DISCOVERY OF A HIGHLY-DEFECTIVE, SHOCK-INDUCED, HIGH-PRESSURE ALBITIC JADEITE, $(Na,Ca,\square_{1/4})(Al,Si)Si_2O_6$: NATURAL OCCURRENCE OF A CLINOPYROXENE WITH EXCESS Si.

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Introduction: Jadeite ($\sim NaAlSi_2O_6$) formed from the dissociation of albitic plagioclase is widely reported in shocked ordinary chondrites [e.g., 1]. Based on static high-pressure, high-temperature experiments, albite ($NaAlSi_3O_8$) breaks down to form jadeite ($NaAlSi_2O_6$) and an SiO_2 phase at high pressures [2]. Here, we report a new vacancy-stabilized, high-pressure and high-temperature clinopyroxene with a composition essentially equivalent to albitic plagioclase and Si on the M1-site. This clinopyroxene formed by shock metamorphism in terrestrial impactites and shocked chondrites. This phase has neither been synthesized nor observed before, providing new insights into shock conditions and impact processes.

During a nanomineralogy investigation of an amphibolite xenolith from the Ries impact structure and EET 13014, EET 13052, TIL 08001 L6 ordinary chondrites, we discovered a highly-defective, shocked-induced, high-pressure albitic jadeite. It has a structural formula of $(Na,Ca,\square_{1/4})(Al,Si)Si_2O_6$ with a high concentration of excess Si on the octahedral cation site M1 and a ¼ vacancy in the M2-site. Its compositions may range from $(Na_{0.75}\square_{0.25})(Al_{0.75}Si_{0.25})Si_2O_6$ to $(Na_{0.50}Ca_{0.25}\square_{0.25})AlSi_2O_6$, which corresponds to plagioclase with An0-An33 compositions. It is convenient to write the formula as a sodic analog to tissintite because this clarifies the connection to plagioclase but tissintite does not have excess Si in the Al M1-site [3]. By nomenclature, this phase would still be jadeite. We characterized the composition, structure and petrography of the albitic jadeite using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), electron back-scatter diffraction (EBSD), electron probe microanalysis (EPMA), and synchrotron X-ray diffraction (SXRD).

Occurrence, chemistry, and crystallography: Albitic jadeite occurs as aggregates crystallized from maskelynite within, or in contact with, shock melt veins (Figs. 1-2). In a Ries amphibolite xenolith (Fig. 1), albitic jadeite forms aggregates of irregular 100-800 nm crystals within a shock melt vein, surrounded by euhedral majoritic garnet. The melt vein is ~50 - 250 µm thick in the plane of the thin section and is surrounded mainly by amphibolite and feldspar, with minor titanite and trace FeS, magnetite, and apatite.

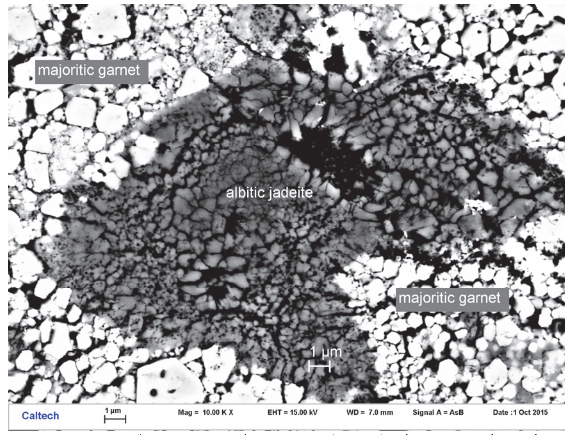

Fig. 1. Backscatter electron (BSE) image showing albitic jadeite with euhedral majorite within a shock melt vein in an amphibolite xenolith from Ries impact crater section ZLN100.

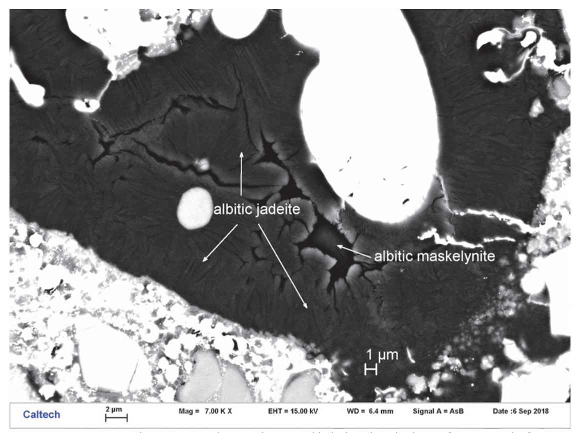

Fig. 2. BSE image showing albitic jadeite formed from maskelynite in a shock melt vein from the TIL08001 L6 chondrite.

The composition of albitic jadeite from Ries (Table 1) yields an empirical formula based on 6 O *apfu* of $(Na_{0.65}Ca_{0.04}K_{0.04}Mg_{0.01}\square_{1/4})(Al_{0.80}Si_{0.19}Fe_{0.01})Si_2O_6$ with a general formula of $(Na,Ca,\square_{1/4})(Al,Si)Si_2O_6$. Vacancies occupy about 25% of the Na-dominant M2-site and excess Si ~20% of the Al-dominant octahedral M1-site. Albitic jadeite is electron beam sensitive, making the EBSD pattern difficult to obtain. Synchrotron X-ray diffraction data were obtained at undulator beamline 13-IDD (GSECARS) at the Advanced Photon Source with primary X-rays of wavelength 0.4133

Table 1. EPMA data for albitic jadeite from Ries.

Constituent wt%	jadeite n=5	SD
SiO_2	65.97	1.99
Al_2O_3	20.51	0.77
Na_2O	10.05	0.96
CaO	1.11	0.19
K_2O	0.85	0.25
FeO	0.51	0.15
MgO	0.14	0.12
Total	99.14	
No. O atoms	6	
Si	2.19	
Al	0.80	
Na	0.65	
Ca	0.04	
K	0.04	
Fe	0.01	
Mg	0.01	
Cation sum	3.74	

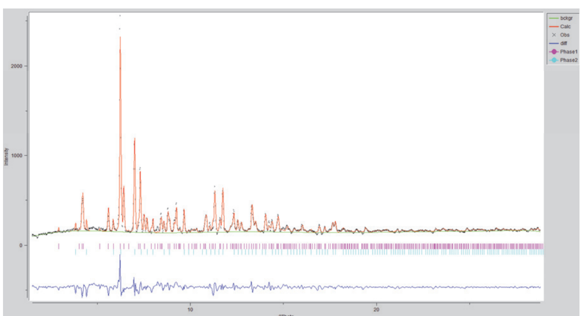

Fig. 3. SXRD pattern of albitic jadeite (blue) and majorite (pink) in the shock melt vein of section ZLN100 from the Ries impact crater (Fig. 1).

Å focused to 2×3 µm. SXRD reveals a monoclinic *C2/c* diopside structure (Fig. 3) with cell parameters a = 9.455 Å, b = 8.598 Å, c = 5.235 Å, β = 107.45°, V = 405.99 Å^3, and Z = 4. The structure refinement shows that the M2-site is only partially occupied while the bulk composition requires excess Si in the M1-site.

Albitic jadeite was also identified in shocked L6 S4 ordinary chondrites EET 13014, EET 13052 and TIL 08001, crystallized from maskelynite (with average compositions of Ab81An11Or8, Ab87An11Or2, and Ab79An11Or10) in melt veins (Fig. 2). Their appearances are similar to those of type tissintite in the Tissint shergottite [3]. The empirical formula of albitic jadeite in the TIL 08001 chondrite by EDS in Fig. 2 is ~ $(Na_{0.54}Ca_{0.08}K_{0.04}\square_{0.32})(Al_{0.8}Si_{0.2})Si_2O_6$ with > ¼ vacancies in M2 due to Na-diffusion by electron beam. The high-pressure phases wadsleyite and majoritic garnet are also found in associated melt veins.

Origin and significance: Albitic jadeites have not been discovered until now. In fact, they were hiding in plain sight. Such pyroxenes are rather common in terrestrial and meteoritic shock-metamorphic environments. These jadeites are high-pressure polymorphs of albite and form through the reaction:

$$3\ NaAlSi_3O_8 \rightarrow 4\ (Na_{0.75}\square_{0.25})(Al_{0.75}Si_{0.25})Si_2O_6.$$

The endmember formula is conventionally broken down as 3/4 $NaAlSi_2O_6$ + 1/4 $\square SiSi_2O_6$ and, therefore, does not define a new mineral but the solid solution between jadeite and a hypothetic endmember. Albitic jadeite adds an important constraint to the NAS phase diagram and accounts for excess Si components in sodic high-pressure pyroxenes.

Besides lingunite, $NaAlSi_3O_8$ in a hollandite-type structure [4], albitic jadeite is the second known high-pressure polymorph of albite. Albitic jadeite is ~21% denser than albite. Lingunite is ~11% denser than albitic jadeite. In ZLN100 (Ries), the silicate hollandite stöfflerite occurs in maskelynite in proximity to the shock-melt vein and this association constrains minimal peak shock pressure to >17 GPa. The presence of calcic sodic majoritic garnet in the melt vein constrains pressure to below ~20 GPa, where garnet of this composition decomposes into zagamiite and stishovite. The composition of garnet that formed from dehydration and transformation of pargasitic amphibole is nearly equal to the garnet reported by [5] for Ries xenolith ZLN114 with a peak shock pressure of 18.5-19.8 GPa based on garnet barometry. Thus, albitic jadeite in the Ries xenolith from ZLN100 formed at pressures between 18.5 and 20 GPa.

Clinopyroxenes with excess Si on the octahedral cation site M1 form at pressures above several GPa. They play a crucial role as hosts of water in sublithospheric mantle. Albitic jadeites with excess Si are possible precursors of omphacites with coesite-exsolution lamellae and are, thereby, indicators of exhumation from great depth on Earth. Since this albitic jadeite is common in shock-metamorphic environments, shock-generated clinopyroxenes should be reexamined with respect to excess Si.

References: [1] Miyahara M. et al. (2013) *Earth and Planetary Science Letters* 373:102–108. [2] Liu L.-G. (1978) *Earth and Planetary Science Letters* 37:438–444. [3] Ma C. et al. (2015). *Earth and Planetary Science Letters* 422:194–205. [4] Gillet P. et al. (2000) *Science* 287:1633–1636. [5] Staehle V. et al. (2010) *Contributions to Mineralogy and Petrology* 161:275–291.