Structural systematics of SFCA-I type solid-solutions in the system CaO–Fe₂O₃–FeO–Al₂O₃

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Received: 3 February 2021 / Accepted: 3 June 2021 / Published online: 23 June 2021
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Abstract
Effects of Fe ↔ Al substitution on triclinic SFCA-I-type compounds with general formula A₄₀O₅₆ (A: Ca, Al, Fe³⁺, Fe²⁺) have been studied using single-crystal X-ray diffraction. Crystals of sufficient quality and size were synthesized in the temperature range between 1200 and 1300 °C. Six samples with Al/FeTot ratios of 0.127, 0.173, 0.216, 0.310, 0.349 and 0.459 have been structurally characterized. SFCA-I can be described with a modular approach involving the stacking sequence <PSS> of “P” and “S” modules that can be imagined as being cut from the well-known pyroxene (P) and spinel (S) structure types. Furthermore, SFCA-I is related to the sapphirine supergroup of minerals. Within the present solid-solution series, the contents in calcium show only minor variations (≈ 6.7 a.p.f.u.). The twenty crystallographically independent tetrahedrally (T) and octahedrally (M) coordinated cation sites exhibit considerable differences concerning the Al uptake. Indeed, Al is preferentially incorporated into the tetrahedra belonging to the single-chains located in the pyroxene modules. Ferrous iron, on the other hand, is restricted to one of the T-positions within the spinel blocks. Most structural aspects from unit-cell parameters and cell volumes to site occupancies, tetrahedral chain kinking as well as polyhedral distortions are defined by linear or nearly linear trends when plotted against the Al/FeTot ratio. Analysis of the <T–O> and <M–O> distances showed a complex interplay between the different coordination polyhedra resulting in a contrasting behavior of these values with positive or negative change rates as a function of composition. Evaluation of the average chemical strain tensor derived from the sets of lattice parameters for the two samples of the abovementioned series showing the highest and lowest Al/FeTot ratios indicated, that the major contraction with increasing Al content is perpendicular to the pyroxene- and spinel modules. Furthermore, the pyroxene module seems to be more affected when compared with the spinel block. There is evidence that the SFCA-I-type solid-solution series is limited on both the Al- and Fe-rich sides. The present investigation provides—for the first time—a detailed crystallographic analysis on the impact of chemical variations on a compound that is of relevance to the field of applied mineralogy related to the technologically important process of iron-ore sintering.

Keywords SFCA-I · Iron-ore sinter · Solid-solution series · Crystal structure · Compositional strain

Introduction
Steel—an alloy of iron and carbon—is a strategic product for the global economy. Its unique properties in combination with low costs make steel an ideal material for a plethora of industrial and engineering applications (Holmes and Lu, 2015). Data available from the Organization for Economic Co-operation and Development suggest that the global steel-producing capacity in 2019 was about 2362.5 million metric tons (OECD 2019).

At the heart of the steel-making process is the blast furnace, where iron ore is reduced to metallic iron. Currently, the group of iron formation-hosted ore deposits including the famous banded iron formations (BIFs) account for the majority of world production (Clout and Manuel, 2015). After a first mechanical processing of the ores, two particle fractions can be distinguished: lump (31.5 to 6.3 mm) and fine (< 6.3 mm) products. Because of blockage of the gas permeability of the furnace, however, the fine fraction of the iron ores cannot directly be used as a feedstock (Kalenga and Garbers-Craig 2010). The fines first need to undergo an agglomeration process that is frequently accomplished...
via sintering. In the European Union alone, about 130 million tons of iron ores have recently been sintered per annum (Fernandez-Gonzalez et al. 2017), making this material one of the most produced inorganic commodities.

During sintering, the loose fine particles are bonded together at temperatures between 1250 and 1350 °C into larger centimeter-sized particles by partial melting of the solids, which is followed by re-crystallization. The resulting porous aggregates consist of ore particles (hematite and magnetite, constituting 40 to 70% vol.) cemented by a matrix of Ca-rich ferrites (20 to 50% vol.), up to 10% vol. quenched melt (glass) and about 10% vol. calcium silicates such as larnite (β-Ca2SiO4) (Patrick and Lovel 2001). Minor phases may include quartz, sulphides, pyroxenes, serpentine and lime, but the total of these rarely accounts for more than a few percent of the sinter volume. The calcium ferrites usually contain some silica and alumina and are thus referred to as Silico Ferrites of Calcium and Aluminum, abbreviated to SFCA (Hamilton et al. 1989; Mumme et al. 1998). Actually, these compounds form the main bonding phase in the sinter (Scarlett et al. 2004).

To date, two representatives have been reported from industrial sinters in larger quantities: SFCA and SFCA-I. According to Scarlett et al. (2004), SFCA has a more prismatic habitus and can be described as columnar or lath-shaped. SFCA-I, on the other hand, should display a more platy morphology and in cross section appears needle-like or acicular. Apart from apparent morphological differences, both compounds are definitely distinct crystallographic phases and powder X-ray diffraction (PXRD) can be used to tell them apart. Their complex crystal structures exhibit low triclinic symmetry, comparatively large unit-cell volumes, and there is a clear structural relationship between them. Indeed, SFCA and SFCA-I belong to a so-called polysomatic series with general composition $A_{14+6n}O_{20+8n}$ ($A$: Ca, Al).

Starting materials for the synthesis experiments were Fe$_2$O$_3$ (99.9%, Alfa Aesar), γ-Al$_2$O$_3$ (99.997%, Alfa Aesar), and CaCO$_3$ (99.995% Merck). Phase purity of the educts was checked by PXRD before they were dried at 300 °C for 24 h. After storing in an evacuated desiccator stoichiometric amounts of the reagents for a total of 2 g were weighed on an analytical balance. Seven different mixtures were prepared for a hypothetical SFCA-I solid-solution series with nominal composition $Ca_8Al_xFe_{32-x}O_{56}$ and $x = 0, 0.8, 2.0, 4.0, 5.0, 6.0$ and $8.0$. For easy reference, we will denote these samples SFCA-I-00 to SFCA-I-06. Homogenization for 45 min was performed in a planetary mill operated at 600 rpm under ethanol. The resulting slurry was dried for 12 h at 50 °C to remove the alcohol completely and manually re-homogenized for 15 min in an agate mortar. Subsequently, 0.5 g of the powder was pressed into pellets with a diameter of about 12 mm and a thickness of about 2 mm. In the next step, two pellets of each mixture were transferred into an open Pt-crucible. Sintering was performed in air using a resistance heated chamber furnace. Samples were fired from 20 °C (with a ramp of 120 °C/h) to the maximum temperature of 1300 °C followed by cooling with a rate of 5 °C/h to 1200 °C where the crucible was immediately quenched in
air. Weight losses were determined from weight differences before and after heating.

Powder diffraction patterns have been collected with a Stoe-MP diffractometer system (STOE & Cie GmbH, Darmstadt, Germany) configured in Bragg–Brentano geometry using a Mythen 1 K detector (Dectris Ltd., Baden-Daettwil, Switzerland). The device is equipped with a primary-beam Ge(111) monochromator yielding Kα1 radiation only. The diffraction studies were performed with a cobalt tube operated at 40 kV and 30 mA. Data were acquired at ambient temperature over a 20 range between 5° and 120° using a 20 step size of 0.015°. The total measurement time per scan was about 48 h. Qualitative phase analysis was performed with the 2018 release of the PDF-4+ Powder Diffraction File database of the International Centre for Diffraction Data (Gates-Rector and Blanton 2019).

Chemical composition of the compounds obtained from the sinter experiments was determined using electron microprobe analysis (EMPA) on a JEOL JXA SUPERPROBE 8100 in wavelength-dispersive mode. For sample preparation, fragments of the pellets were embedded in epoxy resin and polished with diamond paste (10, 5 and 1 μm grain size). After sputter coating with carbon, four-circle measurements were performed with an acceleration voltage of 15 kV, a beam current of 10 nA and counting times of 20 s (on peaks) and 10 s (for background on each side of the peaks). Depending on the size, at least five data points per crystallite were analyzed. Diopside (Ca-Kα), corundum (Al-Kα) and magnetite (Fe-Kα) were used as standard reference materials. Furthermore, a so-called PRZ matrix correction was applied. Finally, the amount of Fe2+ was calculated from the crystal chemical formula obtained by the microprobe measurements (normalized to the expected number of oxygen atoms) and charge balance considerations (Droop 1987).

From each synthesis run between 5 and 8 crystals with diameters up to 200 μm have been retrieved. The single crystals were mounted on the top of glass fibers with nail polish and screened on a Rigaku Oxford Diffraction Gemini R Ultra diffractometer equipped with a four-circle kappagoniometer and a Ruby CCD detector. Measurements were conducted with Mo-Kα radiation at ambient conditions. Pre-experiments aiming at the determination of unit-cell parameters indicated the presence of a so-called α-CFF phase with composition Ca3.43Fe14.39O25 (for SFCA-I-00) as well as SFCA-I-type compounds (in all other cases). As will be outlined further below, the final assignment of different chemical species (Fe3+, Fe2+, Al, Ca) to each of the 20 cation positions was performed using the program OccQP (Wright et al. 2000). Coordinates, site occupancies and equivalent isotropic displacement parameters of the atoms as well as selected inter-atomic distances are summarized in supplementary Tables S1 and S2. Anisotropic displacement parameters are listed in Table S3. Figures showing structural features were prepared with the program VESTA 3 (Momma and Izumi 2011). For the calculation of the difference mean-square displacement parameters, the program XtalDraw (Downs and Hall-Wallace 2003) was employed. Crystallographic Information Files (CIF) for all six compounds have been uploaded as supplementary information.

Results

Synthesis and electron microprobe analysis

For all pellets, a significant reduction in volume was noticed after the heat treatment. On the surface, as well as in the interior of the sintered compacts, blackish crystals with maximum diameters of about 250 μm and a lath-shaped to platy habitus were observed. Notably, a distinct decrease in size with increasing Al-concentration was evident. The partially inter-grown crystals were embedded in a polycrystalline matrix of gray color from which they could be separated mechanically. Subsequent EMP analysis in combination with PXRD proved the multiphase character of most samples. The Al-free specimen (SFCA-I-00) consisted of a phase adopting the so-called α-CFF structure type (Karpinskii and Arakcheeva 1987) as the main constituent. For all other compositions, the platy crystals corresponded to SFCA-I-type compounds with varying Al/Fe ratios. As expected, the analyzed Al-concentrations of the SFCA-I crystals increased with the alumina content of the starting mixtures. Notably, the amounts of calcium and divalent iron remained virtually constant. Table 2 summarizes the average...
Table 1 Crystal data and results of the full-matrix least-squares structure refinements on \( F^2 \) for the different members of the SFCA-I solid-solution series.

|                | SFCA-I-01                        | SFCA-I-02                        | SFCA-I-03                        | SFCA-I-04                        | SFCA-I-05                        | SFCA-I-06                        |
|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Chemical formula | \( \text{Ca}_{6.67}\text{Al}_{3.76}\text{Fe}^{3+} \) | \( \text{Ca}_{6.67}\text{Al}_{3.76}\text{Fe}^{3+} \) | \( \text{Ca}_{6.67}\text{Al}_{3.76}\text{Fe}^{3+} \) | \( \text{Ca}_{6.67}\text{Al}_{3.76}\text{Fe}^{3+} \) | \( \text{Ca}_{6.67}\text{Al}_{3.76}\text{Fe}^{3+} \) | \( \text{Ca}_{6.67}\text{Al}_{3.76}\text{Fe}^{3+} \) |
| Formula weight  | 2896.13                         | 2889.15                         | 2876.59                         | 2766.00                         | 2721.72                         | 2721.72                         |
| Space group     | \( P \bar{1} \)                  | \( P \bar{1} \)                  | \( P \bar{1} \)                  | \( P \bar{1} \)                  | \( P \bar{1} \)                  | \( P \bar{1} \)                  |
| a (Å)           | 10.4436(12)                      | 10.4240(12)                     | 10.4226(8)                      | 10.4061(9)                      | 10.3912(11)                     | 10.3898(11)                     |
| b (Å)           | 10.6096(13)                      | 10.6019(10)                     | 10.5985(7)                      | 10.5783(10)                     | 10.5727(12)                     | 10.5555(12)                     |
| c (Å)           | 11.8528(15)                      | 11.8364(14)                     | 11.8224(10)                     | 11.7905(11)                     | 11.7799(12)                     | 11.7551(14)                     |
| \( \alpha ^\circ \) | 94.130(11)                       | 94.145(9)                       | 94.189(6)                       | 94.240(7)                       | 94.212(9)                       | 94.289(9)                       |
| \( \beta ^\circ \) | 111.276(11)                      | 111.308(10)                     | 111.378(7)                      | 111.381(8)                      | 111.424(9)                      | 111.414(10)                     |
| \( \gamma ^\circ \) | 110.340(11)                      | 110.303(10)                     | 110.226(7)                      | 110.173(8)                      | 110.108(10)                     | 110.076(10)                     |
| Volume (Å\(^3\)) | 1117.62                         | 1113.12                         | 1113.10                         | 1104.43                         | 1101.62                         | 1097.32                         |
| | \( Z \)                         | 1                               | 1                               | 1                               | 1                               | 1                               | 1                               |
| | \( \rho \text{calc.} \)          | 4.333 g/cm\(^3\)                | 4.301 g/cm\(^3\)                | 4.266 g/cm\(^3\)                | 4.205 g/cm\(^3\)                | 4.185 g/cm\(^3\)                | 4.119 g/cm\(^3\)                |
| | θ-Range(°)                       | 3.34 to 26.37°                   | 3.35 to 26.37°                   | 3.42 to 26.37°                   | 3.43 to 26.37°                   | 3.36 to 26.37°                   | 3.37 to 26.37°                   |
| | Reflections collected            | 7087                            | 7133                            | 7005                            | 7384                            | 7260                            | 7361                            |
| | Independent reflections         | 4507                            | 4504                            | 4488                            | 4453                            | 4437                            | 4421                            |
| | Completeness                    | 99%                             | 99%                             | 99%                             | 99%                             | 99%                             | 99%                             |
| | Parameters                      | 451                             | 451                             | 451                             | 451                             | 451                             | 451                             |
| | GoF on \( F^2 \)                | 0.945                           | 0.941                           | 0.965                           | 0.938                           | 0.991                           | 0.973                           |
| Final R indices \( [1 > 2 \sigma (I)] \) | R1 = 0.0437                      | R1 = 0.0389                      | R1 = 0.0411                      | R1 = 0.0309                      | R1 = 0.0421                      | R1 = 0.0387                      |
| | wR2 = 0.0779                     | wR2 = 0.0664                     | wR2 = 0.0718                     | wR2 = 0.0624                     | wR2 = 0.0911                     | wR2 = 0.0698                     |
| R indices (all data)            | R1 = 0.0736                      | R1 = 0.0624                     | R1 = 0.0679                     | R1 = 0.0453                     | R1 = 0.0601                     | R1 = 0.0595                     |
| | wR2 = 0.0953                     | wR2 = 0.0791                     | wR2 = 0.0844                     | wR2 = 0.0699                     | wR2 = 0.0101                     | wR2 = 0.0792                     |
| Largest diff. peak/hole         | 1.206/−1.015 e.Å\(^{-3}\)       | 1.484/−0.853 e.Å\(^{-3}\)       | 0.924/−1.146 e.Å\(^{-3}\)       | 0.877/−0.834 e.Å\(^{-3}\)       | 1.127/−1.475 e.Å\(^{-3}\)       | 1.041/−1.075 e.Å\(^{-3}\)       |

All data have been acquired at 23 °C using graphite monochromatized Mo-Kα radiation. GoF: goodness-of-fit.

compositions of the spot analyses for the different phases that could be identified.

Crystal structure

The refinement calculations confirmed an isotropic relationship between the members of our series and Mumme’s phase. To group the octahedral (M) and tetrahedral (T) sites, we decided to use a slightly different nomenclature and numbering for the cations as the one suggested in the previous investigation.

The crystal structure of SFCA-I contains an alternating sequence of two different types of fundamental layers (I and II) oriented parallel to \( \{2 \bar{0} \bar{1}\} \). Within layer-type I, bands of edge-sharing \( \text{MO}_6 \)-octahedra (M: Ca, \( \text{Fe}^{3+} \), \( \text{Al} \)) running parallel to \( \{010\} \) can be identified (see Fig. 1a). The bands are not planar but exhibit a distinct curvature, i.e. the rims are thicker than the central parts (see Fig. 2a). It is noteworthy, that not all of the potentially available octahedral sites inside the bands are occupied resulting in the formation of ordered vacancies. Actually, central cavities surrounded by the octahedra around M11, M8, M5, M10, M9 and M6 as well as lateral gaps between M1 and M3 can be distinguished. Layer-type II, on the other hand, can be built from \( \text{MO}_6 \)-octahedra as well as \( \text{TO}_4 \)-tetrahedra (T: \( \text{Al} \), \( \text{Fe}^{3+} \), \( \text{Fe}^{2+} \)) (see Fig. 1b). The \( \text{MO}_6 \)-groups around M7 and M12 each share common vertices with two neighboring tetrahedra (T1/T3 and T2/T5, respectively) forming \( \text{MT}_2 \text{O}_{12} \)-clusters or “winged-octahedra”. Linkage between adjacent strips of these moieties is provided by tetrahedral single chains built from the polyhedra about T4, T6, T7 and T8. T1 and T2 are directly connected to these chains by sharing common corners. In the classification of Liebau (1985), the whole assemblage could also be described as an open-branched vierer single chain. Concerning the connectedness of the six \( \text{TO}_4 \)-groups, which is defined as the number of other tetrahedra with which they are connected by sharing common oxygen atoms (Liebau 1985), two primary (Q1: T1, T2), two secondary (Q2: T4, T6) and two tertiary (Q3: T7, T8) tetrahedra can be distinguished inside the chains. The remaining two tetrahedra around T3 and T5 are not linked to the chains. They reside above and below the central octahedral vacancies of layer-type I (see Fig. 2b). The tetrahedra about T1 and T2 in turn “cover” the lateral gaps of the bands of layer-type I from both sides. Notably, the base triangles of the “up” and “down” pointing pairs of \( \text{MO}_6 \)-octahedra (T3 and T5 as well as T1 and T2) are rotated by
about 60° relative to each other, i.e., they are in an almost staggered conformation (see Fig. 2b). One basal plane of each of the four tetrahedra forming the backbone of the abovementioned vierer chain connects adjacent bands from layer-type I by sharing common corners with the three octahedra around M1 and M3.

Alternatively, SFCA-I can be described using a modular approach involving stacking of sequences of “P” and “S” modules that can be imagined as being cut from the well-known pyroxene (P) and spinel (S) structure types. Indeed, these modules are more or less perpendicular to the sheets of type I and II (see Fig. 2a). This modular approach has been already outlined in detail using concepts of OD-theory in several previous publications for the different members of the SFCA family (Merlino & Zvyagin, 1998; Zvyagin & Merlino 2003; Kahlenberg et al. 2019). As can be seen from Fig. 2a, the whole crystal structure of SFCA-I can be understood using the stacking sequence <PSS>.

### Unit-cell parameters

The substitution of a smaller cation like Al for the larger Fe decreases, as expected, the size of the unit-cell volume. Indeed, the volume reduction between SFCA-I-01 and SFCA-I-06 corresponds to −20.3 Å³ or −1.82%. As can be seen from Fig. 3, the volume data do not exhibit a significant deviation from a linear behavior when plotted against the Al/Fe tot ratio. The volume changes are also reflected in a decrease of the lattice parameters \(a\), \(b\) and \(c\) (see Fig. 4), which are reduced by about −0.52, −0.51 and −0.82%, respectively. This indicates that the \(c\) direction is more affected by the aluminum incorporation when compared with \(a\) and \(b\), showing almost identical changes. For the angles \(\alpha\), \(\beta\) and \(\gamma\), two different trends have been observed. While \(\alpha\) and \(\beta\) open with increasing Al content, the angle \(\gamma\) narrows at a roughly doubled rate.

The evolution of the unit-cell volume and the individual lattice parameters as a function of the Al/Fe tot ratio \(X\) can be described by the following linear expressions:

\[
\begin{align*}
V (\text{Å}^3) &= 1124(1) - 60(5) \cdot X, \quad R = -0.986 \\
\alpha (\text{Å}) &= 10.457(8) - 0.16(2) \cdot X, \quad R = -0.946 \\
b (\text{Å}) &= 10.632(5) - 0.16(2) \cdot X, \quad R = -0.983 \\
c (\text{Å}) &= 11.888(6) - 0.29(2) \cdot X, \quad R = -0.992 \\
\alpha (^\circ) &= 94.07(2) + 0.45(4) \cdot X, \quad R = 0.961 \\
\beta (^\circ) &= 111.25(3) + 0.42(9) \cdot X, \quad R = 0.901 \\
\gamma (^\circ) &= 110.42(2) - 0.82(8) \cdot X, \quad R = -0.981.
\end{align*}
\]

### Table 2

| Sample   | Nominal composition of the educts | Composition of the observed phases |
|----------|----------------------------------|-----------------------------------|
| SFCA-I-00| \(\text{Ca}_8\text{Fe}_{32}\text{O}_{56}\) | \(\alpha\)-CFF: \(\text{Ca}_{3.43}(2)\text{Fe}^{3+}_{14.39(2)}\text{O}_{25}\) |
| SFCA-I-01| \(\text{Ca}_8\text{Al}_{0.8}\text{Fe}_{31.2}\text{O}_{56}\) | \(\alpha\)-CFF: \(\text{Ca}_{3.90(3)}\text{Al}_{0.22(2)}\text{Fe}^{3+}_{14.12(2)}\text{O}_{25}\) |
| SFCA-I-02| \(\text{Ca}_8\text{Al}_{1.2}\text{Fe}_{29.8}\text{O}_{56}\) | \(\text{SFCA-I}: \text{Ca}_{6.65(3)}\text{Al}_{1.76(2)}\text{Fe}^{3+}_{28.24(3)}\text{Fe}^{2+}_{1.33(3)}\text{O}_{56}\) |
| SFCA-I-03| \(\text{Ca}_8\text{Al}_{1.2}\text{Fe}_{29.8}\text{O}_{56}\) | \(\alpha\)-CFF: \(\text{Ca}_{3.91(3)}\text{Al}_{0.41(2)}\text{Fe}^{3+}_{14.11(2)}\text{O}_{25}\) |
| SFCA-I-04| \(\text{Ca}_8\text{Al}_{1.2}\text{Fe}_{29.8}\text{O}_{56}\) | \(\text{SFCA-I}: \text{Ca}_{6.71(2)}\text{Al}_{1.88(3)}\text{Fe}^{3+}_{24.12(2)}\text{Fe}^{2+}_{1.29(2)}\text{O}_{56}\) |
| SFCA-I-05| \(\text{Ca}_8\text{Al}_{1.2}\text{Fe}_{29.8}\text{O}_{56}\) | \(\alpha\)-CFF: \(\text{Ca}_{3.90(3)}\text{Al}_{0.22(2)}\text{Fe}^{3+}_{14.12(2)}\text{O}_{25}\) |
| SFCA-I-06| \(\text{Ca}_8\text{Al}_{1.2}\text{Fe}_{29.8}\text{O}_{56}\) | \(\text{SFCA-I}: \text{Ca}_{6.72(2)}\text{Al}_{1.47(3)}\text{Fe}^{3+}_{21.53(2)}\text{Fe}^{2+}_{1.28(2)}\text{O}_{56}\) |

All samples contained minor amounts of almost phase pure \(\text{CaFe}_2\text{O}_4\) with maximal Al-concentrations of 0.1 a.p.f.u. The formulas for the members of the SFCA-I solid-solution series have been normalized to 56 O-atoms p.f.u., corresponding to the content of a single unit cell. Values for the \(\text{Fe}^{2+}\) contents have been derived following the procedure of Droop (1987) (see text).
Cation distributions

For the assignment of the cation species (Ca, Al, Fe$^{3+}$, Fe$^{2+}$) to the different M- and T-positions, the following procedure has been applied: The total scattering power for each site was obtained by allowing for potential Fe$^{3+}$ ↔ Al or Fe$^{3+}$ ↔ Ca substitutions under the assumption of the absence of vacancies. A detailed investigation of all site populations, including an analysis of ferric and ferrous iron contents was performed a posteriori with the program OccQP (Wright et al. 2000). This software uses the full information from chemical analysis (as determined from EMP), refined total scattering powers for the positions (as obtained from single-crystal structure analysis), bond valences and bond distances to find an optimized distribution of the cations. The mathematical algorithm is based on a least-squares method and a weighted linear system. The strength of this approach is the minimization of the residual between formal and apparent valences for an acceptable crystal-chemically solution concerning the site assignments (Wright et al. 2000). However, the program does not provide any standard uncertainties for the optimized site populations.

In the present case, we used the default weights of unity for site scattering, bond-valence, and bond-length terms. Because EMPA results indicated only minor compositional variations from point to point in the SFCA-I-type crystals, for the chemistry term an infinite weight was selected to assure that the resulting bulk chemistry matches the one obtained by the independently performed chemical analysis. Furthermore, Ca-avoidance on the tetrahedral sites has...
been used as an additional constraint. For the six samples, the resulting cation distributions obtained by OccQP for the individual M- and T-sites are listed in supplementary Table S1. The most important points can be summarized as follows.

Calcium cations can be found on all twelve octahedrally coordinated M-sites. Yet, their concentrations differ considerably. The positions M1 and M3 located at the edges of the octahedral bands are exclusively occupied with calcium. The M2-site in the central part of the band is strongly enriched in calcium (about 70%) but contains considerable amounts of Fe$^{3+}$ and Al as well. Within the solid-solution series, the ratios between these three cation species sharing M2 are almost constant. This observation holds also for the M6-site exhibiting Ca-concentrations of about 22%. The remaining eight M-positions (M4, M5, M7–M12) located in the spinel-type modules show significantly lower percentages of calcium (2.7–8.5%). Furthermore, the variation in the calcium levels among individual sites is not pronounced. However, a clear trend concerning the Fe$^{3+}$/Al ratios can be observed (see Fig. 5). With increasing alumina content in the bulk SFCA-I composition, the Al contents of these sites increase by a factor of 2.2–2.7.

For the tetrahedral positions, the following correlations were observed. The T-sites belonging to the central part of the *vierer* single chains (T4, T6, T7 and T8) located in the <P> modules are the primary sink for aluminum (see supplementary Table S1). Within the solid-solution series, these polyhedra show the highest increase rates in Al content. For the T8 site, for example, the Al-occupancy increases from 28% (for SFCA-I-01) to 91% (for SFCA-I-06). From SFCA-I-01 to SFCA-I-06, the tetrahedral centers T1 and T2 representing the branched part of the chains (located in the <S> modules) also incorporate an increasing amount of aluminum, but to a much lesser extent. The corresponding Al contents for the two “insular” T-positions vary between 0.09 and 0.14 (for T5) as well as 0.23 and 0.29 (for T3). The latter site, however, deserves special mention. According to the OccQP analysis divalent iron is solely restricted to this position. Notably, the Fe$^{3+}$/Fe$^{2+}$ ratio for this position is pretty constant: 0.11(2). Further proof for this assignment comes from bond-distance considerations which will be presented in the next section. A graphical representation of the evolution of the Al-concentrations for all tetrahedra can be found in Fig. 6.

### Bond distances and angles

To an upper limit of 3.2 Å, the two pure calcium sites M1 and M3 are coordinated by 6 + 1 oxygen anions. In both cases, the six closest ligands define a strongly distorted octahedron with average bond distances of about 2.39 Å. The gap between the distances to these six next neighbors and the respective additional oxygens (O20, O22) is very pronounced, having a value of about 0.6 Å. Even though these two sites are not directly involved in the Fe$^{3+}$-Al substitution, two opposing trends can be recognized among their M–O bond lengths. With increasing overall Al-concentration of the mixed crystals the <M–O> values for the bonds defining the “inner” octahedrally coordination environments increase by 1.36% (for M1) and 1.43% (for M3), respectively, while the distance to the seventh ligand decreases from SFCA-I-01 to SFCA-I-06 by 0.18 Å or 5.92% (for M1) and 0.24 Å or 7.63% (for M3). Consequently, for the Fe-rich members, the abovementioned gap is much more obvious. The Ca-dominated M2 position located in the central regions of the octahedral bands exhibits only a minor shortening...
of the average M–O distances by 0.38% with increasing Al content.

Most of the remaining M-sites show slightly decreasing <M–O> values with increasing Al/Fetot ratios, directly reflecting the substitution of the smaller Al- by the larger Fe3+-cations (see Fig. 7). The corresponding value for M5, however, is almost constant. In accordance with the only minor reduction of the <M–O> values for the M-sites of layer-type I, the volume of the octahedral vacancy in this sheet decreases negligibly from 14.18 Å³ (for SFCA-I-01) to 13.96 Å³ (for SFCA-I-06).

For each of the two “insular” tetrahedra (T3 and T5) located above and below this vacancy one short and three long T–O distances can be distinguished. This pattern in the distributions of the individual bond lengths can be rationalized by considering the number of cations that are bonded to the corresponding O atoms. Indeed, the oxygen atoms involved in the short distances (O23, O15) are connected to only two additional M-sites, while each of the remaining six oxygens is linked to three other M-positions. For the six tetrahedra of the open-branched vierer single chains, the distances to the non-bridging or terminal oxygens are always significantly longer than the distances to the bridging oxygen ligands. The average T–O values of the latter group are lower than the values for <T5–O> and dramatically lower than those for <T3–O>. This observation compares well...
with the analysis of the site occupancies where the total amount of Fe$^{2+}$ has been allocated to the T3-site.

Concerning the evolution of the $<T-O>$ values as a function of the total Al-concentration in the solid-solution series, two opposing trends have been found. While the values for the tetrahedra around T3 and T5 increase with increasing total Al/Fe$_{Tot}$ ratios, the reverse relationship has been observed for the tetrahedra of the open-branched vierer chains (see Fig. 8). Moreover, for the central four tetrahedra of the chains (T4, T6, T7, T8)—which show the largest variation in individual Al-concentrations—the rate of decrease is by a factor of four larger than for the branched parts (T1, T2).

Another notable change in the solid-solution series is the linear variation of the four angles between the bridging oxygen atoms of the central backbone of the tetrahedral chains (see Fig. 9) which belong to the pyroxene modules ($\phi_1$: O9-O20-O22, $\phi_2$: O20-O22-O21, $\phi_3$: O22-O21-O9 and $\phi_4$: O21-O9-O20; see Fig. 1b). The increase of these angles by 6.0°, 6.8°, 6.9° and 5.9°, respectively, indicates that the chains are becoming more extended with increasing Al/Fe$_{Tot}$ ratio, or in other words, less kinked. As the angles are less than 180°, the chains could be classified as “O-rotated” (Papike et al. 1973). Following the results presented by Thompson & Downs (2001) in a systematic study on structural variations in model pyroxenes as a function of tetrahedral rotation, the $<P>$ modules in SFCA-I can be considered distorted cubic closest packed (ccp), and because $\partial <O-O-O> / \partial (Al/Fe_{Tot}) > 0$, they become less ccp with increasing Al content.

**Difference thermal displacement parameters**

The anisotropic displacement parameters of the cations and anions are generally well behaved. We refrain from providing a detailed discussion of the influence of the total Al/Fe$_{Tot}$ ratio on these parameters but will rather focus on one specific aspect. As mentioned above, site occupancies studied using the OccQp software as well as inspection of the bond distances indicated the presence of ferrous iron on the T3-site. Further evidence for this assumption comes from an analysis of the differences between the anisotropic mean-square displacement parameters of the T and O atoms along the corresponding T–O bonds. According to Kunz and Armbruster (1990) these $<\Delta U>$ values can provide insight into static disorder when averaged over a complete tetrahedron. For the SFCA-I-03 data set, for example, the value for the tetrahedron around T3 ($<\Delta U>=0.022(6) \, \text{Å}^2$) is 3.1 to 7.3 times larger than the corresponding values for the tetrahedra belonging to the branched tetrahedral chains and still 2.4 times larger than the one for the second “insular” tetrahedron (T5)—all of which have been assumed to contain ferric iron only. Consequently, the significantly increased $<\Delta U>$ value observed for T3 would reflect the disorder effects when a comparatively small ion (such as Al$^{3+}$, $r^{4}=0.39 \, \text{Å}$) shares the same position with a much larger cation (such as Fe$^{2+}$, $r^{4}=0.63 \, \text{Å}$) (Shannon 1976).

**Discussion**

In principle, our studies confirm the model for SFCA-I that was published by Mumme et al. (1998) for a synthetic Si-free sample with a comparable chemical composition.
Yet, for several positions, we have obtained strikingly different results concerning the partitioning of the cations. For example, Mumme et al. described M2 to be fully occupied with calcium. This assignment, however, results in a strong overbonding with a bond valence sum as high as 2.6 v.u. Second, based on bond length considerations the content in ferrous iron was exclusively attributed to the octahedral site M6. Our own refinements corroborate that the average bond distances and polyhedral volumes of M6 are slightly bigger when compared to the other M-sites within layer-type I. However, Mumme’s assumption leaves us with a problem that there is no explanation for the dramatically increased size of the tetrahedron about T3—a structural feature that occurred in the former refinement as well, where this site was labelled Fe14 and supposed to contain Fe$^{3+}$ (84%) and Al (16%). As outlined above, we believe that there are strong arguments for the incorporation of Fe$^{2+}$ on this position. Our changes concerning the principal structural model of SFCA-I are minor modifications. Nevertheless, we consider them a valuable improvement and a better description of the crystalchemical features of the SFCA-I series.

Powder X-ray diffraction is the method of choice for the characterization of polycrystalline materials. To study the influence of the cation substitutions, the diffraction patterns of all six members of the SFCA-I series have been calculated (see Fig. 10a–f). They can act as library-of-reference diffractograms for predicting how the Fe ↔ Al substitutions give rise to different signatures in the patterns. In general, the simulated powder diffraction data of the solid-solution series look quite similar. However, there are some features that are especially useful to tell the different members apart. For example, the first observable peak corresponding to the 001-reflection shows the most pronounced dependency of its intensity on the Al content, which increases significantly with increasing Al/Fe$_{\text{Tot}}$ ratio.

Figure 11 summarizes the evolution of the $<T-O>$ values of the tetrahedra obtained for the SFCA-I series as a frequency distribution histogram.
function of their Al-concentrations, \( x_{\text{Al}} \). A similar analysis has been recently performed in the course of a re-investigation of a SFCA-II sample (Kahlenberg et al. 2021) and the corresponding data have been included in the present study. The combined data sets now cover an almost complete range for \( x_{\text{Al}} \) ranging from 0 to 1. Most of the values shown follow a trend that can be adequately described by the following linear relationship:

\[
< T - O > (\text{Å}) = 1.886(3) - 0.151(6) \cdot x_{\text{Al}}, \quad R = -0.962.
\]

Extrapolation of the linear trend to \( x_{\text{Al}} = 0 \) and \( x_{\text{Al}} = 1 \) gives values of 1.886 and 1.735 Å, respectively. Both numbers compare well with the mean bond lengths of 1.875 ± 0.022 (for \( < \text{Fe}^{3+}\text{O} > \)) and 1.746 ± 0.022 Å (for \( < \text{Al} - \text{O} > \)) obtained by Gagné and Hawthorne (2018, 2020) from a comprehensive statistical analysis of individual \([\text{Fe}^{3+}\text{O}_4]\)- and \([\text{AlO}_4]\)-tetrahedra in inorganic compounds.

However, Fig. 11 also shows that there are some outliers. The average bond distances for T3 and two of the tetrahedra in SFCA-II, for example, deviate significantly from the trend line which predicts much lower values when compared with the actual results obtained from crystal structure analyses. It is exactly these polyhedra that have been demonstrated to contain large amounts of Fe\(^{2+}\).

The aforementioned equation could be useful in two ways. First, it may provide an estimation of the Al content of individual tetrahedra in other members of the SFCA family from purely geometrical parameters. Second, it could be employed for the identification of tetrahedra containing appreciable quantities of ferrous iron. With this respect, the OccQp analysis did not support this interpretation.

![Fig. 11](image)

**Fig. 11** Evolution of the \( < T - O > \) values of the tetrahedra obtained for the present SFCA-I series and a recent analysis on SFCA-II (Kahlenberg et al. 2021) as a function of their Al-concentrations, \( x_{\text{Al}} \).

The data given in the results section indicate a complex interplay between chemical composition on the one and structural changes related to individual deformations of the coordination polyhedra on the other hand. To obtain a more holistic picture of the distortion patterns, the evaluation of the so-called compositional strain tensor can be a helpful tool. The derivation of the components of this second-rank tensor from two sets of lattice parameters corresponding to two different compositions has been described by Ohashi and Burnham (1973), for example. The necessary calculations based on the two limiting compositions of the present series (SFCA-I-01 and SFCA-I-06, respectively) have been performed with the program Win_Strain 4.11 (Angel 2011). Using a finite Eulerian strain formalism referred to an orthonormal coordinate system \( \{x, y, z\} \) with \( z // c, x // a^* \) and \( y = z \times x \), the following \( 3 \times 3 \) matrix for an average strain tensor \( \varepsilon_{ij} \) was derived:

\[
\varepsilon_{ij} = \begin{pmatrix}
0.0047(2) & -0.0018(2) & 0.0026(2) \\
-0.0018(2) & 0.0053(2) & 0.0015(1) \\
0.0026(2) & 0.0015(1) & 0.0083(2)
\end{pmatrix}.
\]

With respect to the Cartesian coordinate system of the principal axes \( \{e_1, e_2, e_3\} \), the following three principal strains are obtained: \( \varepsilon_1 = 0.0018(2), \varepsilon_2 = 0.0067(1) \) and \( \varepsilon_3 = 0.0098(2) \) with \( e_1:e_2:e_3 = 1:3.72:5.44 \), indicating a large anisotropy of the strain induced by the Fe\( \leftrightarrow \)Al substitution. As expected for the triclinic case, the principal axes are not related to the directions of the crystallographic coordinate system along \( a, b \) and \( c \). Using Win_Strain, the following angles between the principal and the crystallographic axes have been derived. The values given in parentheses refer to the corresponding vectors with \( a, b \) and \( c \), respectively: \( e_1: (124.3^\circ; 125.2^\circ; 64.9^\circ) \); \( e_2: (34.3^\circ; 144.5^\circ; 97.7^\circ) \); \( e_3: (90.9^\circ; 85.9^\circ; 26.4^\circ) \).

In the next step, the components of the principal axes in the crystallographic coordinate system have been calculated and—after appropriate scaling for better visualization—the corresponding vectors have been plotted together with specific elements of the SFCA-I structure using the program VESTA 3 (see Fig. 12a–d). This approach facilitates a direct comparison of the macroscopic compositional strain and certain structural features of the SFCA-I-type compounds. As can be seen from Fig. 12a showing a single \( < \text{PSS} > \) unit, the direction \( e_3 \) of major expansion (major compression with increasing Al content) is almost perpendicular to the spinel- and pyroxene units, and simultaneously almost parallel to \( e^* \). Further on we tried to separate the contributions of both entities. For this purpose, the thicknesses of the \( < \text{P} > \)- and \( < \text{SS} > \) modules have been approximated by the perpendicular distances between least-squares planes defined by the oxygen atoms located at the boundaries.
of the modules. Figure 13a, b presents the variations of these parameters as a function of the Al/FeTot ratio. While the width of the two spinel modules is virtually constant, the pyroxenes module narrows significantly by 3.36%. The narrowing (widening) of the pyroxene module seems to dominate the contraction (expansion) of the structure in this direction with increasing (decreasing) Al/FeTot ratio. Figure 12b, c demonstrates that the intermediate principal strain axis $\varepsilon_2$ is close to the apical O–M–O bonds in both the pyroxene and spinel modules. $\varepsilon_1$—the least deformable direction—is parallel to the projections of the remaining four equatorial bonds of the octahedra onto the $\varepsilon_1$–$\varepsilon_2$ plane. Furthermore, $\varepsilon_1$ is in line with a system of continuous linear edge-sharing octahedral chains present in both spinel modules that are additionally “stiffened” by two lateral tetrahedra (see Fig. 12d). Finally, the directions of the principal axes can be also related to the underlying distorted ccp arrangements of oxygen atoms that are present in both modules. $\varepsilon_2$ is almost parallel to one of the four $<100>_{ccp}$ directions in the ideal packing, say [001]$_{ccp}$, $\varepsilon_3$ and $\varepsilon_1$, thus, run along [110]$_{ccp}$ and [Â10]$_{ccp}$, respectively.

**Concluding remarks**

Most structural aspects, from unit-cell volumes to site occupancies, tetrahedral chain kinking and polyhedral distortions, are defined by nearly linear trends when plotted against the Al/FeTot ratio. From a thermodynamic perspective, the linear
relationships observed in this study imply that the present SFCA-I solid solution is likely close to be ideal.

When compared with the compositions of the starting mixtures, the retrieved SFCA-I single crystals of the series were consistently depleted in calcium and iron as well as enriched in aluminum. Moreover, all samples contained ferric and minor amounts of ferrous iron. The concentrations of Ca were almost constant. The last observation indicates that under the given experimental conditions the current Ca contents of about 6.6 to 6.7 a.p.f.u. may represent an upper threshold. The fact, that not all of the divalent cations required for electroneutrality are calcium ions is in accordance with earlier studies by Mumme et al. (1998) and Arakcheeva et al. (1991) who consistently reported less than 8 Ca a.p.f.u. to be present in their Si- and Mg-free SFCA-I samples: $\text{Ca}_{8.36}\text{Al}_{2.68}\text{Fe}^{3+}_{29.32}\text{Fe}^{2+}_{1.64}\text{O}_{56}$ and $\text{Ca}_{12}\text{Al}_{18}\text{Fe}^{3+}_{23.82}\text{Fe}^{2+}_{0.88}\text{O}_{56}$, respectively. The incorporation of more than about 7 a.p.f.u. of the large Ca cations into the M-positions located in the octahedral bands is probably not compatible with the short M–O distances implied by the comparatively rigid connectivity of the edge-sharing $\text{[MO}_6\text{]}$-polyhedra. Furthermore, the necessity to match the tetrahedral chains with the octahedra within the pyroxene modules may also induce an upper limit for calcium incorporation.

The four tetrahedra T4, T6, T7 and T8 belonging to the chains in the $<P>$ modules of SFCA-I are the preferred sites for the Al-uptake within the solid-solution series. This observation compares well with the outcome of structural studies on the related SFCA-type $\text{Al}_{14}\text{O}_{20}$ compounds where a similar tendency was recognized (Sugiyama et al. 2005; Murao et al. 2018, 2020).

A further major feature found in the site occupancy patterns of the present SFCA-I solid-solution series concerns the mean Al-concentration $<x_{\text{Al}}>$ of the Q$^1$-, Q$^2$- and Q$^3$-sites in the branched chains as well as the mean connectedness $<Q>$ for Al in the chains. It is evident, that for all members of the series $<x_{\text{Al}}>$ for the Q$^3$-positions (T7, T8) is larger than for Q$^2$ (T4, T6) and Q$^1$ (T1, T2) and $<Q>$ for Al is $>2$. The finding, that the minority species (Al) of the cations in the chains concentrates on the most polymerized sites has also been reported for structurally related compounds containing the same type of branched chains such as sapphireine ($\text{2(Mg,Al)}_6\text{Al}_2\text{Si}_6\text{O}_{20}$), for example (Christy 2009 and references cited therein). For sapphireine, which is isostructural to SFCA, the most abundant species in the chains (Al) is the least polymerized and, conversely, Si as the substituting ion shows a high degree of polymerization. Using Monte Carlo simulations, Christy (2009) demonstrated that this effect is related to the exothermic nature of the Al–O–Si linkages and the same explanation may be applicable for the Fe–O–Al connections in SFCA-I. Studies on the interplay between short- and long-range order as well as configurational entropy in the chains may be an interesting topic for further research activities.

Moreover, one could ask whether there exists an upper limit for the Al content in SFCA-I. For the case that all T-sites within the $<P>$ modules are completely filled with Al, one possibility to accommodate additional aluminum could be realized by increasing the 1:2 ratio between the $<P>$- and $<S>$ modules, which naturally leads to a new structure type. Interestingly, only very recently we demonstrated that for the more alumina-rich starting composition $\text{Ca}_8\text{Al}_{16}\text{Fe}_{16}\text{O}_{56}$, a SFCA-II type phase with a $<\text{PSPSS}>$ stacking sequence ($<P>:<S>$ ratio 2:3) occurred in the same temperature region that was selected for the synthesis experiments of the present study (Kahlenberg et al. 2021). The Al/Fe$_{\text{Tot}}$ ratio in this phase is 0.6. On the other hand, our results indicate that there is probably also a lower threshold for Al-incorporation. Actually, a pure “Fe-SFCA-I” phase could not be obtained. Of course, further experimental work is needed to chart the boundaries between the different members of the SFCA family in the system CaO–Fe$_2$O$_3$–FeO–Al$_2$O$_3$ in more detail and to verify our hypotheses concerning the limits of solid-solution in SFCA-I.

Finally, our investigations on the SFCA-I series may have also implications for mineralogists and petrologists working on new minerals. Natural counterparts to SFCA have been already described from pyrometamorphic rocks...
all over the world including famous localities such as the Hatrirum complex (Negev Desert, Israel) or the Eifel region (Germany). The compositions of these minerals such as khesinite (Ca₂MgFe₁₀SiO₂₀, Galuskina et al. 2017), dorrite (Ca₂MgFe₆Al₅SiO₂₀, Shchipalkina et al. 2019) or devilliersite (Ca₃Fe₁₀SiO₂₀, Krüger et al. 2021) are related to those of the synthetic phases studied in the present investigation. Furthermore, addibischoffite (Ca₂Al₁₂O₂₀)—the natural analog to the pure aluminum end-member of SFCA—has been found in a Ca–Al-rich inclusion of a chondrite meteorite. The compound probably formed under rather exotic conditions from a Ca- and Al-rich melt at high temperature (≈ 1575 °C) and low pressure (≈ 10⁻⁴ to 10⁻⁵ bar) in a solar-like gaseous reservoir near the protosun (Ma et al. 2017). Minerals with equivalent crystal structures to SCFA-I have not yet been discovered, but it is more than likely that their first observation in Nature is only a question of time and of the availability of powerful X-ray sources at synchrotron beamlines dedicated to the study of small crystalline samples. Our crystallographic investigations on synthetic compounds can aid in the identification of these potentially new minerals. Information concerning the synthesis conditions could also be useful to gain a better insight into the formation conditions of the relevant host rocks.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00269-021-01148-4.

Acknowledgements The authors thank Amelie Schickhoff for the preparation of the samples for EMP analysis and Ross John Angel (IGG-CNR, Padova) for providing a development version of the program CrystalPalace that eased the generation of the comprehensive tables from the CIF-files considerably. The manuscript benefited from the helpful comments of two anonymous reviewers.

Author contributions VK: conceived and planned the investigation. He performed the crystal growth experiments, single-crystal structure analyses and wrote the manuscript with the help of HK. HK: carried out the powder diffraction studies. MT: performed the EMP analyses.

Funding Open access funding provided by University of Innsbruck and Medical University of Innsbruck.

Availability of data and material All primary structural information of the six SFCA-I phases is included in the corresponding CIF-files that have been uploaded as well.

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