A ROENTGENOGRAPHIC METHOD FOR DETERMINING PLAGIOCLASES*

FERNAND CLAISSE
Department of Mines, Quebec, Canada.

ABSTRACT

A new *x*-ray diffraction method is described which permits the measurement of the Ab-An percentage composition of plagioclases to 1 or 2 per cent. The determination of line separation instead of absolute line position eliminates several sources of error, and enables the same calibration curves to be used by any laboratory. Several plagioclases of known composition were analyzed in this manner, and calibration curves are given. They indicate that plagioclases do not constitute a single isomorphic series, but rather two such series, with a transition point in the vicinity of Ab_2An_1.

Plagioclases may be considered as solid solutions of albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) the composition of which may vary from $Ab_{100}An_0$ to Ab_0An_{100}. This composition may be determined by various optical methods, but these are not accurate when the sample crystals have been altered, or when the sample is finely powdered.

Since the physical properties of solid solutions vary with their composition, a study of the latter by *x*-ray diffraction is theoretically possible and would overcome the difficulties of the optical methods. The positions of corresponding lines in the diffraction patterns of Ab and An (which crystallize in the same system and with unit cells which have approximately the same dimensions) will be shifted in complementary fashion as the composition of the plagioclase changes. However accurate measurement of these line positions is very difficult, and is subject to several errors, such as those due to eccentricity of the sample in the powder camera, and to film shrinkage during processing. Even when these are corrected the resulting accuracy is usually too low to make the determinations useful, and in general the calibration curves so obtained may not be of any use with other instruments.

In this laboratory, we have analyzed the composition of such solid solutions by measuring the distance between two adjacent lines in the diffraction pattern, instead of the absolute position of one line. This has resulted in much greater accuracy, and eliminates the errors due to sample eccentricity and film shrinkage. In addition, the calibration curves obtained with the powder camera are identical with those obtained with the spectrometer.

PROCEDURES

The percentage compositions of the eight plagioclases examined were first determined by various optical methods to about 1 per cent. The results are given in Table 1.

---

* Published by permission of the Deputy Minister, Department of Mines, Quebec.

TABLE 1. MINERALOGICAL ANALYSIS OF THE PLAGIOCLASES

Plagioclase	Mineralogical Collection	Locality	Composition	Optical Method
Albite	I.I.A.	Amelia Court House, Virginia,	$Ab_{99-100}An_{1-0}$ (a)	(a) Double variation
Pericline	Ward's	Teufelsmühle, Habachtal, Salzburg	$Ab_{91}An_{9}$ (b)	(b) Extinction angle on (010), α':[100]
Oligoclase	I.I.A.	Buckingham, Quebec	$Ab_{82}An_{18}$ (b)	(c) Fedorov
Oligoclase	....	Unknown	$Ab_{69-71}An_{31-29}$ (b)	
Andesine	Ward's	Kragerö, Norway	$Ab_{57}An_{43}$ (b, c)	
Labradorite	Ward's	Near Nain, Labrador	$Ab_{45}An_{55}$ (b)	
Bytownite	Ward's	Crystal Bay, Minnesota	$Ab_{22}An_{78}$ (c)	
Anorthite	I.I.A.	Miakejima, Japan	$Ab_{1-2}An_{99-98}$ (b)	

I.I.A. = Institute of Industrial Arts, Gardenvale, P.Q.

Diffraction patterns of the samples were then obtained in various ways. Three patterns of each sample were taken with a Norelco *x*-ray Diffraction Spectrometer, where the detection is performed by a Geiger-Müller counter with scaling circuit and mechanical register. Tube current and voltage for a copper target were 6 ma and 35 kv respectively. The source slit was 1.5×6 mm. while the detector slit was 0.25×6 mm. The first pattern was drawn by taking readings (counts/min.) every 0.01° as the counter was displaced. The second pattern was taken for 0.05° displacements. For the third pattern, the counter was displaced automatically at the rate of 1° per minute, while its output was recorded on a Brown Electronik potentiometer. Two additional diffraction patterns were taken of each sample using a Norelco 114.59 mm. diameter powder camera. Both copper (20 ma and 35 kv) and iron (15 ma and 30 kv) targets were used.

In examining the diffraction patterns taken of each sample, it was necessary to choose lines satisfying several requirements. They must be (a) prominent so as to be observable even when the sample is diluted; (b) easily recognizable; (c) in a high dispersion region of the pattern for accuracy of measurement; and (d) selected in at least two groups in case one should be masked by impurities. Such conditions are met by the two groups of lines chosen as indicated in Figs. 1 to 8. They are identified as follows:

	LINE	POSITION	RECOGNIZABLE CHARACTERISTIC
Group I	1	2.64 A	Strong line between two weak lines
	2	2.55–2.49 A	
	3	2.51–2.44 A	
Group II	4	1.83–1.82 A	Weak line between two strong lines.
	5	1.79 A	
	6	1.78–1.76 A	

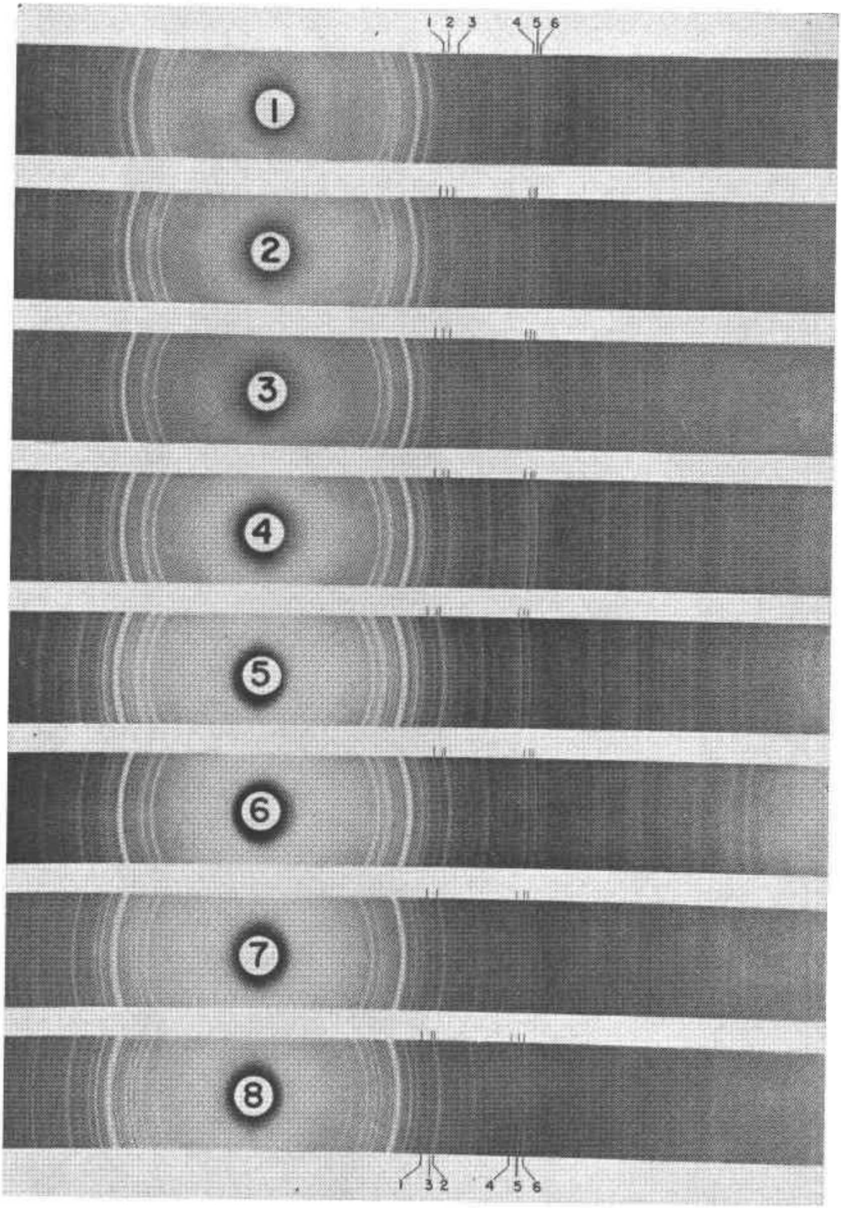

FIG. 1–8. *X*-ray diffraction pattern (Fe$K\alpha$) of a few plagioclases showing positions of the two groups of lines chosen. The inversion in the position of lines 2 and 3 in Fig. 8, following the overlapping of the same two lines in Fig. 7, is to be noted. 1. Albite. 2. Pericline. 3. Oligoclase. 4. Oligoclase. 5. Andesine. 6. Labradorite, 7. Bytownite, 8. Anorthite.

TABLE 2. DISTANCE* BETWEEN THE LINES 1, 2, AND 3 AS OBTAINED BY DIFFERENT MEANS

Plagioclase	Lines	Powder camera			Spectrometer			Average		
		Fe$K\alpha$	$\frac{\mathrm{Fe}K\alpha}{1.31}$†	Cu$K\alpha$	Motor 1°/m.	Manual .05 deg.	Manual .01 deg.	1–2	2–3	1–3
$Ab_{1-2}An_{99-98}$	1–2	2.75	2.10	(1.95)	2.10	2.08	2.11	2.10		
	2–3	−.38	−.29	(.00)	−.25	−.27	−.27		−.27	
	1–3	2.37	1.81	(1.95)	1.85	1.81	1.84			1.83
$Ab_{22}An_{78}$	1–2	2.50	1.91	1.88	1.90	1.87	1.86	1.88		
	2–3	.00	.00	.00	.00	.00	.04		.01	
	1–3	2.50	1.91	1.88	1.90	1.87	1.90			1.89
$Ab_{45}An_{55}$	1–2	2.23	1.70	1.69	1.80	1.70	1.69	1.72		
	2–3	.55	.42	.48	.45	.38	.38		.42	
	1–3	2.78	2.12	2.17	2.25	2.08	2.07			2.14
$Ab_{57}An_{43}$	1–2	2.08	1.59	1.62	1.55	1.57	1.57	1.58		
	2–3	.80	.61	.65	.60	.59	.57		.61	
	1–3	2.88	2.20	2.27	2.15	2.16	2.14			2.18
$Ab_{69-71}An_{31-29}$	1–2	2.00	1.53	1.52	1.60	1.53	1.55	1.55		
	2–3	1.00	.76	.80	.70	.73	.75		.75	
	1–3	3.00	2.29	2.32	2.30	2.26	2.29			2.30
$Ab_{82}An_{18}$	1–2	1.75	1.34	1.37	1.35	1.31	1.32	1.34		
	2–3	1.40	1.07	1.15	1.25	1.20	1.19		1.17	
	1–3	3.15	2.40	2.52	2.60	2.51	2.51			2.51
$Ab_{91}An_{9}$	1–2	1.60	1.22	1.18	1.20	1.20	1.20	1.20		
	2–3	1.90	1.45	1.45	1.35	1.42	1.44		1.42	
	1–3	3.50	2.67	2.63	2.55	2.62	2.64			2.62
$Ab_{99-100}An_{1-0}$	1–2	1.42	1.08	1.02	1.10	1.05	1.05	1.06		
	2–3	2.25	1.72	1.83	1.70	1.77	1.76		1.76	
	1–3	3.67	2.80	2.85	2.80	2.82	2.81			2.82

* The readings are in degrees 2θ.

† Ratio of the dispersion of iron radiation to that of copper radiation in this region.

The distances between the lines in each group were then accurately measured. For the first two diffraction patterns taken with the spectrometer, the counting rate was plotted as a function of counter position, and the distance between line peaks measured in degrees. For the third

TABLE 3. DISTANCE* BETWEEN THE LINES 4, 5, AND 6 AS OBTAINED BY DIFFERENT MEANS

Plagioclase	Lines	Powder camera			Spectrometer		Average		
		Fe*K*α	$\frac{\text{Fe}K\alpha}{1.35}$†	Cu*K*α	Motor 1°/m.	Manual .05 deg.	4–5	5–6	4–6
$Ab_{1-2}An_{99-98}$	4–5	1.58	1.17	1.15	1.20	1.15	1.17		
	5–6	1.25	.93	.98	1.00	.86		.94	
	4–6	2.83	2.10	2.13	2.20	2.01			2.11
$Ab_{22}An_{78}$	4–5	1.45	1.07	1.20	1.20	1.10	1.14		
	5–6	1.00	.74	.73	.70	.75		.73	
	4–6	2.45	1.81	1.93	1.90	1.85			1.87
$Ab_{45}An_{55}$	4–5	1.35	1.00	1.05	1.05	.99	1.02		
	5–6	.98	.73	.66	.70	.71		.70	
	4–6	2.33	1.72	1.71	1.75	1.70			1.72
$Ab_{57}An_{43}$	4–5	1.35	1.00	.97	.95	.87	.95		
	5–6	.80	.59	.62	.60	.65		.61	
	4–6	2.15	1.59	1.59	1.55	1.52			1.56
$Ab_{69-71}An_{31-29}$	4–5	1.29	.95	.95	.85	.89	.91		
	5–6	.80	.59	.55	.60	.59		.58	
	4–6	2.08	1.54	1.50	1.45	1.48			1.49
$Ab_{82}An_{18}$	4–5	1.10	.81	.83	.80	.82	.81		
	5–6	.85	.63	.55	.60	.59		.59	
	4–6	1.95	1.44	1.38	1.40	1.41			1.41
$Ab_{91}An_{9}$	4–5	1.00	.74	—	.75	.70	.73		
	5–6	.67	.50	—	.55	.55		.53	
	4–6	1.67	1.24	1.30	1.30	1.25			1.27
$Ab_{99-100}An_{1-0}$	4–5	.95	.70	—	.60	.65	.66		
	5–6	.70	.52	—	.60	.52		.54	
	4–6	1.65	1.22	1.22	1.20	1.17			1.20

* The readings are in degrees 2θ.

† Ratio of the dispersion of iron radiation to that of copper radiation in this region.

pattern, the distance between lines was measured directly on the Brown potentiometer chart. The films of the powder camera patterns were measured with a Norelco measuring box without magnification. The camera used was such that 1 mm. of film corresponded to 1° 2θ, so that conversion to degrees was simple. The distance between the lines for the two groups are given in Tables 2 and 3.

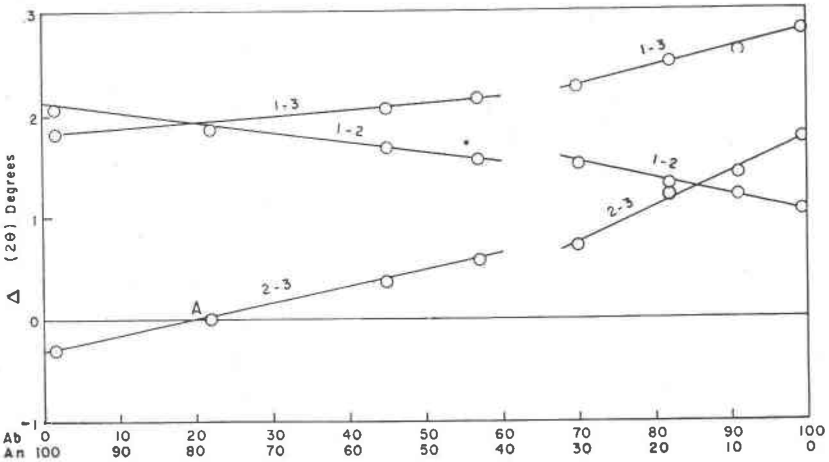

FIG. 9. Distance between lines 1, 2, and 3. These readings are those obtained by using the spectrometer and measuring the intensity of the diffracted rays every 0.05 degree 2θ. The other methods give essentially the same curves.

RESULTS

When the averages of the five measurements of the distances between the lines are plotted as a function of percentage composition, we obtain the curves such as those in Fig. 9 for the first group, and those of Fig. 10 for the second group. It is immediately obvious that the first set may be used to determine percentage composition with far more accuracy than is possible by absolute line position measurement. In particular, the dis-

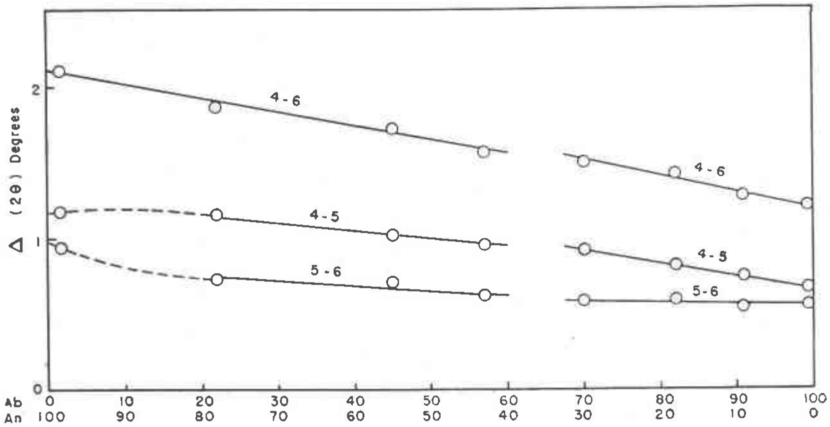

FIG. 10. Distance between lines 4, 5, and 6. These readings are the average of those obtained by different methods and given in Table 3.

tance between the lines 2 and 3 provides a very accurate index which may be obtained quite rapidly with any type of diffraction apparatus. The displacements are given in degrees, and hence these curves may be used in any laboratory.

TABLE 4. ACCURACY EXPECTED IN ANALYSING PLAGIOCLASES USING THE CURVES OF FIG. 1

Method	Absolute error	Curve	Accuracy*	
			$Ab_{100}\rightarrow Ab_{65}$	$Ab_{65}\rightarrow Ab_0$
	degrees		Percentage†	Percentage†
Powder camera, Cu target	±0.05	1–2	±2.9	±8.0
		1–3	3.1	5.3
		2–3	1.5	3.1
Powder camera, Fe target	.05	1–2	2.2	5.4
		1–3	2.6	4.1
		2–3	1.2	2.5
Spectrometer, manual, readings every 0.01 deg.	$.01_5$	1–2	0.9	2.4
		1–3	0.9	1.6
		2–3	0.5	0.9
Spectrometer, manual, readings every 0.05 deg.	.03	1–2	1.7	4.8
		1–3	1.9	3.3
		2–3	0.9	1.9
Spectrometer, motor 1° pm.	.05	1–2	2.9	8.0
		1–3	3.1	5.3
		2–3	1.5	3.1

* The accuracy is given for one measurement; it is greater when three measurements are made.

† Last figure uncertain.

Should lines 2 or 3 be masked by an impurity then one of the other curves of Fig. 9 will also give accurate composition data. However, since the lines 2 and 3 cross each other, the operator may not always be certain which one he is measuring, and consequently may have to choose between two accurate but ambiguous points equidistant from A for samples containing less than 40 per cent Ab (the minority). In this case the ambiguity is easily resolved by the curves of Fig. 10, which permit somewhat less accuracy but immediately indicate in which region of Fig. 9 the sample is located.

PRECISION

From Tables 2 and 3 it is seen that the results obtained by the five recording methods tested agree very well. The spectrometer is seen to be somewhat more accurate, and is also to be preferred for reasons of ease and rapidity of analysis. The greater slope of the curves in the high Ab content region, and the fact that most plagioclases are of this type is a fortunate coincidence. In our tests, the least precise results were obtained in measuring low Ab content samples with $\mathrm{Cu}K\alpha$ radiation in the powder camera.

Summarized in Table 4 are the accuracies which may be expected from the measurement of the distance between two lines by different methods, for two different parts of the percentage range. Should more than one distance be measured, the accuracy will be correspondingly greater, and in general it is possible to make a composition analysis to 1 per cent by this simple and rapid method.

NOTE ON PLAGIOCLASES

It has been pointed out by Taylor, Darbyshire & Strunz (1934) that plagioclases probably do not form a single isomorphous series from $Ab_{100}An_0$ to Ab_0An_{100}, but rather two such series. They base this on their observation that the *c*-axis of low Ab content plagioclases is twice that of high Ab content samples. They explain this by remarking that the dominant Na ion of albite is surrounded by only 6 oxygen atoms, while the dominant Ca ion of anorthite is probably surrounded by 7 or 8 oxygen atoms. This in turn leads them to believe that the transition point between the series will be around the Ab_1An_1 point, where the nature of the dominant atom changes.

However, if their explanation is correct, it seems to us that albite would more easily replace anorthite than vice versa, since the Na atom would find its 6 oxygen atoms in the anorthite structure more easily than the Ca atom could find 7 or 8 in the albite structure. In other words albite will be more soluble in anorthite than the reverse. By the same token the transition point of the two isomorphous series—from albite solutions to anorthite solutions—should not be at the Ab_1An_1 point, but rather displaced so as to show more albite solutions.

The lines of Figs. 9 and 10 all show breaks in the vicinity of 60–70 per cent albite. This supports the theory that two isomorphous series exist, and that their transition point is displaced towards albite.

Acknowledgments. The writer is glad to express his gratitude to Mr. A. O. Dufresne, deputy minister of Mines, for permission to publish this paper. He also gratefully acknowledges the assistance furnished by Mr.

J. Girault who made the optical analyses of the plagioclases used in this work.

REFERENCES

BUHLER, J. S. (1945*a*): Engineering-design development of *x*-ray spectrometer—*Electrical Manufacturing*, **35,** No. 6.

—— (1945*b*): Process quality control with *x*-ray spectrometer—*Instrumentation*, **1,** No. 6.

FRIEDMAN, G. (1945): Geiger-counter spectrometer for industrial research—*Electronics*, **18,** 132–137.

TAYLOR, W. H., DARBYSHIRE, J. A. & STRUNZ, H. (1934): An x-ray investigation of the feldspars—*Zeits. Krist.*, **87,** 482–487.