

Segregation and cation-ordering in sjögrenite and pyroaurite

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SUMMARY. A specimen from Långban, Sweden, was found to consist largely of sjögrenite in which segregation and ordering of the metal cations had occurred, yielding an intergrowth of regions of two main types with compositions probably of or near $\text{Mg}_{2/3}\text{Fe}_{1/3}(\text{OH})_2(\text{CO}_3)_{1/6}(\text{H}_2\text{O})_{0.4}$ and $\text{Mg}_{12/13}\text{Fe}_{1/13}(\text{OH})_2(\text{CO}_3)_{1/26}(\text{H}_2\text{O})_{0.8}$. To a smaller extent segregation had proceeded further, giving regions probably approximating to the end-member $\text{Mg}(\text{OH})_2 \cdot \text{H}_2\text{O}$. It is suggested that the names sjögrenite and pyroaurite be used for the 2H- and 3R- polytypes of this structure irrespective of Mg:Fe ratio, segregation, or cation ordering.

SJÖGRENITE and pyroaurite are two stacking modifications of typical composition $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$. Their crystal structures were determined by Allmann and Lohse (1966), Ingram and Taylor (1967), and Allmann (1968). They consist of brucite-like layers of composition $(\text{Mg}, \text{Fe}^{3+})(\text{OH})_2$, between which occur intermediate layers formed from the H_2O molecules and CO_3^{2-} groups; sjögrenite is the 2H-, and pyroaurite the 3R-polytype. In all the crystals used for the structure determinations by the above workers, the Mg^{2+} and Fe^{3+} ions were found to occupy the same set of octahedral sites, with no indication of ordering, and disorder was also found to occur among the H_2O molecules and CO_3^{2-} ions of the intermediate layers. Small differences exist between the results of Allmann and Lohse and those of Ingram and Taylor regarding the structure of the intermediate layer, but these are unimportant in the present context.

Ingram and Taylor reported that some crystals, which were not used for the structure work, showed splitting of basal X-ray reflections, and that others showed superlattice reflections. Both these effects suggested the occurrence of regions of differing Mg:Fe ratios. They have now been more fully examined, and form the subject of the present paper.

Experimental

The specimen was labelled 'pyroaurite, Långban, Sweden, USNM 93013', and was kindly supplied by the U.S. National Museum. It comprised some 10 mg of material, mostly in a single aggregate of flaky crystals in roughly parallel orientation. Seven fragments (single crystals or polycrystalline aggregates) were picked from it under the microscope. They were 0.1–1.0 mm in their longest dimensions. In general, they were semi-transparent and varied in colour from greyish-white to pale brown, with a pearly lustre on the cleavage. Regions of a deeper brown were observed in some, and one (mentioned later) was deep brown throughout.

Either ω or mean refractive indices were determined; the fragments differed between each other in refractive index but except in one case, also mentioned later, no variation within fragments was observed. Each fragment was also studied by single-crystal X-ray methods, and electron microprobe analyses of three were kindly made by Mr. G. G. Brebner and Mr. G. Taylor, of the Department of Geology and Mineralogy of the University of Aberdeen.

Results and discussion

Four types of crystal were observed in the specimen and will be designated I–IV.

Type I crystals. Four of the seven fragments were of this type, which probably makes up the bulk of the material. Their ω refractive indices were 1.563–1.574. They gave sjögrenite-type single-crystal X-ray patterns, with both splitting of reflections and superlattice reflections. The splitting indicated the existence of two lattices in parallel orientation, with the same a -axial length of 3.12 ± 0.01 Å, but differing layer thicknesses of 7.68 ± 0.01 and 7.84 ± 0.02 Å. Segregation had thus taken place and had yielded an intergrowth of regions of two types, which diffracted independently and were thus each many unit cells thick in the c -direction. The relative intensities of corresponding reflections suggested that the two kinds of region were present in comparable amounts.

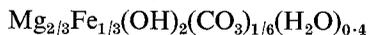
The superlattice reflections were found from oscillation and precession photographs to lie in or near the $h.k.\bar{h}+\bar{k}.0$ plane and to have the positions shown in fig. 1. They fall into two groups. Those of group A correspond to a unit cell with $a = \sqrt{3}a_0$, where a_0 is the value (3.12 Å) of a for the main lattice. Ingram and Taylor (1967) had previously reported the occurrence of this group on electron-diffraction patterns. The reflections of group B can most simply be referred to a twinned lattice with $a = \sqrt{13} \times a_0$, having the two orientations shown in fig. 1.

An electron microprobe analysis of one of the type I crystals gave a Mg:Fe atom ratio of 2.93. The absolute contents of Mg (27.76 %) and Fe (21.73 %) are less meaningful, as partial dehydration occurs in the instrument. A scan across the crystal showed no significant variation in Mg or Fe contents.

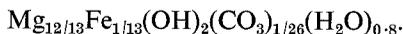
Analogy with the results of Gastuche, Brown, and Mortland (1967) for the corresponding synthetic Mg–Al phases suggests that the 7.68 Å regions have an Mg:Fe atom ratio of or near 2:1. This composition would also readily explain the existence of the group A superlattice reflections. The Mg:Fe ratio may only approximate to 2:1, because the Mg- and Fe-rich sites could have probabilities of occupancy by the respective ions that are less than unity.

Gastuche, Brown, and Mortland (1967) found that a layer thickness of 7.92 Å in the Mg–Al phases was associated with a Mg:Al ratio of about 5:1. The Mg-rich regions in the present case may have a similar Mg:Fe ratio. However, the 7.84 Å layer thickness is more probably associated with the group B superlattice reflections, and if this is so, the idealized Mg:Fe ratio in these regions is probably 12:1. As with the regions discussed earlier, the true ratio may only approximate to the idealized value.

The type I crystals thus contain regions of at least two kinds, with probable compositions of or near



and



In writing these formulae, the occurrence of some vacancies in the oxygen sites of the intermediate layer has been assumed. The conclusion from the X-ray evidence that

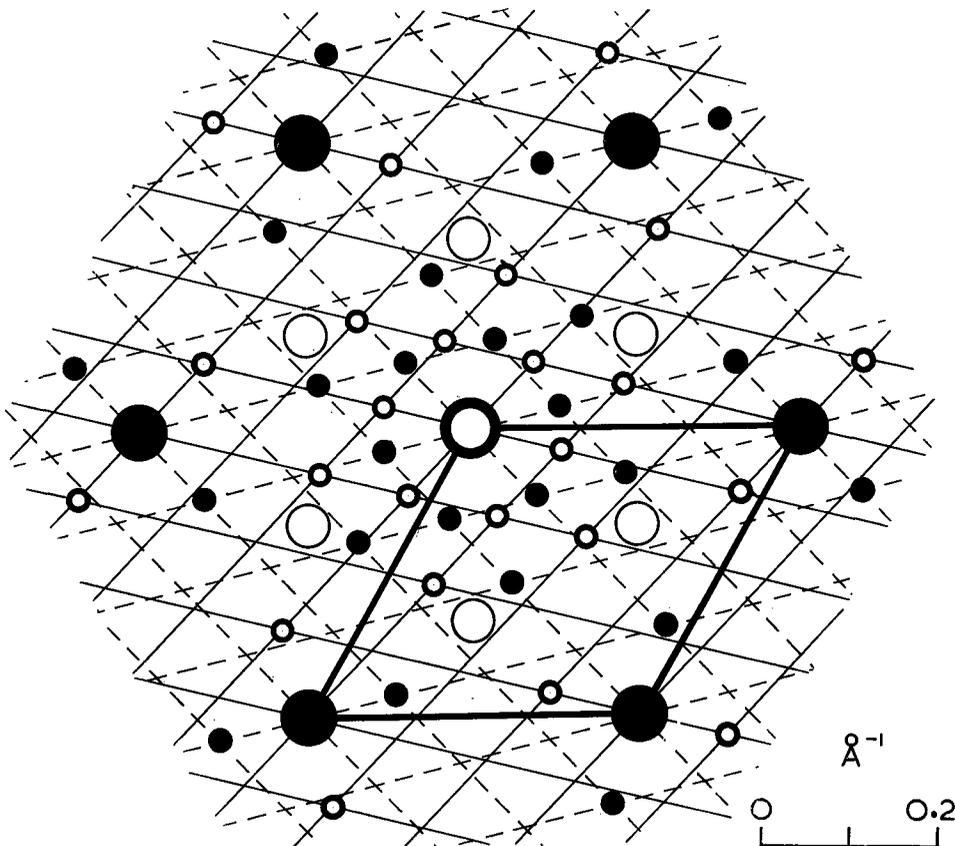


FIG. 1. Central part of the reciprocal lattice of a type I crystal, projected onto the $h.k.\overline{h+k}.o$ plane. Large, full circles represent $\{10\bar{1}0\}$ points of the main lattice; a single reciprocal cell is shown with heavy lines. Medium, open circles represent group A superlattice reflections. Small full and open circles represent respectively group B superlattice reflections of the two twinned orientations. The corresponding reciprocal lattices are shown with thin broken and full lines.

the two kinds of region are present in comparable amounts is compatible with these compositions and the bulk Mg:Fe ratio shown by the microprobe analysis, which in turn agrees with typical analyses for sjögrenite or pyroaurite from the same locality given in the literature (Fron del, 1941). The possibility cannot be excluded that there are also regions in which the cations are disordered. The scale and texture of the inter-

growth are not fully established, but the optical and microprobe evidence suggest that it is on a sub-micron scale. At the same time, the X-ray evidence shows that individual regions of each composition are at least 500–1000 Å thick in the *c*-direction.

Type II crystals. One crystal examined was of this type. It was essentially similar to the type I crystals in that it showed splitting of X-ray reflections and gave both A and B groups of superlattice reflections, but it was pyroaurite and not sjögrenite. The ω index was 1.585. This relatively high value suggests a lower Mg:Fe ratio than in the type I crystals, but the apparent correlation of Mg:Fe ratio with stacking type is probably not significant.

Type III crystals. One crystal examined was of this type. It gave a sjögrenite-type single-crystal X-ray pattern with splitting of reflections but no superlattice effects were observed. The two observed layer thicknesses did not differ significantly from those of the type I crystals, but the reflections from the 7.84 Å regions were very much stronger than those from the 7.68 Å regions. The ω index varied in different parts of the crystal from 1.505 to 1.520. Electron microprobe analyses of two portions of this crystal gave Mg:Fe atom ratios of 11.2 (Mg, 46.35 %; Fe, 9.47 %) and 78 (Mg, 46.75 %; Fe, 1.37 %) respectively.

The X-ray and microprobe results suggest that the type III crystals consist largely of cation-disordered material with a composition approaching that of the Mg-rich end-member, $\text{Mg}(\text{OH})_2 \cdot \text{H}_2\text{O}$, with a little intergrown $\text{Mg}_{2/3}\text{Fe}_{1/3}(\text{OH})_2(\text{CO}_3)_{1/6}(\text{H}_2\text{O})_{0.4}$. The low refractive index further supports this conclusion. If the formula $\text{Mg}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is assumed, the X-ray density is 1.92 g/cm⁻³; subsequent application of the Lorentz-Lorenz equation using the atomic and group refractions quoted by Allmann (1968) gives a calculated value of 1.496 for ω . The observed range of values is slightly higher than this, and this can reasonably be attributed to the presence of a little iron in the crystal.

Type IV crystals. One fragment examined proved to be an aggregate in random orientation of submicroscopic crystals. It was deep brown and had a mean refractive index of 1.705. The X-ray powder pattern (table I) could largely be indexed assuming a hexagonal cell with *a* 3.076, *c* 14.740 Å, which is similar to that of sjögrenite but with a reduced layer thickness of 7.37 Å. However, it is also similar to those of typical layer silicates of the serpentine group, representative data for which were given by Whittaker and Zussman (1956). The suspicion that this phase is a layer silicate of the serpentine or some related group is supported by electron microprobe evidence, which showed that it contained a substantial proportion of silica. However, the refractive index and colour do not agree with those of any known serpentine mineral, and further investigation would be desirable. The similarity between the sjögrenite (or pyroaurite) and serpentine structures may be noted; in both cases trioctahedral layers alternate with single sheets of oxygen atoms. The possibility that the crystals are an oriented intergrowth or interstratified structure of iron-rich members of the serpentine and sjögrenite groups cannot be excluded.

Conclusions: brugnatellite. In the specimen from Långban under examination, segregation into Mg- and Fe-rich regions has occurred, along with ordering of cations. In most of the material, this process appears to have occurred in a sub-micron scale,

and to have given regions with Mg:Fe ratios of or near 2:1 and 12:1. To a lesser extent, the process has gone further, yielding regions some tenths of a millimetre in size and having compositions approximating to the end-member $\text{Mg}(\text{OH})_2 \cdot \text{H}_2\text{O}$. Most of the material is sjögrenite, a little pyroaurite; no correlation is established between stacking type and Mg:Fe ratio. It is suggested that, to avoid introducing new names, the names sjögrenite and pyroaurite should be used to denote respectively the 2H- and 3R-polytypes, irrespective of Mg:Fe ratio, segregation of cations, or occurrence of superlattice effects.

TABLE I. *X-ray powder data for type IV crystals*

7.36 s	2.62 vvw	1.742 w/b	1.417 vvw
4.62 w	2.48 s	1.538 m	1.310 w
4.15 vw/d	2.160 w	1.506 w	1.281 vw
3.66 ms	1.803 vw	1.475 vvw	

Fenoglio (1938) reported X-ray studies on two specimens that had been described as brugnatellite. They had compositions approximating to $\text{Mg}_6\text{Fe}(\text{OH})_{13}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$, and were found to be hexagonal, with a 5.47 ($= \sqrt{3} \times 3.16$), c 15.97 ($= 2 \times 7.99$) Å. The most likely interpretation of these results is that the specimens were of sjögrenite, and contained regions of high Mg:Fe ratio from which no superlattice reflections were observed, and regions with Mg:Fe = 2:1, which gave group A superlattice reflections. The high ratio of CO_3^{2-} to OH^- is unexplained, but it must be considered doubtful whether brugnatellite should be regarded as a species distinct from sjögrenite.

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