Refinement of Iron Ore Sinter Phases: a silico-ferrite of calcium and aluminium (SFCA) and an Al-free SFC, and the Effect on Phase Quantification by X-ray Diffraction

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Abstract

Crystals of a silico-ferrite of calcium and aluminium (SFCA) and an Al-free SFC were prepared from the melt by slow cooling of synthetically prepared mixtures and examined by single-crystal diffraction methods. Both crystals belong to the space group *P*-1. SFC has lattice parameters a = 9.1255(3) Å, b = 10.1189(3) Å, c = 10.6183(2) Å, α = 63.9554(9)°, β = 84.4964(11)°, γ = 65.6706(9)° with a final $R(|F|)$ = 0.024. SFCA has a cell with a = 9.0738(9)Å, b = 10.0474(10)Å, c = 10.5611(10) Å, α = 64.061(3)°, β = 84.356(3)°, γ = 65.722(3)° with a final $R(|F|)$ = 0.030. The SFC structure was transformed to the cell used by Hamilton et al. (1989) and refined to an $R(|F|)$ = 0.024. All the atomic positions are equivalent to those reported by Hamilton et al. (1989) with the exception of one (Ca,Fe) position and two oxygen positions that are displaced from the published positions by 0.5y (Ca,Fe1), 0.5z (O4), or 0.5x (O12). This is ascribed to transcription errors in the published crystal structure data. The calculated powder pattern of SFCA (this study) was compared with the experimental data and it shows that the low angle peak intensities agree significantly better than those calculated from the published atomic positions. Additional electron density is located in proximity to the octahedral and tetrahedral cation sites of the main structure. These positions, coupled with the partially occupied cation sites of the main structure, suggest a minor sharing of cations between the main cation sites and the additional sites.

Introduction

Iron ore sinters are produced by adding lime to fine-grained iron ore and reacting these at temperatures of ~1250°C, by propagating a flame through a bed of intimately mixed ore, lime and carbonaceous char. The sinters are the preferred feedstock for the production of iron in blast furnaces and millions of tons are produced worldwide each year. The sintering reaction takes place at the flame front and redox conditions vary from reducing at the flame to oxidizing during cooling.

Silico-ferrite of calcium and aluminium (SFCA) is an important binding phase that imparts improved strength and reducibility to the sinters produced from iron ores containing variable amounts of Fe, Al, Mg, and Si. As a result the SFCA is variable in its composition and variable in its proportions in the sinters.

The amounts of the different phases, mainly hematite, magnetite, SFCA and a dicalcium silicate are contributing factors to a number of important sinter properties such as extent of sintering, tumble index (strength) and reduction index (reducibility) and are also indicators of temperature and redox conditions during sintering. Phase quantification by powder X-ray diffraction methods is therefore an important method for the correlation of the phase quantities with the different indices. Reliable phase quantification using the Rietveld method is dependent on accurate crystal structure data for the constituent phases being available from the literature for all the phases.

It was however found that the calculated diffraction pattern of SFCA using crystal structure data from Hamilton et al. (1989) and used by the programme Autoquan (Kleeberg and Bergmann 2002) differs substantially from the observed pattern of pure synthesized material. Especially, the calculated peaks at low angles are significantly overestimated as compared to the experimental peaks. This is shown in Figure 1. To resolve this discrepancy it was decided to re-investigate the structure of SFCA. Also, because of the complex cation distribution of SFCA, containing Fe, Ca, Mg, Al and Si on 15 different cation sites, it was deemed necessary to include also a structure analysis of SFC, which contains only Fe, Ca, and Si, as this would simplify the allocation of cations on the various sites considerably.

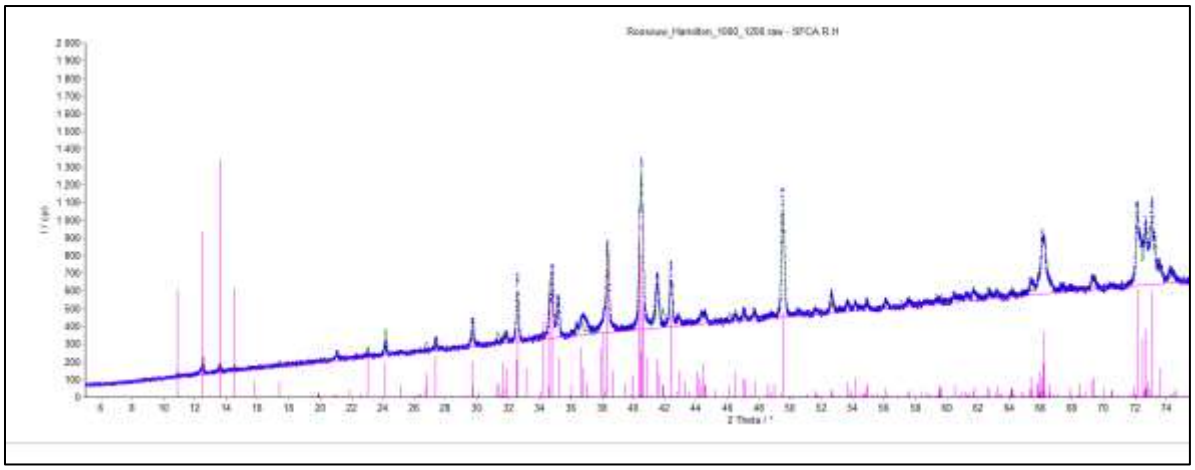

Figure 1 The experimental diffraction pattern of SFCA (Co*K*α) with the superimposed peak positions and intensities calculated from the Hamilton et al. (1989) crystal structure data as vertical lines. The discrepancy is especially evident in the 10-15°2θ region.

Experimental details

The crystal structure of SFCA was determined by Hamilton et al. (1989) using flux-grown crystals. The relation of the structure with those of aenigmatite and sapphirine has been discussed in detail by Mumme (1988). This structure still remains the one most used for phase quantification by the Rietveld method. The cell is given as: a = 9.061Å, b = 10.020Å, c = 10.920Å, with α = 60.30°, β = 73.68° and γ = 65.81°, and space group P-1. In this structure Ca and Fe occupy octahedral sites, and the tetrahedral sites are occupied by Fe, Al and Si.

The structures of two magnesium-containing crystals were determined by Sugiyama et al. (2005). They used the reduced cell setting with a = 8.848Å, b = 9.812Å, c = 10.403Å with α = 64.35°, β = 84.19° and γ = 66.27°, space group P-1. They also mentioned that the structure is isostructural with members of the aenigmatite group, and gave the transformation matrix relating the cell used by Hamilton et al. (1989) to their unit cell. In these structures Ca atoms are located on 7-coordinate sites, Mg and Fe on octahedral sites with Fe and Si on tetrahedral sites. Although bond lengths are not given, the 7-coordination around the Ca atoms is however open to interpretation since one of the Ca-O bonds is significantly longer than the other six.

The sample of SFCA was prepared by a sol-gel technique (Nishio and Tsuchiya 2004) from the metal nitrates, using silica sol as a source of Si, together with citric acid and ethylene glycol, and was reacted at 1200°C for 24 hours, cooled and reground twice. The reacted sample was then heated at 5°C/minute up to 1300°C, held for 24 hours and cooled at a rate of 0.5°C per minute to room temperature. The holding temperature was chosen on the basis of

the study of SFCA by Webster et al. (2012) which showed that SFCA forms below 1288°C from the melt. The sample consisted of inter-grown bladed crystals of SFCA. A number of crystals were selected and one chosen for structure analysis. The average composition of the crystals, as determined by a Cameca SX100 electron microprobe, is $Ca_{2.3}Fe_{8.7}Al_{1.6}Mg_{0.3}Si_{0.9}O_{20}$. Standards used for the various elements were hematite (Fe, O), diopside (Ca, Mg, Si) and Al_2O_3 (Al). The microprobe was run at 20kV accelerating voltage and 20nA probe current.

For the preparation of SFC crystals, the starting composition was prepared from the oxides which were reacted and reground twice. For crystal growth from the melt, the sample was kept at 1240°C to prevent the SFC from decomposing as shown in the study of the system $CaO\text{-}Fe_2O_3\text{-}SiO_2$ by Pownceby et al. (1998). The average composition of the crystals is $Ca_{2.5}Fe_{10.8}Si_{0.7}O_{20}$.

The X-ray crystal structure analyses on SFCA were performed using data collected at room temperature (296 K) on a Bruker D8 Venture diffractometer with a kappa-geometry goniometer, duo Iμ-S sources, a PHOTON CMOS detector and APEX2 control software (Bruker 2014) using QUAZAR-multilayer-optics-monochromated, Mo-*K*α radiation by means of a combination of θ and ω scans. In total, a full-sphere of reciprocal space was collected. The analysis of the diffraction patterns indicated that the SFCA crystal that was finally selected for structural investigation consisted of an intergrowth of two different individuals. The orientation matrices were determined using the program CELL_NOW (Bruker 2014). The interpretation of the matrices suggested a random intergrowth of the individuals rather than non-merohedral twinning. Integration and data reduction was performed using the program SAINT (Bruker 2014) allowing for the appropriate handling of intergrown crystals. The minimum common volume for overlapping reflections was set to a value of 0.04. Furthermore, the intensities were corrected for absorption using TWINABS (Bruker 2014). The structures were subsequently solved by dual-space methods using SHELXT (Sheldrick 2015a) and refined as a two-component crystal by full-matrix least squares using SHELXTL (Sheldrick 2015b) and SHELXL-2014 (Sheldrick 2015b). For SFC, a platy single crystal 0.02 x 0.13 x 0.20 mm^3 in size was selected. Diffraction data were collected on an Oxford Diffraction Gemini R Ultra single-crystal diffractometer using MoK_α radiation. Preliminary diffraction experiments aiming on the determination of the lattice parameters resulted in a triclinic primitive unit cell. Intensities for full data collection corresponding to one full sphere of reciprocal space were acquired at ambient temperature (298 K) with ω-scans using 1.0° scan width per frame. Subsequent integration and data reduction was performed with the

CrysAlis Pro software package (Agilent 2012). Data reduction included Lorentz and polarization corrections and an analytical absorption correction using accurately measured external faces based on the procedure of Clark and Reid (1995). For the calculation of the linear absorption coefficient the results from the chemical analysis were used. Notably, the prominent basal plane of the platy fragment corresponded to the (110) plane. Crystal and experimental data for the two compounds are given in Table 1. For drawing of structural details the programs DRAWxtl (Finger et al. 2007) as well as Mercury (Macrae et al. 2008) have been used.

Results and discussion

SFC and SFCA structural description

The structures of SFCA were described in detail by Hamilton et al. (1989) and Sugiyama et al. (2005) and the SFC and SFCA structures will be discussed only briefly here. The cations form layers with Fe, Ca and Mg in octahedral (or 7 coordinate) sites alternating with predominantly tetrahedral layers containing Fe, Al and Si. Rows of vacant octahedral sites are present between the two Ca rows parallel to the c axis (perpendicular to the view). The layers of O atoms either side of this octahedral row expand outwards around the Ca and vacant rows. This is shown in Figure 2 for the SFC structure. The crystal data for SFC and SFCA in the reduced cell setting also used by Sugiyama et al. (2005) are given in Table 1. The atomic positional parameters and site occupation parameters for the extra low occupancy sites of SFC and SFCA in the reduced cell setting are given in Table 2. For these sites, the isotropic atomic displacement parameters were kept constant at 0.02 A^2. Other atomic positional and all interatomic distances, etc. have been deposited as supplementary data. In each of the predominantly Ca-O polyhedra (around Ca14 and Ca15) of the SFC structure, six of the Ca—O bonds vary between 2.31 to 2.45Å, with the other Ca—O distances significantly longer, 2.97-3.18Å. Since the contributions of these longer bonds to the bond valence sums are only small (~0.07 v.u.) it can be concluded that the Ca—O polyhedra should be considered as 6-coordinate and not 7-coordinate.

Table 1 Experimental details for SFC and SFCA. Data collections for both compounds have been performed at 296 K.

	SFC	SFCA
Crystal data		
Chemical formula	$Ca_{5.10}\ Fe_{21.70}\ O_{40}\ Si_{1.30}$	$Al_{2.72}Ca_{4.48}Fe_{17.56}Mg_{0.28}O_{40}Si_{1.52}$
M_r	2092.87	1924.12
Z	1	1
Crystal system	triclinic	triclinic
Space group	*P* -1	*P* -1
a, *b*, *c* (Å)	9.1249(4), 10.1192(3), 10.6123(5)	9.0738 (9), 10.0474 (10), 10.5611 (10)
α, β, γ (°)	63.955(4), 84.482(4), 65.671(4)	64.061 (3), 84.356 (3), 65.722 (3)
V (Å^3)	797.90(6)	785.35 (14)
μ (mm^{-1})	10.529	8.85
Crystal size (mm)	0.20 x 0.13 x 0.02	0.18 × 0.14 × 0.03
Data collection		
T_{min}, T_{max}	0.470 , 0.749	0.471, 0.837
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3883, 3883, 3431	4788, 4788, 4407
R_{int}	0.031	0.042
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.691	0.714
Refinement		
$R[F^2 > 4\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.067, 1.01	0.030, 0.072, 1.17
No. of reflections	4424	4788
No. of parameters	330	325
No. of restraints	2	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.795 , −0.98	1.51, −0.74
Ratio of intergrown components	-	0.748:0.252 (3)

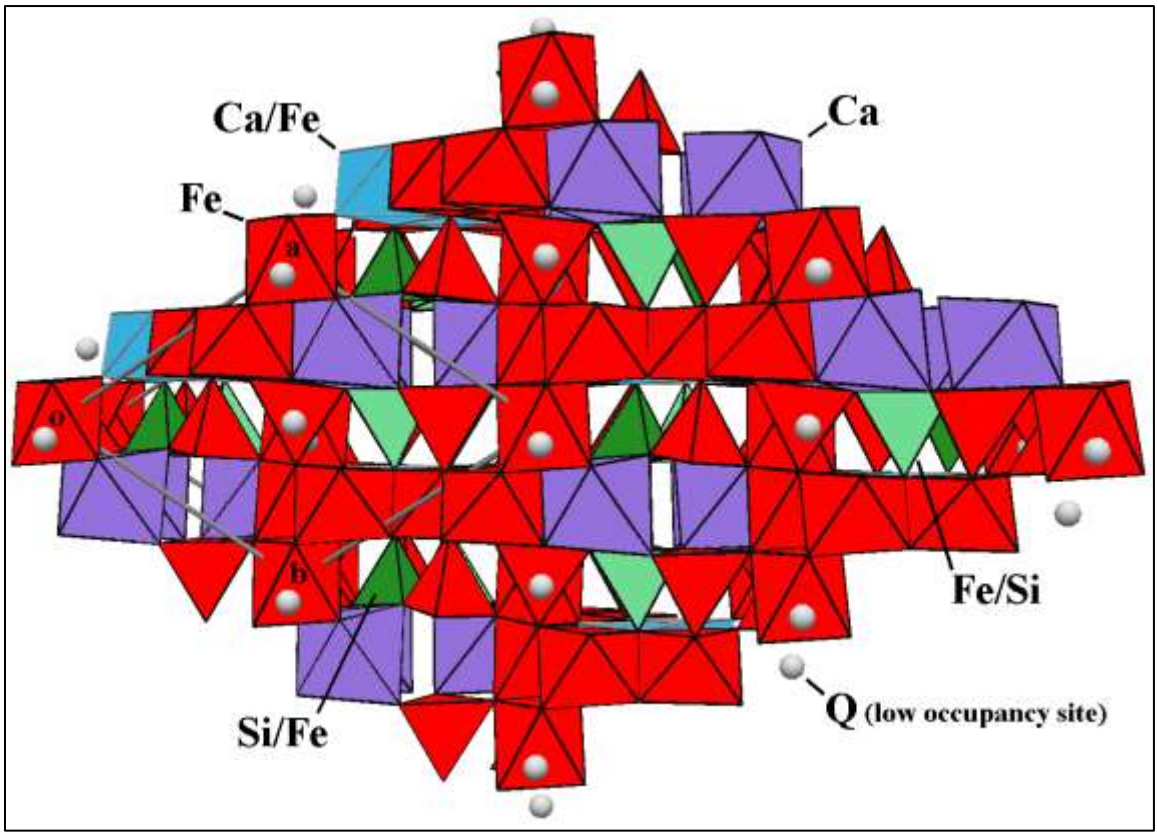

Figure 2 Diagram of the SFC structure projected along the c-axis. The octahedral layers comprise Fe (red), Ca/Fe (light blue) and Ca (light purple) octahedra. The predominantly tetrahedral layers comprise Fe (red), Fe/Si (light green) and Si/Fe (dark green) polyhedra. For all mixed occupancy sites the higher occupancy cation is given first. Oxygen atoms form the vertices of the polyhedra. Low occupancy (Q) sites are shown as small grey spheres.

Table 2 Atomic coordinates (reduced cell) and site occupation factors for positions containing additional electron density in SFC and SFCA and assigned as low-occupancy Fe sites.

SFC	*x*	*y*	*z*	*sof*
Q(1) (Fe)	0.255(2)	0.758(2)	0.746(2)	0.041(2)
Q(2) (Fe)	0.5000	0.5000	0.0000	0.023(1)
Q(3) (Fe)	0.0000	0.0000	0.5000	0.038(1)
Q(4) (Fe)	0.566(2)	0.450(2)	0.694(1)	0.046(2)
Q(5) (Fe)	-0.054(2)	0.066(2)	0.801(2)	0.042(2)
SFCA				
Q(1) (Fe)	0.267(4)	0.755(4)	0.745(4)	0.018(2)
Q(2) (Fe)	0.5000	0.5000	0.0000	0.009(1)
Q(3) (Fe)	0.0000	0.0000	0.5000	0.007(1)
Q(4) (Fe)	0.568(4)	0.435(4)	0.692(4)	0.017(2)
Q(5) (Fe)	-0.040(4)	0.066(4)	0.798(3)	0.019(2)

SFC and SFCA cation distributions

The crystal structure of SFC contains three sites with mixed occupancy: Ca/Fe(5), Fe/Si(8) and Si/Fe(11). The occupancies of each cation on each of the sites were refined, however, the three Fe occupancies were restrained to sum to 1.70(1) and the two Si occupancies were restrained to sum to 0.66(1) so that the overall composition of the crystal matched that obtained by microprobe analysis.

The crystal structure of SFCA is very similar to that of SFC, the only difference being the presence of Al and a small amount of Mg in the structure, which complicates the allocation of the cations on the various sites considerably. The linear programme OccQP (Wright et al. 2000) was used to allocate the different cations to the various sites. The programme uses a quadratic programming approach to assign the cations to the sites by considering the mean scattering at each site and the overall chemical composition. The bond lengths can also be included in the calculation. The programme also calculates the vacancy distribution on each cationic site. In this case Fe5 does show a significant vacancy fraction of 0.22 for that site. The resultant cation distribution was included in the final refinement, and can be obtained from the CIF.

Comparison with published structure data

The data of the SFC crystal were transformed to the Hamilton et al. (1989) unit cell for direct comparison using the transformation matrix (given as columns): [-1 0 0 / 0 -1 0 / 0 -1 1]. Refinement of the transformed reflection data resulted in an R-factor of R = 0.024. The crystal data, atomic parameters, and site occupation parameters may be obtained from the CIF file. Experimental details which differ from the data in Table 1 are given in Table 3. The refined atomic positions correspond closely to the published data, but with the exception of three atomic positions, Ca,Fe(1), which is displaced by 0.5*y*, O(4) displaced by 0.5*z* and O12 displaced by 0.5*x*. These are denoted by a suffix N in the atom names (supplementary data). Coordinates which differ from those reported by Hamilton et al. (1989) are given in Table 4. Selected interatomic distances for SFC determined in this study, those for SFCA given in Hamilton et al. (1989) Table 6, and those calculated from their published atomic parameters are given in Table 5. From Table 4 it is clear that the erroneous data are due to transcription errors and not due to errors in structure determination or refinement.

It can therefore be concluded that the atomic parameters of Ca,Fe(1), O(4) and O(12) (their notation) are in error. Revised coordinates and site occupation factors for the SFC structure (Hamilton cell) which differ from those reported by Hamilton et al. (1989) in their Table 5.

Table 3 Experimental details for SFC Hamilton cell. Only parameters that differ from SFC (reduced cell) are shown.

	SFC Hamilton cell
Crystal data	
a, *b*, *c* (Å)	9.1249(4), 10.1192(3), 10.9871(7)
α, β, γ (°)	60.204(3), 73.384(5), 65.671(4)
V (Å^3)	797.90(8)
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.024, 0.070, 1.00
No. of reflections	3883
No. of parameters	330
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −0.97

Table 4 Atomic positions that differ from the ones given in Hamilton et al data.

	x	*y*	*z*	*sof*
Ca(1)	0.55532(7)	0.90411(7)	0.15725(6)	0.517(17)
Fe(1)	0.55532(7)	0.90411(7)	0.15725(6)	0.430(11)
O(4)	0.5542(3)	0.8432(3)	0.9848(3)	1.0
O(12)	0.0291(3)	-0.0455(3)	0.8331(2)	1.0

Table 5 A comparison of selected bond lengths (Å) from this study, from Table 6 of Hamilton et al. (1989) and calculated from the Hamilton et al. atomic parameters in their Table 5.

	This study (Hamilton cell)	Hamilton et al. (Table 6)	From Hamilton et al. atomic coordinates (Å)
M2 – O12	2.017	2.037	2.859
M5 – O12	1.852	1.810	3.081
M7 – O4	2.065	2.063	5.152
Fe10 – O12	2.026 (x2)	2.025 (x2)	4.525
Ca,Fe1 – O4	2.190	2.121	3.606
Ca,Fe1 – O4	2.268	2.210	
Ca3 – O12	2.411	2.416	5.067
Si,Al12 – O4	1.706	1.706	4.830

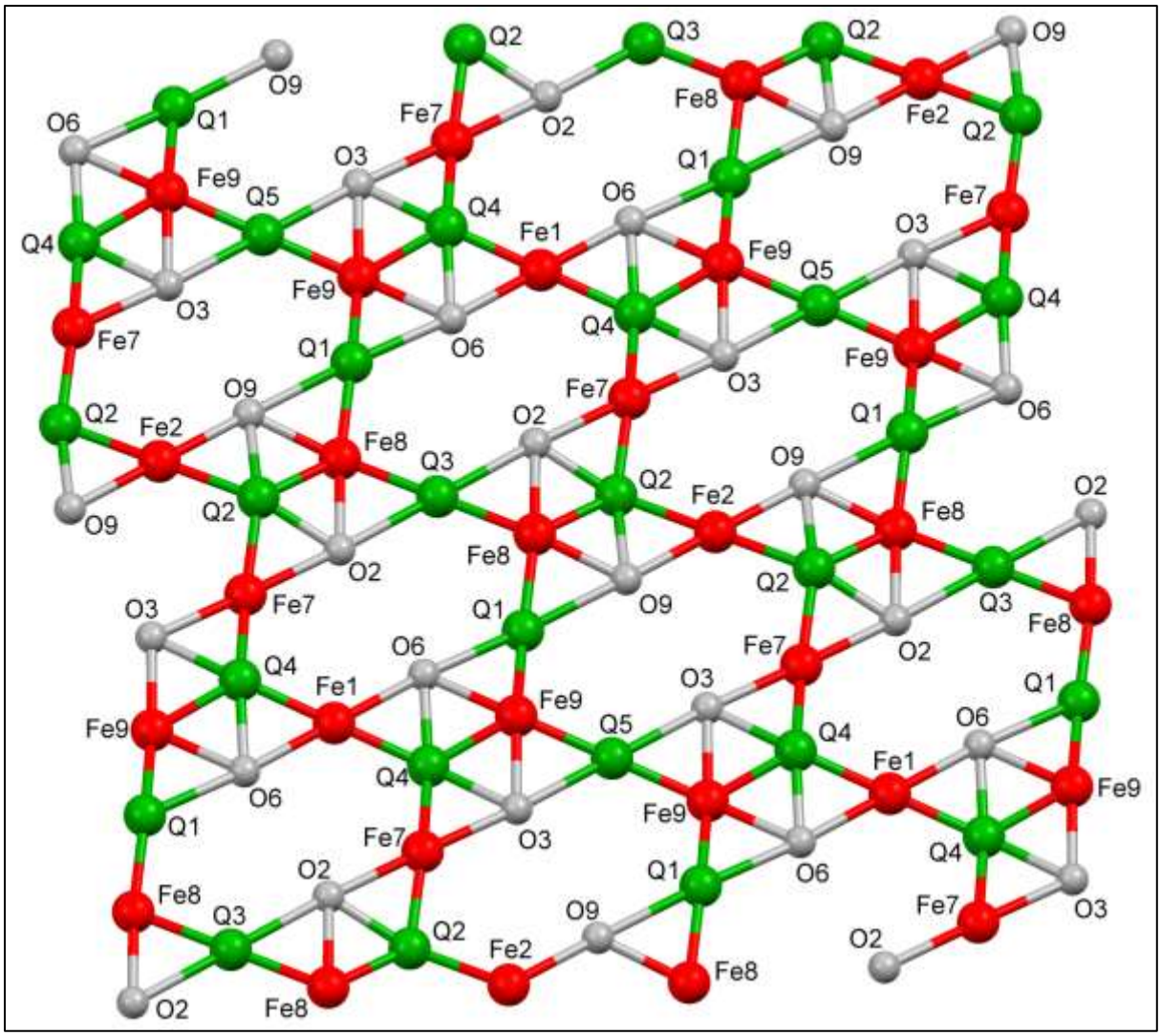

Figure 3 Positions of the sites (Q1 to Q5) showing residual electron density (green), normal to the (110) plane. Distances from these positions to the atomic sites of both cations (red) and oxygen atoms (grey) vary from 1.8 to 2.3 Å. The crystallographic axes are all oblique to this plane.

Additional electron density maxima

From the refinement of the basic structure of both SFC and SFCA, additional electron density (~ 4 e/Å) was present at the atomic positions shown as Q1 to Q5. These were included in the structural models as low occupancy Fe positions. The occupancies of these sites all refined to be in the range 0.041 to 0.046 for SFC and 0.014 to 0.019 for SFCA. The Q1 positions occur interstitially in the octahedral layer and are situated at bonding distances both from the iron and oxygen atoms. Q2, Q3 and Q5 are situated in one tetrahedral layer with Q2, Q4 and Q5 in the next tetrahedral layer. Figure 3 shows the layer normal to the [110] direction with the additional positions shown as Q1 to Q5. These are all on the same slice with a width of 2.5 Å. Further examination of the additional positions shows that they also have octahedral and

tetrahedral coordination with the oxygen atoms, but they are also within short contact distances of certain cations in the main structure. However, the partial occupancies of the cation and Q sites means that there is no requirements for any two such adjacent sites to be simultaneously occupied. This implies that these positions compensate for the partial vacancies in cationic sites of the main structure. According to the OccQP calculation for SFCA, the vacancy on the Ca/Fe5 site is 0.22, on the Fe/Si11 site is 0.14 and on the Fe13 site is 0.10. The sum of the electron density of all the additional sites represents 0.02 of an iron atom. This is not enough to postulate a stoichiometry of the compounds different from $M_{14}O_{20}$.

Calculated powder diffraction pattern

The calculated diffraction pattern of SFCA from this study is shown in Figure 4. This shows a closer correspondence to the experimental diffraction pattern, especially in the low angle region. It is expected that the latest crystallographic data for SFC and SFCA will give lower discrepancy factors and more accurate quantification of these phases. As an example, eight synthetic mixtures of magnetite, hematite, SFCA, magnesioferrite, larnite, silicon and glass were quantified using the published (Hamilton) and revised (this study) structures by means of TOPAS (Bruker 2009). The results are shown in Figure 5 and indicate an improved agreement (especially for SFCA) when the revised structural data is used.

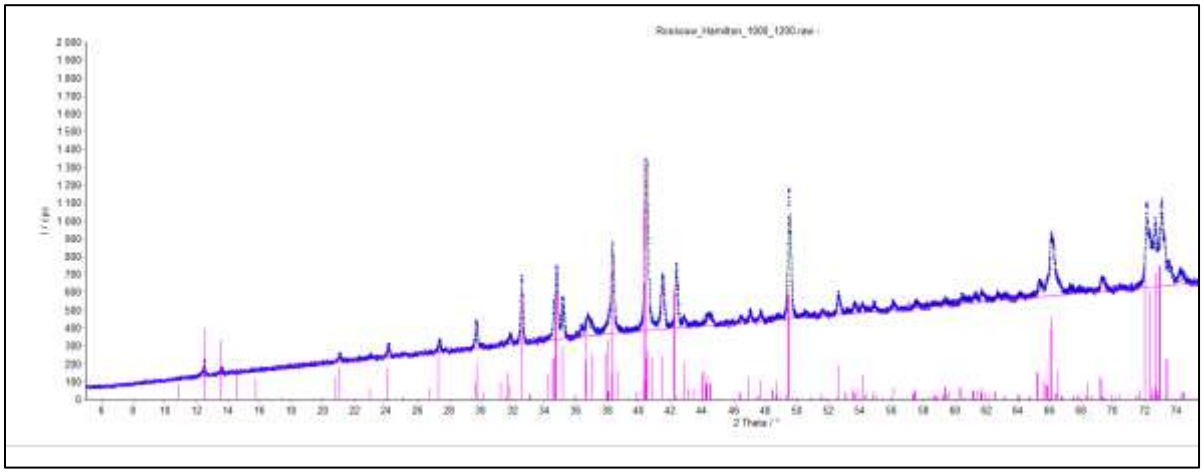

Figure 4 The experimental diffraction pattern of SFCA (Co-*K*α) with the superimposed peak positions and intensities calculated from this study as vertical lines. The calculated peak intensities in the 10-15°2θ region are now much reduced.

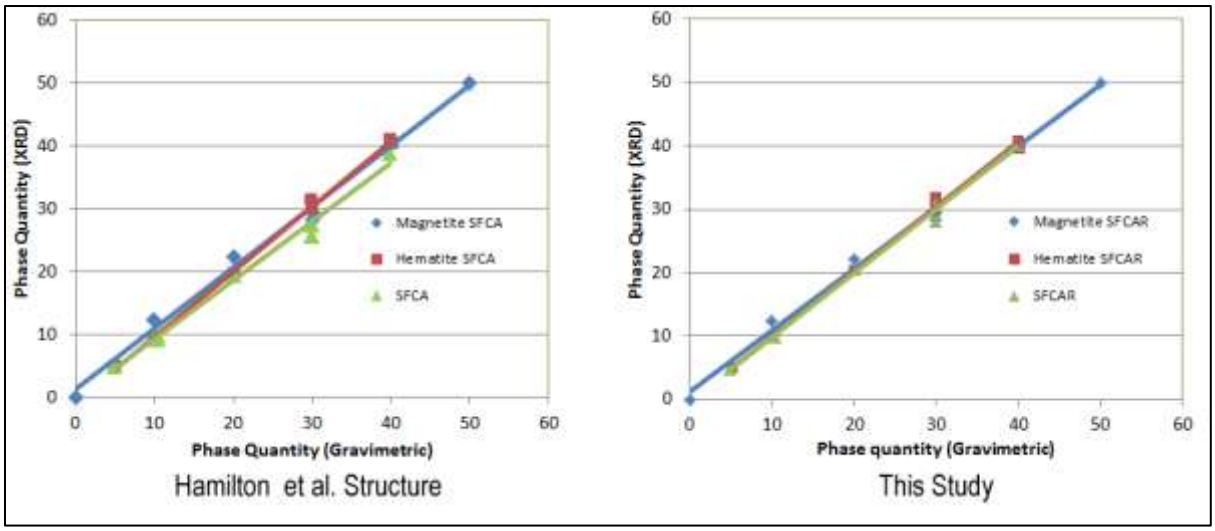

Figure 5 Eight synthetic mixtures of magnetite, hematite, magnesioferrite, larnite, silicon and glass quantified using the published and revised structures by means of TOPAS (Bruker 2009).

Concluding remarks

The crystal structures of magnesium, aluminium-free SFC and SFCA have been determined and refined in the reduced cell setting. After transformation, both structures differ from the published SFCA structure in that the original published structure contains errors in three atomic positions.

Additional electron density is present (in both SFC and SFCA) on 5 additional cation sites in both the octahedral and tetrahedral layers, and their proximity to the main cationic sites means that cations are shared between both the main and the additional sites.

The calculated powder X-ray diffraction pattern of SFCA using the new crystal structure corresponds better to the experimental pattern and should lead to a better quantification of this phase in industrial iron ore sinters. Furthermore, the corrected set of coordinates will help to avoid dubious structure refinements of SFC-related materials that have been published only recently by Ding and Guo (2014), for example.

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Supplementary Data for SFC and SFCA

SFC

Table 1. Crystal data and structure refinement for jdvsfc_1.

Identification code	shelx	
Empirical formula	Ca5.10 Fe21.70 O40 Si1.30	
Formula weight	2092.87	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1249(4) Å	α= 63.955(4)°.
	b = 10.1192(3) Å	β= 84.482(4)°.
	c = 10.6123(5) Å	γ = 65.671(4)°.
Volume	797.90(7) $Å^3$	
Z	1	
Density (calculated)	4.356 Mg/m^3	
Absorption coefficient	10.529 mm^{-1}	
F(000)	1004	
Crystal size	0.160 x 0.120 x 0.020 mm^3	
Theta range for data collection	3.096 to 29.402°.	
Index ranges	-12<=h<=11, -13<=k<=13, -14<=l<=13	
Reflections collected	12979	
Independent reflections	3883 [R(int) = 0.0309]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3883 / 2 / 330	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0666	
R indices (all data)	R1 = 0.0297, wR2 = 0.0698	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.823 and -0.979 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for jdvsfc_1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	5000	5000	5000	6(1)
Fe(2)	0	0	0	6(1)
Fe(3)	1680(1)	6511(1)	415(1)	5(1)
Fe(4)	8472(1)	3290(1)	4506(1)	5(1)
Ca(5)	9447(1)	4386(1)	6573(1)	7(1)
Fe(5)	9447(1)	4386(1)	6573(1)	7(1)
Fe(6)	591(1)	5589(1)	8478(1)	5(1)
Fe(7)	2584(1)	7574(1)	2459(1)	6(1)
Fe(8)	6606(1)	7382(1)	7335(1)	6(1)
Si(8)	6606(1)	7382(1)	7335(1)	6(1)
Fe(9)	6485(1)	7301(1)	2388(1)	6(1)
Fe(10)	7612(1)	8517(1)	9317(1)	5(1)
Si(11)	7709(1)	8437(1)	4267(1)	5(1)
Fe(11)	7709(1)	8437(1)	4267(1)	5(1)
Fe(12)	4335(1)	5509(1)	8094(1)	6(1)
Fe(13)	9528(1)	655(1)	2993(1)	6(1)
Ca(14)	3819(1)	8727(1)	9208(1)	8(1)
Ca(15)	6276(1)	1184(1)	5463(1)	8(1)
O(1)	8449(3)	5523(3)	7973(3)	11(1)
O(2)	8359(3)	5417(3)	2828(3)	11(1)
O(3)	2625(3)	5422(3)	9201(2)	7(1)
O(4)	2721(3)	5594(3)	4248(2)	8(1)
O(5)	6301(3)	3626(3)	8769(2)	6(1)
O(6)	3755(3)	6219(3)	6158(2)	6(1)
O(7)	4860(3)	7091(3)	8077(3)	12(1)
O(8)	4709(3)	7124(3)	3331(2)	7(1)
O(9)	6052(3)	8231(3)	500(3)	12(1)
O(10)	6279(3)	8256(3)	5397(3)	16(1)
O(11)	9497(3)	6577(3)	9811(2)	7(1)
O(12)	9458(3)	6720(3)	4848(3)	17(1)
O(13)	9609(3)	2352(3)	3202(2)	9(1)
O(14)	602(3)	7735(3)	1596(2)	8(1)
O(15)	1189(3)	8747(3)	8863(2)	6(1)
O(16)	1402(3)	8711(3)	3738(2)	6(1)

O(17)	7957(3)	66(3)	4083(3)	13(1)
O(18)	7867(3)	293(3)	9240(2)	8(1)
O(19)	6984(3)	8738(3)	2723(3)	16(1)
O(20)	6646(3)	8983(3)	7638(3)	13(1)
Q(1)	2549(17)	7584(16)	7460(15)	20
Q(2)	5000	5000	0	20
Q(3)	0	0	5000	20
Q(4)	5657(16)	4503(15)	6943(14)	20
Q(5)	-537(17)	657(16)	8013(15)	20

SFCA

Table 2. Crystal data and structure refinement for SFCA.

Identification code	shelx	
Empirical formula	Al0.68 Ca1.12 Fe4.39 Mg0.07 O10 Si0.38	
Formula weight	481.03	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.0738(9) Å	α= 64.061(3)°.
	b = 10.0474(10) Å	β= 84.356(3)°.
	c = 10.5611(10) Å	γ = 65.722(3)°.
Volume	785.35(14) $Å^3$	
Z	4	
Density (calculated)	4.068 Mg/m^3	
Absorption coefficient	8.854 mm^{-1}	
F(000)	927	
Crystal size	0.180 x 0.140 x 0.030 mm^3	
Theta range for data collection	2.469 to 30.508°.	
Index ranges	-12<=h<=12, -12<=k<=14, 0<=l<=15	
Reflections collected	4788	
Independent reflections	4788 [R(int) = ?]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4788 / 0 / 325	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0673	
R indices (all data)	R1 = 0.0352, wR2 = 0.0695	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.555 and -0.734 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for twin5_x. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca(1)	5000	5000	5000	6(1)
Fe(1)	5000	5000	5000	6(1)
Mg(2)	0	0	0	7(1)
Ca(2)	0	0	0	7(1)
Fe(2)	0	0	0	7(1)
Mg(3)	1702(1)	6502(1)	421(1)	7(1)
Ca(3)	1702(1)	6502(1)	421(1)	7(1)
Fe(3)	1702(1)	6502(1)	421(1)	7(1)
Mg(4)	8481(1)	3284(1)	4512(1)	7(1)
Ca(4)	8481(1)	3284(1)	4512(1)	7(1)
Fe(4)	8481(1)	3284(1)	4512(1)	7(1)
Ca(5)	9450(1)	4392(1)	6566(1)	7(1)
Fe(5)	9450(1)	4392(1)	6566(1)	7(1)
Ca(6)	586(1)	5576(1)	8477(1)	7(1)
Fe(6)	586(1)	5576(1)	8477(1)	7(1)
Ca(7)	2586(1)	7578(1)	2456(1)	6(1)
Fe(7)	2586(1)	7578(1)	2456(1)	6(1)
Al(8)	6627(1)	7368(1)	7344(1)	6(1)
Si(8)	6627(1)	7368(1)	7344(1)	6(1)
Fe(8)	6627(1)	7368(1)	7344(1)	6(1)
Al(9)	6502(1)	7293(1)	2404(1)	6(1)
Fe(9)	6502(1)	7293(1)	2404(1)	6(1)
Al(10)	7620(1)	8500(1)	9338(1)	6(1)
Fe(10)	7620(1)	8500(1)	9338(1)	6(1)
Al(11)	7714(1)	8411(1)	4288(1)	5(1)
Si(11)	7714(1)	8411(1)	4288(1)	5(1)
Fe(11)	7714(1)	8411(1)	4288(1)	5(1)
Fe(12)	4341(1)	5517(1)	8086(1)	6(1)
Fe(13)	9526(1)	655(1)	2992(1)	6(1)
Ca(14)	3862(1)	8747(1)	9193(1)	11(1)
Fe(14)	3862(1)	8747(1)	9193(1)	11(1)
Ca(15)	6258(1)	1155(1)	5480(1)	11(1)
Fe(15)	6258(1)	1155(1)	5480(1)	11(1)
O(1)	8431(3)	5543(3)	7948(3)	14(1)

O(2)	8361(3)	5442(3)	2843(3)	14(1)
O(3)	2631(3)	5407(3)	9200(3)	12(1)
O(4)	2717(3)	5586(3)	4237(3)	12(1)
O(5)	6288(3)	3613(3)	8780(3)	9(1)
O(6)	3764(3)	6234(3)	6149(3)	10(1)
O(7)	4899(3)	7099(3)	8057(3)	16(1)
O(8)	4740(3)	7122(3)	3323(3)	12(1)
O(9)	6082(3)	8228(3)	537(3)	17(1)
O(10)	6322(3)	8246(3)	5452(3)	20(1)
O(11)	9484(3)	6583(3)	9827(3)	11(1)
O(12)	9436(3)	6717(3)	4838(3)	17(1)
O(13)	9617(3)	2361(3)	3193(3)	12(1)
O(14)	589(3)	7724(3)	1608(3)	11(1)
O(15)	1204(3)	8753(3)	8861(3)	10(1)
O(16)	1410(3)	8727(3)	3724(3)	10(1)
O(17)	7970(3)	33(3)	4090(3)	15(1)
O(18)	7868(3)	270(3)	9246(3)	11(1)
O(19)	6931(4)	8720(3)	2776(3)	20(1)
O(20)	6673(3)	8925(3)	7677(3)	18(1)
Q(1)	2670(40)	7550(40)	7450(40)	20
Q(2)	5000	5000	0	20
Q(3)	0	0	5000	20
Q(4)	5680(40)	4350(40)	6920(40)	20
Q(5)	-400(40)	660(40)	7980(30)	20