

SHOCK-GENERATED LABRADORITE POLYMORPHS IN TERRESTRIAL IMPACT ROCKS AT MANICOUAGAN

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Introduction: A characteristic of strong shock waves is their ability to transform the structural state of a given mineral during the contact/compression stage of crater formation. This study characterizes the crystal chemistry and structure of plagioclase, and reveals the high pressure – high temperature behavior of polymorphs in the $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ system. We report here the finding of two new natural occurrences of shock-generated polymorphs in the form of monoclinic- and tetragonal-structured plagioclase of labradorite (An58) composition. The plagioclase polymorphs are developed in shock veins pervading anorthosite from the central uplift of the Manicouagan impact structure, Canada. The study provides information that helps us understand shock conditions of plagioclase polymorph formation in a natural terrestrial target body.

An58 polymorphs: Photomicrographs and secondary (SE) and back-scattered electron (BSE) images reveal that in the shocked anorthosite, plagioclase with planar fractures (PF) and planar deformation features (PDFs) occurs adjacent to zones of comminution and shock-generated melt veins (SMV) (Figures 1 and 2). Clusters of subhedral to euhedral, short rectangular micrograins (<1 to 2-5 μm) of monoclinic labradorite occur in the comminution zones and near SMVs (Figure 2). In addition, tetragonal labradorite as nano-prismatic/tabular crystallites (<0.2 x ~5 μm) is developed as interstitial crystals between micro-grains of mono-labradorite in closer proximity to and within SMVs. Energy dispersive x-ray spectrometry reveals that both the mono- and tetra-labradorite have a composition equivalent to that of the host rock labradorite, with an An content of 54-58 ($\text{Ab}_{43}\text{An}_{56}\text{Or}_1$). Furthermore, within the matrix in the center of SMVs, sub-micron crystallites of the labradorite polymorphs coexist with stishovite.

Raman spectra of pristine host rock plagioclase and shocked plagioclase with PDFs display similar intense Raman bands of triclinic labradorite at 480 and 510 cm^{-1} . The mono-labradorite fragments display distinct Raman bands at 372-378, 694-696, 904-914, and 997-1030 cm^{-1} , with low intensity at 285, 424, 490, 520-524, 620, 639, 853 cm^{-1} , corresponding to the Raman spectrum of a crystal structure analogous to $C2/c$ monoclinic jadeite [1]. The crystallography of the labradorite polymorphs was further examined by Electron Backscattered Diffraction (EBSD) attached to the field emission scanning electron microscope, and via selected area electron diffraction (SAED) patterns via

transmission electron microscope (TEM) analysis. The diffraction patterns of the mono-labradorite grains are comparable to the lattice planes of a monoclinic crystal structure with $C2/c$ symmetry (Figure 3a). The mono-labradorite cell parameters are $a = 9.45 \text{ \AA}$, $b = 8.594 \text{ \AA}$, $c = 5.233 \text{ \AA}$, $\alpha = 90$, $\beta = 107.57$ and $\gamma = 90$, with a calculated density of 3.34 g/cm^3 . The observed reflections determined by synchrotron X-ray diffraction analysis were derived from a mixture of phases adjacent to and within the SMV; including garnet, amorphous material, triclinic- and mono-labradorite. In addition, the EBSD and SAED patterns of the nano-tabular crystals of tetra-labradorite can be unambiguously indexed in terms of the tetragonal hollandite structure $I4/m$ symmetry, with cell parameters $a = 9.31 \text{ \AA}$, $b = 9.31 \text{ \AA}$, $c = 2.72 \text{ \AA}$, $\alpha = 90$, $\beta = 90$ and $\gamma = 90$, respectively (Figure 3b). The corresponding density is 3.82 g/cm^3 . The tetragonal $(\text{NaCa})(\text{Al,Si})_4\text{O}_8$ -labradorite has similar crystal structure to the silicate hollandite found in shock veins of the Sixiangkou L6 chondrite [2, 3].

The close relationship, both in spatial occurrence and chemical composition, between normal triclinic labradorite, PDF-bearing labradorite and mono-labradorite within the vicinity of SMVs, as well as a well defined crystal structure of the polymorph, together suggest that mono-labradorite is a newly identified polymorph. We believe it is generated as a result of shock-induced displacive transformation of the crushed host rock labradorite triclinic $C\bar{1}$ - monoclinic $C2/c$ high pressure phase transition. In highly fragmented zones, mono-labradorite displays a residual thermal stress feature as resorbed grain margins and/or shredded edges, with strings of nano-prismatic crystals of tetra-labradorite (Figures 2b and c). The occurrence of the neo-crystallites between mono-labradorite suggests that localized heating induced melting at grain boundaries and initiated crystallization of tetra-labradorite from a labradorite melt. This study interprets that the labradorite polymorphs in the Manicouagan anorthosite were formed due to shock compression, high pressure compaction and hot isostatic pressing within the shock-induced fractured zones and shock melt veins. The coexistence of natural occurrences of high pressure – high temperature phase assemblages, mono- and tetra-labradorite with stishovite, and the absence of a calcium ferrite-structured phase sets an upper bound for local shock conditions in the highly comminuted zones to $P > 19\text{-}25 \text{ GPa}$ and T

~2400-2500 °C [4, 5, 6]. The mono- and tetra-labradorite are new natural occurrences of high pressure and high temperature polymorphs in the Ab-An system. The discovery is one of a few findings of such minerals within a terrestrial impact crater.

References: [1] Yang et al., (2009) *Am. Mineral.* 94, 942-949. [2] Chen M. et al. (2000) *European Journal Min.* 12: p30. [3] Gillet P. (2000) *Science.* 287: 1633-1636. [4] Langenhorst F. and Poirier J.P. (2000) *Earth Planet. Sci. Lett.* 176: 259-265. [5] Liu X. (2006) *Earth Planet. Sci. Lett.* 246: 317-325. [6] Agarwal A. et al. (2016) *Sci. Rep.* DOI:10.1028/erep25991

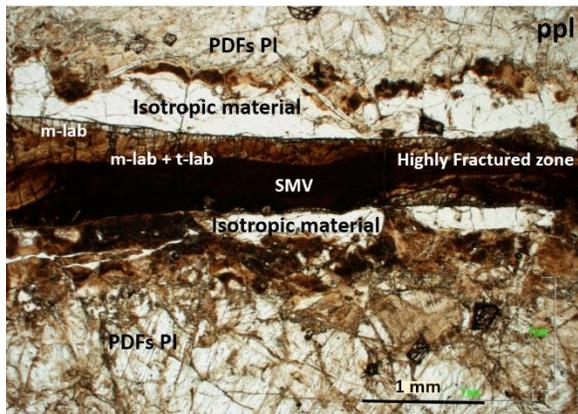


Figure 1. Photomicrograph of shock-induced melt vein under plane polarized light displaying vein structure and margins, and plagioclase polymorph occurrences (m-lab = monoclinic labradorite; t-lab = tetragonal labradorite; SMV = shock-induced melt vein).

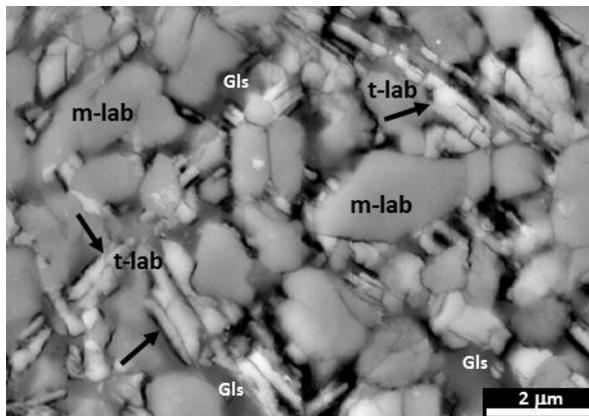


Figure 2. SE images showing cluster of mono-labradorite (m-lab) and bright contrast tetra-labradorite (t-lab, black arrows) fragments within highly fractured zones. Note amorphous phase between minerals as interstitial glass (Gls).

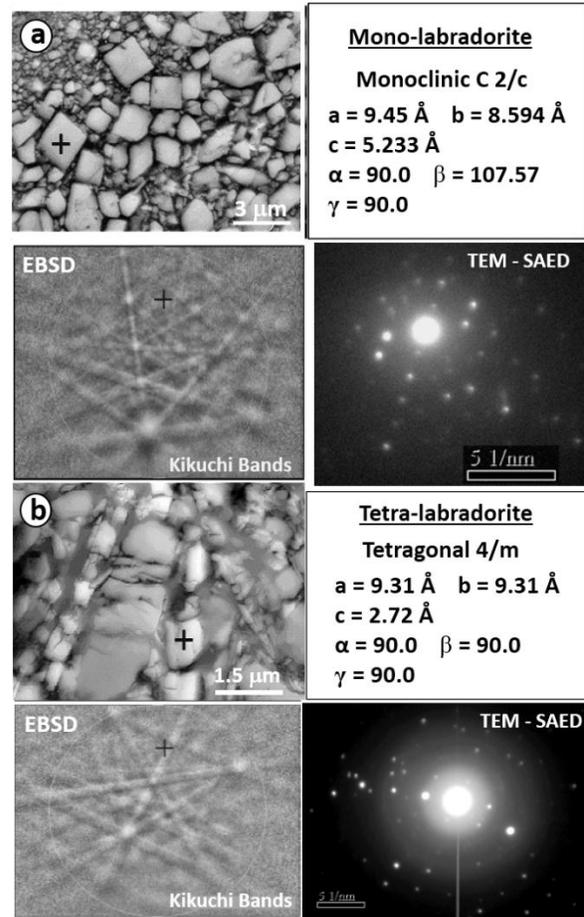


Figure 3 EBSD and SAED-TEM diffraction patterns reveal that the two polymorphs have monoclinic crystal structure with $C2/c$ symmetry (a), and tetragonal crystal structure with $I4/m$ symmetry (b), respectively.

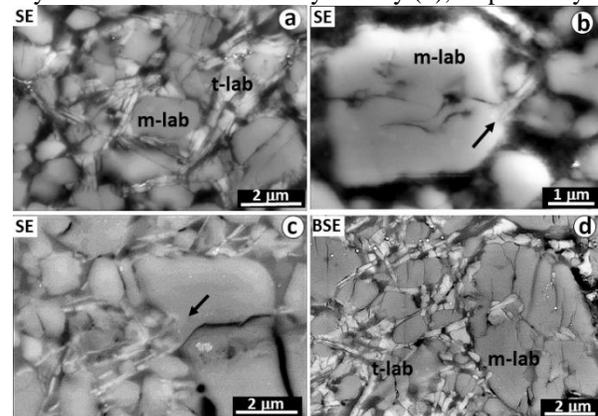


Figure 4. SE and BSE images of mono-labradorite (m-lab) and tetra-labradorite (t-lab) displaying intra-granular fractures and high temperature features (ductile edges). Strings of submicron prismatic crystals of t-lab (b and c) are attached to the rims of m-lab grains.