BARIUM FELDSPARS FROM BROKEN HILL, N.S.W.

M.Sc. THESIS.

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BARIUM FELDSPARS FROM BROKEN HILL, N.S.W.

At a locality known as The Piggery, on the outskirts of the township of Broken Hill, certain gneisses were found by   to contain a high percentage of barium. The present investigation was undertaken to ascertain the form in which the barium was present. The existence of barium feldspar at this spot has been known for some time, and is the subject of an investigation by S.R. Nockolds, who, however, evidently did not receive for examination specimens of the rocks richest in barium.

S.R. Nockolds, Min. Mag., Dec., 1933. Vol. 23, pp. 448 - 457.

The rocks under examination were light coloured gneiss containing up to 15% BaO.

The Barium was found to occur in four different feldspars, one being a new variety of celsian. The minerals studied were:-

celsian

Calcio-celsian

hyalophane

barium plagioclase

A careful search was made for other barium silicate minerals such as sanbornite, but none could be found.

CELSIAN.

This mineral was found in two specimens only, both collected from within a few feet 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 grainsize of the order of 0.2mm. Feldspar is the chief mineral constituent. It makes up 85 to 90% of the rock, the other 10 - 15% being chiefly quartz and hornblende. The latter is concentrated along gneissic bands in the rock. It is a green variety, strongly pleochroic X = pale greenish yellow, Y = dark green, Z = blue green. Accessory minerals are plentiful, and include epidote, sphene, garnet, apatite, zircon, orthite, chlorite, biotite and muscovite.

Two feldspars are present - celsian and plagioclase; both are quite fresh, and practically undistinguishable 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 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 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 optical properties are as stated below. Its 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 ½ way

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2V		-88°
RI	α	1.579 ± .001
	β	1.583
	γ	1.588 ± .001
D.R.		.010
$Z \wedge \alpha$		28°
Y = b		

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, with the aid of an electromagnet the ferromagnesian minerals were removed from the celsian. This yielded a fairly pure sample, contaminated with plagioclase, but very little else. An analysis of this sample is recorded as I in the table below. An attempt was made to determine BaO on the main fusion by recovering it from the Al_2O_3, the 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 to 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 grams were obtained altogether for the analysis.

	I	II	III	IV	
SiO_2	3.75	--	35.1	2.11)	4.00
Al_2O_3	27.8	--	26.8	1.89)	
Fe_2O_3	nil	--			
CaO	2.3	4.8			
MgO	nil	--			
BaO	(30.1)	24.6	35.8	.84)	1.01
K_2O	1.9	--	2.3	.17)	
Na_2O	.4	--			
Loss on ign.	(.9)	.9			
Total	100.9				

The calcium and soda (evidently present as plagioclase) were calculated as constituents of anorthite and albite. This gave a plagioclase closely equivalent to that determined optically, namely, An4 Ab1. The theoretical amount of BaO in column 1 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 feldspar.

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 Italy, Sweden, Alaska, Wales, Japan and California. The optical properties, specific gravity and essential parts of the chemical analyses of all these are listed below together with those of this new record from Broken Hill, N.S.W.

	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_2O_3	26.55	27.28	25.6	27.40	26.8	30.23	23.61	
BaO	39.72	38.94	37.75	37.45	35.8	34.38	25.50	
Na_2O	.16	nil	-	.77	-	-	1.85	
K_2O	.22	.18	-	.32	2.3	-	5.10	
2V		nearly 90°	close to 90°	86°22'	88°	88°39'	80.5°	77°
Sign		±ve	±ve	-ve	-ve	-ve	-ve	-ve
RI		1.580	1.584	1.5935	1.579	1.592	1.564	1.590
		- 1.590	1.589	1.5886	1.583		1.568	
		1.590	1.596	1.5941	1.588		1.572	
			30°		28°			28°
S.G.		3.31		3.384	3.3-3.2	3.325	3.003	

I. Celsian, Jakobsberg, H. Sjogren, Geol. For. Forh., Stockholm, 1895, Vol. 17, p. 578.

II. Celsian, Wales. L.J. Spencer, Min. Mag., 1942, Vol. 26, p. 236.

III. Celsian, Alaska. W.T. Schaller. Am. Min., 1929, Vol. 14, pp. 319-322.

IV. Celsian, Jakobsberg. J.E. Standmark, Geol. For. Forh., Stockholm, 1903, Vol. 25. p. 298.

V. Celsian, The Piggery, Broken Hill.

VI. Celsian, Italy. E. Tacconi, Zeit. Fur. Kryst. & Min., 1907, Vol 43, p. 4244, Vol. 4, p. 365.

VII. Kasoite, Japan. T. Yosimura, Journ. Fac. Sc., Hokkaido Univ., 1939, Ser. 4, Vol. 4, p.365.

VIII. Celsian, California, A.F. Roger, Am. Min. 1932, Vol. 17, p. 171.

No chemical analysis of the California occurrence is available. A universal stage measurement of 2V was made by the author on a thin section of a specimen from this locality.

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

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's (1) or Yosimura's (2) variation diagrams for

(1) Winchell - Elements of Optical Minerlaogy. 1933, p. 354.
(2) Yosimura, Op. Cit., p. 372.

Ba - K feldsaprs, little or no agreement is found. There seems to be no continuous variation of optical properties from the pure potash to the pure barium feldspar as shown in Winchell's Graph.

Bragg (3) indicated that there is probably a change in the structure

(3) Bragg, W.L. "Atomic Structure of Minerals", p.239.

when a composition of about 15% BaO is reached. A break in properties at about this composition is indicated in Yosimura's diagrams, 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 colsian end of the series) to usefully construct such diagrams. Yosimura's graph does not agree with the properties of the this 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 feldspar series.

CALCIO-CELSIAN.

The specimen (5081) containing calcio-celsian in white in colour, containing only occasional patches and lenticles of biotite up to 2cm. 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 .2mm. Fine grained irregular intergrowths of quartz and feldspar are to be frequently seen.

Feldspar 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 latter altered, causing radial expansion cracks in the surrounding feldspar.

The biotite is the common red brown variety with pleochroism X = pale yellow, Y = Z = deep red brown, and occasional pleochroic haloes

Two feldspars are again present - plagioclase and calcio-celsian - They are both quite unaltered.

The plagioclase is generally twinned, albite and pericline being the only types of twinning seen. The extinction angle of albite twins ($X' \wedge 010$) 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} to An_{90}.

The second feldspar 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 precentage of barium than the original rock.

In thin section of the rock, however, most, possibly all, of the untwinned feldspar is calcio-celsian. 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 calcio-celsian and heavy minerals sinking. This was repeated several times on the heavy fraction. The heavy minerals were then removed by electromagnet, the resulting powder being used for the analysis.

Material between 60 and 100 mesh was treated similarly, the powder here obtained being 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 below:

% Celsian Mol.		I	II	III
2V		86°22'	88°	76°
Sign		+ve	-ve	-ve
RI	α	1.5835	1.579	1.572 ± .001
	β	1.5886	1.583	
	γ	1.5941	1.588	1.584 ± .001
Z∧a			28°	29°
D.R.		.0106	.010	.012
S.G.		3.384	3.1-3.2	
Cleavages			2 very perfect	2 distinct (on grains)

I. Celsian, Jakobsberg. J.E. Strandmark

II. Celsian, The Piggery, Broken Hill.

III. Calciocelsion, The Piggery, Broken Hill.

The chemical composition of the mineral is set out below, together with the analysis of the lighter part of the gneiss.

	ROCK	CALCIOCELSIAN	METAL IONS.	
SiO_2	49.10	42.0	2.33	4.00
TiO_2	.17			
Al_2O_3	25.43	25.8	1.67	
Fe_2O_3	.04			
FeO	.19			
MnO	.005			
MgO	—			
CaO	7.65	4.0	.24	.93
Na_2O	1.68	.3	.3	
K_2O	.73	1.4	.10	
H20 +	.35			
H_2O -	.08			
P_2O_5	.06			
S	.04			
BaO	14.72	25.8	.56	
Cl	.04			
	100.28	99.8		

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 in the CaO:Na_2O ratio in the mineral analysis, and the unusual composition is reflected by the change in optical properties, particularly 2V and RI. The absence of clear cleavages in thin section, in contrast to the perfect cleavages of the Broken Hill celsian is a notable feature.

HYALOPHANE.

Hyalophane has been noted in two of the rocks collected, namely 5938 and 5945. 5945 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 feldspars were searched for.

The rock is almost entirely feldspar, two of which are present - hyalophane and plagioclase, in about equal proportions.

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.

It was identified by its low D.R., low R.I., 2V = 76° and negative sign, and by the fact that only .96% BaO was found in the acid soluble portion of the rock, hyalophane being insoluble in acid.

5938 is a coarser rock containing 4.64% BaO. It is white in colour, the chief accessory being ilmenite.

In this rock, plagioclase of composition $An_{75}Ab_{25}$ predominates, quartz and hyalophane being less abundant.

The hyalophane forms crystal grains up to 1mm. in diameter, not easily distinguishable at first sight from the quartz. It is occasionally intergrown in a microperthitic 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°. From Winchell's information this would indicate a composition of about $Or_{75}Cn_{25}$.

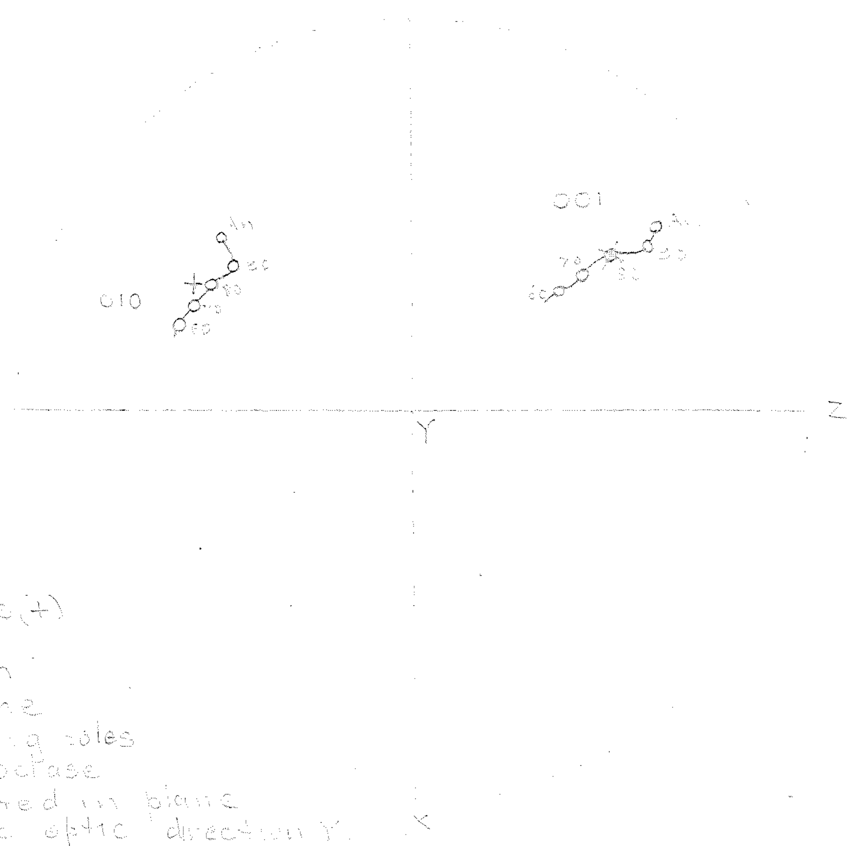
It was unfortunately found impossible to separate material for analysis from either of the specimens.

BARIUM PLAGIOCLASE.

A barium plagioclase from this locality is the subject of a paper by S.R. Nockolds. No comparable rock has been found in the series under examination; only one was found to have a similar barium content as Nockolds' rocks and that was 5938, containing hyalophane. The relative BaO contents of Nockolds' rock and feldspar (4.8% and 5.7% respectively) is also peculiar in view of the fact that the rock was only 50% - 60% feldspar. 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 2.22%, 1.44%, .80%, .68% and .64%, about half these figures being obtained for the acid soluble portion of the analyses. The feldspars in each case were similar in appearance, and only one or two will therefore be described.

No. 5936 contained 2.22% BaO. It is moderately coarse rock with not a great deal of quartz. It contains abundant sphene, often surrounding what is probably ilmenite. Hornblende, biotite, chlorite, apatite, zircon, and zoisite are also present.

The feldspar is generally twinned - albite and pericline were the only twin laws determined. The maximum extinction angle of the albite twins in section perpendicular to 010 was about 44°, while the optic axial angle was 89°, with negative sign. These indicate a compos-



Position of Cleavage poles (+) of the barium plagioclase in relation to the corresponding poles of the plagioclase series; oriented in plane normal to the optic direction Y.

ition of $An_{74}Ab_{26}$ and $An_{71}Ab_{29}$ respectively on the ordinary plagioclase variation diagrams of Chudoba. It will be seen from the stereographic projection of the elements of this plagioclase that its optical orientation is quite normal (Emmon's 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 feldspar.

However, as the amount of BaO present only represents about 7% - 8% of the celsian molecule in the feldspar, 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.

No. 5080 A is a similar rock with only 1.44% BaO. The properties of the feldspar 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 feldspars in these, as would be expected, appeared quite normal plagioclases.

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 was not found.

Distribution of the Barium feldspars with respect to the amount of barium Present.

The different feldspars 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. Alling 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 .64% to 2.22%.

(2) The barium has combined with potash present 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 formed celsian.

Rock No. 5936, containing 2.22% BaO is chiefly quartz, and allowing for the amount of this 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 feldspar 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 with 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 more straightforward. A specimen containing 7.06% BaO was found to be rich in hyalophane, but on reaching 10%, 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 as 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 should 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 connection 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 as this grade is shown by the fact that the specimens containing celsian and calciocelsian were collected within a few inches.

SUMMARY.

A series of barium rich gneisses have 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,

Barium plagioclase.