PRELIMINARY INVESTIGATION OF TISSINTITE FORMATION USING *IN-SITU* SYNCHROTRON X-RAY DIFFRACTION AND MULTI-ANVIL TECHNIQUES. M. J. Rucks[1], T. D. Glotch[1], M. L. Whitaker[1], and J. B. Parise[1], [1]Stony Brook University (Melinda.rucks@stonybrook.edu).

Introduction: Impact-induced shock pressures and temperatures often result in the formation of mineral phases with unique properties. If the stability fields of these phases are known, they can be used to suggest upper and lower bounds of impact conditions. Thus, the study of high pressure phases through static and shock experiments is vital to our interpretation of impacts from meteorite samples and terrestrial impactites. Here, we report the results of our initial investigation into the formation of the newly discovered phase, tissintite. Raman spectra of our synthetic material matches the spectra published for tissintite [1]. This is the first report of synthetic tissintite. 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". Thus, the presence of this phase has potential to provide strict constraints to impact condition estimates.

Methods: We performed 3 different 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 mullite as the pressure medium and a graphite furnace and compressed relatively fast (~2 h) to peak pressure. Two heating protocols were used: stepped heating by increasing temperature by 200˚C every 60 seconds, and spike heating to the peak temperature in ~1s and quenched after 60 s. Our target pressure and temperature was 8 GPa and at least 1200˚C. The actual peak pressures and temperatures varied from run to run due to minor variations within the sample cell assemblies. 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 scanning electron microscopy (SEM) 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. SEM images were collected at SBU with a LEO1550 SFEG-SEM with a Robinson backscatter detector operated at 20 kV and 8mm working distance.

Results: The crystalline starting material was used for two of the three runs, denoted here as Lab-01 and Lab-02. Runs Lab-01 and Lab-02 were compressed to ~8.2 and 8.5 GPa respectively, and a different heating approach was used for each. Lab-01 was initially step heated to a maximum T of 1400˚C and quenched after 60 s. We then tested the feasibility of the spike heating protocal on the same sample while at pressure.

In experiment Lab-02, only the spike heating method was used. *In-situ* diffraction patterns collected in both experiments show broadening and disappearance of some labradorite peaks during compression, Lab-01 shown in Fig. 1. In Lab-01, a jadeite-like structure began to appear during step heating around 1000˚C (Fig. 2). Lab-02 was spike heated to ~1200˚C and quenched after 60s. The same jadeite-like pattern began to appear within 15 s (Fig. 2).

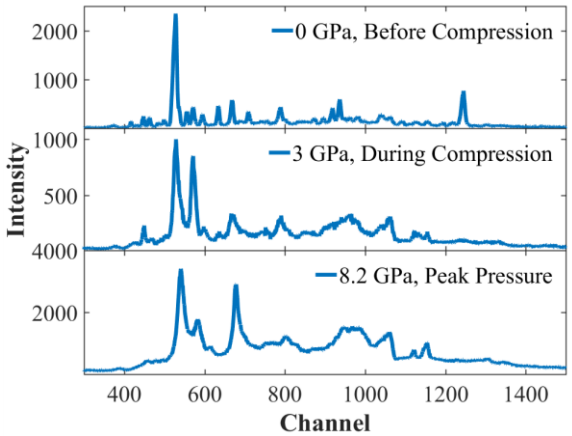

Figure 1. The progression of the crystal pattern during the compression for run Lab-01. The same structure changes were seen for run Lab-02 (not shown here).

Run Lab-03 started with the amorphous material, and was compressed to a peak pressure of ~ 6 GPa. The sample was spike heated to a peak temperature of ~1250˚C, and quenched after 60 seconds. The sample showed only an amorphous phase during compression. Diffraction patterns were collected every 15 s during the spike heating (Fig. 2.), where the same jadeite-like pattern appeared within the first 15 s, similar to run

Lab-02. Raman spectra for runs Lab-01 and Lab-03 are shown in Fig. 3. The major peak positions for Lab-01, Lab-03, and tissintite [1] are shown in Table 1.

Discussion: Based on studies of [1-2], and high pressure experiments on the amorphization of labradorite [3] we estimated the most probable P-T-t range for tissintite formation to be 7-12 GPa, 1000-2000˚C, and <60 s. Here, we have tested the lower values of this range. We also considered the effect of the crystallinity of starting material, as discussed in [1] by using both a powdered crystalline and amorphous starting material. We also attempted to replicate time scales put forth by Kubo et al., 2010 and Walton et al., 2014., with rapid heating and quench time.

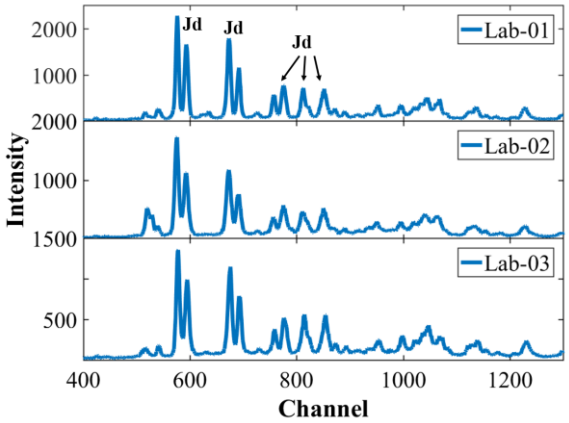

Figure 2. Representative diffraction patterns of each run after decompression. The annotation in the top plot shows peaks that are consistent with natural jadeite.

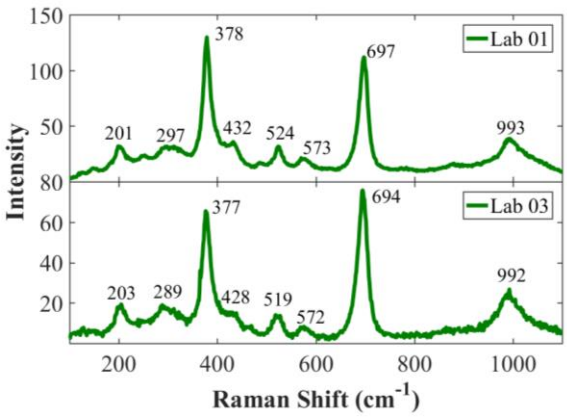

Figure 3. Representative Raman spectra of run Lab-01 and Lab-03.

Tissintite has been described as the Ca-analog to jadeite. However, a complete refined crystal structure has not been reported for natural tissintite due to difficulty of analysis within meteorite thin-sections. Our synthetic material has a diffraction pattern similar to jadeite, with some apparent peak shifts and peak broadening. These differences are most likely due to the high Ca-content of our samples and disorder within the structure (vacancies?). We have yet to complete a crystal structure refinement and thus cannot confirm the presence or absence of vacancies within the structure.

Raman spectra collected for our samples are nearly identical to published data for tissintite [1]. During our investigation we did not find any accompanying silicate phase, such as stishovite, which commonly forms with jadeite at high pressures and temperatures. Natural tissintite is found with no other crystalline phase, similar to occurences of jadeite in L6 chondrites [4-5].

Lab-01	Lab-03	Tissintite [1]
201	203	203
297	289	NA
378	377	377
432	428	417
524	519	523
573	572	573
697	694	693
993	992	997

Table 1. Peak positions for samples Lab-01, Lab-03, and tissintite [1].

When observed with SEM there was no discernable contrast within the material that resembled textures observed within the natural meteorite samples, i.e the "wormy" and "rind" textures observed by [1]. However, our samples begin with homogeneous, pure starting materials. This may indicate that the these textures result from cases in which crystallization of tissintite in meteorites is influenced by surrounding clinopyroxenes and other phases. Thus, occurences of tissintite may be more common and just overlooked without the unique texture.

Conclusion: Based on a comparison of Raman and X-ray diffraction data for known tissintite and our synthetic samples, we have produced a material that matches tissintite. Despite difficulties in using static or shock experiments as a direct proxy to impact processes, understanding the behavior of materials, such as tissintite will aid in our understanding of the impact shock process.

Future Work: A refined crystal structure for each sample will be obtained. We will also expand our experiments further into our designated P-T range to identify the stability field of tissintite, including different compositions.

References: [1] Ma C., et al., *EPSL*., 422, 194-205. [2] Walton, E., et al. (2014) *Geochim. Cosmochim. Acta*, 140, 334-348. [3] Kubo, T., et al., (2010) *Nat. Geosci*., 3, 41-45. [4] Ozawa, S., et al., (2009) *Meteorit. Planet. Sci.*, 44, 1771-1786. [5] Miyahara, M., et al., (2013) *Earth Planet. Sci. Lett.*, 373, 102-108.

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