

TETRAGONAL MAJORITE: NEW CONSTRAINT ON SHOCK HISTORIES OF METEORITES.

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Introduction: Majorite is a garnet-structured mineral in the system $(\text{Mg,Fe})\text{SiO}_3$ – $(\text{Mg,Fe})_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Al-free majorite samples synthesized by Kawai-type multianvil apparatus are known to have a tetragonal symmetry (space group $I4_1/a$) [1]. However, natural Al-free majorite samples found in shocked chondrites have been reported to be cubic ($Ia-3d$) [2]. Only exception is tetragonal majorite having a high-Ca composition ($\text{W}_{0.27}\text{En}_{64}\text{Fs}_{10}$) previously reported in the Tenham chondrite. The majorite occurred as submicrometer-sized symplectic intergrowth with amorphous Fe-Mg silicate as a dissociation product of subcalcic pyroxene [3]. Its crystallographic characterization was limited due to the extremely fine grain size. By way of contrast, we provide unequivocal evidence for $(\text{Mg,Fe})\text{SiO}_3$ tetragonal majorite in Tenham based on single-crystal electron diffraction analysis.

Experimental methods: A polished thin section of Tenham was initially examined by polarized microscopy, SEM and Raman spectroscopy to observe a 400- μm thick shock vein and fragments of host rocks therein. The portions of Al-free majorite in the fragments were processed into two ultrathin foils by FIB (Hitachi SMI4050) and then studied using an TEM (JEOL ARM-200F) equipped with a 100-mm² silicon drift EDS detector at the Kochi Institute for Core Sample Research, JAMSTEC.

Results and Discussion: The TEM samples consist of monomineralic aggregates of euhedral or subhedral grains with 450 ± 200 nm in size. Its chemical composition ($\text{W}_{0.2}\text{En}_{79}\text{Fs}_{19}$) is almost identical to that of low-Ca pyroxene ($\text{W}_{0.2}\text{En}_{78}\text{Fs}_{20}$) in the host rock. The occurrence suggests that the majorite was formed through a solid-state transformation from the low-Ca pyroxene. All the single crystal electron diffraction patterns taken from the grains were consistent with the cubic garnet structure with space group $Ia-3d$. However, the diffraction patterns along the [010] zone axis showed faint extra spots which violate the extinction rule on the Bragg diffraction for $Ia-3d$. Although the unit-cell is metrically cubic within the analytical uncertainty associated with electron diffraction under TEM [$a=1.152(12)$ nm, $c=1.151(12)$ nm], the extra diffraction spots clearly showed that the symmetry of the majorite was tetragonal.

Based on phase equilibria studies, $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ majorite is bounded within the pressure range of 17–20 GPa at 1800 °C [4] and the temperature range of 1900–2100 °C at 20 GPa [5]. The liquidus temperature of the bulk chondrite of ~2000 °C at 20 GPa [6] corresponds to the upper temperature limit for tetragonal majorite formation in a solid-state reaction, because low-Ca pyroxene in the host rock should be melted with coexisting minerals above this temperature. Hence, $(\text{Mg,Fe})\text{SiO}_3$ tetragonal majorite in Tenham would have formed at 1900–2000 °C and 17–20 GPa.

The crystal symmetry of $(\text{Mg,Fe})\text{SiO}_3$ majorite is complex. Based on group theory, MgSiO_3 majorite forms by a symmetry reduction from the space group $Ia-3d$ to $I4_1/a$ through the Mg-Si ordering in the octahedral sites upon cooling [7]. The transition temperature in $(\text{Mg,Fe})\text{SiO}_3$ was estimated to be lower than ~1950 °C by the density contrast of twinning structures [8]. Therefore, the discrepancy in the symmetry of $(\text{Mg,Fe})\text{SiO}_3$ majorite between meteoritic and synthetic samples can be explained by the difference in cooling rates from the temperatures above the phase boundary. In the current study, both meteoritic and synthetic $(\text{Mg,Fe})\text{SiO}_3$ majorite showed a tetragonal symmetry. However, extra reflections for the tetragonal phase in meteoritic majorite are significantly weaker than those of synthetic majorite. This suggests that cations in the octahedral sites of meteoritic majorite were less ordered, even though its symmetry became tetragonal. In high-pressure synthesis, the sample in a Kawai-type apparatus is cooled at the rate of 10^3 °C/s [9], whereas $(\text{Mg,Fe})\text{SiO}_3$ tetragonal majorite in Tenham would have been cooled more rapidly.

The cooling rate of the shock vein further constrains the shock temperature of the overall meteorite sample, because locally extremely heated shock veins are cooled by surrounding host rock after the passage of the shock wave. On the basis of observed cation order degree in synthetic and natural samples and calculated cooling path of shock veins by the 1-D thermal conduction model, the above-mentioned cooling rate of shock vein sets the upper bound for the shock-temperature increase in the bulk meteorite at ~900°C.

References: [1] e.g. Angel, R.J. et al. 1989. *American Mineralogist* 74:509–512. [2] e.g. V. Voegelé et al. 2000. *European Journal of Mineralogy* 12:695–702. [3] Xie, Z. and Sharp, T. 2007. *Earth and Planetary Science Letters* 254:433–445. [4] Ohtani, E. et al. 1991. *Earth and Planetary Science Letters* 102: 158–166. [5] Kato, T. 1986. *Earth and Planetary Science Letters* 77: 399–408. [6] Agee, C. et al. 1995. *Journal of Geophysical Research* 100:17725–17740. [7] Hatch, D.M. and Ghose, S. 1989. *American Mineralogist* 74: 1221–1224. [8] Tomioka, N. et al. 2002. *European Journal of Mineralogy* 14:7–14. [9] Heinemann, S. 1996. thesis, Universität Bayreuth.