Ferric iron in Al-bearing akimotoite coexisting with iron-nickel metal in a shock-melt vein in an L-6 chondrite

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ABSTRACT

We report evidence for high ferric iron to total iron (Fe3+/ΣFe) ratios in Al-bearing akimotoite coexisting with other high-pressure silicates and Fe-Ni metal from shock-melt veins in the Sixiangkou (L-6) chondrite. The measurements were made using electron energy-loss near-edge structure (ELNES) spectroscopy. The results demonstrate that akimotoite in shock-melt veins of this meteorite has high proportions of Fe3+, with a Fe3+/ΣFe ratio of 0.67(3). In contrast, the coexisting majoritic garnet and ringwoodite, which are the typical Fe-bearing phases in shock veins in this meteorite, are enriched in Fe2+ rather than Fe3+, with Fe2+/ΣFe ratios of 0.10(5) and 0.15(5), respectively. We conclude that the higher affinity of Fe3+ for akimotoite, rather than for the other dense silicate phases, is related strongly to the substitution mechanism of trivalent cations. This mechanism is described as $\text{V1}0\text{Mg}2+ + \text{V1}0\text{Si}4+ = \text{V1}0\text{Mg}^++ \text{V1}0\text{Si}^{4+}$ in the ABO3 structural formula of MgSiO3-ilmenite under high pressures and temperatures, and operates even at a low oxygen fugacity where Fe-Ni metal is stable.

Keywords: Meteorite, L-6 chondrite, electron microscopy, Fe-bearing silicates, akimotoite, high pressure, shock-melt vein

INTRODUCTION

Melt veins in many shocked L-6 chondrites contain complex mineral assemblages indicative of formation at high pressures and temperatures during dynamic events on parent asteroids (Agee et al. 1995; Chen et al. 1996). These assemblages include ringwoodite and majorite formed by solid-state phase transformation in addition to the liquidus pair majorite-pyrope solid-solution + magnesiowüstite indicative of crystallization at $P < 23$ GPa and $T < 2000$ °C (Agee et al. 1995; Chen et al. 1996). Akimotoite, the ilmenite-structured dense polymorph of (Mg,Fe)SiO3 pyroxene, newly described in shocked chondrites, was found to contain variable amounts of Al2O3 (Sharp et al. 1997; Tomioka and Fujino 1997; Xie et al. 2006). This observation raises the question of the possibility of the presence of Fe3+ to maintain charge balance by the substitution mechanism: $\text{Fe}^{2+} + \text{Al}^{3+} = \text{Mg}^{2+} + \text{Si}^{4+}$, as demonstrated for aluminous silicate perovskite (e.g., McCammon 1997; Lauterbach et al. 2000; Frost and Langenhorst 2002). To explore for the presence of Fe3+, we have examined a shock-melt vein in the Sixiangkou meteorite (e.g., Chen et al. 1996) that is rich in akimotoite, using an analytical TEM equipped with electron-energy-loss spectrometer (EELS).

SAMPLE AND METHODS

We examined several polished thin sections of the Sixiangkou (L-6) chondrite (Chen et al. 1996) using reflected- and transmitted-light optical microscopy and scanning electron microscopy, to select a region containing heavily shocked melt veins surrounding a single crystal of olivine for TEM foil preparation (Fig. 1). The sample was prepared by mounting 3 mm Cu-grids onto the area of interest in a petrographic thin section. The grid with the sample attached was removed from the thin section and thinned to electron transparency using a Gatan Ar-ion milling holder (Gatan 666 PEELS). A stationary defocused electron beam with a spot size of about 100 nm was used for EDXS and PEELS measurements. To reduce electron irradiation damage during EELS measurements, the TEM thin foil was cooled to nearly liquid nitrogen temperature (ca. 100 K) in a Gatan cooling holder. Two-dimensional EDXS element maps were obtained in the scanning probe mode. Qualitative EDXS spectra in the TEM mode were collected with 100 seconds live time and were quantified according to the procedure of van Cappellen and Doukhan (1994). We corrected EDXS spectra for X-ray absorption on the basis of the principle of electroneutrality taking into account the Fe2+/Fe3+ ratio obtained from Fe Lt2 edge electron energy-loss near-edge structure (ELNES) of the sample was examined in a 200 kV analytical scanning transmission electron microscope (Philips CM20T/FEG) equipped with a STEM unit equipped with an energy dispersive X-ray spectrometer (EDXS, NORAN Vantage system with a Ge detector) and a parallel electron energy-loss spectrometer (PEELS, Gatan 666 PEELS). A stationary defocused electron beam with a spot size of about 100 nm was used for EDXS and PEELS measurements. To reduce electron irradiation damage during EELS measurements, the TEM thin foil was cooled to nearly liquid nitrogen temperature (ca. 100 K) in a Gatan cooling holder. Two-dimensional EDXS element maps were obtained in the scanning probe mode. Qualitative EDXS spectra in the TEM mode were collected with 100 seconds live time and were quantified according to the procedure of van Cappellen and Doukhan (1994). We corrected EDXS spectra for X-ray absorption on the basis of the principle of electroneutrality taking into account the Fe2+/Fe3+ ratio obtained from Fe Lt2, ELNES and semi-quantitative oxygen contents obtained from EDXS. The k factors were calibrated using a natural garnet having a known chemical composition obtained by chemical analysis using an SEM, by using the parameter-less correction method (van Cappellen 1999).

ELNES spectra were collected in diffraction mode with convergence and collection semiangles of $\alpha = 6\text{ mrad}$ and $\beta = 1.45\text{ mrad}$, an energy dispersion of 0.1 eV per channel and 5–10 seconds integration time per read-out. The incident beam current was about 6 nA, and the fluence rate was $9 \times 10^8$ e/Å/s. The energy resolution of 0.8–0.9 eV was measured as the width of the zero-loss peak (ZLP) at half height. Spectral processing included subtraction of the dark current, alignment, and summation of offset spectra to reduce channel-to-channel gain variations, background subtractions of the form $\alpha E$, deconvolution of the ZLP to remove the multiple scattering effect on the core-loss edge using a Fourier ratio technique (Egerton 1996). The energy scale was calibrated using the Fe Lt2 edge maximum of predominantly Fe5+ and Fe3+-bearing phases at 707.8 and 709.5 eV, respectively (Garvie et al. 1994) and subtraction of the continuum intensity.