

Barium-felspars from Broken Hill, New South Wales.

(With Plate XIV.)

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AT two localities on the outskirts of the township of Broken Hill—near the De Bavay shear zone, and at 'The Piggery'—W. R. Browne¹ reported unusual rock types rich in barium. His statement is accompanied by an analysis by H. P. White (analyst to the Mines Dept.) of one of these rocks, which contains 9.23% BaO. Subsequently S. R. Nockolds and E. G. Zies² examined the felspars of the rock analysed by White with a view to ascertaining whether they are barium-containing varieties.

In view of the very high barium content of some of the occurrences now being investigated, much higher than that of the rock examined by Nockolds and Zies, a further mineralogical investigation was undertaken with the results recorded below. The rocks under examination were light-coloured gneisses containing up to 15% BaO. They are distributed as lenses and streaks in an acid gneiss. A specimen of the latter rock was analysed and found to contain only 0.09% BaO. The barium was found to occur in four felspars, one being a new variety of celsian. The minerals studied were celsian, calciocelsian, hyalophane, and barium-plagioclase. A careful search was made for other barium silicate minerals such as sanbornite, but none was found.

CELSIAN.

This mineral was found in two specimens only, both collected from within a few inches of one another. They are light grey in colour and do not differ appreciably in appearance from the other barium-gneisses of the locality. In thin section the rock is seen to have an equigranular structure with grain-size of the order of 0.2 mm. Felspar is the chief mineral constituent. It makes up 85–90% of the rock, the other 10–15% being chiefly quartz and hornblende. The last is concentrated along gneissic bands in the rock; it is a green variety, strongly pleochroic, α pale greenish-yellow, β dark green, γ blue-green. Accessory minerals are plentiful, and include epidote, sphene, garnet, apatite, zircon, orthite, chlorite, biotite, and muscovite.

Two felspars are present—celsian and plagioclase; both are quite fresh, and practically indistinguishable under ordinary microscopic examination. The plagioclase is only rarely twinned, twin-laws observed being albite and pericline. The optic axial angle (2V) measured on the universal stage is 82°, with negative sign, and this, together with the high extinction-angle of the albite twins, indicates a composition of $An_{82}Ab_{18}$. This agrees with the specific gravity, 2.74, found

¹ W. R. Browne, Mem. Geol. Surv. N.S.W., 1922, no. 8, appendix 1, p. 337.

² S. R. Nockolds and E. G. Zies, Min. Mag., 1933, vol. 23, pp. 448–457.

by floating the powder in heavy solution of diluted methylene iodide. There is therefore no evidence to suggest that this might be a barium-bearing plagioclase comparable with that in some of the other rocks examined. During the examination of this slide on the universal stage, about one crystal in three was found, in a random survey, to be celsian. This amount of celsian would account for the total BaO content of the rock, namely 11.79%.

The celsian (pl. XIV, fig. 1) is perfectly clear, and never twinned. It commonly exhibits two perfect cleavages at 90°, fragments being perfectly rectangular in shape in broken parts of the section. The double refraction was determined in thin section by means of the Berek compensator, and the refractive indices determined in sodium-light by the immersion method; β was taken half-way between α and γ , 2V being nearly 90°. Other constants were measured on the universal stage:

$$\alpha \text{ 1.579, } \beta \text{ 1.583, } \gamma \text{ 1.588} \pm 0.001, \gamma - \alpha \text{ 0.010, } 2V \text{ 88}^\circ, \text{ negative, } \beta = b, \gamma : a = 28^\circ.$$

To obtain material for analysis the rock was crushed and the portion between -100 and -200 mesh was used. The plagioclase and quartz were floated off in slightly diluted methylene iodide. This operation was repeated twice on the heavy sample. After drying, the ferromagnesian minerals were removed from the celsian with the aid of an electromagnet. This yielded a fairly pure sample, contaminated with plagioclase, but very little else. An analysis of this sample is recorded under I in table 1. An attempt was made to determine BaO on the main fusion by recovering it from the Al_2O_3 and CaO, and precipitating the remainder as sulphate before MgO, but this was not successful. This method, as was indicated by some previous experimental work, tends to yield a BaO result several per cent. low. Therefore, another sample was separated yielding the result shown in II. This sample was richer in plagioclase. 0.3 gram was obtained altogether for the analysis.

TABLE 1. Analysis of celsian from Broken Hill, N.S.W.

	I.	II.	III.	IV.
SiO ₂	37.5	—	35.1	2.11
Al ₂ O ₃	27.8	—	26.8	1.89
Fe ₂ O ₃	nil	—	—	—
MgO	nil	—	—	—
CaO	2.3	4.8	—	—
BaO	(30.1)	24.6	35.8	0.84
Na ₂ O	0.4	—	—	—
K ₂ O	1.9	—	2.3	0.17
Loss on ign.	(0.9)	0.9	—	—
	100.9		100.0	

The calcium and sodium (evidently present as plagioclase) were calculated as constituents of anorthite and albite. This gave a plagioclase closely equivalent to that determined optically, namely An_4Ab_1 . The amount of BaO in column I was then calculated from II, and this figure (30.1%) is seen to yield a fairly satisfactory total. All the potash is reserved for the celsian, as basic plagioclases are poor in this constituent; in any case, in the presence of barium the potash would tend to go into the celsian. Column III will therefore approach very close to the actual composition of the felspar. Column IV gives the ratios of the metal ions, calculated with respect to O = 8.

Comparison of the Broken Hill celsian with that of other occurrences.

There have been published descriptions of celsian from Sweden, Italy, Alaska, Wales, Japan, and California. The optical properties, specific gravity, and essential parts of the chemical analyses of all these are listed in table 2, together with those of this new record from Broken Hill, N.S.W.

On examining table 2 it will be observed that at the celsian end of the celsian-potash-felspar series there are too few data available for determining the relation between optical properties and composition. Only occurrences IV, V, and VII have sufficient data to work upon. Tacconi's analysis lacks alkalis, as well as having a peculiarly high alumina content. This could possibly be due to the retention of some BaO by the alumina precipitate; the BaO, if determined on a separate sample, would not, of course, be affected.

The present occurrence will be seen to occupy, in regard to its composition, a position between IV and VII. It is therefore interesting to note that all the optical and physical properties of V also lie between those of IV and VII. When the properties of the Broken Hill celsian are plotted on Winchell's¹ or Yosimura's (loc. cit., p. 372) variation diagrams for Ba-K-felspars, little or no agreement is found. There seems to be no continuous variation of optical properties from the pure potash- to the pure barium-felspar as shown in Winchell's graph.

TABLE 2. Comparison with celsian from other localities.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO ₂ ...	32.43	32.68	33.9	32.23	35.1	35.06	38.48	—
Al ₂ O ₃ ...	26.55	27.28	25.6	27.40	26.8	30.23	23.61	—
BaO ...	39.72	38.94	37.7	36.45	35.8	34.38	25.50	—
Na ₂ O ...	0.16	nil	—	0.77	—	—	1.85	—
K ₂ O ...	0.22	0.18	—	0.22	2.3	—	5.10	—
2V ...	—	nearly 90°	close to 90°	86° 22'	88°	83° 39'	80.5°	77°
Sign ...	positive	positive	positive	positive	negative	positive	negative	positive
α ...	—	1.580	1.584	1.5835	1.579	1.592	1.564	1.590
β ...	—	—	1.589	1.5886	1.583	—	1.568	—
γ ...	—	1.590	1.596	1.5941	1.588	—	1.572	—
γ : α ...	—	28°	30°	28° 3'	28°	—	28-29°	28°
Sp. gr. ...	3.37	3.31	—	3.384	3.1-3.2	3.325	3.003	—

- I. Celsian, Jakobsberg, Sweden. H. Sjögren, Geol. För. Förh. Stockholm, 1895, vol. 17, p. 578.
- II. Celsian, Benallt mine, Rhiw, Wales. L. J. Spencer, Min. Mag., 1942, vol. 26, p. 236.
- III. Celsian, Alaska range, Alaska. W. T. Schaller, Amer. Min., 1929, vol. 14, p. 321. [M.A. 4-237.]
- IV. Celsian, Jakobsberg, Sweden. J. E. Standmark, Geol. För. Förh. Stockholm, 1903, vol. 25, p. 298.
- V. Celsian, 'The Piggery', Broken Hill, New South Wales.
- VI. Celsian, Candoglia, Piedmont, Italy. E. Tacconi, Zeits. Kryst. Min., 1907, vol. 43, p. 424; 1914, vol. 54, p. 388.
- VII. Kasoite, Kaso mine, Japan. T. Yosimura, Journ. Fac. Sci. Hokkaido Univ., Ser. 4, 1939, vol. 4, p. 380. [M.A. 7-412.]
- VIII. Celsian, Incline, Mariposa Co., California, A. F. Rogers, Amer. Min., 1932, vol. 17, p. 171. [M.A. 5-145.] The value for 2V was determined by the present author in a thin section on the universal stage.

¹ A. N. Winchell, Elements of optical mineralogy. 1933, p. 354.

Bragg¹ indicates that there is probably a change in the structure when a composition of about 15% BaO is reached. A break in properties at about this composition is indicated in Yosimura's diagram, and it seems that the relations of the members of this series can be best shown as two separate graphs. There is, however, need for additional accurate data (particularly towards the celsian end of the series) usefully to construct such diagrams. Yosimura's graph does not agree with the properties of the new celsian, and is based on data from very few occurrences. Much emphasis is also put upon the properties of kasoite, a mineral of peculiar composition, very deficient in silica. A re-examination of many of the occurrences with a view to obtaining more precise optical or chemical data is called for. Until then, it is hardly possible to establish a diagram which can with any accuracy represent the variation in properties with the composition of the celsian-potash-felspar series.

CALCIOCELSIAN.

The specimen (5081) containing calciocelsian is white in colour, containing only occasional patches and lenticles of biotite up to 2 cm. in length. It was collected within a few inches of the specimen containing ordinary celsian. It is an equigranular rock, the grain-size being about the same as the rock containing ordinary celsian, namely about 0.2 mm. Fine-grained irregular intergrowths of quartz and felspar are to be frequently seen. Felspar is the chief mineral constituent, making up about 90% of the rock. The rest is chiefly quartz, with a little biotite. Accessory minerals are apatite, magnetite, sphene, zircon, and orthite, the last altered, causing radial expansion cracks in the surrounding felspar. The biotite is the common red-brown variety with pleochroism α pale yellow, β and γ deep red-brown, and occasional pleochroic haloes. The felspars—plagioclase and calciocelsian—are both quite unaltered. The plagioclase is generally twinned, albite and pericline being the only twin-laws determined. The extinction-angle, α' : (010), of albite twins in section normal to the (001) cleavage is 43° , and the optic axial angle ($2V$), 80° , with negative sign. These agree quite well for plagioclase of the composition $An_{88}-An_{90}$.

The second felspar is a variety of celsian containing about 4% CaO. The name calciocelsian is suggested for this mineral as indicating its relationship to the parent mineral, and at the same time indicating the point at which the difference occurs. The mineral is virtually indistinguishable from the plagioclase in sections. Its presence was only discovered when it was found that a fraction of the crushed rock sinking in bromoform contained a much higher percentage of barium than the original rock. In thin section of the rock, however, most, possibly all, of the untwinned felspar is calciocelsian. It rarely shows cleavages, and so, owing to the lack of crystallographic directions, is readily overlooked, even on the universal stage.

For analysis and determination of properties a portion of the rock was crushed and sieved. Material between -100 and -200 mesh was separated with bromoform, the calciocelsian and heavy minerals sinking. This was repeated several times on the heavy fraction. The heavy minerals were then removed with an electromagnet, the remaining powder being used for the analysis. Material between 60 and 100 mesh was treated similarly, the powder here obtained being

¹ W. L. Bragg, *Atomic structure of minerals*. 1937, p. 239.

used for the determination of optical properties. A Canada-balsam mount of the powder was prepared for universal stage work. The properties thus obtained are set out and compared with other occurrences of celsian in table 3.

It can be seen from the table that the introduction of calcium into the celsian molecule, while not altering the orientation, has effected a considerable change in the optical properties, the change in 2V being the most striking. A very notable change in physical properties is the cleavage. While the celsian from this locality had two exceptionally clear cleavages in thin section, cleavages could only be occasionally seen in the grain mounts of the calciocelsian.

TABLE 3. Optical data of calciocelsian compared with those of celsian.

	I.	II.	III.
2V	86° 22'	88°	76°
Sign	positive	negative	negative
α	1.5835	1.579	1.572 \pm 0.001
β	1.5886	1.583	—
γ	1.5941	1.588	1.584 \pm 0.001
$\gamma : a$	28° 3'	28°	29°
	$\beta = b$	$\beta = b$	$\beta = b$
$\gamma - \alpha$	0.0106	0.010	0.012
Sp. gr.	3.384	3.1-3.2	—
Cleavages	(001), (010)	2 very perfect	2 distinct (on grains)

I. Celsian, Jakobsberg, Sweden. J. E. Strandmark, loc. cit., 1903.

II. Celsian, 'The Piggery', Broken Hill, New South Wales.

III. Calciocelsian, 'The Piggery', Broken Hill, New South Wales.

TABLE 4. Analyses of gneiss and calciocelsian.

	Rock.	Calciocelsian.	Metal ions.
SiO ₂	49.10	42.0	2.33
TiO ₂	0.17	—	—
Al ₂ O ₃	25.42	25.8	1.67
Fe ₂ O ₃	0.04	—	—
FeO	0.19	—	—
MnO	0.005	—	—
MgO	nil	—	—
BaO	14.72	25.8	0.56
CaO	7.65	4.0	0.24
Na ₂ O	1.68	0.3	0.03
K ₂ O	0.73	1.4	0.10
P ₂ O ₅	0.06	—	—
S	0.04	—	—
Cl	0.04	—	—
H ₂ O+	0.35	—	—
H ₂ O-	0.08	—	—
	<u>100.28</u>	<u>99.3</u>	

The chemical composition of the mineral is set out in table 4 together with the analysis of the lighter part of the gneiss. The deficiency of Ca, Ba, Na, K ions is to be accounted for by the solubility of the calcium oxalate. Small amounts only were obtained for analysis, and considerable volumes had to be taken to ensure separation from barium. The sample is considered to be free from

appreciable plagioclase. This is borne out by the increase of the $\text{CaO} : \text{Na}_2\text{O}$ ratio in the mineral analysis, and the unusual composition is reflected by the change in optical properties, particularly $2V$ and the refractive indices.

HYALOPHANE.

Hyalophane has been noted in two of the rocks collected, namely 5938 and 5945. The latter is a dark grey rock with occasional white veins running through it. It has the smooth weathered surface of many of the gneisses, owing to solution weathering. An analysis of the rock yielded 7.06% BaO, so that barium-felspars were searched for. The rock consists almost entirely of felspar, two of which are present—hyalophane and plagioclase—in about equal proportions. The plagioclase is a fine irregular intergrowth in patches in the hyalophane. Its refractive index is greater than that of the hyalophane; it is untwinned and has an optic axial angle ($2V$) of about 87° positive, indicating a composition in the region of $\text{An}_{70}\text{Ab}_{30}$.

The hyalophane occurs throughout the rock as a rather fine equigranular aggregate and it is clear, very rarely twinned or cleaved, looking remarkably like quartz (pl. XIV, figs. 2 and 3). It was identified by its low birefringence and low refractive indices, $2V$ 76° , and negative sign, and by the fact that only 0.96% BaO was found in the acid soluble portion of the rock, hyalophane being insoluble in acid.

Specimen 5938 is a coarser rock containing 4.64% BaO. It is white in colour, the chief accessory being black iron-ore, probably ilmenite. In this rock plagioclase of composition $\text{An}_{75}\text{Ab}_{25}$ predominates, quartz and hyalophane being less abundant.

The hyalophane forms crystal grains up to 1 mm. in diameter, not easily distinguishable at first sight from the quartz. It is occasionally intergrown in a micropertthitic fashion with plagioclase. It was distinguished by the same means as that in 5945, the optic axial angle ($2V$) measured on the universal stage being about 77° , negative. According to Winchell (loc. cit., p. 360) this would indicate a composition of about $\text{Or}_{75}\text{Cn}_{25}$. It was unfortunately found impossible to separate satisfactory material for analysis from either of the specimens.

BARIUM-PLAGIOCLASE.

A barium-plagioclase from this locality is the subject of a paper by S. R. Nockolds and E. G. Zies (loc. cit.). No comparable rock has been found in the series under examination; only one was found to have a similar barium content, and that was 5938 containing hyalophane. The relative BaO contents given by Nockolds and Zies for rock and felspar (4.8% and 5.7% respectively) are also peculiar in view of the fact that the rock contains only 50–60% felspar. However, certain of the rocks examined have a much lower barium content, and it would seem probable that in these cases the barium is contained in the plagioclase. A number of specimens were analysed; BaO contents were found in different specimens to be as follows: 5936, 2.22%; 5080A, 1.44%; 5934, 0.80%; 5935, 0.62%. About half these figures were obtained for the acid soluble portion of the analyses. The rocks generally contain about 20% quartz. The felspars in each case were similar in appearance, and only one or two will therefore be described.

Specimen 5936 is a moderately coarse rock with some quartz. It contains abundant sphene, often surrounding black iron-ore, probably ilmenite. Hornblende, biotite, chlorite, apatite, zircon, and zoisite are also present. The BaO content indicates that the felspar contains about 3% BaO. The felspar is generally twinned; albite and pericline were the only twin-laws determined. Optical properties determined by the immersion method in sodium-light and on the universal stage are:

$$\alpha \ 1.564, \gamma \ 1.573 \pm 0.001, \ 2V \ 89^\circ, \ \text{negative}, \ \alpha': (010) = 44^\circ.$$

The optic axial angle and extinction-angle indicate a composition of $An_{74}Ab_{26}$ and $An_{71}Ab_{29}$ respectively on the ordinary plagioclase variation diagrams of Chudoba.¹ The refractive indices are those of a normal plagioclase of this

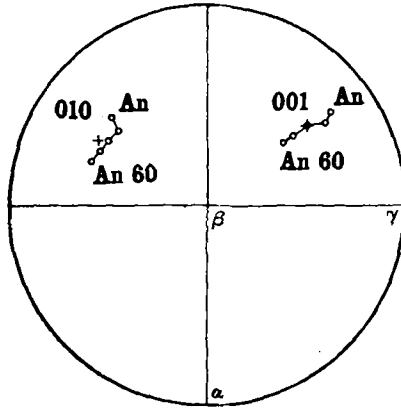


FIG. 1. Stereogram of the optic elements of plagioclase. Cleavage poles projected on to the plane normal to β (after Emmons). Positions of cleavage poles of the felspar of rock 5936 indicated by +.

composition. It will be seen from the stereographic projection of the elements of this plagioclase (text-fig. 1) that its optical orientation is quite normal (Emmon's² graphs being used), the cleavage poles falling close to An_{80} . This slight discrepancy in values could possibly be caused by the barium content of the felspar.

However, as the amount of the BaO present only represents about 7-8% of the celsian molecule in the felspar, it would not be safe to state definitely that the above variations are real. This is further enhanced by the fact that the orientation variation diagrams as given by different workers vary slightly, resulting in a variation band rather than line, this no doubt being due to the unknown effect of potash in the plagioclase series.

Specimen 5080A is a similar rock with only 1.44% BaO. The properties of the felspar are almost identical with the above, except that the optic axial angle ($2V$) was found to be 86° with negative sign. Numerous specimens were found to contain smaller amounts of BaO. The felspars in these, as would be expected, appeared quite normal plagioclases.

¹ K. Chudoba, The determination of the felspars in thin section. 1933. [M.A. 5-386.]

² R. C. Emmons, The universal stage. Mem. Geol. Soc. Amer., 1943, no. 8. [M.A. 9-18.]

In view of the appearance of hyalophane in some of the specimens, this mineral was searched for, on the possibility that the barium might be present in that form in the rocks of low BaO content, but it was not found.

Distribution of the barium-felspars with respect to the amount of barium present.

The different felspars into which the barium enters is of special interest when considered in relation to the total amount of barium present. It is not known to what extent barium can enter into the plagioclase framework; the open nature of the structure will, however, allow of a certain amount of replacement of calcium and sodium by the larger ion. The plagioclase structure is somewhat contracted as compared with the orthoclase structure, so that the introduction of barium over a small amount would render the framework unstable. As to how much barium could be introduced, there is no real data. Winchell (loc. cit., p. 319), with information from Alling,¹ has published a diagram of the miscibility fields of albite-orthoclase-anorthite. The miscibility field of orthoclase-anorthite is shown to be small, orthoclase entering into the anorthite molecule only to the extent of 5% at low temperatures, and rising to 14% at high temperatures.

The rocks at present under examination may be divided up into three groups:

(1) Those in which the barium has entered into the plagioclase structure. The BaO content of these varied from 0.62 to 2.22%.

(2) Those in which the barium has combined with the available potash to form hyalophane, this accompanying a normal plagioclase. The two specimens in this group contained 4.64 and 7.06% BaO respectively.

(3) Those of high barium content, which form celsian.

Rock no. 5936, containing 2.22% BaO consists chiefly of quartz, and allowing for the amount of mineral present, the plagioclase would contain about 8% of the celsian molecule.

Turning now to rocks of higher barium content, we see the next example (5938) contains 4.64% BaO, in this case as hyalophane. It would seem then, that at a certain maximum but low barium concentration, this ion cannot be further absorbed in the plagioclase structure, but immediately combines with potash present to form hyalophane. This change, then, apparently takes place somewhere in between a 3 and 5% BaO content of the total felspar molecules present. It seems probable, then, that basic plagioclases can only contain up to about 10% of the celsian molecule without radically altering the structure. It is reasonable to suppose that the celsian and orthoclase molecules would enter into the plagioclase structure in comparable amounts, owing to the similar ionic radii of Ba and K. It is therefore interesting to note the similarity between these figures, and those of Alling given above for anorthite-orthoclase mixtures.

Another consideration in respect to this is the amount of potash present. The assumption has been made above that enough potash would be present to form hyalophane. In the present case this condition appears to have been satisfied. If potash were lacking, the excess barium would either have to come out as celsian, or to remain in the plagioclase to a greater extent than intimated above.

The behaviour of the barium as it reaches higher concentrations is the more straightforward. A specimen containing 7.06% BaO was found to be rich in

¹ A. L. Alling, Journ. Geol. Chicago, 1921, vol. 29, p. 193. [M.A. 3-33.]

hyalophane, but on reaching 10% BaO celsian was found to be the barium-bearing mineral. This is what is to be expected in this series of gneisses rich in both barium and calcium. The increase of these two constituents would have to be at the expense of the alkalis, resulting in a K : Ba ratio too low for the formation of hyalophane. Celsian would, then, have to be formed.

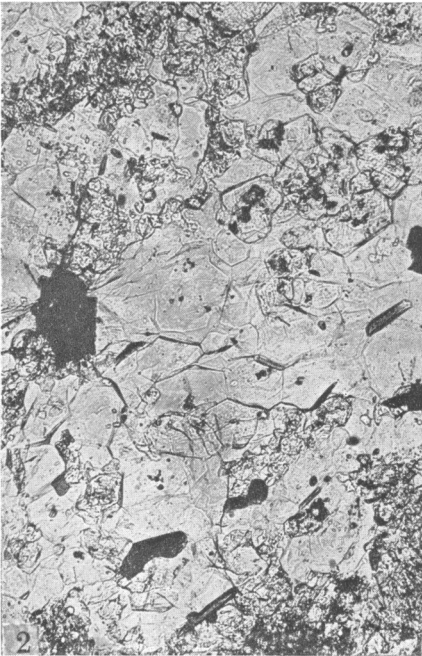
The position of the calciocelsian in this discussion is peculiar. Why and how it would form must have been dependent on special local conditions of composition. The high calcium content of the rock may have some bearing on the case. It is interesting to note, in connexion with this, the low diffusion limits, even in rather high grades of metamorphism. Garnet has been noted in a number of the specimens; the small diffusion at this grade is shown by the fact that the specimens containing celsian and calciocelsian were collected within a few inches.

The author is indebted to Mr. A. W. Kleeman, M.Sc., for useful suggestions and advice during the investigation, and to Mr. H. E. E. Brock for the photographs.

Summary.—A series of barium-rich gneisses has been examined with a view to finding the form into which barium enters into the mineral composition. Four barium-containing feldspars have been described, one being a new variety of the barium-feldspar celsian. The described minerals are celsian, calciocelsian, hyalophane, and barium-plagioclase.

EXPLANATION OF PLATE XIV.

- FIG. 1. Celsian, showing two perfect cleavages at 90°. Plagioclase, quartz, hornblende (dark), sphene (high-relief grains near hornblende), and apatite also present. Ordinary light. $\times 55$.
- FIG. 2. Hyalophane, clear and untwinned. The smaller turbid grains are chiefly untwinned plagioclase. Ordinary light. $\times 76$.
- FIG. 3. Same as fig. 2, crossed nicols. Shows zoning in some hyalophane crystals.
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E. R. SEGNI: BARIUM-FELSPARS FROM BROKEN HILL, NEW SOUTH WALES.