THE BEHAVIOR OF CALCIUM-RICH PLAGIOCLASE UNDER IMPACT RELEVENT CONDITIONS AND IMPLICATIONS FOR IMPACT STUDIES. M. J. Rucks[1], T. D. Glotch[1], M. L. Whitaker[1], T. G. Sharp[2], C. Fudge[2] D. Lindsley[1], T. Catalano[1] and H. Nekvasil[1], [1]Stony Brook University, [2]Arizona State University (Melinda.rucks@stonybrook.edu).

Introduction: Shock pressures and temperatures achieved during impact events can often result in the formation of high-pressure mineral phases with unique properties. These phases and the assemblages they form can be used to infer the extent of shock that a particular meteorite has experienced. Tissintite is a clinopyroxene with a calcic-plagioclase composition and ~25% structural vacancies in the M2 site ($(Ca,Na,\_)AlSi_2O_6$), and has been interpreted by [1] to form within a tight P-T-t-X "Goldilocks Zone". Tissintite was first synthesized by [2] using multi-anvil techniques. In that work, we determined tissintite forms from an An_{60} at pressures of 4.5 – 8.5 GPa and temperatures 1000℃ and above.

It is important to note here that many mineral assemblages observed in meteorites are kinetically controlled and may not reflect the behavior of the chemical system under equilibrium conditions. By expanding the work of [2] to concentrate on the first 5 seconds of this reaction, we are gaining insight into the processes that occur during and after impact for these common minerals. Here we explore the effects of composition and kinetics on the formation of tissintite through variation of starting materials composition between An_{40} and An_{80} and residence times of 5 – 60s.

Methods: We performed high-pressure and temperature (HP-HT) 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 performed additional HP-HT experiments using the large volume multi-anvil press coupled with *in-situ* angle dispersive diffraction available at the National Synchrotron Light Source II at Brookhaven National Laboratory at the XPD 28-ID-D beamline. Using this technique we were able to collect X-ray diffraction patterns every second, which allows us to probe in detail the structural changes happening on the second timescale. Our starting materials are fused glasses of An_{40}, An_{60}, An_{80}, and An_{85} compositions. All glasses were synthesized from either natural or synthetic crystalline plagioclase in the Stony Brook Experimental Petrology Laboratory following the procedure used for An_{60} in [2].

Each sample was loaded into a high-pressure cell assembly 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, 10, or 60 seconds. Our target pressure ranged from 3 GPa to above 14 GPa. The temperatures of the spike heatings were also varied between 800℃ to 1500℃. Diffraction patterns of each sample were collected during compression, during the spike 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.

In addition, one of our samples reported in [2] was revisited using TEM microscopy. A FIB slice was taken of the sample using the FEI Nova 200 NanoLab and analyzed using the FEI CM200FEG in the Eyring Materials Center at ASU. Product phases were analyzed using a combination of energy dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED).

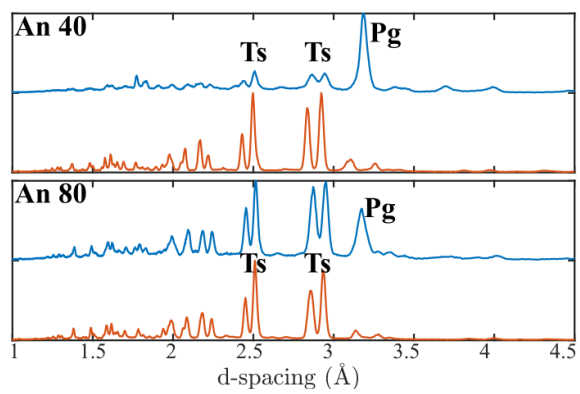

Figure 1. An_{40} (top) and An_{80} (bottom) results from 4.5 GPa (blue) and 9 GPa (orange) Major peaks for tissinite, Ts, and plagioclase, Pg, are annotated.

Results: For each composition, at pressures between 5 and 8 GPa, temperatures ~1350℃, and quench times of 5 to 60 s, we did not observe a marked difference in the reaction of these new composition materials compared to previous work on An_{60}. Within this pressure range we only observe tissintite in the *in-situ* X-ray diffraction data and Raman spectra of the recovered

samples. In Figure 1, we show the final X-ray diffraction patterns for An_{40} (top) and An_{80} (bottom) starting compositions with peak pressures of 4.5 GPa (blue) and 9 GPa (orange), representing lower and upper boundary for An_{60} tissintite stability.

At pressures below 4.5 GPa we observed both the formation of tissintite and plagioclase in both starting materials. In addition, the An_{60} starting material was compressed to ~3 GPa and spike heated to a similar temperature for 5 seconds. In this run we observed only the formation of plagioclase and no tissintite.

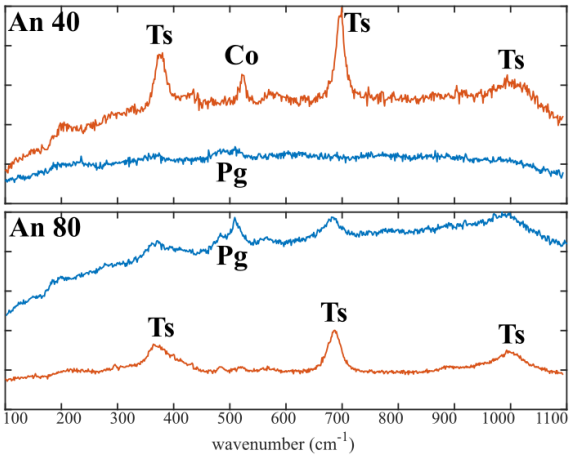

Figure 2. Raman spectra for An_{40} (top) and An_{80} (bottom) at 4.5 GPa (blue) and 9 GPa (orange) Major peaks for tissinite, Ts, and plagioclase, Pg, and coesite (Co) are annotated.

At pressures above 10 GPa, the An_{40} and An_{80} starting materials behave similarly to An_{60}. We see formation of tissintite accompanied by garnet and silica. When compressed to 9 GPa and spike heated for 5 seconds, we observe only tissintite formation for An_{40} and An_{80} compositions, whereas we see the 3 mineral assemblage from the An_{60} composition glass. However, when the recovered samples were analyzed using Raman spectroscopy, we were able to identify an additional phase, possibly coesite, in the An_{40} starting material. Coesite is absent in the An_{80} sample, where only peaks common to tissintite are observed. Representative Raman spectra for An_{40} and An_{80} at both low and high pressures are shown in Figure 2 with the major peaks for each phase labeled.

Discussion: We determined that 4 – 5 GPa is likely a formation boundary, where both tissintite and plagioclase form together, whereas only plagioclase forms at ~ 3 GPa, and only tissintite forms at 5 GPa. While this behavior is seen in all compositions studied, tissintite appears to form more readily within An_{80} and plagioclase forms more readily within An_{40}. In previous experiments we identified 9 GPa as an upper bound for tissintite formation in An_{60}. This holds true for An_{40}, where we also observe coesite, but does not for An_{80} where we only observe tissintite. This raises the possibility that calcic tissintite could form with no coexisting phases at higher pressures.

To better understand both the structure of our synthetic tissintite as well as the kinetic variable that controls its formation we revisited one of our initial samples, Lab 3 [2], using TEM. This sample was compressed to ~6 GPa, and spike heated to ~1350℃ for 60 s. We observed a single phase, tissintite, in both the *in-situ* data and Raman analysis of the recovered sample. However, TEM analysis reveals a 3 phase system. While tissintite is the most abundant phase, we also observe long blade-like crystals that readily degrade in the electron beam when collecting EDS data. We determined these other phases are a kyanite and a CaAlSi phase that is not yet identified. Figure 3 shows the sample and an example of each crystal type. This three phase system is not surprising given this sample was allowed to stay at temperature for 60 s before quenching.

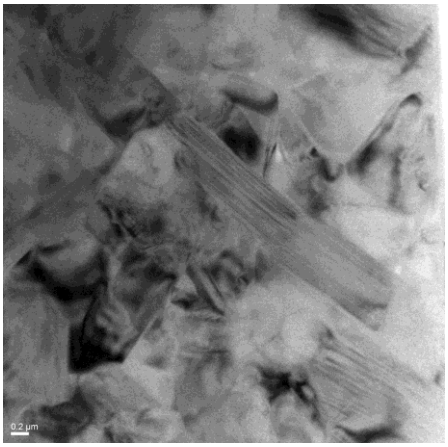

Figure 3. TEM image of Lab 03 showing irregular grains of tissintite, and blade-like

Conclusion: This study is a continuation of work completed in [2], with the goal of understanding how plagioclase composition glass reacts under impact relevant conditions. We have observed that varying the composition of the starting material can have an effect on the minerals that form under HP-HT conditions. In addition, we have also seen that quench times and heating durations are the driving factor in what phases will form and must be taken into consideration.

Future work: Further characterization of recovered samples is needed to fully understand the behavior of these glasses under these range of conditions.

References: [1] Ma C., et al., (2015) *EPSL*., 422, 194-205. [2] Rucks, M. et al., (2018) *Am. Min.*, 103, 1516-1519.

The natural labradorite samples were supplied through collaboration with Darby Dyar. This work is supported through an NESSF fellowship award. We acknowledge use of the Eyring Materials Center.