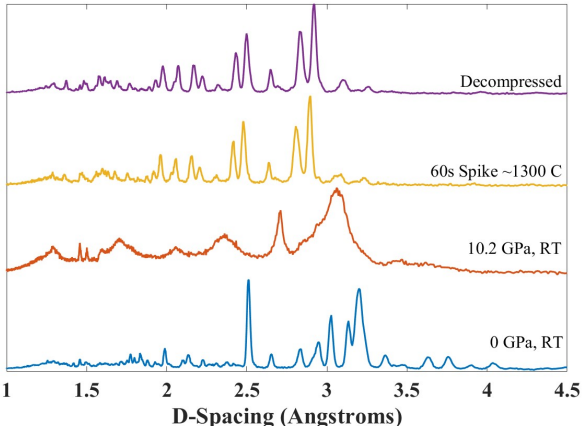


**Figure 1**. The progression of the labradorite crystal pattern before compression (bottom) and after decompression (top).

In these experiments, we observed tissintite formation accompanied by peaks that indicate the possible formation of garnet and stishovite. In Figure 2, we show the diffraction patterns of 3 runs after decompression: L06, L08 and L09. The starting material type and the length of time of the heating spike is noted to the right within the figure. Runs L06, L08, and L09 were compressed to 10.4, 9, and 10.2 GPa, respectively before spike heating to ~1300˚C. The characteristic peaks for tissintite, garnet and stishovite are annotated.

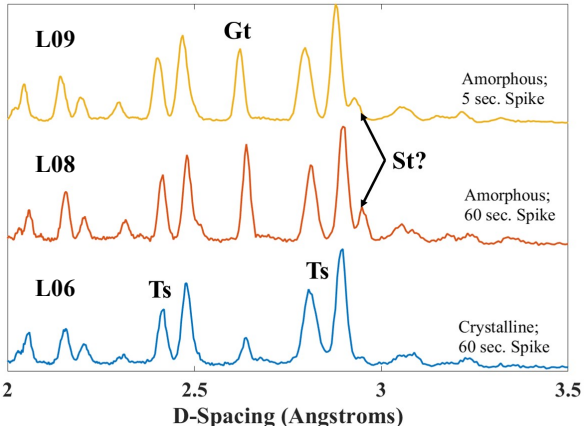


**Figure 2**. Comparison of 3 experimental runs with the major peaks for tissintite (Ts), garnet (Gt) and stishovite (St) annotated.

Here we can see that a 5 s heating spike is sufficient to produce substantial amounts of garnet and possibly stishovite at pressures ~10 GPa within an amorphous precursor.

In addition, we performed an experimental run (L05) using crystalline starting material, in which the pressure did not build above 4 GPa. When this sample was spike heated no additional phases formed and the crystalline plagioclase remained. Figure 3 shows Raman spectra of recovered samples for the runs L05, L06, L08 and L09 as well as a Raman spectrum for natural tissintite provided by Dr. Chi Ma (personal communication). The presence of tissintite + garnet in runs L06, L08 and L09 are confirmed though no stishovite is apparent. This may be due to poor crystallinity of stishovite or crystal size on the nano-scale.

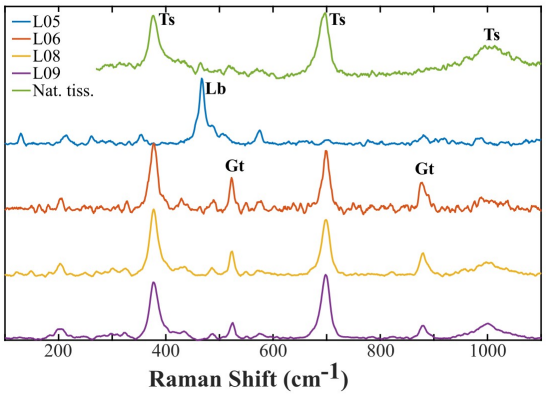


**Figure 3**. Raman spectra for Natural tissintite, and experimental runs L06, L08, and L09. Mineral phases observed are labradorite (Lb), tissintite (Ts), and garnet (Gt), major peaks labeled.

**Discussion:** The purpose of this study is to define conditions at which tissintite will form with no accompanying phases, as it is observed in meteorites, from an $An_{60}$ precursor as well as establishing what factors may influence its formation. Here, we have built upon previous data [3-4] and defined an upper and potential (?) lower bound for the formation of tissintite.

In our previous experiments [3-4] we found tissintite forms readily in both crystalline and amorphous material during spike heating and step heating across the pressure range of 6 to 8.5 GPa. However, spike heating was not sufficient enough to completely transform crystalline labradorite into tissintite, indicating that tissintite forming in an amorphous precursor for this pressure range is most probable.

In this study we observed formation of tissintite accompanied by garnet and the possible presences of stishovite from both crystalline and amorphous material from 9 to 10.4 GPa. Given that natural tissintite has been observed with no coexisinting phases, we can infer that the upper pressure boundary for tissintite formation with no coexisting phases to be between 8.5 and 9 GPa. In run L09 where the amorphous material was spike heated for only 5 s, we observed the same tissintite + garnet + stishovite mineral assemblage. We suggest the formation of tissintite may be kinetically driven more so than dependent upon pressure. A similar study of labradorite at higher pressure but subsolidus temperatures, [5] shows that jadeite or a jadeite-like material (tissintite?) began to form at 12.6 GPa at 930˚C after ~ 10 s, followed by garnet formation at ~600 s, then followed by stishovite at ~ 900s. If a similar formation sequence is occurring in our experiments it is happening at a rate < 5 s and beyond our observational abilities. It is important to note, that for $An_{60}$ an upper limit to tissintite formation alone is likely 9 GPa. We must consider the time scales of our experiments when applying this knowledge to impact events where impact generated melts vitrify within 1 s to several seconds. Further, in run L05 crystalline labradorite was compressed to 4 GPa then spike heated to ~1300˚C. No phases were observed to form and crystalline labradorite was retained. This suggests a lower limit to the formation of tissintite to lie between 4 and 6 GPa.

We have defined a pressure range for the formation of tissintite as well as establishing that it likely forms from an amorphous material rather than crystalline material. This supports several hypotheses for shock condition of martian meteorites: (1) multiple impact, (2) amorphization of plagioclase during compression followed by tissintite formation during but not after compression. (3) small impact size (4) meteorites ejected from areas further away from central peak.

**Conclusion:** Here we have defined the formation pressure range for tissintite of $An_{60}$ composition at shock relevant temperatures (~1300˚C) and time scales to be 4 to 9 GPa. While this is a strict formation range, it may not be useful in telling the peak pressure of the impact itself, but it can be an indicator for the evolution of an impact.

**Future Work:** Further work will include TEM analysis of all recovered samples, as well as a refined crystal structure for our synthetic tissintite. Additionally we will refine the upper and lower bounds reported here to include other compositions across the plagioclase solid solution.

**References:** [1] Ma C., et al., *EPSL*., 422, 194-205. [2] Walton, E., et al. (2014) *Geochim. Cosmochim. Acta*, 140, 334-348. [3] Rucks, M. et al., (2017) LPSC Abs # 2427 [4] Rucks, M. et al., *in preparation* [5] Kubo, T., et al., (2010) *Nat. Geosci*., 3, 41-45.

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