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ARTICLES

Xieite, a new mineral of high-pressure $FeCr_2O_4$ polymorph

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Xieite, a new mineral, occurs in the shock vein of the Suizhou meteorite. The mineral has an orthorhombic structure and its space group is *Bbmm*. The cell parameters are *a* = 9.462(6) Å, *b* = 9.562(9) Å, *c* = 2.916(1)Å. The crystal-chemical formula is $(Fe_{0.87}Mg_{0.13}Mn_{0.01})_{1.01}(Cr_{1.62}Al_{0.25}Ti_{0.08}V_{0.02})_{1.97}O_4$, or simply formula $FeCr_2O_4$. Stronger X-ray diffraction lines are [*d* (Å), I/I_o]: (2.675, 100), (2.389, 20), (2.089, 10), (1.953, 90), (1.566, 60), (1.439, 15), (1.425, 15), (1.337, 40). Xieite is a high pressure polymorph of $FeCr_2O_4$ and formed by solid-state transformation of chromite under shock-induced high pressure and temperature, in association with other high-pressure minerals including ringwoodite, majorite, lingunite and tuite. The *P-T* condition for the formation of xieite is estimated to be 18—23 GPa and 1800—1950℃, respectively. Xieite has recently been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2007-056). The mineral name, xieite, is named after Xiande Xie.

xieite, chromite, high-pressure, polymorph, new mineral, shock, Suizhou meteorite

GEOLOGY

Chromite, $FeCr_2O_4$, belongs to spinel group, and it occurs mainly in meteorites and the Earth's ultramafic igneous rocks, for instance, peridotite. In the late 1960s, Reid and Ringwood[1] proposed if there be high pressure phase transitions of spinels in the deep Earth, it would convert from a cubic structure to dense orthorhombic $CaFe_2O_4$-, $CaMn_2O_4$- or $CaTi_2O_4$-type structure. In order to investigate the high-pressure phase transition of spinels, several dense high-pressure phases with spinel compositions, for instance, Mn_3O_4, Fe_3O_4, $CaAl_2O_4$, $MgFe_2O_4$, $MgAl_2O_4$ oxides, have been synthesized by laboratory experiments[1−5]. It was not until 2003 that the first natural occurrence of high-pressure polymorph of chromite with orthorhombic $CaTi_2O_4$-type structure was reported in the shock-metamorphosed Suizhou meteorite[6]. Recently, this new mineral, xieite, has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association. The meteorite sample containing xieite is deposited in the Geological Museum of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. This paper describes the occurrence, chemical composition, physical properties, crystallography, possible formation mechanism and its geological significance of this new mineral.

1 Occurrence

Xieite occurs in the shock-produced veins of Suizhou L6 chondrite, which fell in Suizhou County, Hubei Province, China, in 1986[7]. The rock-forming minerals of the meteorite include olivine, pyroxene, plagioclase, kamacite, taenite and troilite, in addition to the accessory components chromite, ilmenite, whitlockite and chlorapatite.

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The Suizhou meteorite contains small amounts of networks of thin shock veins about 20－300 μm thick, mostly 20－90 μm. The chondrite is intersected by shock veins, which are composed of coarse-grained mineral fragments and fine-grained matrix. The coarse-grained minerals are polycrystalline aggregates of ringwoodite, majorite, lingunite and tuite, transformed from olivine, pyroxene, plagioclase and whitlockite, respectively, whereas the fine-grained matrix is an assemblage of garnet plus ringwoodite crystallized from a shock-induced dense chondritic melt[6,8]. Metal and troilite in the shock veins were molten and occurred as eutectic FeNi-FeS grains or droplets of metal and troilite.

The xieite is formed through solid-state transformation of chromite, and its occurrence is intimately associated with the shock veins of meteorite. Xieite occurs within the shock veins, or in the chondritic portion adjacent to the shock veins within a distance of less than 40 μm (Figure 1).

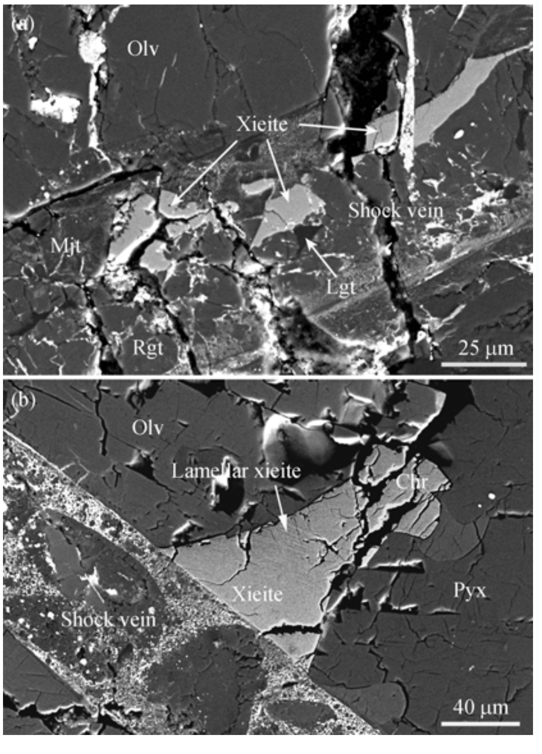

Figure 1 Back-scattered electron image of the shock vein of Suizhou meteorite. (a) The polycrystalline aggregates of high-pressure minerals in the vein including ringwoodite (Rgt), majorite (Mjt), lingunite (Lgt) and xieite. The fine grained matrix is distributed among the aggregates. (b) A chromite (Chr) grain in chondritic portion is cut off by the shock vein. One part of this grain in contact with the vein was transformed to massive xieite, whereas other part of this grain apart from the vein is still chromite. The middle part of this chromite grain is of a lamellar texture composed of layers of xieite. Olv, olivine; Pyx, pyroxene.

2 Appearances

The xieite occurs as compact polycrystalline aggregates of about 5－40 μm in grain size and commonly displays as pseudomorph of chromite crystals or its fragments. The aggregates are composed of crystallites of less than 1 μm in size. Inside the shock veins, grains of chromite are completely transformed to massive xieite (Figure 1(a)). In the chondritic area adjacent to the shock veins, xieite may replace chromite completely for those grains closer to the vein, whereas those chromite grains relatively apart from the vein could only be replaced by lamellar xieite along fractures or special crystallography orientation (Figure 1(b)).

3 Chemical compositions

Electron microprobe analyses of xieite yielded an average composition of 2.47wt% MgO, 29.35wt% FeO, 0.55wt% MnO, 2.71wt% TiO_2, 57.46wt% Cr_2O_3, 6.07 wt% Al_2O_3, 0.92wt% V_2O_3, and 99.53wt% in total. The empirical formula of xieite is $(Fe_{0.87}Mg_{0.13}Mn_{0.01})_{1.01}$-$(Cr_{1.62}Al_{0.25}Ti_{0.08}V_{0.02})_{1.97}O_4$, based on 4 oxygen atoms per formula unit. The simplified formula for xieite is given as $FeCr_2O_4$. Empirical formula of chromite in the chondritic portion is $(Fe_{0.88}Mg_{0.13}Mn_{0.01})_{1.02}(Cr_{1.61}Al_{0.25}$-$Ti_{0.08}V_{0.02})_{1.96}O_4$. The xieite has the same composition as chromite.

4 Physical properties

Physical properties including colour, streak, lustre, tenacity, cleavage, fracture, and parting are unknown because of the polycrystalline nature of xieite aggregates, extremely small size of crystallites. Based on polishing relief, xieite is harder than chromite (a Mohs' hardness of 5.5). Calculated density is 5.342 g/cm^3 with empirical formula of xieite.

5 Raman spectroscopy

There is a distinct difference in feature of Raman spectra between xieite and chromite. The spectrum of xieite obtained by Raman microprobe shows a strong band at 605 cm^{-1} and a shoulder at 665 cm^{-1}, whereas the Raman spectrum of chromite displays distinct bands at 217, 280, 396, 595, and 680 cm^{-1} (Figure 2). The Raman spectroscopic analyses demonstrate that the polycrystalline aggregates of xieite within the shock veins consist of single phase of xieite, indicating a complete transformation from previous chromite to xieite, whereas those chromite grains with lamellar texture in the chondritic portion adjacent to the shock vein show only partial transformation to xieite in the lamellar layers (Figure 2). Chromite in chondritic portion far from the shock veins remains a spinel structure.

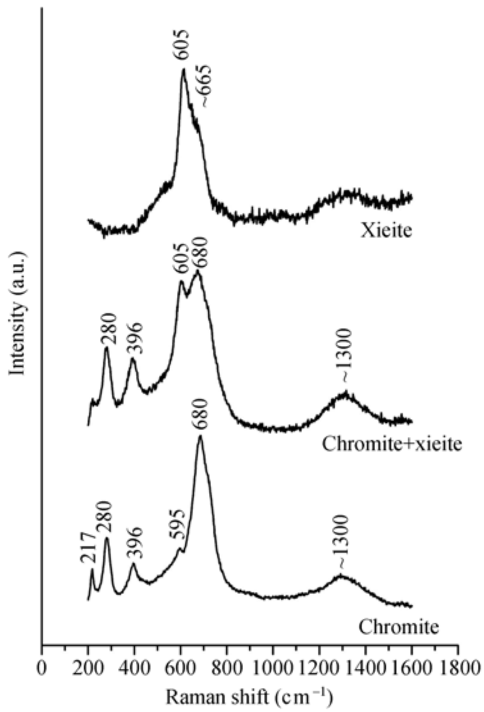

Figure 2 Raman spectra showing xieite, chromite and a mixture consisting of both chromite and xieite. The upper is a xieite spectrum recorded from a polycrystalline aggregate of xieite occurring within a shock vein. The lower is a chromite spectrum measured from a chromite grain in the chondritic portion apart from the shock veins. The middle is a mixture spectrum from chromite plus xieite obtained from a chromite grain with lamellar texture in chondritic portion adjacent to a shock vein.

6 Optical properties

Colour of xieite under reflected light is grey. Bireflectance, pleochroism, anisotropy and internal reflections could not be observed because of an occurrence of crystallite aggregate of xieite. The average reflectance values of xieite in air for the standard COM wavelengths are 19.9% (470 nm), 19.7% (546 nm), 18.6% (589 nm), 17.6% (650 nm) and 18.5% (white light).

7 Crystallography

The crystal structure of xieite was measured *in-situ* on polished sections of meteorite by using synchrotron X-ray diffraction analyses[6]. Figure 3 shows two X-ray diffraction patterns recorded at different orientations of the sample, which show the polycrystalline nature of analyzed xieite grains. Table 1 lists the indexed peaks of X-ray diffraction pattern and Miller indices for xieite. The strongest lines in the X-ray powder-diffraction pattern are [d (Å), I/I_o]: (2.675, 100), (2.389, 20), (2.089, 10), (1.953, 90), (1.566, 60), (1.439, 15), (1.425, 15), (1.337, 40). Xieite is isostructural with synthesized

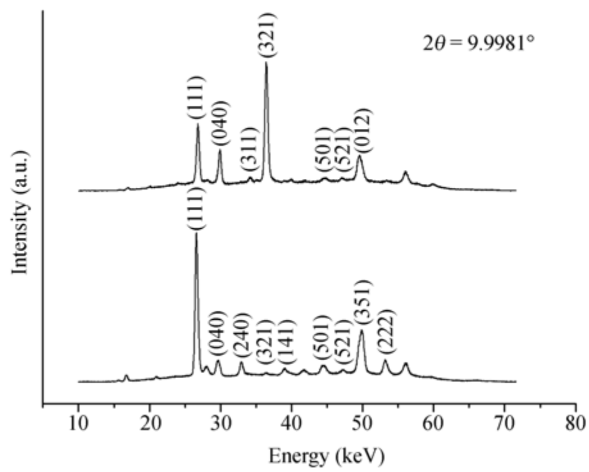

Figure 3 X-ray diffraction patterns of polycrystalline aggregate of xieite obtained from two different orientations of the sample. The numbers listed at diffraction peaks are the Miller indices representative of the orientation of atomic planes in a crystal lattice.

Table 1 X-ray diffraction data of polycrystalline xieite[a)]

h k l	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I/I_o
1 1 1	2.6747	2.6754	100
0 4 0	2.3890	2.3905	20
2 4 0	2.1306	2.1336	5
4 2 0	2.1220	2.1203	5
3 1 1	2.0887	2.0895	10
3 2 1	1.9526	1.9542	90
1 4 1	1.8138	1.8144	8
5 0 1	1.5881	1.5875	10
5 1 1	1.5661	1.5661	60
5 2 1	1.5060	1.5066	5
0 1 2	1.4394	1.4414	15
3 5 1	1.4247	1.4263	15
2 2 2	1.3373	1.3377	40
4 1 2	1.2292	1.2309	2
6 0 2	1.0717	1.0706	6
2 6 2	1.0502	1.0490	5
6 3 2	1.0140	1.0149	8
6 4 2	0.9775	0.9771	7
1 2 3	0.9479	0.9477	2
3 2 3	0.9138	0.9119	3
3 3 3	0.8900	0.8918	4

a) The data of *hkl*, d_{meas} and d_{calc} are from Chen et al.[6].

$CaTi_2O_4$ with space group *Bbmm* and orthorhombic symmetry[9,10]. Cell parameters are: a = 9.462(6) Å, b = 9.562(9) Å, c = 2.916(1) Å (numbers in parentheses are standard deviations for the last significant digits), Z = 4, V = 263.8(4) $Å^3$. Figure 4 is a schematic view of xieite structure showing and edge- and corner-sharing octahedral and dodecahedral sites, where cations of Cr^{3+} and Al^{3+} occupy octahedral sites, whereas Mg^{2+} and Fe^{2+} occupy dodecahedral sites.

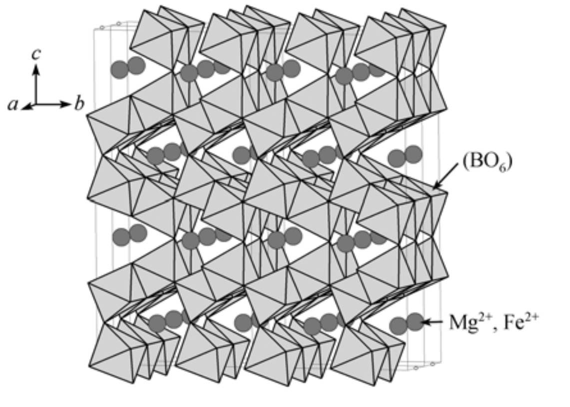

Figure 4 Schematic view of xieite structure showing that Cr^{3+} and Al^{3+} occupy octahedral sites (BO_6), whereas Mg^{2+} and Fe^{2+} occupy dodecahedral sites.

8 Pressure and temperature condition

The veins of meteorite experienced a high pressure and temperature event induced from shock waves, which resulted in melting, partially melting, and recrystallization of veins. Recent studies demonstrated that the high-pressure mineral assemblages from shock veins of meteorites can be compared to those produced from high-pressure melting experiments of chondritic meteorites, and that it is possible to use the phase diagrams of the meteorite to estimate pressure and temperature condition of shock veins of meteorites[6,8,11,12]. The liquidus assemblage in the fine-grained matrix of the shock vein of Suizhou meteorite is garnet plus ringwoodite. Based on the phase diagram[13], the pressure (18 to 23 GPa) and temperature (1800 to 1950℃) are estimated for the shock vein, for which a solid state transformation from chromite to xieite takes place. High pressure and temperature experiments confirmed that xieite can be synthesized from above *P-T* condition[14]. Outside the shock vein, shock-induced pressure and temperature reduce continuously along with an increasing of distance to the vein, hence resulting in a complete or partial transformation from chromite to xieite. Far from the shock veins (>40 μm), no high-pressure phase transformation was observed in chromite probably because of lower pressure and temperature there.

9 Mineral name

In February 2008, the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association approved this new mineral and its name “xieite” (IMA 2007-056). The mineral name, xieite, is for Professor Xiande Xie, the former president of the International Mineralogical Association from 1990 to 1994, in honor of his contribution to mineralogy and shock effects of minerals.

10 Geological significance

The collision between asteroids may cause extremely high pressure and temperature in meteorites, and results in high-pressure phase transformation of minerals as well as other physical and chemical effects. The structural transitions of minerals are also believed to take place in the deep Earth where a high pressure and temperature environment is expected. Because of extensive occurrence of spinels in the upper Earth, its structural transitions under high pressure and temperature have been an important topic for mantle mineralogy. According to the features in occurrence, chemical composition, crystallography of xieite in the Suizhou meteorite, it appears that xieite is a high-pressure polymorph of $FeCr_2O_4$. Xieite is about ten percent denser than chromite and should occur in a pressure regime equal to a depth >500 km from the surface of Earth. If the high-pressure polymorphs of chromite could form in the deep Earth, it could be preserved in some natural mantle rocks, for example, as inclusion mineral in diamonds from kimberlites and related rocks[15]. Since chromite is a common accessory mineral occurring in meteorites and Earth’s mantle rocks, xieite could be another potential pressure gauge not only for shock-metamorphosed meteorites, but also for the rocks exhumed from the deep Earth.

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1 Reid A F, Ringwood A E. Newly observed high pressure transformations in Mn_3O_4, $CaAl_2O_4$, and $ZrSiO_4$. Earth Planet Sci Lett, 1969, 6: 205—208

2 Irifune T, Fujino K, Ohtani E. A new high-pressure form of $MgAl_2O_4$. Nature, 1991, 349: 409—411

3 Funamori N, Jeanloz R, Nguyen J H, et al. High-pressure transformations in $MgAl_2O_4$. J Geophys Res, 1998, 103: 20813—20818

4 Fei Y, Frost D J, Mao H K, et al. In situ structure determination of the high-pressure phase of Fe_3O_4. Am Mineral, 1999, 84: 203—206

5 Andrault D, Bolfan-Casanova N. High-pressure phase transformations in the $MgFe_2O_4$ and Fe_2O_3-$MgSiO_3$ system. Phys Chem Mineral, 2001, 28: 211—217

6 Chen M, Shu J, Xie X, et al. Natural $CaTi_2O_4$-structured $FeCr_2O_4$ polymorph in the Suizhou meteorite and its significance in mantle mineralogy. Geochim Cosmochim Acta, 2003, 7: 3937—3942

7 Xie X, Chen M, Wang D. Shock-related mineralogical features and P-T history of the Suizhou L6 chondrite. Eur J Mineral, 2001, 13: 1177—1190

8 Xie X, Minitti M E, Chen M, et al. Tuite. γ-$Ca_3(PO_4)_2$: A new mineral from the Suizhou L6 chondrite. Eur J Mineral, 2003, 15: 1001—1005

9 Bertaut E F, Blum P. Determination de la Structure de Ti_2CaO_4 par la Méthode Self-Consistante d'Approche Directe. Acta Cryst, 1956, 9: 121—126

10 Bright N F H, Rowland J F, Wurm J G. The compound CaO. Ti_2O_3. Can J Chem, 1958, 36: 492—495

11 Chen M, Sharp T G, El Goresy A, et al. The majorite-pyrope + magnesiowüstite assemblage: constraints on the history of shock veins in chondrites. Science, 1996, 271: 1570—1573

12 Gillet P, Chen M, Dubrovinsky L, et al. Natural $NaAlSi_3O_8$-hollandite in the shocked Sixiangkou meteorite. Science, 2000, 287: 1633—1636

13 Agee C B, Li J, Shannon M C, et al. Pressure-temperature phase diagram for the Allende meteorite. J Geophys Res, 1995, 100: 17725—17740

14 Chen M, Shu J, Mao H K, et al. Natural occurrence and synthesis of two new post-spinel polymorphs of chromite. Proc Natl Acad Sci USA, 2003, 100: 14651—14654

15 Green H W II. Shock-induced minerals in meteorite provide prospecting tools for mineral physics. Proc Natl Acad Sci USA, 2004, 101: 6—7