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## SYNTAXIC INTERGROWTHS IN THE ANDORITE SERIES\*

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### ABSTRACT

Most specimens of andorite are syntaxial intergrowths of two distinct species, which have also been observed separately. Rather than revive the name sundtite, we propose to call them andorite IV and andorite VI because their  $c$  translations are multiples,  $4c'$  and  $6c'$ , of a common pseudo-period  $c' = 4.29 \text{ \AA}$ . They have identical  $a$  and  $b$  translations, equal to 13.03 and 19.15  $\text{\AA}$  respectively. They have different morphological developments, already noted by Ungemach, with morphological aspects  $P^*ca$  and  $Pn^*a$  referred to the true cells. Weissenberg and precession  $x$ -ray patterns yield diffraction aspects  $P^{**}a$  and  $Pn^*a$ ; they also show a strikingly marked pseudo-aspect  $Bb^{**}$ , for the pseudo-cell  $abc'$ , common to both species. Specific gravity determinations on polycrystals give values ranging from 5.23 to 5.44, suggesting different chemical compositions for the two species. Ramdohrite = andorite VI.

### INTRODUCTION

Andorite  $PbAgSb_3S_8$  was first found at Felsöbánya and was described by Krenner (1892). Sundtite, announced as  $(Ag_2, Cu_2, Fe) Sb_2S_6$  by Brögger (1893), came from Oruro, Bolivia. Stelzner (1895) described a mineral under the name webnerite. Prior and Spencer (1897) re-examined these minerals and concluded that both sundtite and webnerite were identical with Krenner's andorite, with up to 2 per cent copper substitution in the case of sundtite. Ahlfeld (1930) described a mineral of composition  $Pb_3Ag_2Sb_6S_{13}$  or  $Pb_6Ag_4Sb_{10}S_{23}$  from Potosí, Bolivia, and named it ramdohrite. It is known to have a powder pattern "very similar" to that of andorite (Strunz, 1949).

Ungemach studied the Oruro material, on which he noted two distinct types of morphological development. On this basis he suggested that

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† This paper presents some of the unpublished data discussed in the presidential address *Edifices of Periodic Matter*, which was delivered in Toronto, on November 10, 1953, to the Mineralogical Society of America.

sundtite should be reinstated. His results are mentioned in the literature (Ungemach, 1923) though not fully discussed. Preliminary  $x$ -ray results obtained by the senior author (J. D. H. Donnay, 1941) showed that the andorite-sundtite problem was still unsolved and needed further study. Nuffield (1945) gave cell dimensions and space groups for andorite, ramdohrite, and fizelyite.

#### MORPHOLOGICAL RESULTS

Ungemach's notebooks, which had been bequeathed by him to one of us (JDHD), were carefully examined. He had measured 24 "crystals" from Oruro. Although he was not aware that nearly all of them are syntaxitic intergrowths of two species (see below, under  $x$ -ray results), he separated his specimens into two types, which he considered distinct species. His conclusion rested on two facts, which an admirable power of observation and patient scrutiny had enabled him to establish, namely: (1) differences in the morphological developments of the two types of "crystals"; (2) small angular differences in their interfacial angles.

For the type of crystals described by Brögger, Ungemach found the axial ratios:

$$0.6773:1:0.4429.$$

He referred to them as "sundtite" (=our andorite IV, see below). For other crystals, which he called "andorite" (=our andorite VI), he multiplied the  $c/b$  ratio by 3 and gave the numerical values:

$$0.6807:1:1.3346 = 0.6807:1:0.4449 \times 3.$$

The axial ratios given for andorite in the literature (Strunz, 1949),

$$0.6771:1:0.4458,$$

are those of Brögger (1893).

The only emendations required by Ungemach's conclusions stem from the fact that the edifices he measured, although they simulated crystals of a single species, actually were intergrowths of crystals of two species in parallel orientations. The term *polycrystal* (G. Donnay, 1953) can be applied to such an intergrowth.

The numerical values reported by Ungemach for the axial ratios will probably have to be refined because some of the interfacial angles used in the calculations were due to the species intergrown with the species under consideration. For example on a polycrystal in which andorite IV was predominant, and which Ungemach accordingly treated as an andorite IV crystal, he would have included the angle (001):(091) among those on which to base his  $c/b$  ratio, and yet (091) would have been a face of andorite VI.

Ungemach stated that Brögger's (331) must be chosen as the new unit

face in the case of andorite VI. We confirm this statement by morphological analysis. All the crystals of andorite VI plainly show the morphological aspect  $Pn^*a$ , with Brögger's  $c$  trebled (Fig. 1), so that the morphological space group is either  $Pnma$  ( $D_{2h}^{16}$ ) or  $Pn2a$  ( $C_{2v}^9$ ).

Ungemach also stated that Brögger's unit face (111) was correctly chosen for andorite IV. Our own morphological analysis, on the contrary,

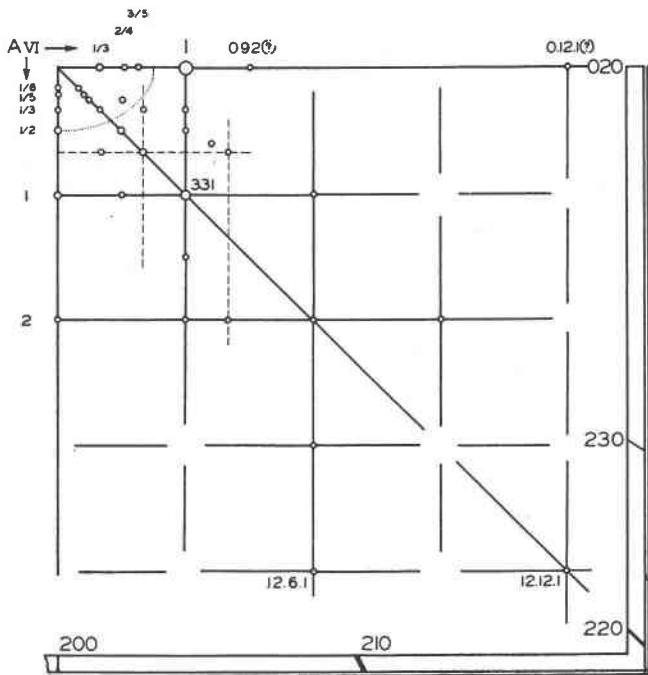


FIG. 1. Gnomonic projection $\ddagger$  of a polycrystal, dominantly composed of andorite VI, referred to Brögger's axial elements. The pole indexed 331 in Brögger's notation should be taken as 111 for andorite VI. Some poles, connected by dashed lines, belong to andorite IV. The space group can be read directly from the projection ( $Pnma = D_{2h}^{16}$ ). Ungemach's specimen B425.

indicates that the face to be selected as the new unit face is Brögger's (221). The first layer of the reciprocal lattice of andorite IV is then remarkably brought out, on the gnomonic projections of all the polycrystals on which andorite IV predominates, by such faces as Brögger's (221), (241), (261), (281), (441), (481), which can be seen on Fig. 2, and (2.12.1), (661), (12.12.1), (24.12.1), (12.6.1), which were observed on other speci-

$\ddagger$  The gnomonic projections (Figs. 1-3) have been distorted by shrinking the  $a^*$  direction in the ratio of 3 to 2, so that the rectangular mesh can be represented by a square. The sphere of projection becomes an ellipsoid.

mens. On some crystals (Fig. 2) it may be difficult to decide whether the aspect is  $P^{**}a$  or  $P^{*}ca$ . On the whole, however, the frequency data collected on the  $(h0l)$  forms definitely point to Brögger's (101) = new (102) as the dominant face in the zone. The zone of the  $(h0l)$  faces, moreover, is of the simple type, as the next frequent faces are (in the new notation) (104) and (206), and the multiple indices of the latter are confirmed by (308) and (3.0.10), both observed. The zone of the  $(hkl)$  faces is an outstanding example of a simple zone with (210) dominant (Fig. 2). The

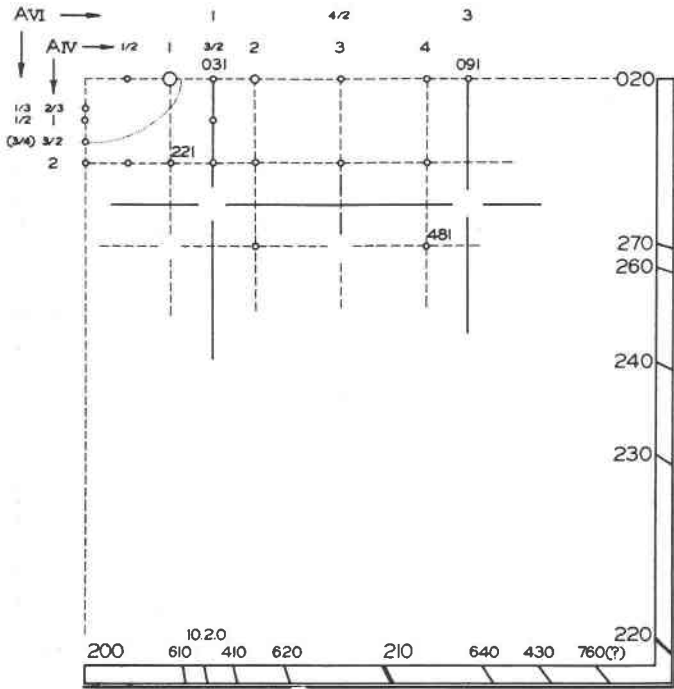


FIG. 2. Gnomonic projection of nearly pure andorite IV, referred to Brögger's axial elements. The pole indexed 221 in Brögger's notation becomes 111 for andorite IV. Pole 091 belongs to a double series (031-061-091) due to andorite VI. The zone of the  $h0l$  poles can be interpreted either as simple with unit face dominant (mirror) or as simple with dominant face shifted toward the  $c$  face ( $c$  glide plane). The morphological space group is read as  $Pmma(D_{2h}^8)$  or  $Pmca(D_{2h}^{11})$ . Ungemach's specimen A356.

morphology thus unmistakably indicates aspect  $P^{*}ca$ , and the morphological space group is either  $Pmca(D_{2h}^{11})$  or  $P2ca(C_{2v}^5)$ .

The gnomonic projection plotted for the original andorite, according to the data published by Krenner (1892), shows that both andorite IV and andorite VI are present in an intergrowth but that andorite IV predominates. Using Brögger's notation we see that  $q(221)$ ,  $r(121)$ , and  $\gamma(021)$

belong to andorite IV, whereas  $\beta(131)$  and especially  $\gamma(031)$  and  $t(091)$  can be referred only to andorite VI. Some faces, such as  $x(011)$  and all the  $(hk0)$  faces, are compatible with either species. Koch (1928) studied new material from Felsöbánya. His data confirm the above conclusion, based on Krenner's results. He found some new forms, among which  $\pi(032)$ , a rather frequent one, will find its place as a secondary form of andorite VI to be expected between  $\gamma$  and  $x$ .

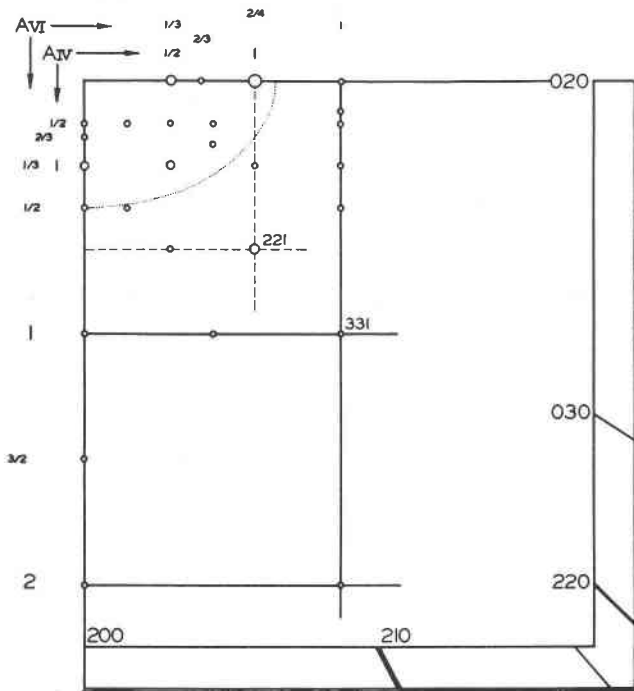


FIG. 3. Gnomonic projection of a polycrystal of andorite VI (zone lines solid) and andorite IV (zone lines dashed), referred to Brögger's axial elements. The zone of the  $Ok\bar{l}$  poles is a simple zone for andorite IV, and a double zone for andorite VI. The zone of the  $h0l$  poles shows the simple zone, with Brögger's 301 dominant, of andorite VI and another simple zone, with Brögger's 101 dominant, due to andorite IV. The zone of the  $hk0$  poles is the same for both species; it is a simple zone with 210 dominant. Ungemach's specimen B485.

Brögger's data (1893) on sundtite from Oruro yield a gnomonic projection remarkably similar to that of the Krenner specimens. Additional faces of andorite IV are  $f(101)$  and  $h(102)$ . Andorite VI acquires  $d(601)$  and  $e(302)$ , although (301) is not reported. Andorite IV is again preponderant.

From the confrontation of such similar data, the conclusion reached by

Prior and Spencer (1897), that andorite and sundtite were one and the same species, was inevitable. We were fortunate in finding, in Ungemach's material, a specimen (No. B 426) that is almost exclusively andorite VI. Its gnomonic projection displays even more forms of andorite VI than does that shown in Fig. 1. For instance—again in Brögger's notation—(091) and (061), the former larger than the latter, fit in the double zone of the ( $0kl$ ) faces, while (901) and (902) complete the simple zone of the ( $h0l$ ) faces. The difference between this projection and that of Fig. 2, which represents an almost pure andorite IV (No. A 356), is indeed striking. There is no doubt that, if Prior and Spencer had had such crystals available, sundtite would never have been discredited.

#### X-RAY RESULTS

Rotation, Weissenberg, and precession photographs were taken, with copper and molybdenum radiations, on fragments of the polycrystals that had been measured by Ungemach, on the material studied by Nuffield (1945), and on fragments of a ramdohrite specimen, from the mine Chocaya la Vieja, Potosí, Bolivia, borrowed from the Harvard University Museum.

The lengths of  $a$  and  $b$  are the same for both species within the limits of error of our measurements,

$$a = 13.03 \pm 0.04, \quad b = 19.15 \pm 0.06 \text{ \AA}.$$

The  $c$ -axis rotation photographs show an intense layer line, which yields a pseudo-translation

$$c' = 4.29 \pm 0.02 \text{ \AA},$$

the same for both species. The small angular differences observed by Ungemach between corresponding interfacial angles of the two species, which led him to slightly different axial ratios (see above), cannot be confirmed by the present  $x$ -ray work. The first strong layer line on the  $c$ -axis rotation patterns is the fourth layer line in the case of one species, which is called andorite IV for this reason, and the sixth layer line in the case of the other species, which is accordingly designated andorite VI. The true  $c$  is therefore equal to  $4c' = 17.16 \text{ \AA}$  for andorite IV and  $6c' = 25.74 \text{ \AA}$  for andorite VI. Although the intermediate layer lines are clearly visible on a 2-hour rotation photograph superimposed on a 2-hour  $10^\circ$ -oscillation photograph,<sup>1</sup> exposures of the order of 20 hours are required to bring out the weak spots on precession pictures taken with

<sup>1</sup> Such a combined photograph gives the same information as a rotation photograph if the crystal is properly adjusted. If the crystal is maladjusted, the arc corrections can be obtained from the film so that it is not necessary to take a separate adjustment picture (Donnay and Donnay, 1952).

nickel-filtered copper radiation. The Weissenberg photographs of the strong layer lines were exposed for 22 hours; those of the weak layer lines for twice that time.

The reflections that lead to the pseudo-cell  $abc'$  show "systematic" omissions, so that the space group of the pseudo-cell can be determined. Let  $l'$  designate the index that refers to the pseudo-translation  $c'$ . The following reflections are observed:  $hkl'$  with  $(h+l')$  even;  $0kl'$  with  $k$  and  $l'$  both even. The diffraction aspect is therefore  $Bb^{**}$  and the space group of the pseudo-cell is  $Bbmm$  ( $D_{2h}^{17}$ ),  $Bb2m$  ( $C_{2v}^{12}$ ), or  $Bbm2$  ( $C_{2v}^{16}$ ). The diffraction aspect is the same for both species. Inasmuch as the omissions considered in its determination are due to features of the crystal structure, that is, are *structural extinctions* rather than *space group extinctions*, the aspect of the pseudo-cell is only a pseudo-aspect. The pseudo-symmetry is so pronounced in the present case, however, that the pseudo-aspect of the pseudo-cell could safely be assumed in all but the final stages of a crystal-structure determination. The reflections due to the pseudo-cells of the two species are so nearly identical that the crystal structures must only differ in details.

Systematic omissions among reflections indexed with respect to the true cells were obtained from zero-layer and first-layer  $c$ -axis Weissenberg patterns, for the  $hk0$  and the  $hk1$  reflections, and from precession patterns, for the  $0kl$  and the  $h0l$  reflections. The following reflections were observed.

In andorite VI:  $hkl$  present in all orders;  $0kl$  with  $(k+l)$  even;  $h0l$  in all orders;  $hk0$  with  $h$  even. The diffraction aspect is therefore  $Pn^*a$ , and the possible space groups  $Pnma$  ( $D_{2h}^{16}$ ) and  $Pn2a$  ( $C_{2v}^9$ ).

In andorite IV:  $hkl$  present in all orders;  $0kl$  in all orders;  $h0l$  in all orders;  $hk0$  with  $h$  even. The diffraction aspect is  $P^{**}a$ , compatible with three space groups:  $Pnma$  ( $D_{2h}^5$ ),  $P2ma$  ( $C_{2v}^2$ ), and  $Pm2a$  ( $C_{2v}^4$ ).

Although the observations have been given for each species separately, most films showed the superimposed patterns of the two species in syntaxial intergrowth. All the specimens used by Nuffield were polycrystals, which accounts for his erroneous interpretation (Fig. 4). What would be called "andorite XII" in our nomenclature does not exist, and the systematically missing layer lines are no longer puzzling. Dr. Nuffield has re-examined his films and confirms our findings (personal communication).

A ramdohrite crystal from the type locality, Potosí, Bolivia, was studied by Nuffield (1945), who reported cell dimensions identical, within limits of error, with those of our andorite VI. We obtained crystals from the same locality and confirmed the identity of ramdohrite and andorite VI. No andorite IV was found on the specimen. We also confirmed Nuf-

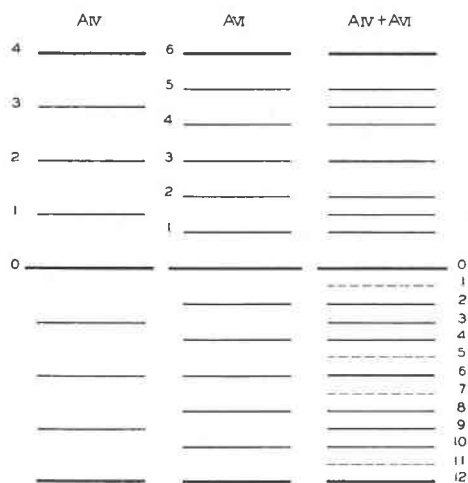


FIG. 4. Schematic representation of layer lines on rotation  $x$ -ray patterns. The pseudo period of  $4.29 \text{ \AA}$  along the  $c$  axis is shown by the first strong layer line, which is the fourth one in andorite IV and the sixth one in andorite VI. The effects observed with a polycrystal (IV+VI) are due to the superposition of the two patterns; they could be mistaken for those of a single crystal, in which the first strong line would be the twelfth one and in which the systematically absent first, fifth, seventh, and eleventh lines would be ascribed to structural extinctions.

field's results on fizelyite, which is definitely not an "andorite II" (Donnay and Donnay, 1952).

No material described as webnerite was available to us or to Nuffield.

Gnomonic projections of all the Ungemach's measured polycrystals were plotted, and the zone lines of the two species drawn with solid and dashed lines (cf. Figs. 1 to 3). In this way it was possible to see which of the two species controlled the morphological development and was presumably dominant. The  $x$ -ray photographs of the same polycrystals did not in every case confirm the morphological conclusion. The reason for this is simple: the  $x$ -ray beam may penetrate only one crystal, especially when the tip of the edifice, which is usually bathed in the beam, is homogeneous or happens to contain a preponderance of the species that is the minor constituent of the polycrystal.

The comparison of the  $x$ -ray results with the morphological ones shows that Brögger's axial elements,

$$0.6771:1:0.4458,$$

are those of a cell twice as high as the pseudo-cell, which has height  $c' = 4.29 \text{ \AA}$ . For Brögger's cell our  $x$ -ray results yield the ratios

$$0.680:1:0.448.$$



This cell probably represents the best compromise if one tries to refer the forms of both species to a single cell, but it is inadequate to express the morphology of either species. The true cell governs the morphological development in each species. The morphological space groups are the same as the structural space groups, with one deviation—the morphology of andorite IV demands a  $c$  glide plane perpendicular to the  $(h0l)$  faces, whereas its crystal structure requires either a mirror or no symmetry plane at all. It is admittedly hard to see how a structural mirror would cease to be a mirror when morphology is concerned. This anomaly suggests the absence of symmetry planes normal to the  $b$  axis in the crystal structure and thereby makes the space group  $Pm2a$  the most likely one.

#### REMARKS ON CHEMICAL COMPOSITION

The very occurrence of two species in syntaxial intergrowth was taken by Ungemach (1923) to mean that they were polymorphic forms (*polytypes*), but it is now known that such is not necessarily the case. It is true for carborundum (Ramsdell, 1947; Donnay, 1943) and for zinc sulfide (Frondel and Palache, 1950). In the bastnaesite-synchisite series, however, chemically different species have been found to intergrow (Donnay and Donnay, 1953). In that series of minerals (bastnaesite, parisite, roentgenite, synchisite), a pseudo-cell is common to all the species though one of its dimensions—namely its  $c$  length—varies from species to species. In the present case of andorite IV and andorite VI, there also exists a common pseudo-cell, but we have not been able to detect a variation in any of its dimensions. At first sight, this situation would seem to favor the assumption of identity of chemical composition. The density, of course, would have to be constant too, and it provides a way of attacking the problem of the composition. The available chemical analyses vary a great deal; that of ramdohrite (by Brendler, on type material) departs considerably from the others.

Five new determinations of the specific gravity were made on polycrystals from Oruro by means of the Berman balance. They are: 5.23 (on 31 mg), 5.23 (on 14 mg), 5.33 (on 8 mg), 5.36 (on 19 mg), 5.44 (on 20 mg). The last one was obtained on material that was predominantly andorite VI, judging from its gnomonic projection. One of the 5.23 values was obtained on 31 mg of material in which andorite IV was preponderant. The relative proportions of andorite IV and andorite VI in the other polycrystals cannot be estimated as easily. The highest value in the literature is 5.43, reported for ramdohrite by Frondel (in Nuffield, 1945). The values found by Prior and Spencer (1897) were 5.38 (Oruro) and 5.33 (Felsöbánya). This range of specific gravities suggests that the compositions of andorite IV and andorite VI may be different.

The pseudo-cell  $abc'$  has volume  $V' = 1070 \text{ \AA}^3$ . With 4 formula units of composition  $\text{PbAgSb}_3\text{S}_6$ , the calculated specific gravity is 5.41. If it were to contain 1 formula unit of  $\text{Pb}_6\text{Ag}_4\text{Sb}_{10}\text{S}_{23}$ , one of the compositions suggested for ramdohrite, the calculated specific gravity would be 5.63, 4% higher than the maximum value observed. This means either that no pure andorite VI specimen has as yet been used for specific gravity determination or that this formula is not the correct one. The alternate formula for ramdohrite,  $\text{Pb}_3\text{Ag}_2\text{Sb}_6\text{S}_{13}$ , is even less probable, as it leads to a calculated specific gravity as high as 6.16. As to the lowest value observed namely 5.23, it will require a "molecular weight" equal to 3,370 in the pseudo-cell. This is 121 less than the formula weight of  $\text{Pb}_4\text{Ag}_4\text{Sb}_{12}\text{S}_{24}$ .

Chemical analyses of pure samples of each species are needed to solve the problem. In the meantime we propose to use the designations andorite IV and andorite VI to stress the structural relationship of the two species.

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