

THE HIGH-PRESSURE ASSEMBLAGE MAJORITE-PYROPE SOLID SOLUTION + MAGNESIOWÜSTITE : A NEW CONSTRAINT ON THE HIGH PRESSURE AND TEMPERATURE HISTORY OF SHOCK MELT VEINS IN CHONDRITES. M. Chen^{1,3}, T. G. Sharp², A. El Goresy¹, B. Wopenka⁴ X. Xie³. ¹Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany; ²Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany; ³Guangzhou Institute of Geochemistry, Academia Sinica, 510640 Guangzhou, China; ⁴Department of Earth and Planetary Sciences, Washington University St. Louis MO 63130, USA.

Two coexisting distinct high pressure assemblages were discovered in shock melt veins of the Sixiangkou (L6) chondrite: (1) majorite-pyrope_{ss} + magnesiowüstite and (2) ringwoodite + low-Ca majorite. The majorite-pyrope_{ss} + magnesiowüstite evidently crystallized from a dense melt of bulk Sixiangkou composition that was produced by shock-fusion under high pressures and temperatures, whereas ringwoodite and low-Ca majorite in the second assemblage were formed by solid state transformation of olivine and low-Ca pyroxene originally present in the meteorite. The two high pressure assemblages indicate a duration over a time on the order of seconds under a high pressure (20 - 24 GPa) and high temperature (2050 - 2300 °C) regime.

Introduction: Mg-Fe olivine transforms to the more dense polymorphs modified spinel (wadsleyite) and spinel (ringwoodite) in the Earth's transition zone [1], and dissociates at $P > 23$ GPa and $T \geq 1600$ °C to perovskite plus magnesiowüstite in the Earth's lower mantle [2]. Majorite (garnet) is a stable phase in the pressure range 19 - 24 GPa and at temperatures between 1700 - 2600 °C and is believed to be a significant component of the transition zone [3]. At higher pressures majorite transforms to a perovskite type structure [3]. The phase transitions and dissociation reactions are of vital importance to the understanding of the evolution and the dynamic nature of the Earth. Along with experimental investigations, mineral assemblages in shock-melt veins in meteorites can reveal crucial constraints to the pressure and temperature conditions that lead to phase transformations and dissociation reactions. Here we report the occurrence of two coexisting, but distinct high pressure assemblages in shock-induced black veins of the Sixiangkou (L6) chondrite: (1) a fine-grained intergrowth of a majorite-pyrope solid solution and magnesiowüstite and (2) large rounded grains consisting of polycrystalline aggregates of ringwoodite and low-Ca majorite.

Analytical Techniques: The shock-melt veins were investigated in polished thin sections (PTS) using different techniques in the given sequence: BSE techniques in SEM, Electron Probe Microanalyses (EPM) of individual grains and broad-beam analysis of bulk vein compositions, laser Raman microprobe (LRM) spectroscopy of individual and selected areas of grains, high resolution transmission electron microscopy (HRTEM) and analytical electron microscopy (ATEM). The areas of interest were cored out of the PTS for HRTEM and ATEM using a high precision microdrill.

Petrography: Sixiangkou is a heavily shocked L6 chondrite and it is intersected by a number of shock-induced black veins ranging in width from 0.1 to 2 mm [4]. The veins consist of two distinct lithologies: (1) a fine-grained matrix constituting more than 60 vol. % of the veins that consist of Al-, Na-, Ca-, and Cr-bearing majorite and magnesiowüstite. This part of the vein is sprinkled with fine-grained metal and troilite blebs; (2) mostly unfractured rounded large aggregate grains of ringwoodite and low-Ca majorite that are 15 - 300 μ m in diameter, diaplectic plagioclase glass 10 - 60 μ m in size, and metal-troilite eutectic intergrowths up to 300 μ m in size [4,5].

Majorite-pyrope_{ss} + magnesiowüstite assemblage: The garnet in the matrix is a majorite-pyrope solid solution rich in Al, Ca, Na, and Cr (58.18 % SiO₂, 28.02 % MgO, 2.19 % CaO, 0.34 % MnO, 11.45 % FeO, 0.11 % TiO₂, 3.67 % Al₂O₃, 0.55 % Cr₂O₃, 0.99 % Na₂O, 0.03 % V₂O₃, Totals: 99.53) [4] and its compositional formula can be expressed as: $Mj_{73.8}Na_{-}Mj_{4.7}Ca_{-}Mj_{4.2}Py_{15.8}Uv_{1.5}$. Usually these majorite-pyrope_{ss} grains have equant forms with mostly typical idiomorphic garnet crystal habits (rhombododecahedra, icosidodecahedra, or hexaoctahedra) indicating that they have crystallized as such from the melt and not through inversion of perovskite to garnet upon decompression [6]. The majorite-pyrope_{ss} do not display any dendritic textures [6]. Their sizes range from 1 to 4 μ m. SAED of the majorite-pyrope_{ss} indicates a cubic symmetry. In the interstices of majorite-pyrope_{ss} grains irregularly-shaped blebs of magnesiowüstite (Mg_{0.54}Fe_{0.46})O up to 5 μ m long and thin veneers of silicate glass that wets grain boundaries and fills triple junctions between garnets and magnesiowüstite were encountered [6,7]. The amount of magnesiowüstite ranges between 15 and 20 vol. % of the metal-troilite-poor lithology. SAED indicates that these irregular magnesiowüstite blebs are segments of multibranching single crystals that engulf one or more garnet crystals.

Ringwoodite + low-Ca majorite assemblage: The large aggregate grains of ringwoodite and low-Ca majorite have the same compositions as the olivine and low-Ca pyroxene, respectively (Mg_{1.49}Fe_{0.49}Mn_{0.01})SiO₄, (Mg_{3.09}Fe_{0.82}Ca_{0.06}Mn_{0.03})Si₄O₁₂ in the chondrite part outside the veins [4]. Laser Raman microprobe

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investigations showed that they are ringwoodite and majorite, respectively. The Raman spectra display sharp narrow bands which are characteristic for good crystallinity. TEM and selected area electron diffraction (SAED) showed that the grains are polycrystalline aggregates of ringwoodite and majorite, respectively. The ringwoodite aggregates consist of grains up to 6 μm in size with abundant stacking faults and dislocations. Highly disordered spinelloid structures were not observed [7]. The majorite aggregates contain grains up to 10 μm in size. No evidence for partial transformation as found in experiments were observed [7,8]. All of the SAED patterns collected in the low-Ca majorite were consistent with cubic symmetry.

Discussion: The large aggregate grains of polycrystalline ringwoodite and low-Ca majorite must have formed directly from olivine and low-Ca pyroxene through solid-state reactions without the incorporation of additional elements from the matrix melt. Because both olivine and low-Ca pyroxene in the chondritic part contain very little Al, Na, Ca and Cr, the majorite - pyrope_{SS} must have crystallized from a melt that was enriched in these elements through fusion of plagioclase and chromite along with olivine and pyroxene. Broad-beam analyses of the metal-troilite poor areas of the majorite-pyrope_{SS} + magnesiowüstite intergrowth revealed a composition (47.53 % SiO₂, 26.39 % MgO, 2.19 % CaO, 0.40 % MnO, 17.17 % FeO, 0.18 % TiO₂, 2.71 % Al₂O₃, 0.53 % Cr₂O₃, 1.03 % Na₂O, 0.03 % V₂O₃, Totals: 99.14%) identical to that of bulk Sixiangkou (45.21 % SiO₂, 28.49 % MgO, 2.18 % CaO, 0.41 % MnO, 18.39 % FeO, 0.12 % TiO₂, 3.04 % Al₂O₃, 0.64 % Cr₂O₃, 1.17 % Na₂O, 0.13 % V₂O₃, 0.23 % P₂O₅) [9]. These findings lead to the conclusion that the shock event formed a silicate melt of Sixiangkou bulk composition and that both majorite-pyrope_{SS} and magnesiowüstite crystallized from this dense melt under high pressures and temperatures. The occurrence of two distinct textural and compositional types of garnets in the same vein pays witness to the two different reaction mechanisms. The microtextures seen in the aggregate grains are very similar to those produced experimentally [10,11] through polymorphic solid-state reactions where large overstepping of the equilibrium phase boundaries results in high nucleation rates and fine-grained polycrystalline aggregates.

Evidently all Na, the majority of Al and Ca, and some Cr in the melt were scavenged by the majorite-pyrope_{SS}. Cr was also partitioned to magnesiowüstite. The location of magnesiowüstite in the interstices between majorite grains indicates that the garnet crystallized prior to magnesiowüstite and was therefore the liquidus phase in the Sixiangkou melt. Experiments [12-14] constrain the temperatures and pressures during the crystallization of majorite-pyrope_{SS} + magnesiowüstite to range from 2050 to 2300 °C and 20 to 24 GPa, respectively. The presence of ringwoodite rather than wadsleyite in the polycrystalline lithology constrains the pressure to be higher than \approx 20 GPa. Furthermore, the lack of perovskite or garnet pseudomorphs of perovskite crystals in the fine-grained lithology indicate that the pressure did not exceed \approx 24 GPa during the crystallization of the dense Sixiangkou silicate melt [6].

The peak pressures and temperatures that prevailed during the formation of the shock melt veins in the Sixiangkou L6 chondrite can be constrained by the following findings: (1) solid state transformation of olivine and low-Ca pyroxene to relatively coarse-grained aggregates of ringwoodite and majorite respectively, (2) fusion of the low pressure mineral constituents of the chondrite, (3) partial melting of the polycrystalline ringwoodite and low-Ca majorite under high pressure, and (4) subsequent crystallization of majorite-pyrope_{SS} + magnesiowüstite from the dense silicate melt under high pressures and temperatures. An anticipated short duration of the peak pressures (microseconds to milliseconds) and temperatures that may have prevailed during the passage of the shock wave cannot account for these observations for the following reasons: (1) the relatively coarse-grained nature of the polycrystalline ringwoodite and majorite (up to 6 and 10 μm , respectively) strongly argues for annealing at high pressure, (2) silicate liquids of chondritic and peridotitic composition develop dendritic textures during the 1 to 2 seconds it takes to quench from high temperatures at high pressures in a multianvil apparatus [13,15]. Hence, the lack of dendritic textures in the majorite-pyrope_{SS} + magnesiowüstite assemblage argues against rapid quenching of the dense liquid and implies that the melt crystallized at high pressures and temperatures over a time period on the order of seconds. Our findings lead inevitably to the conclusion that both lithologies were kept at high pressures and temperatures for a much longer time period than would be predicted by the models of shock metamorphism.

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