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RESEARCH ARTICLE

X-ray diffraction investigation of native Si-Fe alloy minerals from Luobusha, Tibet

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Abstract The origin of native Si-Fe alloy mineral is thought to be related with mantle and aerolite. The native Si-Fe alloy minerals from podiform chromites of the Luobusha ophiolite in the Yarlong Zangbo suture zone were examined by a new method for powder-like diffractograms of small single crystals, using an SMART APEX-CCD area-detector X-ray diffractometer. The powder diffraction pattern shows that the minerals are composed of FeSi, $FeSi_2$, β-$FeSi_2$[1)] and native silicon. The association of these minerals suggests that the crystallization order of the mineral may be from early to late FeSi→$FeSi_2$→native silicon, accompanied by gradually increasing deoxidization.

Keywords native Si-Fe alloy mineral, X-ray diffraction, crystal structure, mantle mineral, Tibet

The natural origin of Si-Fe alloy mineral was first discovered in epidotic hornblende rocks and Devonian sandstone in Russia in the 1960s. In the 1980s, some natural Si-Fe alloy minerals were found in ultramafic rocks, metamorphic rocks and granite in various places in China, including Tibet, Xinjiang, Anhui, Liaoing, Jiangsu, and Zhejiang (Hu, 1995).

Natural Si-Fe alloy minerals, except the ones named as gubeiite (Fe_3Si) and xifengite (Fe_5Si_3), some different kinds of Fe_xSi_y were found in aerolite. The natural origin of Si-Fe alloy mineral has always been a matter of debate. Ferdisilicite ($FeSi_2$) and fersilicite (FeSi) have not been approved as valid mineral names by the IMA-CNMMN because their natural origin is in doubt.

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The podiform chromites of the Luobusha ophiolite in the Yarlong Zangbo structure zone have an unusual mineral assemblage including ultra-high pressure minerals such as diamond and moissanite (SiC), as well as a number of highly reduced phases such as graphite, native chromium, iron, and nickel. An unnamed chromium carbide iron silicide (Fe-Si), and native W, Cr, Cu, Mn, Ag, Au and Si are also present (Bai et al., 2003b, 2004b). $Fe_{0.84}Si_{2.00}$, Fe_7Si_3, Fe_6Si_4 and $Fe_4Ti_3Si_2P$, have been found in the heavy-mineral fractions of the chromites (Bai et al., 2003a). However, it is impossible to get powder X-ray patterns to determine constituents by using a conventional X-ray diffraction instrument, because of the rarity of the minerals and their tiny crystallization. A new method for powder-like diffractograms of small crystals with SMART APEX-CCD area-detector X-ray diffractometer was developed by the Crystal Structure Laboratory at China University of Geosciences (Beijing) (Li, 2005). The powder XRD data of these rare alloy minerals were obtained by using this new method, and the structure of $FeSi_2$ was also determined by signal crystal X-ray diffraction.

1 Chemical composition of Si-Fe alloy minerals

The composition of the Si-Fe alloy minerals in this area was obtained by using electronic probe microscopy analysis (Bai et al., 2004a). This mineral group mainly consists of Fe and Si, which change content levels within a certain range, and there is a small amount of Al and Ti. The range of several elements is as follows (number of atoms): Fe: 29.63–31.98, Si: 66.48–69.85, Al: 0.56–2.24. The powder X-ray Diffraction (XRD) analysis indicates that most alloys were the $FeSi_2$ phase and a few were FeSi. Fe: 50.75 and Si: 49.75. The rare natural silicon inclusions were detected in $FeSi_2$.

[1)] β-$FeSi_2$ was denominated a new mineral, Luobusaite (2005-52a) on August 2006 by the IMA-CNMMN

2 Powder X-ray diffractometry

2.1 A new method for powder-like diffractograms of small single crystals

In this contribution we used a new method for powder-like diffractograms of small single crystals using an SMART APEX-CCD detector X-ray diffractometer in the X-Ray Laboratory of China University of Geosciences. A repeat rotation method and a supporting software program were developed. The motivation for this work was to make available for analysis the powder diffraction data for small crystal grains. Using this method we have obtained many powder diffraction data of native Si-Fe alloy minerals from podiform chromites of the Luobusha ophiolite in Tibet.

The experimental samples are from the Luobusha chromites, in heavy-mineral concentrates separated from the chromites. The alloy minerals were hand-picked from several size-fractions, irregular grains up to 1.5 mm, but most are between 0.1–0.3 mm in diameter and are grey in color. The powder X-ray diffraction was performed on an SMART APEX-CCD area-detector diffractometer using MoKα radiation, 45 kV, 35 mA, repeat rotation with $\Delta\omega = 10°–20°$. The exposure time was 60–120 s. The new method was used by taking powder diffraction Debye image with a small crystal grain (Li, 2005), and very clear Debye ring images were obtained. The powder diffraction pattern and diffraction data were obtained using Gadds software.

2.2 X-ray Diffractometry analysis and results

2.2.1 $FeSi_2$ phase

The $FeSi_2$ phase is also common in the Luobusha chromites. Figure 1 shows the powder X-ray diffraction patterns corresponding to tetragonal symmetry $FeSi_2$ phase. As can be observed, four patterns show similar characteristics. The main diffraction peaks are 1.85 (100), 5.22 (90), 2.37 (80), and 1.89 (80) Å (Table 1). Besides the main phase $FeSi_2$, samples 32-12 and 32-3-8 were found to contain small inclusions of native Si. Its typical X-ray diffraction peaks are 3.122, 1.894, and 1.629 Å (Fig.1).

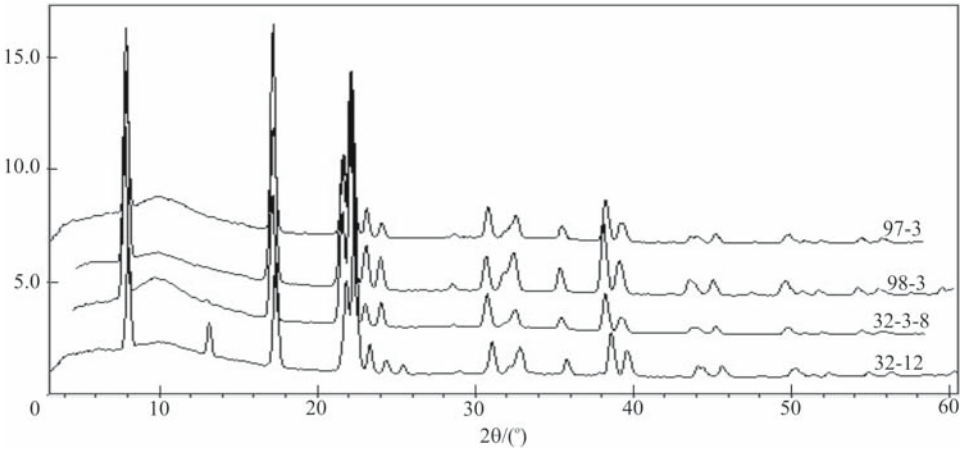

Fig. 1 The X-ray powder diffraction pattern of $FeSi_2$

Table 1 X-ray powder diffraction data of $FeSi_2$

32-3-8		38-3		97-3		32-12		ICDD73-1843	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
5.150	5 773	5.163	7 963	5.142	4 759	5.092	3 770	5.128 0	999
2.373	3 988	2.376	8 661	2.377	3 320	2.372	3 595	2.684 0	8
1.895	3 689	1.899	4 101	1.897	2 286	1.894	2 552	2.564 0	3
1.848	6 049	1.851	6 880	1.851	4 438	1.847	5 466	2.378 0	710
1.776	654	1.774	1 369	1.776	795	1.773	905	1.897 9	520
1.704	780	1.708	995	1.707	402	1.699	416	1.854 0	925
1.436	72	1.440	180	1.439	96	1.434	82	1.779 9	148
1.340	891	1.342	1 044	1.341	812	1.339	936	1.709 3	80
1.297	77	1.299	378	1.300	83	1.297	151	1.525 4	4
1.267	461	1.271	903	1.269	535	1.267	743	1.441 8	30
1.167	349	1.169	729	1.169	363	1.167	500	1.342 0	131
1.086	1 171	1.087	2 139	1.088	1 239	1.085	1 368	1.298 3	38
1.061	455	1.061	919	1.063	554	1.059	798	1.282 0	47
0.957	197	0.958	450	0.959	258	0.956	258	1.270 1	92
0.926	336	0.927	433	0.949	198	0.948	147	1.200 3	3
0.847	172	0.846	487	0.927	290	0.925	319	1.189 0	2
0.813	84	0.779	310	0.845	317	0.844	331	1.168 7	83
								1.156 8	2

2.2.2 β-$FeSi_2$ phase

The β-$FeSi_2$ phase is a rare mineral in Luobusha chromites. The powder X-ray diffraction pattern is shown in Fig. 2. It is similar to that of synthetic orthorhombic $FeSi_2$ (ICDD71-642). All strong lines coincide with the strong lines of this β-$FeSi_2$ very well. The main diffraction peaks are 3.060 3 (100), 1.833 0 (43), 1.961 2 (27), and 1.634 9 (11) Å (Table 2). We are of the opinion that it may be a natural phase of β-$FeSi_2$.

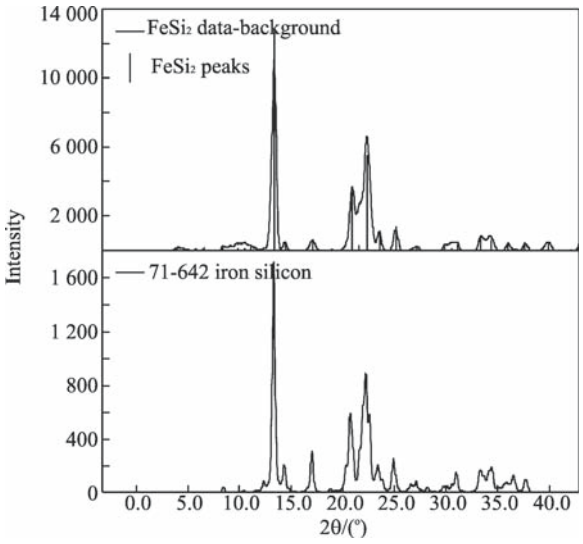

Fig. 2 The X-ray powder diffraction pattern of β-$FeSi_2$

Table 2 The X-ray diffraction data of β-$FeSi_2$

h	*k*	*l*	*d*/Å	*I*
2	0	0	4.860 7	2
0	0	2	3.886 6	1
2	2	0	3.060 3	100
2	2	1	2.837 7	4
2	2	2	2.398 3	5
0	2	3	2.155 7	1
0	4	0	1.961 2	27
0	4	1	1.897 1	2
4	2	2	1.833 0	43
0	2	4	1.741 7	9
2	2	4	1.634 9	11
1	5	1	1.511 1	2
0	4	4	1.377 7	2
7	1	1	1.348 9	1
1	5	3	1.326 4	3
3	5	3	1.237 6	6
5	1	5	1.202 9	5
4	6	0	1.149 3	4
1	7	1	1.100 2	4
7	3	4	1.041 2	4
4	6	4	0.988 9	1
7	5	3	0.968 2	4
2	4	7	0.944 0	3
0	6	6	0.911 8	1
3	7	5	0.872 9	1
1	7	6	0.840 6	1

2.2.3 FeSi phase

The powder diffraction data of the FeSi phase are shown in Table 3 and Fig. 3. As well as the main FeSi phase, we found some small inclusions of $FeSi_2$. After the FeSi unit cell was refined by CHKCELL software, the cell parameter was $a = 4.452\ 7\ (4)$ Å with cube symmetry. The main diffraction peaks are 1.990, 1.816, and 2.568 Å. According to the FeSi crystal structure, Fe and Si tend to form a covalent bond. The Fe-Si bond distance is 2.288–2.346 Å.

Table 3 X-ray powder diffraction data of FeSi

Sample 97-8-2					ICDD86-795	
h	*k*	*l*	*d*/Å	*I*	*d*/Å	*I*
1	1	0	3.148	360	3.154 3	200
1	1	1	2.568	436	2.575 5	166
2	0	0	2.222	73	2.230 4	61
2	1	0	1.990	1 820	1.995 0	999
2	1	1	1.816	1 011	1.821 1	487
2	2	0	1.573	74	1.577 2	3
2	2	1	1.485	62	1.487 0	32
3	1	0			1.410 7	23
3	1	1	1.344	182	1.345 0	93
2	2	2			1.287 8	23
0	2	3			1.237 2	49
1	2	3			1.192 2	216
4	0	0			1.115 2	58

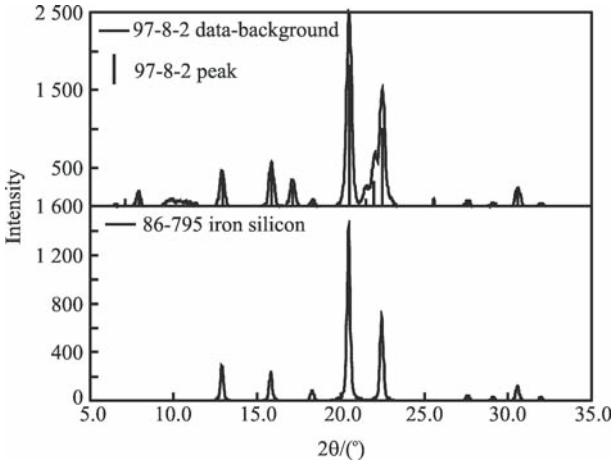

Fig. 3 The X-ray powder diffraction pattern of FeSi

3 Structure determination of the $FeSi_2$

A crystal approximately 0.2 mm × 0.1 mm × 0.1 mm was used. Single crystal X-ray diffraction data were collected on a Bruker APEX SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, $\lambda = 0.710\ 73$ Å) operating at 45 kV and 35 mA. A hemisphere of intensity data was collected at room temperature in 1 265 frames with ω scans (frame width 0.30°

and exposure time 10 s per frame). The refined unit cell parameters were determined by a least squares fit of 304 reflections in the range h: −3 − 3, k: −3 − 4, l: −5 − 7. An absorption correction and PL correction based on symmetry equivalent reflections were applied using the SADABS program. The crystal structure was refined with 245[R(int) = 0.03] independent reflections at an $F_0 > 3\sigma F_0$.

The $FeSi_2$ space group was analyzed by XPREP in the SHELXTL 5.1 for NT software group. The crystal structure was solved by the direct methods with *P4/mmm*. Once the positions of Si and Fe atoms had been determined the anisotropic displacement parameters and occupancy were refined (Table 4). Finally, the crystal structure of $FeSi_2$ was refined to $R[F^2 > 2\sigma(F^2)] = 0.057$, w$R2(F^2) = 0.153$, $\Delta\rho_{max}$(eÅ^{-3}) = 1.456; $\Delta\rho_{min}$(eÅ^{-3}) = −1.828.

Table 4 Atom coordinates and equivalent isotropic displacement parameters for $FeSi_2$

	x	*Y*	*Z*	*U* (eq)
Fe	1/2	1/2	0	0.002 (1)
Si	0	0	0.271 3 (2)	0.006 (1)

The structure of $FeSi_2$ has tetragonal symmetry, space group *P4/mmm* with the following cell parameters, a = 2.725 (3) Å, b = 2.725 (3) Å, c = 5.202 (10) Å, Z = 1, V = 38.62 (9) Å^3, D = 4.817 g/cm^3. Atom parameters are given in Table 4. The Fe-Si distance in the structure is 2.388 (2) Å, the Fe-Fe distance is 2.725 (3) Å, and the Si-Si distance is 2.379 (5) Å. The structure is shown in Figs. 4 and 5.

The structure of $FeSi_2$ can be regarded as a layer of Fe-Si_8 cube parallel to the (001) plane (Fig. 4). The Si lies on the zenith of the cube, and the Fe occupies the center of the cube. Two layers are connected by Si.

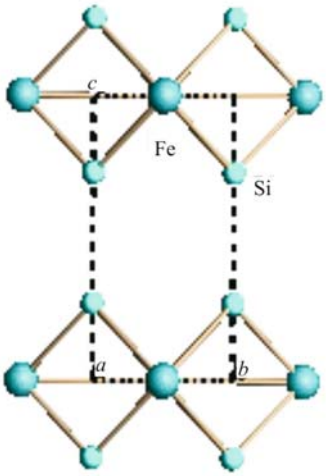

Fig. 4 The cell structure of $FeSi_2$

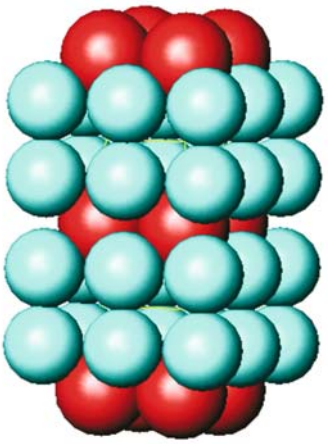

Fig. 5 The structure of $FeSi_2$

Table 5 Crystal chemistry parameters for native Si-Fe alloy

Name of mineral		*β*-$FeSi_2$ phase	$FeSi_2$ phase	FeSi phase	Gubeiite	Xifengite	Fersilicite*	Ferdisilicite*
Formula		$Fe_{0.84}Si_2$	Fe Si_2	Fe Si	Fe_3Si	Fe_5Si_3	FeSi	$FeSi_2$
Crystal system		Orthorhombic	Tetragonal	Cubic	Cubic	Hexagonal	Cubic	Tetragonal
Unit cell parameters	*a*/Å	9.874 (14)	2.725 (3)	4.452 (7)	5.644	6.741 6	4.495	2.684
	b/Å	7.784 (5)	2.725 (3)	4.452 (7)	5.644	6.741 6	4.495	2.684
	c/Å	7.829 (7)	5.202 (10)	4.452 (7)	5.644	4.707 9	4.495	5.128
	V/Å^3	601.70 (8)	38.62 (9)	88.28	179.79	185.30	90.82	36.94
	Z	16	1	4	4	2	4	1
Space group		*Cmca*	*P4/mmm*	*P 2$_1$3*	*Fm3m*	*P6$_3$/mcm*	*P2$_1$3*	*P4/mmm*
Chemical composition (electron probe)	Si	54.58 (11)	52.89	33.85	14.10 (5)	23.70 (3)	33.46	53.55 (6)
	Fe	45.35 (11)	47.23	66.17	84.80 (5)	75.50 (3)	66.54	45.47 (6)
	Ni				0.80 (5)	0.30 (3)		
	Mn				0.70 (5)	0.20 (3)		
	Total	99.93	100.12	100.02	100.40	99.70	100.00	99.02
Data source		Our work (powder)	Our work	Our work (powder)	ICSD 53545	ICSD 42585	ICSD 402761	ICSD 24360

*Names not approved by the IMA-CNMMN.

4 Discussion

Up to now, the natural intermetallic compounds of Si-Fe have been discovered as the following mineral species: gubeiite (Fe_3Si), α-Fe_3Si, xifengite (Fe_5Si_3), FeSi and $FeSi_2$. Their unit cells are listed in Table 5. Their characteristics are high symmetry and small cell volume. The atoms tend to the closest packed structure in the crystal structure. The bonds between Fe and Si tend to covalent bond, and the Fe-Si bond lengths are 2.288–2.346 Å in FeSi, Fe_5Si_3 and Fe_3Si. But in the $FeSi_2$ the bond lengths are 2.349 Å and 2.359 Å for Fe-Si and Si-Si, respectively. The bond length is 2.335 Å in the natural silicon.

The intermetallic compounds of Si-Fe originated in high temperatures and extremely low oxygen fugacity. Knittle et al. (1991) carried out an experiment in which the reaction of liquid iron and (Mg, Fe) SiO_3 at a high temperature and high pressure was simulated as similar to the mantle and core boundary. The experiment validated the form mechanism of Fe-Si intermetallic compounds. This kind of natural condition only occurs in the unusual UHP ultramafic mantle or planetary body. The diffraction pattern shows that $FeSi_2$ occurs as an inclusion in FeSi, and other $FeSi_2$ grains find natural silicon inclusions. In this case, the crystalline order of FeSi-$FeSi_2$-Si probably exists. It can be presumed that the deoxidization degree was increased by the crystalline order. Therefore, the formation of intermetallic compounds of Fe-Si can be considered a result of the early differentiation in the evolution of the earth. When the liquid-state Fe-Ni materials were raised by plume to shallow area the chemical reaction between the liquid-state Fe, Ni and D" layer materials occurred and the Fe-Si intermetallic compounds were formed (Shi et al., 2005).

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