Chain Periodicity Faults in Babingtonite, $Ca_2Fe^{2+}Fe^{3+}H[Si_5O_{15}]$

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Abstract

Based on the observations in rhodonite $(Mn,Ca)_5$-$[Si_5O_{15}]$, errors in the periodicity of the tetrahedral chains in babingtonite were expected; they are confirmed by high-resolution electron microscopy. These errors are arranged mainly into planar chain periodicity faults (CPF). Deviations of the faults from planarity, such as terminations and alterations of the fault units, have been found. ^{57}Fe Mössbauer studies show that the frequency of CPF's is not controlled by positional disorder of the cations.

I. Introduction

In a large number of crystalline phases tetrahedral groups such as $[SiO_4]$, $[PO_4]$, *etc.* are linked together and form one-dimensionally infinite chains. The number of tetrahedra within the repeat unit of the chain, *i.e.* within the chain unit, is defined as the periodicity p of the chain. The number of single chains linked to a multiple chain is called the multiplicity m (Liebau, 1972, 1980). In such phases there are three types of planar faults:

(1) Faults in the periodic packing or arrangement of otherwise undisturbed chains (neglecting minute distortions at the fault). Such faults have been known for a long time in chain silicates and were described as stacking faults, antiphase boundaries or twin boundaries (*e.g.* Wenk, 1969).

(2) Faults caused by chains of wrong multiplicity, which were described as chain width errors a few years ago (Hutchison, Irusteta & Whittaker, 1975).

(3) Faults caused by errors in the periodicity of the chains. Such faults have only recently been discovered (Ried, Schröpfer & Korekawa, 1979; Czank & Liebau, 1979).

For these three different types of planar faults, the terms chain arrangement fault (CAF), chain multiplicity fault (CMF) and chain periodicity fault (CPF) have been suggested (Czank & Liebau, 1980).

According to Czank & Liebau, a wrong unit interspersed into the periodic sequence of chain units is called a chain periodicity error (CPE); a CPF is then a group of CPE's located at correlated positions within adjacent chains. The term fault unit should be used for a region of the crystal which is one wrong unit thick.

So far, CPF's have been observed by electron microscopy in rhodonite $(p = 5)$ (Ried & Korekawa, 1980; Czank & Liebau, 1980; Franco, Jefferson, Pugh & Thomas, 1980), pyroxmangite $(p = 7)$ (Czank & Liebau, 1980) and in pyroxferroite $(p = 7)$ (Ried & Korekawa, 1980). These are single chain silicates of the pyroxenoid group having the general formula $(Mn, Fe, Ca, Mg)_p [Si_p O_{3p}]$ with $p = 2n + 1$, n an integer. Since the structure of the triclinic mineral babingtonite, $Ca_2Fe^{2+}Fe^{3+}H[Si_5O_{15}]$ (Araki & Zoltai, 1972; Kosoi, 1976), is closely related to that of rhodonite, the existence of CPF's in babingtonite was suspected, and an electron microscopic study of this phase has now been carried out.

II. Electron microscopic investigations

II.1. *Samples and techniques*

Natural babingtonites from Arendal, Norway, from Cummington, Mass., USA, and from Hampden Quarry, West Springfield, Mass., USA, are the object of the present study. Their chemical compositions are given in Table 1.

The specimens were ground and deposited on perforated carbon films. Since babingtonite has good cleavage parallel to the chains, *i.e.* parallel to the c axis, most crystals were elongated in this direction and were lying with c almost perpendicular to the electron beam. Therefore, a number of crystals could be oriented with c^* perpendicular to the beam to observe the (001) lattice fringes.

The electron microscope used was a Philips EM 400, operated at 100 kV and provided with a tilting stage. The micrographs shown in the figures were taken at the conditions of critical alignment, underfocus, *etc.* as described by Buseck & Iijima (1974).

Table 1. *Chemical composition (wt%) of the babing-tonites*

Column 1: babingtonite from Arendal, Norway; column 2: babingtonite from Cummington, Massachusetts; column 3: babingtonite from West Springfield, Massachusetts.

The H content is not considered in the analysis.

Sample	1	2	3
SiO_2	52·40	51·68	53·15
Al_2O_3	0·20	0·44	0·39
V_2O_3	0·02	0·08	0·12
Fe_2O_3	13·57	13·10	21·25*
FeO	6·79	9·78	
MnO	4·12	1·41	0·72
MgO	0·90	0·76	1·32
CaO	19·50	19·78	19·80
Total	97·51	97·00	96·75

* No ^{57}Fe Mössbauer study was done on this sample.

II.2. *High-resolution lattice images*

As expected, crystals from all three localities contain CPF's with (001) as the fault plane.

For all the CPF's observed, the differences $\Delta p = p'$ (fault unit) $-p$ (ordered chains) were found to be a multiple of 2. The number of tetrahedra in a chain unit (wrong units as well as 'right' units) can be deduced from the spacings of the fringes in the corresponding lattice images. Referring to the cell parameters and settings reported by Liebau, Hilmer & Lindemann (1959) for pyroxenoids, the values of $d_{(001)}$ are 7·1, 11·5 and 15·9 Å for silicates containing chains with *dreier*, *fünfer* and *siebener* chain units, respectively. Increasing the chain units by steps of two tetrahedra ($\Delta p = +2$) leads to spacings 20·3, 24·7, 29·1 Å, *etc.* for *neuner*, *elfer*, *dreizehner*, ... chain units ($p = 9, 11, 13, ...$) respectively.

In the *fünfer* chain structure of babingtonite, CPF's characterized by *dreier* ($\Delta p = -2$) and by *siebener* ($\Delta p = +2$) fault units were observed most frequently. *Neuner* ($\Delta p = +4$) and *elfer* ($\Delta p = +6$) fault units occur less frequently, and only in a very few cases were fault units with $p' > 13$ ($\Delta p \geq +8$) detected.

Fig. 1 shows images of several types of CPF's. The ordered sequence of the (001) lattice planes is interrupted by various faults. The numbers given at the edge of the crystal represent the numbers of tetrahedra in the wrong units of the corresponding CPF.

Although *dreier* fault units and *siebener* fault units should lead to different spacings in the one-dimensional fringe pattern, distinction between both types of CPF may be difficult, if operating conditions are such that additional fringes, which correspond to structural details smaller than the chain unit (*i.e.* subperiodicities of double tetrahedra, *cf.* Fig. 2b), appear between the main fringes. For this reason it is often necessary

to take several micrographs at different contrast conditions.

Another way to identify CPF's in pyroxenoids unambiguously is to look along fringes parallel or almost parallel to the chain direction as, for example, the (010) fringes in Fig. 2(a). A kink then becomes recognizable in each of these fringes when crossing a CPF (Fig. 2a). As seen in this figure, a kink to one side of the fringe direction is visible when $\Delta p \geq +2$, a kink to the other side when $\Delta p = -2$. Comparison with a schematic drawing of the structure (Fig. 2b) helps to decide which kink direction belongs to which fault. By incorporating a wrong unit of three tetrahedra ($\Delta p = -2$) within the periodic sequence of the *fünfer* chain units, one obtains a kink of the chain towards [110]. A wrong unit of seven tetrahedra ($\Delta p = +2$) gives rise to a kink in the opposite direction. The angle of the kink depends on the value of Δp. The assignment of fault units in Figs. 1 and 2(a) has been verified according to this procedure.

Quite often, *dreier* and *siebener* fault units occur in pairs. A recombination of *dreier* and *siebener* fault units to two *fünfer* units can take place without visible strain as indicated by the contrast (Fig. 3). In some cases it was found that CPF's can recombine although they are not direct neighbours. In one instance, 'finite' planar faults have been observed, which are produced by recombination of *dreier* and *siebener* fault units which are terminated at both ends; they could be described as a loop.
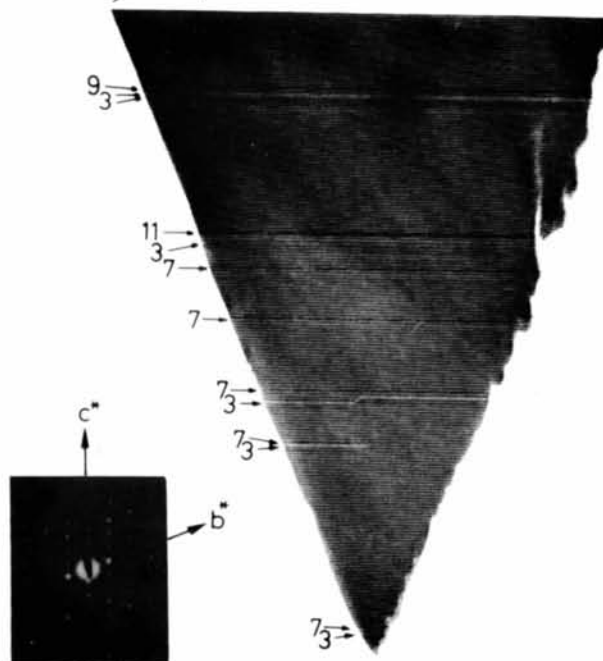

Fig. 1. Two-dimensional fringe pattern of babingtonite from Arendal, Norway. Several chain periodicity faults (CPF's) parallel to (001) are indicated. The numbers 3, 7, 9 and 11 give the number of tetrahedra within the wrong chain units of the corresponding CPF.

Alteration of fault units has also been observed, *e.g.* two *siebener* fault units change to a *neuner* fault unit and a *fünfer* unit (Fig. 4), and this without visible strain.

Although the (001) plane is the most likely one for the CPF's, other planes have also been observed. In Fig. 5, a *dreier* fault unit changes its orientation from (001) to approximately (0$\bar{2}$5).
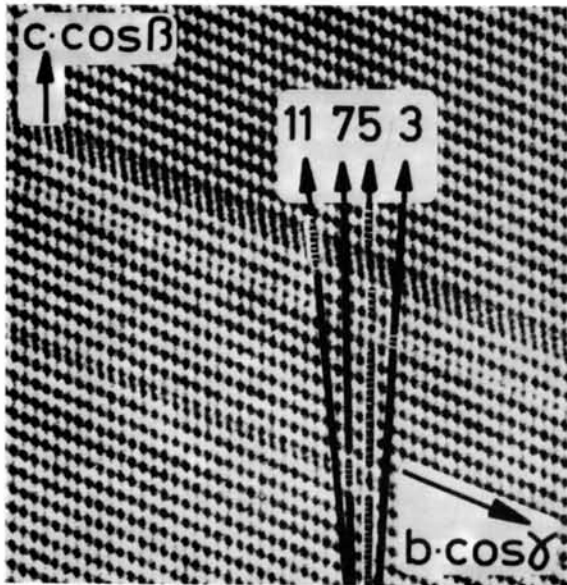
(a)
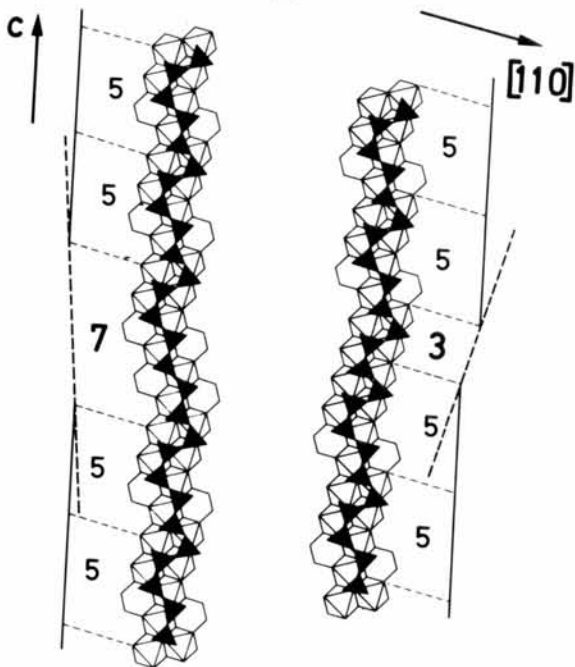
(b)

Fig. 2. Changes in the chain direction by incorporation of wrong chain units, visualized in a two-dimensional lattice image (a) and in a schematic drawing (b). If one looks along the *c* axis, the kink in the chains is easy to recognize. (a) A section enlarged from Fig. 1. For the schematic representation in (b), the projection along [1$\bar{1}$0] has been chosen because of the better recognizability of the kink.

Fig. 3. Termination of periodicity faults by recombination of a pair of adjacent *dreier* and *siebener* fault units to two layers of 'right' *fünfer* chain units (section enlarged from Fig. 1).
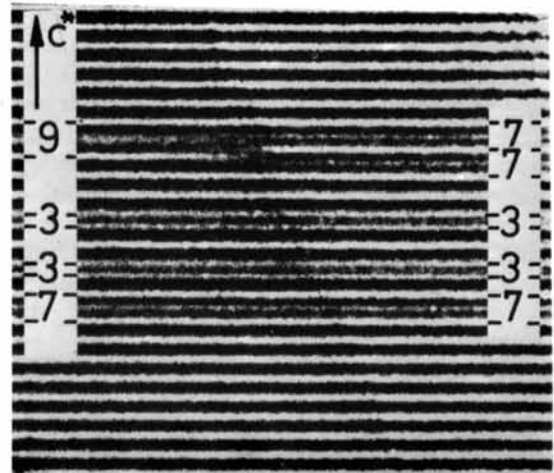

Fig. 4. Change of two adjacent *siebener* fault units into one *neuner* fault unit and a layer of one 'right' *fünfer* chain units.
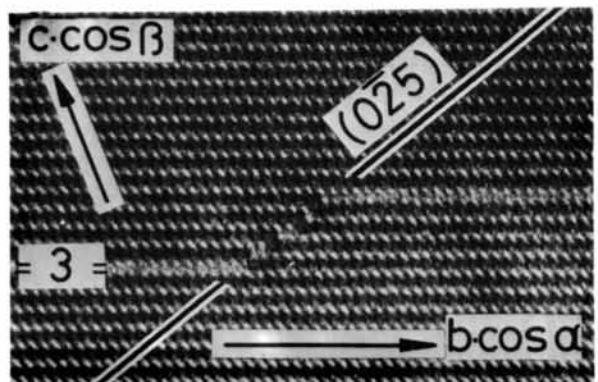

Fig. 5. A CPF changes direction. The fault plane turns from (001) to approximately (0$\bar{2}$5) and back.

III. Discussion

The present EM study of babingtonites was suggested by observations on rhodonites. Therefore, a brief comparison of the faults in the two minerals is appropriate.

In natural rhodonites, no other fault units than *siebener* fault units ($\Delta p = +2$) were found, and all CPF's observed were strictly planar layers oriented parallel to (001) (*cf.* Czank & Liebau, 1980). In babingtonites, CPF's occur more frequently. Not only does one find different types of fault units, such as *dreier* ($\Delta p = -2$), *siebener* ($\Delta p = +2$), *neuner* ($\Delta p = +4$), *elfer* and higher ($\Delta p \geq +6$) fault units, but one observes also various kinds of deviations from planarity of the CPF's.

Compared with rhodonite, it seems that the substitution of ($Fe^{3+} + H^{+}$) for two M^{2+} cations promotes the formation of CPF's.

As suggested for the pyroxenoids (Czank & Liebau, 1980), CPF's should be suitable to provide information on the genesis of minerals and the rocks in which they occur. Babingtonites from localities in Massachusetts contain considerably fewer CPF's than the crystals from Arendal, but their fault features do not differ significantly. The difference in fault frequency of the two samples may be controlled not only by their different chemical composition, but also by the pressure and thermal history of the crystals, and possibly by a difference in the cation distribution.

An ^{57}Fe Mössbauer study of the samples from Arendal and from Cummington yielded Mössbauer spectra nearly identical to those reported by Amthauer (1980). In particular, the line widths of the two samples are small and nearly identical.

It can be concluded from the spectra that in both samples the iron atoms occupy distinct positions and are ordered. The higher concentration of CPF's in the Arendal sample is therefore neither connected with a sufficient number of iron atoms in the Ca sites (no additional absorption features), nor with an Fe^{3+}/Fe^{2+} disorder over their corresponding sites (no line broadening). The two samples differ, however, in the relative intensities of the doublets assigned to Fe^{2+} and Fe^{3+}, respectively. The intensity ratio has been used to derive the Fe^{2+}/Fe^{3+} ratio when calculating the crystallo-chemical formulae.

It is clear from Table 1 that the higher Fe^{3+}/Fe^{2+} ratio of the Arendal sample is associated with the higher Mn content. Since for the octahedral cations the ratio M^{3+}/M^{2+} is almost the same in both samples (from Arendal and from Cummington), a significant difference in the H content can be excluded. Therefore, the higher CPF frequency in the samples from Arendal may be caused by the higher Mn content.

However, at present no clear correlation reveals itself. Further studies on synthetic and natural pyroxenoid minerals are being carried out to clarify this point.

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