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Metal-troilite-magnetite assemblage in shock veins of Sixiangkou meteorite

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Abstract—The first natural occurrence of metal-troilite-magnetite assemblage composed of Fe-Ni metal and magnetite dendrites and a groundmass of troilite was identified in the shock veins of the Sixiangkou L6 chondrite, which contain abundant high-pressure minerals. This assemblage suggests a liquid miscibility among metal, FeS, and iron oxide, and subsequently quenching under pressure. Components of magnetite could be, in origin, related to chromite that was embedded and dissolved in an Fe-Ni-S liquid. Cr_2O_3 dissociated from chromite was mainly incorporated into garnet and magnesiowüstite in the fine-grained matrix of shock veins, in which chromium behaves as a lithophile element at the P-T conditions experienced by the shock veins. The occurrence of metal-troilite-magnetite assemblage suggests that the shock veins were still under pressure at temperatures from 900 to 950°C during solidification of Fe-Ni-S or Fe-Ni-S-O liquid, hence indicating a long duration of high pressure in the shock veins. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Shock-induced melt veins (shock veins) are pervasive in many chondritic meteorites (Fredriksson et al., 1963; Rubin, 1985; Stöffler et al., 1991), and melting temperatures of up to 1500°C or more have been indicated (Begemann and Wlotzka, 1969; Taylor and Heymann, 1971; Smith and Goldstein, 1977; Chen et al., 1996). The shock veins consist of recrystallizing silicate, oxide, iron-nickel metal and sulfide, and trace amounts of silicate melt glass in interstices (Price et al., 1979; Scott, 1982; Rubin, 1985; Stöffler et al., 1991; Chen et al., 1995; Langenhorst et al., 1995; Chen et al., 1996; Chen and Xie, 1996). Metal and sulfide phase in the shock veins were commonly molten and occur as rapidly solidified metal-troilite eutectic with dendritic or cellular texture, in which metallic dendrites were enclosed in a troilite groundmass (Scott, 1982; Rubin, 1985; Chen et al., 1995). The investigation of textures, compositions and microstructures in the metal-troilite eutectic might shed light on the postshock thermal histories of reheated chondritic meteorites (Begemann and Wlotzka, 1969; Taylor and Heymann, 1971; Smith and Goldstein, 1977; Scott, 1982; Rubin, 1985; Chen et al., 1995; Leroux et al., 2000).

Shock veins in chondritic meteorites contain either a common low-pressure mineral assemblage or a high-pressure mineral assemblage that could be predominating in the Earth's mantle (Binns, 1970; Price et al., 1979; Rubin, 1985; Stöffler et al., 1991; Chen et al., 1995; 1996; Chen and Xie, 1996; Sharp et al., 1997b; Gillet et al., 2000). In this paper, we report the first occurrence of a metal-troilite-magnetite assemblage in the shock veins of Sixiangkou meteorite with abundant high-pressure minerals and discuss the pressure and temperature history of the shock veins.

2. SAMPLE AND ANALYTICAL METHODS

The Sixiangkou meteorite fell on August 15, 1989, in the village Sixiangkou of Taizhou in Jiangsu, China. In total, 375 g of the Sixiangkou meteorite were collected. The major portion of Sixiangkou meteorite is now preserved in the Purple MT Observatory, Chinese Academy of Sciences, Nanjing. The meteorite containing abundant shock veins was classified as an L6 chondrite, and its shock classification stage is S6 (Chen et al., 1994).

The chondritic portion of the Sixiangkou meteorite consists of rock-forming minerals, including olivine, pyroxene, maskelynite (plagioclase glass), kamacite, taenite, and troilite, and accessory minerals chromite and phosphates (Fig. 1a). Shock veins range in width from 0.01 to 10 mm. The high-pressure minerals, including ringwoodite, majorite, hollandite-structured $(Na,Ca,K)AlSi_3O_8$, majorite-pyrope garnet, and magnesiowüstite, were identified in the shock veins above 0.05 mm in width (Fig. 1b) (Chen et al., 1996; Gillet et al., 2000). Both garnet and magnesiowüstite occur in the fine-grained matrix of shock veins. Metal and troilite inside and close to the shock veins mostly occur as metal-troilite grains, occur in the interstices of silicate in the fine-grained matrix of veins, or fill in the cracks and fracture in the silicates in the chondritic portion.

Polished thin sections were prepared from the Sixiangkou meteorite. The mineral assemblages were characterized with an optical microscope and a Hitachi S-3500N scanning electron microscope in backscattered electron mode. Compositions of minerals were quantitatively determined by a CAMECA SX-51 electron microprobe at 15 kV accelerating voltage and 10 nA beam current at the Institute of Geology, Chinese Academy of Sciences. Raman spectra of minerals were recorded with a Renishaw RM-1000 instrument at the China University of Geology. The device and spectra were calibrated by a source of neon light. A microscope was used to focus the excitation beam (Ar^+ laser, 514-nm line) to a 2-μm spot and to collect the Raman signal. Accumulations lasting from 120 to 150 s were made. The laser power was 26.8 mW.

3. RESULTS

3.1. Metal-Troilite Eutectic

Iron-nickel metal and troilite inside and next to the shock veins of the Sixiangkou meteorite were melted during a shock event, and commonly occur as metal-troilite eutectic (Figs. 1b to 1d). This eutectic has a quench texture composed of metallic dendrites and a groundmass of troilite. The cell widths of the dendrites range from 0.5 to 10 μm. The eutectic occurs either as irregular grains ranging in size from several micrometers to a hundred micrometers or as veinlets. The volume ratios of

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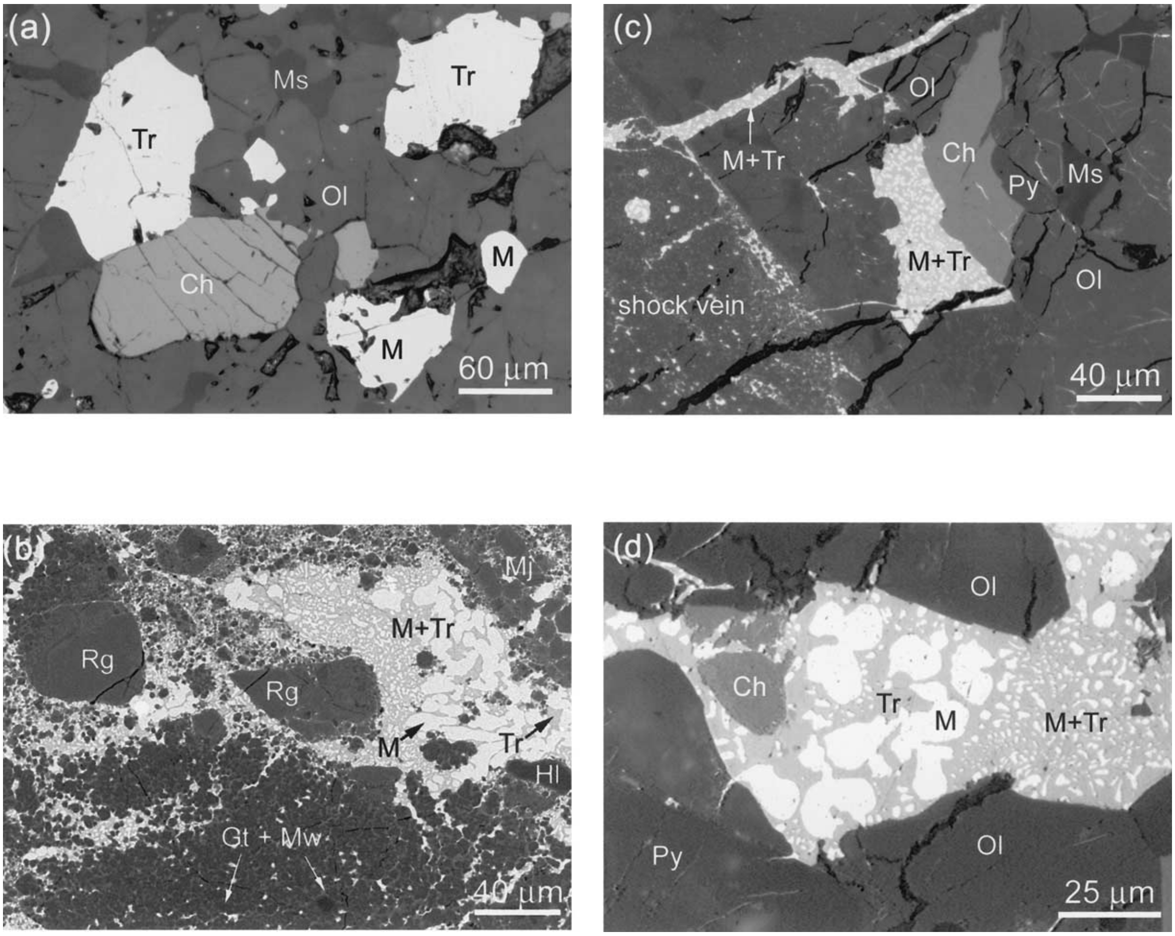

Fig. 1. (a) Chromite (Ch) in the chondritic portion contains abundant cracks and fractures. Reflected light. Ol = olivine; Ms = maskelynite; M = iron-nickel metal; Tr = troilite. (b) Back-scattered electron image shows that the shock vein is composed of metal-troilite (M + Tr) eutectic, ringwoodite (Rg), majorite (Mj), hollandite-structured (Na,Ca,K)$AlSi_3O_8$ (Hl), and fine-grained matrix consisting of garnet (Gt) plus magnesiowüstite (Mw). (c) In the chondritic area close to the shock vein, chromite was molten, which shows a rather smooth surface, and the metal-troilite eutectic was identified. Py = pyroxene. Reflected light. (d) Some molten chromite fragments were enclosed in a metal-troilite grain in the chondritic portion closed to the shock vein. Reflected light.

metal and troilite (metal/metal + troilite) in these eutectic grains are from 0.3 to 0.6.

In the regions of shock veins, there are plenty of cracks nearly perpendicular to the shock veins. These cracks might cut through the shock veins and extend into the chondritic area. Obviously, these cracks were produced during or after solidification of shock-produced silicate melt. Some of these cracks are filled with metal-troilite eutectic (Figs. 1c and 2a). This indicates that the Fe-Ni-S liquid should have been injected into the cracks after solidification of the silicate melt.

The average Ni- and Fe-contents of dendrites are ~8.98 and 87.37 wt.%, respectively (Table 1). Some dendrites consist of a Ni-rich rim (<1 μm wide) with up to 15 wt.% of Ni and a Ni-poor interior with 7 to 8 wt.% of Ni. This Ni-zoning profile of metal dendrites could be produced by rapid nonequilibrium solidification of Fe-Ni-S liquid (Begemann and Wlotzka, 1969; Smith and Goldstein, 1977; Chen et al., 1995) or in association with the vaporization of S into cracks near the shock veins, in which vaporized S scavenged Fe from nearby metal grains, hence resulting in higher Ni-contents at the rims of metal grains (Rubin, 2002). The chemical compositions of metallic dendrites are distinct from both kamacite (~7 wt.% Ni) and taenite (~25 wt.% Ni) in the chondritic portion of the meteorite (Table 1).

3.2. Metal-Troilite-Magnetite Assemblage

Small amounts of metal-troilite eutectics in the shock veins contain the portions of metal-troilite-magnetite assemblage consisting of metallic dendrites, magnetite dendrites, and a groundmass of troilite (Figs. 2a to 2d). Magnetite dendrite has cellular or dendritic texture 0.5 to 2.5 μm wide and up to 10 μm long. In reflected light, the magnetite is gray-black with a metallic luster. The abundance of magnetite in the metal-troilite-magnetite assemblage ranges from a few percent by volume up to 35 vol.%. Fig. 2d shows such a typical area of metal-troilite-magnetite assemblage, with 35 vol.% of magnetite, 45 vol.% of troilite, and 20 vol.% of iron-nickel metal.

Compositional analyses indicate that the magnetite contains 68.00 wt.% of Fe_2O_3, 30.60 wt.% of FeO, and 1.00 wt.% of

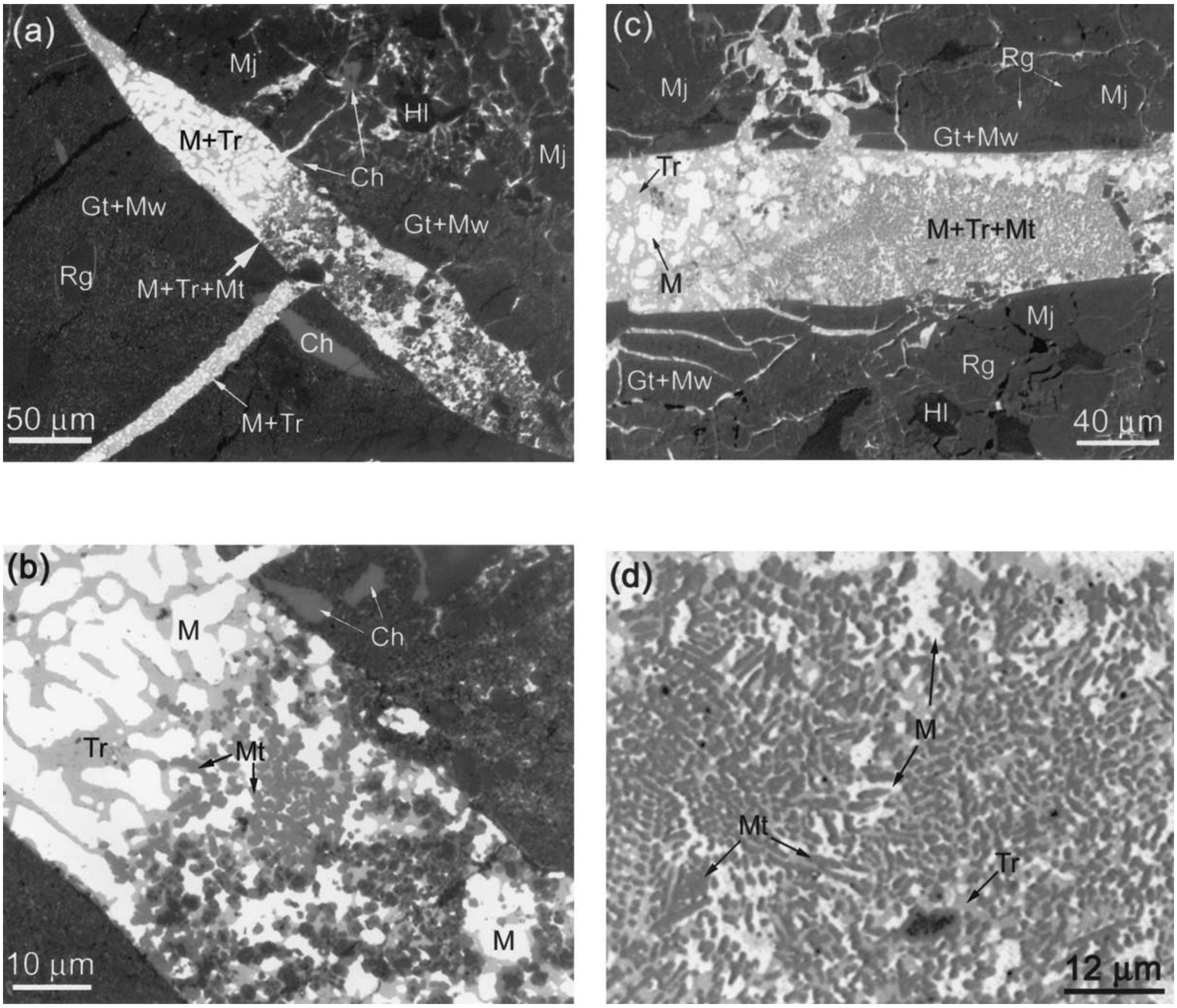

Fig. 2. Some metal-troilite grains in the shock veins contain a portion of the metal-troilite-magnetite assemblage. Both magnetite and metal enclosed in a groundmass of troilite have dendritic or cellular texture. Reflected light. M = metal; Tr = troilite; Mt = magnetite; Ch = chromite; Gt = garnet; Mw = magnesiowüstite; Rg = ringwoodite; Mj = majorite; Hl = hollandite-structured $(Na,Ca,K)AlSi_3O_8$. (a) A metal-troilite veinlet contains a portion of the metal-troilite-magnetite assemblage. A fracture of the fine-grained matrix of shock vein was filled with metal-troilite eutectic. The occurrence of this fracture is perpendicular to the shock veins. Neighboring the metal-troilite veinlet, some partially melted chromites are enclosed in a fine-grained matrix of shock vein. (b) Enlarged picture of (a) showing cellular magnetite. (c) A metal-troilite-magnetite assemblage occurring in a metal-troilite veinlet. (d) Enlarged picture of (c) showing a metal-troilite-magnetite assemblage with dendritic and cellular magnetite.

Cr_2O_3 (Table 2). A Raman spectrum of magnetite displays a strong peak at 665 cm^{-1} and three weak peaks at 541, 406, and 291 cm^{-1} (Fig. 3), which is in agreement with the magnetite vibration mode (Bell et al., 2000; Wang et al., 2001). Fig. 3 also shows that the spectrum of magnetite is distinct from that of chromite, which has a strong peak at 680 cm^{-1} and three weak peaks at 593, 496, and 340 cm^{-1}.

It should be noted that most of the metal-troilite eutectic grains in the shock veins contain no magnetite and that magnetite was never encountered in the metal-troilite eutectic outside the shock veins.

3.3. Molten Chromite

The chondritic portion of the meteorite contains ~1.5 vol.% of chromite. These intact chromites contain abundant fractures or cracks (Fig. 1a). The average compositions of chromite are 30.90 wt.% of FeO and 57.47 wt.% of Cr_2O_3 (Table 2). Within the shock veins, there are some residues of chromite fragments occurring as inclusions enclosed in the fine-grained matrix, and these chromite fragments usually have round or island outlines, hence indicating that these grains were partially melted into the shock-produced silicate melt (Fig. 2a). Inside or closed to the shock veins, most chromites were evidently molten during shock events and display rather smooth surfaces in comparison to the chromite in the chondritic portion (Figs. 1c and 2a). It shows that most previous fractures or cracks in chromite were erased because of shock-induced melting. The compositions of these molten chromites are identical to those of intact chromite in the chondritic portion.

The inclusions of molten chromite fragments were also iden-

Table 1. Compositions of metal and sulfide by microprobe analyses (wt.%)..

	Chondritic portion						Shock vein			
	Taenite		Kamacite		Troilite		Metallic dendrite		Troilite	
	(12)	SD	(12)	SD	(12)	SD	(15)	SD	(15)	SD
Fe	72.16	3.13	91.08	0.52	63.23	1.15	87.37	2.96	63.56	1.02
Ni	25.88	2.50	7.03	0.28	0.03	0.01	8.98	1.88	0.07	0.02
Co	0.38	0.20	0.82	0.22	0.05	0.02	0.68	0.31	0.09	0.03
Mg	0.03	0.02	0.03	0.01	0.02	0.01	n.d.		0.02	0.01
Mn	0.02	0.01	n.d.		n.d.		n.d.		n.d.	
Cr	n.d.		n.d.		0.04		n.d.		n.d.	
Si	n.d.		n.d.		n.d.		0.04	0.02	0.07	0.03
S	n.d.		n.d.		35.87	0.55	0.51	0.25	35.64	0.67
P	n.d.		n.d.		0.02	0.01	0.06	0.02	0.03	0.01
Totals	98.47		98.96		99.26		97.64		99.48	

n.d. = not detected. Numbers in parentheses are the numbers of analyses.

tified in the metal-troilite eutectic grains outside the shock veins (Fig. 1d). Inside the shock veins, neither the metal-troilite grains nor the metal-troilite-magnetite grains contain residues of molten chromite.

4. DISCUSSION

Usually, L chondrites do not contain magnetite. It can be excluded that the magnetite in the Sixiangkou meteorite is a terrestrial alteration product for the following reasons: (a) The Sixiangkou meteorite is a fall, and our sample is very fresh and far from the fusion crust of the meteorite; (b) most magnetite occurs in the interior of metal-troilite-magnetite grains. If the magnetite was formed by the oxidation of the metal phase in the metal-troilite eutectic grains, most of them should have been developed mainly from the rim, then to the interior; (c) the composition of magnetite with 1 wt.% of Cr_2O_3 argues against its origin through oxidation of FeNi metal; and (d) the dendritic texture of magnetite indicates crystallization from a liquid.

Table 2. Compositions of oxides and silicates by microprobe analyses (wt.%).

	Chromite		Magnetite		Garnet[a]	Mw[a]
	(12)	SD	(12)	SD		
SiO_2	n.d.		n.d.		52.18	1.11
TiO_2	2.68	0.23	0.07	0.03	0.11	0.29
Al_2O_3	6.01	0.67	0.19	0.33	3.67	
Cr_2O_3	57.37	0.56	1.00	0.10	0.55	0.86
V_2O_3	0.16	0.04	n.d.		0.03	
Na_2O	n.d.		n.d.		0.99	
K_2O	n.d.		n.d.			
MgO	2.67	0.13	0.14	0.03	28.02	34.85
CaO	0.09	0.03	n.d.		2.19	
FeO	30.90	0.28	30.60[b]	1.08	11.45	62.85
Fe_2O_3			68.00[b]	1.08		
MnO	0.27	0.07	n.d.		0.34	
P_2O_5	n.d.		n.d.			
Totals	100.15		100.00		98.81	99.96

n.d.= not detected.Mw = magnesiowüstite.

[a] Data from Chen et al (1996).

[b] The contents of FeO and Fe_2O_3 were recalculated based on the formula of magnetite and the results of microprobe analyses.Numbers in parentheses are the numbers of analyses.

Sharp et al. (1997a) reported that the fine-grained matrix of shock veins of the Tenham L6 chondrite consists mainly of majorite-pyrope garnet and magnetite and that the magnetite could be either a high-pressure phase crystallized from shock-produced melt or formed as an alteration product of magnesiowüstite or wüstite. Different from the Tenham meteorite, the fine-grained matrix of shock veins of the Sixiangkou meteorite consists mainly of majorite-pyrope garnet and magnesiowüstite. Only tiny magnetite with nanometer sizes was identified, occurring in magnesiowüstite as inclusions, which represents the breakdown of wüstite to magnetite plus metallic iron (Sharp et al., 1996). Obviously, the magnetite in the metal-troilite-magnetite assemblage of the Sixiangkou was not related to the magnesiowüstite in origin. Otherwise, magnetite should have been encountered in the majority of metal-troilite eutectic grains throughout the shock veins. This fact shows that only small amounts of metal-troilite eutectic contain the portion of metal-troilite-magnetite assemblage.

Leroux et al. (2000) reported that the metal-sulfide globules embedded in an amorphous silicate glass matrix of shock veins of Tenham contain 13 wt.% of FeO. They believe that the shock-melting event was accompanied by oxidation of metallic iron-nickel and that appreciable amounts of FeO incorporated into the metal phase at high pressure and temperature. Our electron microprobe analyses of the metal phases in the metal-troilite grains of the shock veins of Sixiangkou show no abnormal concentrations of FeO. The occurrence of magnetite in Sixiangkou also does not support the hypothesis that the origin of magnetite in the metal-troilite-magnetite assemblage was related to such a possible source of shock-oxidized FeO in the shock-produced silicate melt, as in Tenham, because the shock veins of Sixiangkou contain abundant silicate melt subsequently solidified as fine-grained matrix, and magnetite was found only occurring in small amounts of metal-troilite grains.

Our observations might support the hypothesis that the magnetite in the metal-troilite-magnetite assemblage could be, in origin, related to chromite that was embedded and dissolved in an Fe-Ni-S liquid, because (a) chromite is a major Cr-Fe oxide in the chondritic portion of Sixiangkou; (b) some inclusions of

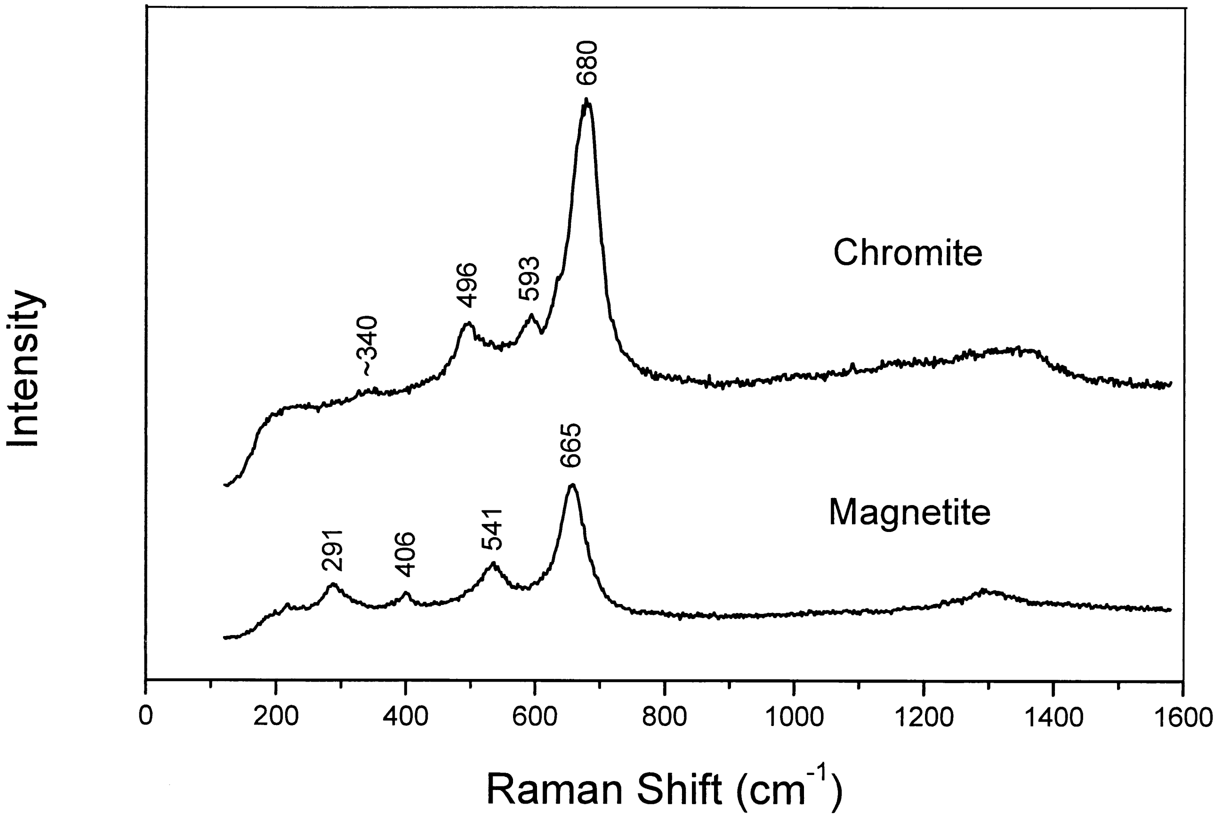

Fig. 3. Raman spectra of magnetite from a metal-troilite-magnetite assemblage and chromite from the chondritic portion of the Sixiangkou meteorite.

molten chromite fragments are enclosed in the metal-troilite eutectic at the chondritic region outside shock veins and were never encountered either in the metal-troilite eutectic or the metal-troilite-magnetite assemblage within shock veins; (c) magnetite was never identified in the metal-troilite eutectic outside the shock veins; (d) the metal-troilite-magnetite assemblage usually occurs as a portion of some metal-troilite eutectic grains, and the majority of metal-troilite eutectic grains in the shock veins do not contain magnetite; (e) partially melted chromite was found in the fine-grained matrix of shock veins, and residues of molten chromite were also encountered adjacent to metal-troilite-magnetite grains; and (f) the magnetite contains small amounts of Cr_2O_3, which are indicative of a component inherited from its parent mineral. These considerations indicate that outside the shock veins, molten chromite embedded in shock-produced Fe-Ni-S liquid was not dissociated under high temperature and low pressure. Only those chromites embedded in Fe-Ni-S liquid in the shock veins were dissociated under high pressure and temperature, hence producing an Fe-Ni-S-O liquid. The more chromite was dissolved into Fe-Ni-S liquid, the more magnetite was produced. A number of studies indicate that stoichiometric FeO as a metastable intermediate phase would decompose to iron and magnetite (Broussard, 1969; Greenwood and Howe, 1972; Hentschel, 1970). Magnetite instead of wüstite occurring in the metal-troilite-magnetite assemblage might be the result of wüstite decomposition to magnetite plus metallic iron at decreased temperature (Shen et al., 1983).

P-T condition has an important effect on the mineral assemblage in the shock veins of meteorites. Chen (1992) reported that some fine-grained idiomorphic chromite crystallized in Fe-Ni-S liquid in the shock veins of Yanzhuang H chondrite, in which the shock veins consist mainly of low-pressure mineral olivine plus pyroxene. The shock veins of the Sixiangkou meteorite experienced a peak pressure and temperature of ~23 GPa and ~2000°C, which was well constrained by the high-pressure mineral assemblages in the shock veins (Chen et al., 1996; Gillet et al., 2000). The metal-troilite-magnetite assemblage may have implications for a high-pressure history in the shock veins, during which Fe-Ni-S or Fe-Ni-S-O liquid was produced and solidified.

Silicate-metal partitioning experiments indicated that chromium behaves as lithophile element at 10 to 25 GPa and 1650 to 2000°C and preferentially partitions into garnet, magnesiowüstite, and other silicate minerals (Kato and Ringwood, 1989). Our microprobe analyses reveal that the metallic dendrite and the troilite in the metal-troilite-magnetite assemblage contain nearly undetectable Cr content. However, both majorite-pyrope garnet and magnesiowüstite in the shock veins, which crystallized from shock-produced dense melt at high pressure and temperature, contain 0.55 and 0.86 wt.% of Cr_2O_3, respectively (Chen et al., 1996). These results are in good agreement with the result of Kato and Ringwood's (1989) experiments. Other high-pressure minerals, such as ringwoodite, majorite, and hollandite-structured (Na,Ca,K)$AlSi_3O_8$, contain lower Cr_2O_3 concentrations ($<$0.13 wt.%) (Chen et al., 1996; Gillet et al., 2000). After subtraction of metal and troilite, the Cr_2O_3 contents in the bulk shock-induced melt (fine-grained matrix) and the bulk chondrite are 0.53 and 0.64 wt.%, respectively (Chen et al., 1996). The composition of bulk matrix is close to the bulk chondrite. On one hand, this fact indicates that the chromium of chromite that was directly melted into shock-produced silicate melt was mainly incorporated into the garnet and magnesiowüstite. On the other hand, chromium from chromite that dissolved in a Fe-Ni-S liquid was also mainly moved into the silicate melt of the veins and subsequently incorporated into garnet and magnesiowüstite. Only a small amount of chromium remained in the Fe-Ni-S-O liquid and was finally incorporated into magnetite.

Experiments by Urakawa et al. (1987) demonstrated that the oxygen solubility in the Fe-Ni-S-O system is pressure dependent and will increase with pressure and that the region of liquid immiscibility in the Fe-Ni-S-O system might disappear above 20 to 25 GPa at $>$900°C. The dendritic texture of metal-troilite-magnetite assemblage in the Sixiangkou displays a eutectic relation among these phases and suggests a liquid miscibility of metal, troilite, and Fe oxide at ~23 GPa and ~2000°C. The Fe-Ni-S eutectic temperature is 950 to 1000°C (Smith and Goldstein, 1977). The eutectic temperature in the system Fe-Ni-O-S is ~900°C at pressures above 15 GPa (Urakawa et al., 1987). The eutectic texture of the metal-troilite-magnetite assemblage indicates that the formation of this assemblage was under pressure. Therefore, the occurrence of high-pressure minerals and the metal-troilite-magnetite assemblage has implications for a long duration of high pressure in the shock veins, in which the high pressure persisted for a time period that lasted from the shock-induced melting of chondritic material to the crystallization of high-pressure minerals (~2000°C) and until the solidification of Fe-Ni-S-O liquid (~900°C).

On the basis of the high-pressure mineral assemblages in shock veins of the Sixiangkou meteorite, a duration of high pressure and temperature of up to some seconds was estimated for the formation of high-pressure minerals (Chen et al., 1996). There is no doubt that the reverse transformation to the low-pressure phase at high temperature is rapid when the pressure decreases. Therefore, the occurrence of high-pressure mineral assemblages in Sixiangkou indicates that the shock veins must have been quenched under pressure. DeCarli (personal communication, 2002) suggested that an approximate calculation of cooling histories of shock veins would help better understand the pressure duration of the impact event. In this heat flow estimation, a thermal conductivity of ~10 W/mK (DeCarli, personal communication, 2002) and peak temperatures of 2000°C in the interior of a vein and 600°C in the material adjoining the veins were considered. Our results show that the cooling time ranges from ~60 μs for a thin vein (0.05 mm) to 11 s for thick veins (10 mm). It should be indicated that those numbers used in the heat flow estimation are uncertain but allow an order of magnitude estimate (DeCarli, personal communication, 2002). Our results reveal that a time period of up to a few seconds could be required to quench the veins to a temperature at which ringwoodite, majorite, hollandite, and a metal-troilite-magnetite assemblage could survive on release of pressure. If the chondritic material was in the deep interior of a larger body, a long duration of high pressure up to seconds is possible because the duration of shock pressure is limited by the time for the release wave to propagate from the nearest free surface (DeCarli, personal communication, 2002).

It has been suggested that both oxygen and sulfur could be the most important light elements in the Earth's outer core (Birch, 1952, 1964). As the Earth might have grown through accretion of planetesimals composed of chondritic rocks (Mason, 1966; Ringwood, 1975; Morgen et al., 1980), the discovery of the metal-troilite-magnetite assemblage in the shock veins of the Sixiangkou meterorite might suggest that a certain amount of iron oxide in the Earth's primitive mantle may have been scavenged by Fe-Ni-S liquid, which subsequently ended up in the Earth's core.

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