$An_{60}Ab_{40}$ glass $Ca_{.6}Na_{.4}Al_{1.6}Si_{2.4}O_8$ plus FeO .001

	% ANAB		
	Element	Oxide	Oxide % calc. from formula
Na	.0337	.046	.0454
Ca	.0883	.125	.1235
Al	.1585	.300	.2994
Si	.2480	.524	.5305
Fe	.00064	.0010	.00082
Oxygen	.4709	-	-
Total	1.0000	.996	1.0000

Z = 11.453

A3

ALBITE, TIBURON, CA $An_{.2}Or_{.5}$

	% TAB	
	Element	Oxide
Na	.087	.117
K	.0008	.00096
Ca	.0003	.00042
Si	.3213	.6873
Al	.1029	.1944
Oxygen	.4877	-
Total	1.0000	1.0000

Z = 10.716

D3

ORTHOCLASE (Ingamells)

% ORTH

	Element	Oxide
Si	.3010	.6439
Al	.0983	.1858
Fe	.0002	.0003
Sr	.00029	.00035
Ba	.0073	.0082
Na	.0085	.0114
K	.1239	.1492
Rb	.0003	.0003
Oxygen	.4602	-
Total	1.0000	1.0000

$Z = 12.057$

C3

ANORTHITE, An_{100} glass $CaAl_2Si_2O_8$

% AN

large grain 2-8-63; 2 small grains 2-4-63

	Element	Oxide
Ca	.1441	.2016
Al	.1940	.3665
Si	.2019	.4319
Oxygen	.4599	-
Total	1.0000	1.0000

$Z = 11.910$

J. A. SPEER

P.H. Ribbe 10

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X-RAY-EMISSION MICROANALYSIS OF ROCK-FORMING MINERALS

IV. PLAGIOCLASE FELDSPARS[1]

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ABSTRACT

Forty-two chemically analyzed and eleven synthetic plagioclase feldspars have been analyzed by microprobe X-ray-emission methods for sodium, magnesium, aluminum, silicon, phosphorus, potassium, calcium, titanium, manganese, iron, strontium, cesium, and barium. The highest concentrations (weight per cent) of the minor elements are: phosphorus, 0.11; potassium, 0.55; titanium, 0.04; iron, 0.53; strontium, 0.13. Magnesium, manganese, cesium, and barium were not detected at the 0.02 wt. per cent level, although barium was found in intergrown potassium feldspar. With a few exceptions, phosphorus, potassium, titanium, and iron were found at lower levels than those given by bulk chemical analyses, as might be expected from the occurrence of inclusions in many specimens. Strontium analyses for one suite of specimens showed a systematic bias, probably attributable to a calibration error in the optical spectrographic technique. Major elements were referred to synthetic plagioclase glasses and to devitrified synthetic albite as standards. For sodic plagioclases (especially glasses) it was necessary to use either low counting rates or wide electron beams to reduce alkali loss. Microprobe and chemical analyses for calcium show a good, almost unbiased, correlation, but for sodium they have a poor correlation, microprobe results tending to be higher than chemical. Microprobe analyses of aluminum and silicon tend to be lower and higher, respectively, than chemical analyses. Only three of forty analyses yield oxide totals outside the 99.0–101.0 per cent range, but totals of feldspar molecules calculated from sodium, potassium, calcium, and strontium have a wider range, 97.5–102.5 per cent, with thirty-three between 99 and 101 per cent. The average iron content increases with calcium as expected from the increasing Al^{3+} sites and the generally higher temperatures of formation of calcic plagioclases. Strontium and potassium reach their highest concentrations in the range An_{20}–An_{40}.

INTRODUCTION

This paper is the fourth in a series on the X-ray-emission microanalysis of rock-forming minerals. Part I (Smith, 1965) describes the theoretical approaches and experimental methods; Parts II (Smith, 1966) and III (Smith and Ribbe, 1966) describe microprobe analyses of olivines and alkali feldspars. In keeping with the rationale of the program, Part IV compares microprobe and chemical analyses of yet another mineral series, the plagioclase feldspars, seeking to establish calibration curves and appropriate correction factors for the microprobe analyses and to detect inaccuracies in either analytical method.

To accomplish this, forty-two chemically analyzed plagioclases and eleven synthetic glasses at 10 mole per cent intervals over the range $Ab_{100}An_{0}$–$Ab_{0}An_{100}$ were carefully analyzed using an ARL electron microprobe. Contributors of these specimens and references are listed in table 1.

TECHNIQUE

A representative sample of grains from each specimen was mounted with epoxy cement in a brass disk and polished by standard methods. The disks containing all specimens were simultaneously sputtered with a thin, conductive carbon coat. Five to ten grains of each specimen were analyzed for the major elements and at least two for the minor elements. When significant differences were found for the minor elements, more spots were analyzed. The experimental conditions are similar to those for the alkali feldspars, and the correction factors have already been described in Part III (see particularly tables 2 and 3). A few additional remarks will appear later.

DISCUSSION

It is convenient to examine the analyses of each element in turn, attempting to establish thereby the relative accuracies and

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limitations of X-ray emission and chemical methods and seeking suitable calibration curves and correction factors. In relating X-ray counts to the chemical analysis of each major element, it has been necessary first to apply a small correction factor for minor elements, thus deriving the corresponding counting rate for a feldspar lying at the nearest point on the ideal binary join $NaAlSi_3O_8$–$CaAl_2Si_2O_8$. The factors were derived from table 3, *B*, of Part III and were usually within 1 per cent of unity. After establishment of calibration curves using factors from table 3, *A*, of Part III, analyses for the major elements were derived graphically. For the minor elements, analyses were numerically determined. Table 2 shows the resulting elemental analyses; the oxide per-

TABLE 1

SPECIMENS, CONTRIBUTORS, AND REFERENCES FOR ANALYZED PLAGIOCLASES

Sample	Contributor	Reference	Comments
E1–E32.	R. C. Emmons	Emmons (1953)	E2, 3, 4, 5 contain quartz estimated from the chemical analysis to amount to 3, 5, 19, 35 per cent excess SiO_2
All KN specimens.	H. S. Yoder	Kracek and Neuvonen (1952)	
Haddam.	S. W. Bailey	Jeffries (1936)	Peristerites—unmixing on a submicron scale
Monteagle Township Villeneuve Monteagle Valley . .	S. W. Bailey	Meen (1933)	Peristerites—unmixing on a submicron scale
BM1940, 27.	P. M. Game	Game (1949)	Peristerites—unmixing on a submicron scale
Howie 2270 Howie 464ZA	R. A. Howie	Howie (1955)	
Lambert RB561 Lambert RB579	P. Gay	Lambert (1959)	Unanalyzed, but compositions determined optically are An_{31} and An_{32}
SK4145 SK4272	P. Gay	Gay and Muir (1962)	Zoned
EH201 EH20	I. D. Muir	Muir (1955)	Zoned
H92 G98	I. S. E. Carmichael	Carmichael (1964)	Zoned (see fig. 5)
Juvinas.	P. Gay	Game (1957)	From Juvinas meteorite
Anorthite (Japan).	J. R. Goldsmith	. . . .	Unanalyzed
Hakone 1 Hakone 3	P. Gay	Kuno (1950)	
Miyake 99.	P. Gay	Gay (1953)	Unanalyzed
Synthetic glasses	D. Lindsley	. . . .	Assumed stoichiometric*

* Prepared by repeated fusion at 1,525–1,535° C. (1,625° for anorthite) from weighed amounts of Lisbon, Md., quartz inverted at 1,520° C., Baker's lot 19641 $CaCO_3$, Fisher's lot 723140 $NaHCO_3$ and Al_2O_3 made from 99.999 per cent aluminum wire. Spectroscopic analysis of the Al_2O_3 showed silicon 0.050 per cent, iron 0.015 per cent, sodium and potassium 0.000 per cent.

centages calculated using expected valences; the percentages of feldspar molecules calculated from sodium, calcium, potassium, and strontium; and the atomic proportions. Table 3 lists the atomic contents recalculated to thirty-two oxygen atoms and the molecular percentages of Or, Ab, An, Cn, and Sr-F recalculated to 100 per cent in the standard manner of recording used by Deer, Howie, and Zussman (1963).

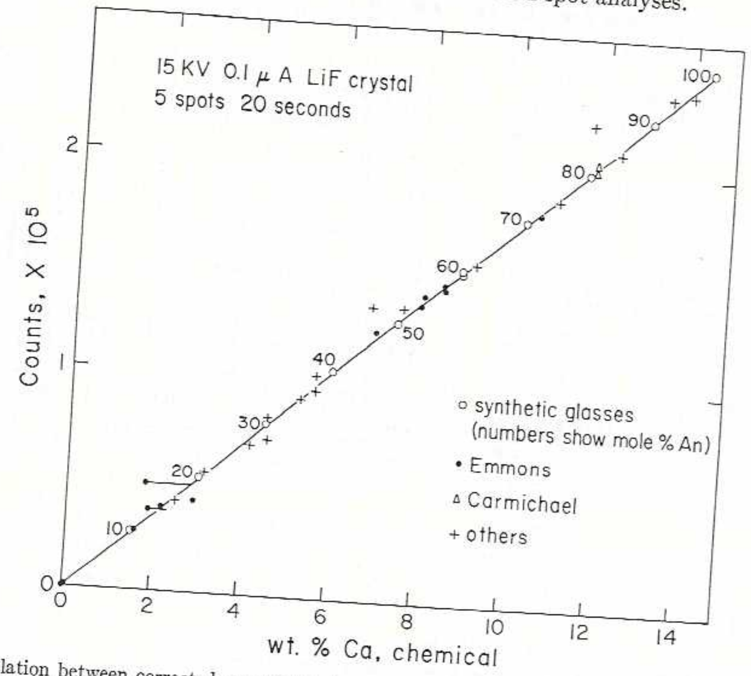

FIG. 1.—Relation between corrected, accumulated counts and weight per cent calcium determined by gravimetric analysis for natural specimens or by weighing for synthetic samples. Correction was made by applying the factors of table 3B of Part III to the estimates of minor elements in order to change the accumulated counts to those for a binary sodium, calcium feldspar. The shape of the calibration curve was calculated by applying the factors of table 3A to a linear relation, and the curve was adjusted to pass through the datum for synthetic anorthite. The horizontal lines for Emmons 4 and 5 are corrections for the presence of quartz on the bulk sample which was analyzed chemically (see table 1).

MAJOR ELEMENTS

Calcium.—Two sets of analyses for calcium were made, the first in conjunction with aluminum and silicon and the second with sodium and barium. Figure 1 shows the relation for the first set between corrected, accumulated counts for calcium versus the chemical determination, while figure 2 shows the relation between the corrected, accumulated counts for the second set and the average calcium content derived from the calibration curve of figure 1. About one-quarter of the specimens show zoning of 5 per cent An or greater, thus making it difficult to obtain a good estimate of bulk composition from spot analyses.

In order to prove that the variations of counting rate for some samples displayed in figure 2 were caused by chemical zoning, plots were made between simultaneous spot measurements of sodium and calcium. Two such plots are superimposed in figure 3 for ten spots each from specimens G98 and H92. The deviations from the best straight line can be explained almost entirely by statistical counting fluctuations. For the homogeneous specimens (including the syn-

TABLE 2—*Continued*

WEIGHT PER CENT MOLECULES					ATOMIC PROPORTIONS												SPECIMEN
An^{II}	Or	Ab	Sr-F	Total	Si	Ti+P	Al	Fe	Sr	Ca Mean	K	Na	Si$_{calc}$‡	Δ_1§	Al$_{calc}$‖	Δ_2#	
0.0	0.3	100.0	0.0	100.3	1,159	4	390	0	0	0	1	381	1,146	+ 17	382	+ 8	E1
0.2	0.6	98.2	0.0	99.0	1,141	3	389	0	0	1	2	375	1,131	+ 13	379	+ 10	E30
0.1	0.8	99.4	0.0	100.3	1,143	0	382	0	0	0	3	379	1,143	0	382	0	Amelia (KN)
7.6	1.3	91.6	0.0	100.5	1,111	0	402	2	0	27	4	349	1,113	− 2	407	− 3	Monteagle Township
8.9	N.d.	91.5	N.d.	100.4+	1,114	N.d.	411	N.d.	N.d.	32	N.d.	349	1,111+	+ 3	413	− 2	Haddam
9.7	0.9	89.7	0.0	100.3	1,100	0	412	0	0	35	4	342	1,104	− 4	416	− 4	Villeneuve
10.0	0.6	87.3	0.1	98.0	1,102	0	419	1	0	36	2	333	1,111	− 9	407	+ 13	BM1940, 27
10.4	0.4	89.9	0.1	100.8	1,105	0	421	1	0	39	1	343	1,110	− 5	422	0	E2
12.4	1.2	87.1	0.1	100.8	......	0	.....	2	0	44	4	332	1,096	......	424	......	Monteagle Valley
16.0	1.3	82.0	0.1	99.4	1,081	0	437	0	0	56	4	313	1,063	+ 18	429	+ 8	E4
15.5	0.9	83.5	0.1	100.0	1,078	0	437	1	0	56	3	318	1,075	+ 3	433	+ 5	E3
17.0	2.0	81.4	0.2	100.6	1,084	0	436	1	1	61	7	311	1,072	+ 12	442	− 5	81822 (KN)
17.0	3.9	80.1	0.2	101.2	1,059	0	435	1	1	61	14	305	1,081	− 22	443	− 7	E32
19.4	1.4	76.9	0.1	97.8	1,047	0	449	1	0	71	5	293	1,036	+ 11	440	+ 10	E5
21.5	3.6	77.3	0.1	102.5	1,062	0	456	1	0	79	13	295	1,082	− 20	466	− 9	80165 (KN)
28.2	3.5	68.4	0.5	100.6	1,026	0	469	1	1	101	12	261	1,023	+ 3	477	− 7	97490 (KN)
29.4	2.8	66.2	0.3	98.7	1,009	0	469	2	1	105	10	252	998	+ 11	474	− 3	Howie 2270
30.4	0.6	68.8	N.d.	99.8+	1,021	0	481	2	1	110	2	262	1,014	+ 7	486	− 5	Lambert RB561
30.9	1.6	68.2	0.4	101.1	1,015	0	485	1	1	112	6	260	1,024	− 9	492	− 6	Lambert RB579
33.6	1.7	65.7	0.2	101.2	1,016	0	491	1	1	120	6	251	1,013	+ 3	499	− 7	Howie S347
35.7	2.7	60.9	0.2	99.5	998	0	481	6	1	130	10	232	988	+ 10	504	− 17	SK4145
38.5	2.1	58.9	0.2	99.7	981	1	497	6	1	138	8	224	974	+ 8	510	− 7	SK4272
41.4	1.8	55.8	0.1	99.1	981	1	511	1	0	148	6	213	953	+ 29	515	− 3	Howie 4642A
47.8	2.7	47.7	0.3	98.5	931	0	547	2	1	175	10	182	928	+ 3	544	+ 5	E9
50.7	1.9	47.2	0.2	100.0	918	1	553	6	1	188	7	180	939	− 20	565	− 6	EH201
52.5	1.9	45.9	0.1	100.4	922	1	553	6	0	192	7	175	930	− 7	566	− 7	EH20
55.5	0.5	42.8	0.2	99.0	907	1	571	1	1	198	2	163	893	+ 15	563	+ 9	E13
55.2	0.4	42.9	0.2	98.7	904	0	574	2	1	201	1	164	899	+ 5	569	+ 7	E12
59.0	0.6	40.0	0.3	99.9	897	0	581	1	1	210	2	153	887	+ 10	577	+ 5	E16
56.9	0.4	41.5	0.3	99.1	901	0	588	3	1	208	1	158	895	+ 6	577	+ 9	E14
62.5	0.7	35.7	0.2	98.9	881	1	579	6	1	225	2	136	866	+ 16	590	− 5	Clear Lake
70.3	0.4	27.6	0.0	98.3	......	0	.....	5	0	253	1	105	824	......	612	......	Crystal Bay (KN)
72.1	0.0	26.5	0.3	98.9	830	0	627	2	1	260	0	101	825	+ 5	623	+ 6	E23
75.5	1.1	23.5	0.1	100.2	824	0	631	2	0	272	4	90	826	− 2	638	− 5	7510 (KN)
81.1	0.3	19.3	0.1	100.8	790	0	646	9	0	292	1	74	809	− 19	659	− 4	H92
80.1	0.2	20.1	0.1	100.5	781	0	645	9	0	293	1	77	820	− 39	660	− 6	G98
84.7	0.4	14.6	0.0	99.7	785	0	658	5	0	305	2	56	784	+ 1	658	+ 15	EB18 (KN)
90.6	0.1	6.8	N.d.	97.5	767	N.d.	671	N.d.	N.d.	324	1	26	729	+ 38	675	− 4	Juvinas
94.3	N.d.	4.9	0.1	99.3	748	0	685	9	0	337	N.d.	19	731	+ 17	693	+ 1	Anorthite (Japan)
95.4	0.0	3.8	0.1	99.3	744	0	686	7	0	343	0	14	728	+ 16	700	− 7	Hakone 1
95.8	0.0	2.6	0.3	98.7	737	0	691	8	1	344	0	10	718	+ 21	700	− 1	Hakone 3
95.1	0.0	3.1	0.1	98.3	740	0	692	7	0	344	0	12	724	+ 16	700	− 1	Miyake 99
0.0	.....	56.5	......	56.5	1,187	0	407	1	0	0	0	215	645	+542	215	(+193)	An_{0} glass
11.0	.....	47.9	......	58.9	1,160	0	447	1	0	39	0	183	627	+533	261	(+187)	An_{10} glass
21.5	.....	50.6	......	72.1	1,098	0	481	1	0	77	N.d.	193	733	+365	347	(+135)	An_{20} glass
31.7	.....	53.5	......	95.2	1,032	0	501	1	0	114	N.d.	204	740	+292	432	(+ 70)	An_{30} glass
41.9	.....	57.1	......	99.0	968	0	526	0	0	151	N.d.	218	956	+ 12	520	(+ 6)	An_{40} glass
52.1	.....	48.6	......	100.7	926	0	554	1	0	186	0	185	927	− 1	557	− 2	An_{50} glass
61.4	.....	38.6	......	100.0	872	0	588	1	0	222	N.d.	147	885	− 13	591	− 2	An_{60} glass
71.3	.....	28.6	......	99.9	838	0	618	1	0	257	N.d.	109	841	− 3	623	− 4	An_{70} glass
80.8	.....	18.3	......	99.1	801	0	651	1	0	291	N.d.	70	792	+ 9	652	0	An_{80} glass
90.7	.....	8.9	......	99.6	755	0	687	1	0	326	N.d.	34	754	+ 1	686	+ 2	An_{90} glass
99.8	.....	0.0	......	99.8	719	0	718	1	0	359	0	0	718	+ 1	718	+ 1	An_{100} glass

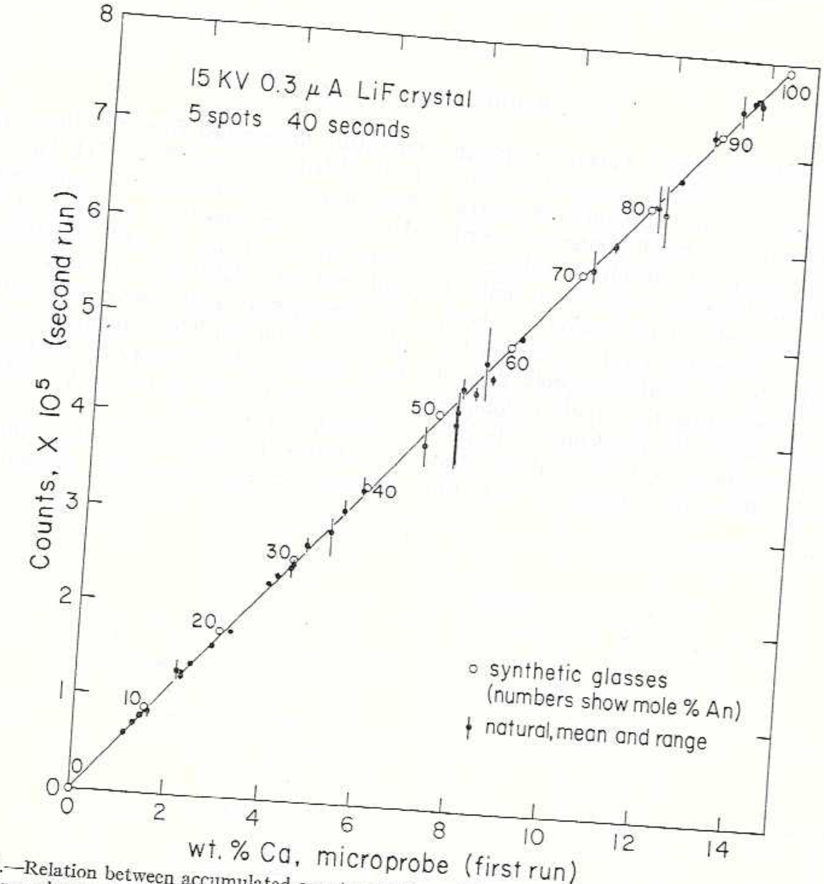

FIG. 2.—Relation between accumulated counts and the weight per cent calcium deduced from the first set of microprobe results shown in fig. 1.

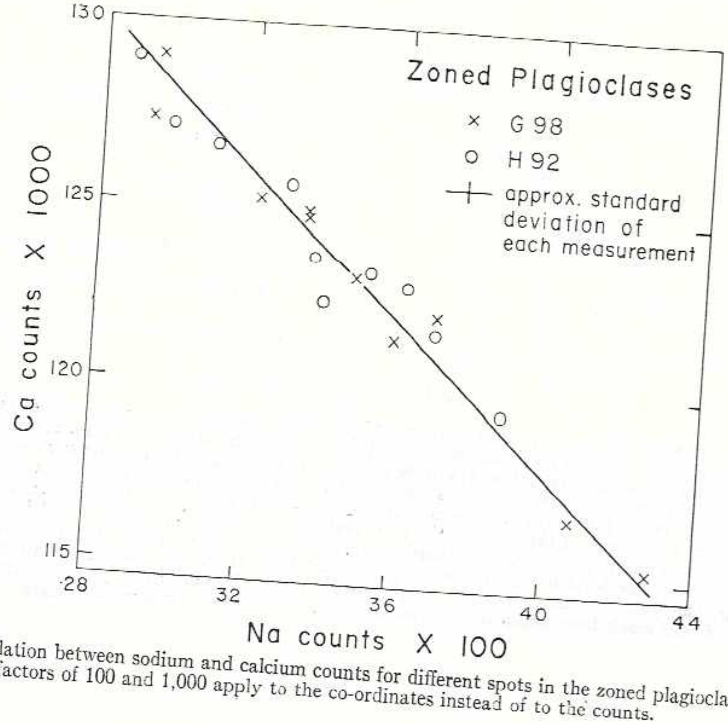

FIG. 3.—Relation between sodium and calcium counts for different spots in the zoned plagioclases G98 and H92. The factors of 100 and 1,000 apply to the co-ordinates instead of to the counts.

counts and the weight per cent determined chemically. Because no preamplifier was fitted then to the counter, extraneous signals were detected, making it inadvisable to lower the beam current below 0.3 μa. Using a 20–50-μ electron-beam diameter, no volatilization of sodium was recorded for crystalline plagioclases, but the synthetic sodic glasses suffered severe reduction in the counting rate. Figure 5 shows the relation between the counting rate for sodium, aluminum, and silicon for the synthetic albite glass for which the counts were collected in successive 30-sec. periods for a total of 5 min. The initial fall of the sodium readings, together with the small increase in the aluminum and silicon counting rate, can be explained by volatilization of sodium, with a corresponding increase of the aluminum and silicon, which are assumed to be involatile. A pit can be seen to form and grow larger at the impact area of the electron beam. (The increased absorption of the emerging X-rays would explain the low oxide total in table 2 for the synthetic albite.) The later reversal in the trends is hard to explain unless sodium diffuses from the body of the albite to concentrate in the region of primary X-ray excitation. No attempt has been made thus far to systematically study this phenomenon as a function of beam loading, but various scattered measurements have suggested that in alkali feldspars, as the beam loading increases from a level for which no significant variation occurs in repeated analyses, both increasing and decreasing counting rates can be obtained. Measurements of potassium X-rays in alkali feldspars just above the critical beam loading have indicated a small increase followed by a prolonged decrease. Consequently, it is advisable to analyze at least three times at each spot of alkali feldspars and sodic plagioclases in order to test for anomalous counting rates. Alkali-bearing glasses are very unstable in the electron beam, and it is necessary to use very low beam currents (0.005 μa) on fine spots (~ 1–5 μ) in order to obtain steady readings. Calcium stabilizes the feldspar glasses such that those above An_{40} are immune to beam damage for reasonable beam currents.

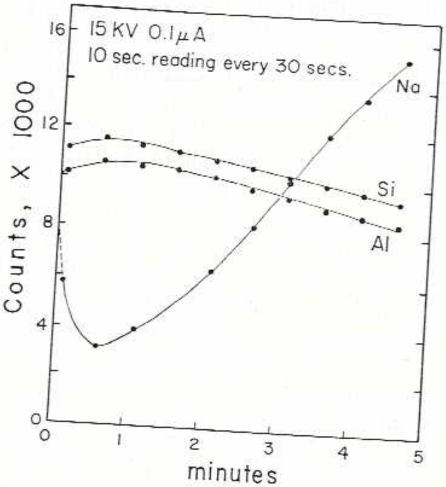

FIG. 5.—The variation of X-ray output of sodium, aluminum, and silicon using a small spot and a 15-kv. and 0.1 μamp electron beam. Readings were made for 10 sec. every 30 sec. and plotted at the midpoint of each counting period.

In order to provide a more stable standard for albite, samples of the glass were crystallized hydrothermally in open and sealed tubes and analyzed with respect to natural albites. By this means, they were referred to the other specimens which had been analyzed at an earlier time. The crystals grown in a sealed tube were rather small (~ 5–20 μ), and it was necessary to use a beam focused to 5–10-μ diameter and to extrapolate all readings to zero time to correct for a small reduction of the counting rate during analysis. The crystals grown in an open tube were large, but it was feared that some alkali might have been leached away. However, the counting rate for the latter was about 2.0 per cent higher than for the former, a difference greater than the statistical counting error of about 0.5 per cent. The calculated factor for sodium in An referred to an Ab standard, based on the data of Part I, is 1.06. It was not possible to prepare a suitable calibration curve using this factor; it was therefore decided to use a factor of 1.10 and to draw the curve through the mean of the two sets of data for syn-

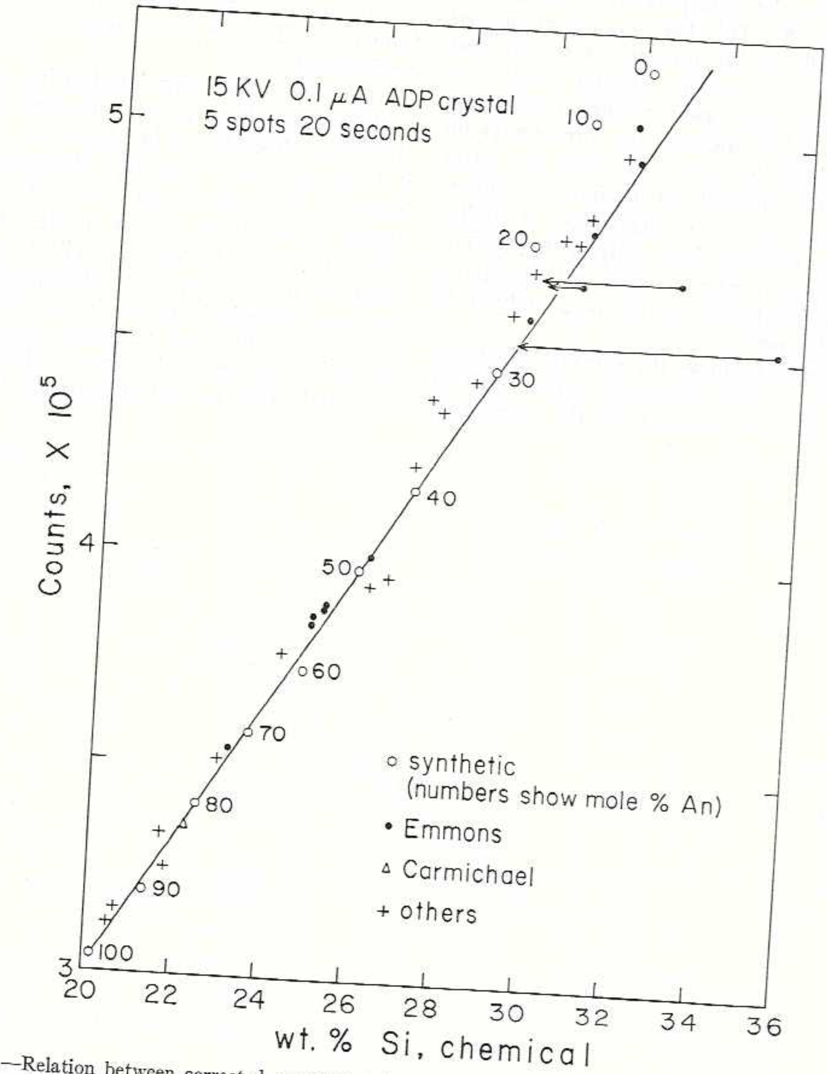

FIG. 6.—Relation between corrected, accumulated counts and weight per cent silicon determined by chemical analysis for natural specimens or by weighing for synthetic samples. The correction was made by applying the factors of table 3B of Part III to the estimates of minor elements in order to change the accumulated counts to those for a binary sodium, calcium feldspar. The shape of the calibration curve was calculated by applying the factors of table 3A to a linear relation, and the curve was adjusted to pass through the datum for synthetic anorthite. The horizontal lines for three of the Emmons specimens show corrections for the presence of excess silica arising from quartz impurity in the samples analyzed chemically. The deviations for the sodic synthetic specimens arise from damage as shown in fig. 5.

have a systematic bias, being about twice as high as the microprobe analyses. Because the generation and absorption of X-rays in alkali and plagioclase feldspars are similar and the agreement with the Carmichael data is good, it seems reasonable to ascribe a systematic error to the analyses of the Emmons specimens. Figure 10 demonstrates that strontium content, like the potassium content, increases with increasing sodium to a maximum in the range An_{40-20} and is small for the albites. Anorthoclase (Part III) may carry large amounts of strontium. There is no obvious crystal-chemical explanation for the relation between strontium and sodium contents, but it is noteworthy that there is no direct correlation between strontium and potassium contents in plagioclase in spite of the afore-mentioned parallelism.

Barium and cesium.—These elements were not detected at the 0.02 wt. per cent level, although Harrison and Miller (Em-

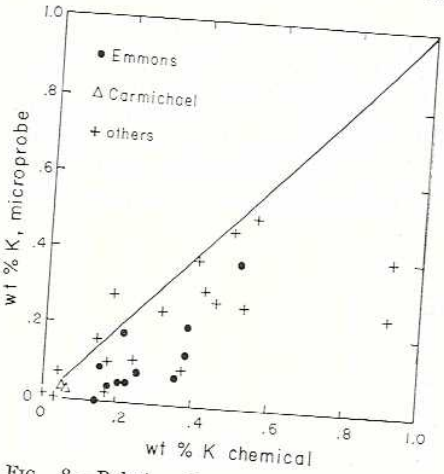

FIG. 8.—Relation between microprobe and chemical estimates of the potassium content of plagioclase. Presence of potassium-rich impurities would lead to deviations to the right of the line of agreement.

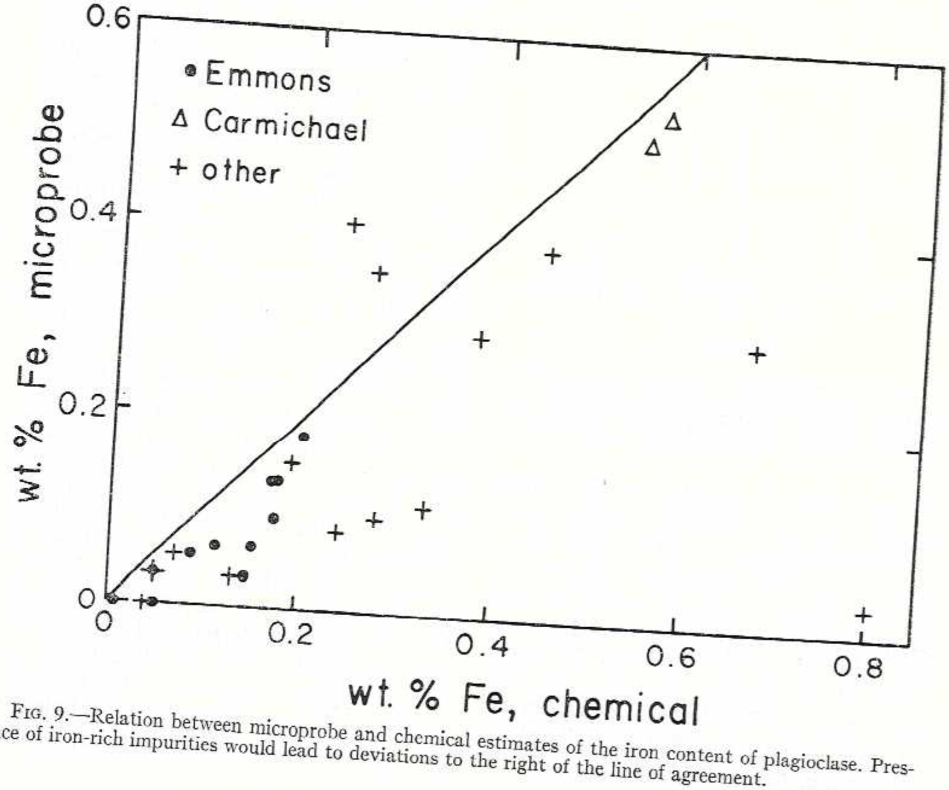

FIG. 9.—Relation between microprobe and chemical estimates of the iron content of plagioclase. Presence of iron-rich impurities would lead to deviations to the right of the line of agreement.

the meantime it seems best to assume that at least most of the iron atoms occupy tetrahedral sites.

Titanium.—With a limited detection level of 0.01 wt. per cent, titanium was found in several plagioclases: the maximum concentration was 0.04 per cent. Whether titanium goes into silicon or aluminum sites, and what is its valence state, are interesting problems for future study. Chemical analyses of bulk specimens are generally unreliable because of the possible presence of titanium-rich impurities.

Phosphorus.—Chemical data for phosphorus are also likely to be unreliable in providing estimates of the phosphorus content of the plagioclase because of the common occurrence of apatite inclusions, which are, however, readily detected in the microprobe by the contrast in the luminescence properties (usually yellow for apatite and blue for plagioclase). The highest level de-

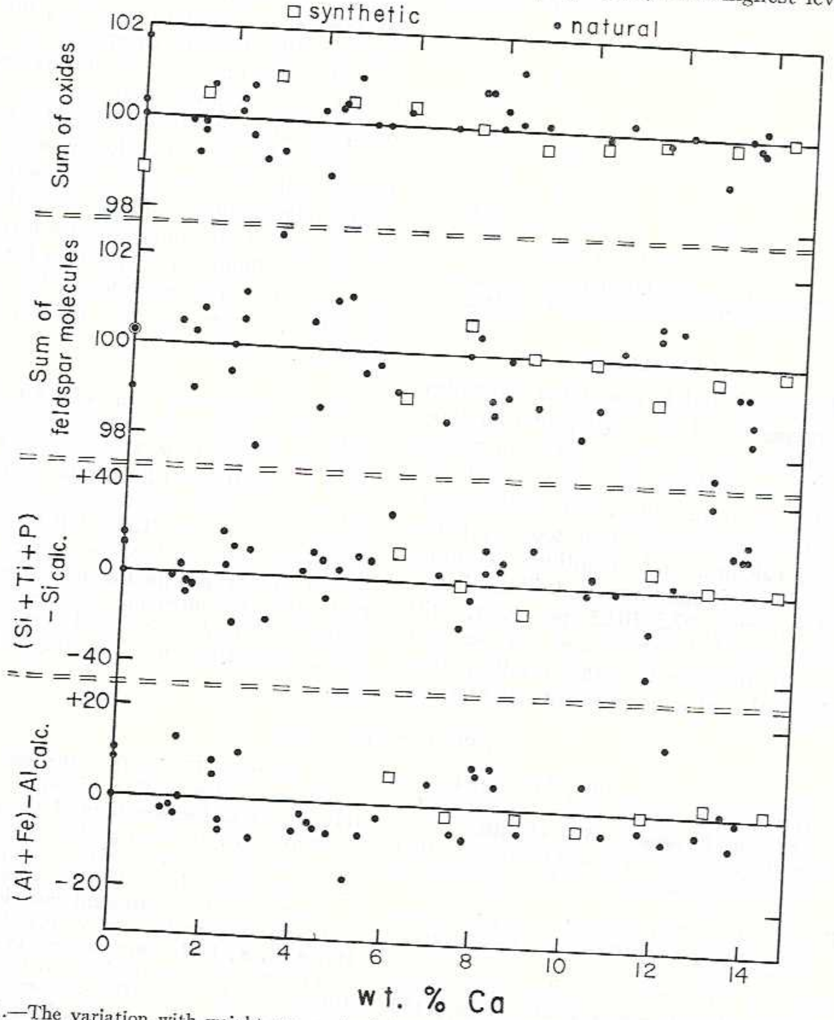

FIG. 11.—The variation with weight per cent calcium of the sum of oxides, feldspar molecules, and differences between atom proportions (data from table 2).

tected by microprobe methods is 0.11 per cent. Presumably phosphorus substitutes for silicon rather than for aluminum because of its more favorable charge and ionic size. Since completion of the manuscript, Koritnig (1965) has shown by colorimetric analysis that the phosphorus content of twelve feldspars leached to remove apatite varies from 0.0005 to 0.1060 per cent, which values are similar to those reported here.

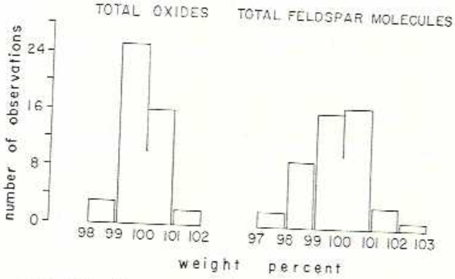

FIG. 12.—Frequency distributions of the sums of oxides and feldspar molecules listed in table 2.

CONCLUSION

Figures 11 and 12 summarize some overall properties of the microprobe analyses. Only three out of forty analyses of natural plagioclase yield oxide totals outside the 99–101 per cent range, but total feldspar molecules calculated from sodium, potassium, calcium, and strontium (assuming stoichiometric aluminum and silicon) have a wider range, 97.5–102.5 per cent, with thirty-three between 99 and 101 per cent. A small increase in totals resulting from substitution of minor elements such as iron should be made. The average oxide sum of the natural plagioclases is 99.9 per cent, and the average of the molecule sums is 99.7 per cent. After correction for replacement of aluminum by iron, the average molecule sum is close enough to 100.0 per cent to suggest that natural plagioclase feldspars on the average are stoichiometric within experimental error. The atomic proportions (Si + Ti + P) tend to be 0.3 per cent higher than the values calculated from sodium, potassium, calcium, and strontium (twenty-six positive vs. twelve negative), but the bias is within possible experimental errors. The (Al + Fe) atomic proportions tend to be 0.2 per cent lower than the calculated ones, but this could be explained by bias in the calibration curve for aluminum, as suggested earlier. In conclusion it appears that microprobe analyses of plagioclase feldspars can be carried out routinely with a relative accuracy of about 1.0–2.0 per cent for major elements and an absolute level of detection of 0.01–0.04 per cent for various minor elements.

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mons, 1953) report barium levels greater than this (one up to 0.058 per cent barium) in six of Emmons' plagioclases, which have been reanalyzed by microprobe methods. Since barium commonly occurs in substantial amounts in antiperthitic orthoclase of labradorites (Ribbe and Doman, manuscript in preparation) it is possible that the barium recorded spectroscopically actually occurs in potassium feldspar avoided by the microprobe beam. This possibility is enhanced by the fact that the chemical analyses of these six specimens average 1.5 per cent Or greater than the microprobe analyses. It is also pertinent that the two plagioclases in Deer *et al.* (1963) showing the most BaO (0.06 and 0.11 per cent) are classified as antiperthites and contain 6.0 and 8.7 wt. per cent Or. Thus it appears that plagioclase crystallized at high temperature may contain barium at the 0.0x per cent level, but that exsolved alkali feldspar will incorporate most of the barium, leaving an essentially barium-free plagioclase.

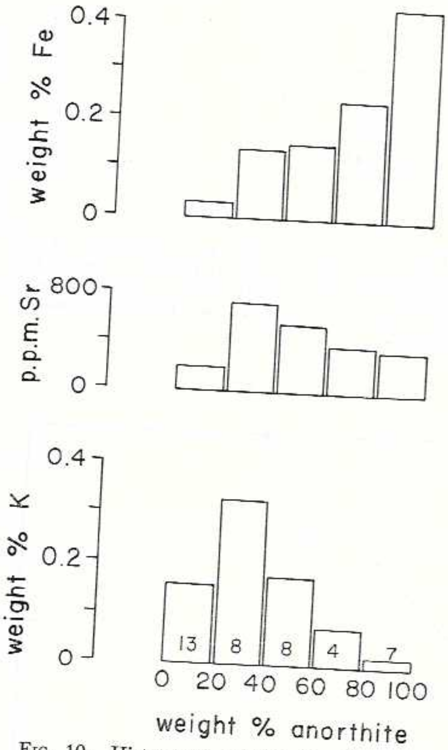

FIG. 10.—Histograms showing for the present specimens the average levels of iron, strontium, and potassium in five equal compositional ranges. The numbers of specimens are shown in the lowest boxes.

Iron.—Because of the likely occurrence of iron-rich impurities such as ilmenite, hematite, and magnetite, the bulk chemical analyses should tend to be higher, but not lower than microprobe analyses. This is true except for two specimens (fig. 9). (Heier 1962) does not discuss iron analyses in his review of trace elements because of likely presence of impurities. The microprobe analyses indicate a steady increase of average iron content from 0.0x per cent near albite to 0.5 per cent at anorthite (fig. 9), which can be readily explained by the generally higher temperatures of crystallization of the calcic specimens and by the increasing proportion of Al^{3+} sites which presumably provide sites for Fe^{3+} ions. Alternatively, it may be considered that the iron atoms substitute for the calcium atoms by analogy with pyroxene, either by a straight substitution Ca → Fe^{II} or by a coupled substitution Ca^{II} + Si^{IV} → Fe^{III} + Al^{III}. Again, the amount of substituted Fe should increase from albite to anorthite. The present analyses are in favor of substitution of aluminum atoms rather than calcium atoms. The thirteen specimens containing over 0.2 per cent iron yield an average sum of feldspar molecules in table 2 of 99.6 per cent. These feldspar molecules were calculated for only alkali and alkaline-earth metals in the interstices and only aluminum and silicon in the tetrahedral framework. If iron substitutes for aluminum, the average rises to 99.7 per cent. If iron occupies the interstices in the framework, the average sum of feldspar molecules rises to 101.8 per cent. There is a similar deterioration in the comparison between atomic proportions. Those calculated for iron occupying tetrahedral sites are almost balanced (table 2), while those for iron occupying interstices are more unbalanced. Application of resonance techniques may permit location of iron atoms, but in lower than the corresponding chemical analyses (fig. 8). This bias can be attributed principally to the presence of sericite and intergrown potassium feldspar (antiperthite), which were easily avoided in the microprobe analyses because the former gave no appreciable luminescence while the latter yielded an intensity of luminescence different from that of the plagioclase. A similar relation exists for iron analyses (fig. 9). The potassium contents were usually fairly steady for the five to ten spots analyzed in the microprobe.

Potassium shows the expected tendency to increase with increasing sodium content (fig. 10). The reduction for the range An_0–An_{20} results from the predominance of pegmatite and vein specimens. Anorthoclases from Part III would have raised the value considerably.

Strontium.—No strontium-bearing impurities (apart from minor potassium feldspar) have been found in plagioclase, and it seems necessary to ascribe discrepancies between microprobe and chemical techniques to deficiency in one or the other. Figure 8 of Part III shows excellent agreement (with one exception) between microprobe and chemical analyses by Carmichael of strontium in alkali feldspars; however, the optical spectrographic analyses by Harrison and Miller quoted in Emmons (1953)

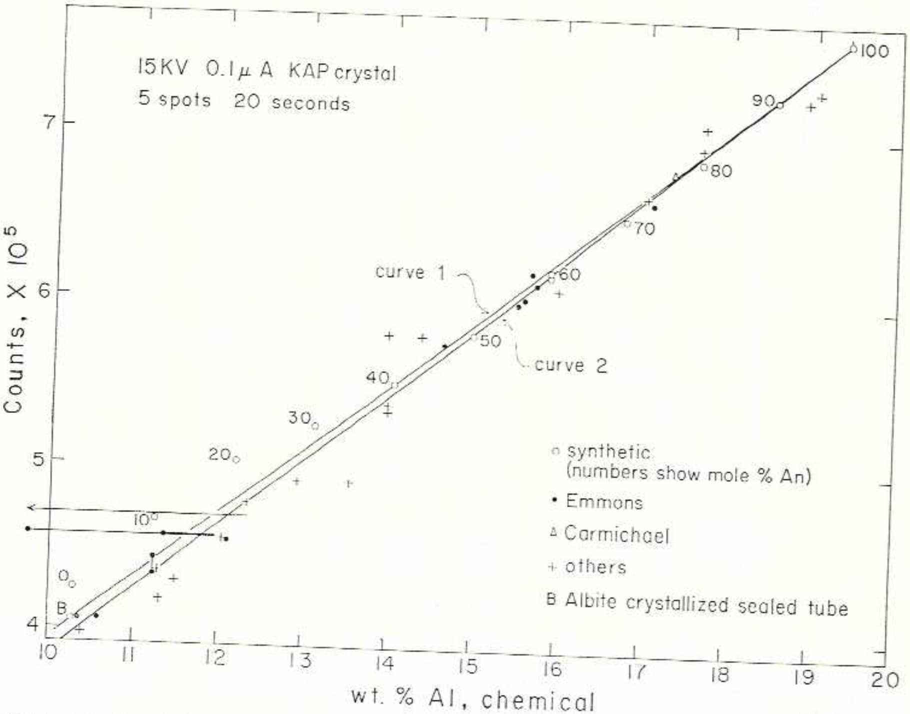

FIG. 7.—Relation between corrected, accumulated counts and weight per cent aluminum determined by chemical analysis for natural specimens or by weighing for synthetic samples. Both calibration curves were adjusted to pass through the datum for synthetic anorthite. Curve *1* was obtained by passing a line through the datum *B* for a synthetic albite crystallized in a sealed tube, while curve *2* was obtained by calculation using the factors of table 3A of Part III derived from formulas of Part I. The latter curve is preferred because it gives an excellent fit to the data for synthetic calcic plagioclase. The deviations for the synthetic sodic plagioclase arise from damage as shown in fig. 5. The horizontal lines for three of the Emmons specimens show corrections for the presence of excess silica arising from quartz impurity in the samples analyzed chemically.

thetic crystallized albite. The resulting curve fits well with the data for the stable calcic glasses but is strongly biased with respect to the chemical analyses for the natural sodic plagioclases. As mentioned in Part II, because $CaAl_2Si_2O_8$ and $KAlSi_3O_8$ have similar scattering and absorbing properties for X-rays, similar correction factors would be expected for plagioclase and alkali feldspars. The factor 1.12 was used for measurements on orthoclase made at 20 kv., based on flame photometer analyses and assumptions of stoichiometry and completely filled cation sites. Thus the empirical factor of 1.10 for data taken at 15 kv. is consistent within an estimated uncertainty of 0.02, for a lower value would be expected at the lower voltage. The sodium content of Amelia albite determined in Part III from the alkali feldspar calibration curve is 8.62 per cent, to be compared with the value of 8.71 per cent obtained from the plagioclase calibration. The difference is less than the claimed relative accuracy of about 2 per cent for sodium.

Most of the chemical analyses for sodium were probably made by gravimetric techniques for which the co-operative studies of G1 and W1 have revealed large variations (Stevens and Niles, 1960). Comparison of gravimetric and flame photometer analyses shows that the former tend to be lower than the latter (G1, 3.31 vs. 3.41; W1, 2.7 vs. 2.21). Thus it is reasonable to place the microprobe calibration curve at higher sodium values than those given by older chemical analyses. A similar situation exists for the alkali feldspars (Part III).

Silicon.—Figure 6 shows the relation between corrected, accumulated counts for silicon and weight per cent silicon determined chemically. The calibration curve was obtained by use of factors derived from the formulas of Part I (table 3 of Part III) and the data for pure synthetic anorthite. Apart from the datum for An_{60} there is excellent agreement for the synthetic calcic plagioclases. The synthetic sodic plagioclases give higher counting rates for calcium because of the assumed volatilization of sodium. The chemical analyses tend to lie on the lower side of the calibration curve, in accordance with the bias suggested in Part III for alkali feldspars and that suggested for gravimetric chemical analyses in the study of G1 and W1 (Stevens and Chodos, 1960). Three specimens contain large amounts of quartz impurities, thus explaining their high chemical values for silicon.

Aluminum.—Figure 7 shows the relation between corrected, accumulated counts and the respective weight per cent aluminum. A tentative calibration curve was drawn between the data for synthetic anorthite and the synthetic albite devitrified in a sealed tube. This calibration curve resulted in a factor of 0.98 for aluminum in An referred to unity for an Ab standard, which differs markedly from the value of 0.95_8 calculated from the data and formulas of Part I. Furthermore, the curve is displaced from the data for the synthetic calcic plagioclases which do not suffer alkali loss. A second calibration curve, passing through the datum for anorthite glass and using the Part I factor, gave a much better fit with the synthetic calcic plagioclase data. As mentioned earlier, the closeness of atomic numbers of the elements in orthoclase and anorthite should result in similar correction factors, and the good agreement with the factor from Part I for aluminum analyses of alkali feldspars in Part III suggests that the Part I factor should also be valid for plagioclase feldspars. The aluminum contents for the calculated calibration curve agree quite closely with the values for the stoichiometric formula, in contrast to those for the tentative calibration curve which are lower than theoretical. Consequently, the calculated calibration curve has been adopted in preference to the tentative one, and it was assumed that the experimental data on the synthetic albite are in error by about 1.5 per cent.

Whether the tentative or calculated calibration curve is used, the chemical analyses tend to lie at higher values than the calibration curves.

MINOR ELEMENTS

Potassium.—With but three exceptions, the microprobe analyses of potassium are thetic specimens) there is a good correlation between the two sets of microprobe analyses; but for the zoned specimens the agreement, of course, is much poorer in accordance with sampling difficulties. Taking account of the presence of quartz in some of the specimens and of the zoning of others, there is a reasonably good correlation between the chemical and microprobe data of figure 1, suggesting that both techniques give good analyses for this element. The calibration curve in figure 1 was made to fit at synthetic albite and anorthite, with the curvature determined from the theoretical factor listed in table 2 of Part III. The calibration curve fits well with the experimental data for the intermediate synthetic plagioclases; the small bias for sodic specimens is explained by volatilization of sodium and the consequently higher percentage content of other elements. The consistency of the data indicates that microprobe analyses of calcium can be carried out with a relative precision of 1 per cent.

Sodium.—Figure 4 shows the relation for sodium between corrected, accumulated

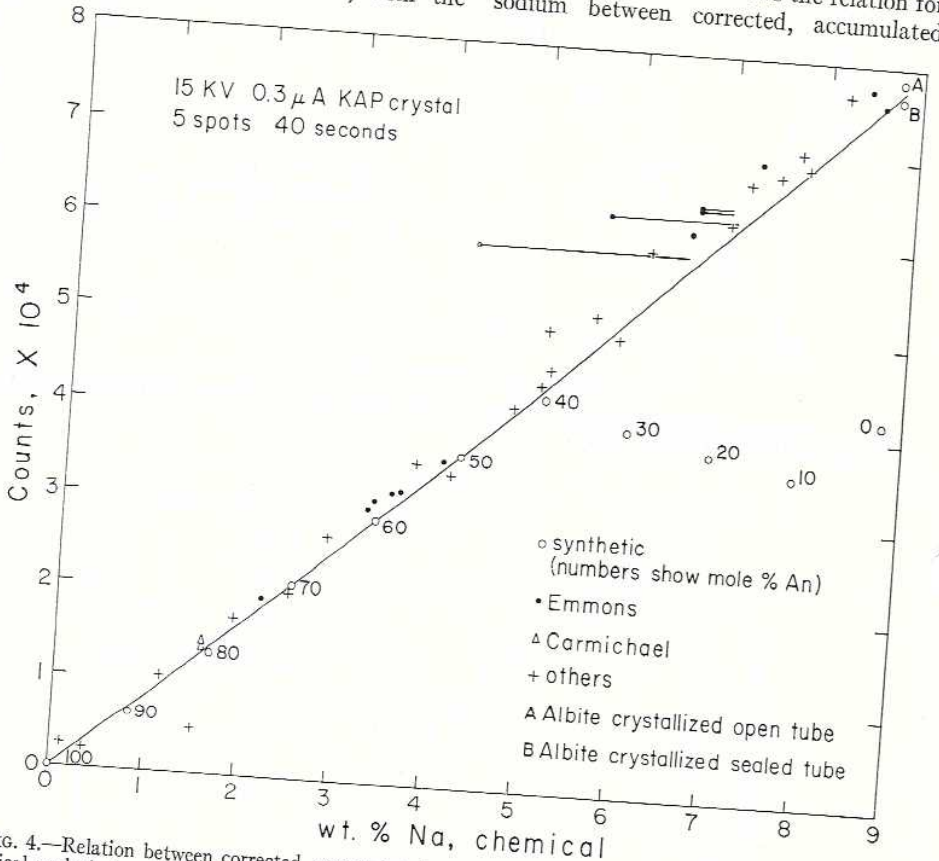

FIG. 4.—Relation between corrected, accumulated counts and weight per cent sodium determined by chemical analysis for natural specimens or by weighing for synthetic samples. The correction was made by applying the factors of table 3B of Part III to the estimates of minor elements in order to change the accumulated counts to those for a binary sodium, calcium feldspar. The shape of the calibration curve was calculated by applying the factor 1.10 to the X-ray emission of An referred to unity for Ab, and the curve was adjusted to pass through the mean of the data for the two crystallized albites. The factor of 1.06 listed in table 3A of Part III would lead to a more linear calibration curve and to a strong deviation from the data for synthetic calcic plagioclase. The deviations for specimens labeled 0, 10, 20, 30, and 40 arise from alkali loss as discussed in the text. The horizontal lines correct for the presence of excess silica in three Emmons specimens (table 1). The pair of lines result from duplicate measurements for one of these Emmons specimens.

TABLE 3

ATOMIC PROPORTIONS AND MOLECULAR PERCENTAGES OF FELDSPAR MOLECULES

	P	Si	Ti	Al	Fe³⁺	Ca	Sr	Na	K	Z	X	Molecular Per Cent			
												Or	Ab	An	Sr-F
E1	0.036	11.954	0.000	4.021	0.000	0.000	0.000	3.934	0.010	16.01	3.94	0.3	99.7	0.0	0.0
E30	.030	11.925	.000	4.066	.000	0.007	.001	3.914	.021	16.02	3.94	0.5	99.3	0.2	.0
Amelia	.000	11.988	.000	4.012	.000	0.002	.000	3.975	.029	16.00	4.01	0.7	99.2	0.0	.0
Monteagle Township	.003	11.722	.000	4.240	.021	0.289	.001	3.687	.049	15.99	4.03	1.2	91.6	7.2	.0
Villeneuve	.003	11.626	.000	4.361	.004	0.369	.001	3.615	.035	15.99	4.02	0.9	89.9	9.2	.0
BM1940, 27	.000	11.613	.000	4.414	.005	0.376	.003	3.508	.024	16.03	3.91	0.6	89.7	9.6	.1
E2	.000	11.585	.000	4.410	.005	0.404	.002	3.594	.012	16.00	4.01	0.3	89.6	10.1	.0
E4	.000	11.411	.000	4.610	.000	0.587	.002	3.303	.049	16.02	3.94	1.2	83.8	14.9	.1
E3	.000	11.386	.000	4.615	.010	0.590	.002	3.363	.035	16.01	3.99	0.9	84.3	14.8	.1
81822	.003	11.397	.000	4.582	.005	0.640	.007	3.266	.076	15.99	3.99	1.9	81.9	16.0	.2
E32	.003	11.324	.000	4.646	.005	0.653	.006	3.264	.151	15.98	4.07	3.7	80.1	16.0	.2
E5	.000	11.206	.000	4.810	.012	0.756	.002	3.138	.055	16.03	3.95	1.4	79.4	19.1	.1
80165	.003	11.168	.000	4.798	.005	0.832	.003	3.101	.135	15.97	4.07	3.3	76.2	20.4	.1
97490	.000	10.958	.000	5.013	.010	1.074	.016	2.789	.135	15.98	4.01	3.4	69.5	26.8	.4
2270	.000	10.908	.000	5.066	.017	1.131	.101	2.727	.110	15.99	3.98	2.8	68.6	28.4	.3
RB561	.003	10.856	.000	5.114	.017	1.170	.010	2.789	.021	15.99	3.99	0.5	69.9	29.3	.3
RB579	.003	10.808	.000	5.163	.012	1.188	.012	2.771	.063	15.99	4.03	1.6	68.7	29.5	.3
S347	.003	10.767	.000	5.201	.015	1.269	.007	2.655	.065	15.99	4.00	1.6	66.4	31.8	.2
SK4145	.000	10.717	.004	5.168	.069	1.393	.007	2.496	.104	15.96	4.00	2.6	62.4	34.8	.2
SK4272	.000	10.558	.006	5.350	.068	1.487	.006	2.417	.083	15.98	3.99	2.1	60.5	37.2	.2
4642A	.014	10.494	.000	5.471	.010	1.583	.002	2.276	.068	15.99	3.93	1.7	57.9	40.3	.1
E9	.000	10.077	.000	5.921	.017	1.894	.009	1.968	.105	16.01	3.98	2.6	49.5	47.6	.2
EH201	.000	9.292	.009	5.978	.068	2.038	.006	1.948	.075	15.98	4.07	1.8	47.9	50.1	.2
EH20	.000	9.950	.009	5.961	.061	2.067	.004	1.887	.072	15.98	4.03	1.8	46.8	51.3	.1
E13	.006	9.825	.000	6.180	.012	2.146	.008	1.766	.019	16.02	3.94	0.5	44.8	54.5	.2
E12	.003	9.784	.000	6.208	.025	2.175	.008	1.770	.013	16.02	3.97	0.4	44.6	54.8	.2
E16	.000	9.711	.002	6.295	.005	2.275	.009	1.653	.025	16.01	3.96	0.6	41.7	57.4	.2
E14	.000	9.685	.000	6.315	.034	2.240	.010	1.701	.013	16.03	3.96	0.3	42.9	56.5	.3
Clear Lake	.000	9.603	.007	6.305	.069	2.457	.007	1.484	.028	15.98	3.98	0.7	37.3	61.8	.2
E23	.000	9.106	.000	6.885	.025	2.859	.009	1.107	.000	16.02	3.98	0.0	27.8	71.9	.2
7510	.000	9.037	.004	6.914	.030	2.982	.005	0.982	.045	15.98	4.01	1.1	24.5	74.3	.1
H92	.000	8.735	.004	7.142	.105	3.234	.003	0.813	.011	15.99	4.06	0.3	20.0	79.6	.1
G98	.000	8.692	.004	7.177	.100	3.259	.003	0.852	.009	15.97	4.12	0.2	20.7	79.0	.1
EB18	.000	8.664	.000	7.268	.057	3.367	.001	0.615	.017	15.99	4.00	0.4	15.4	84.2	.0
Japan	.000	8.302	.000	7.598	.098	3.742	.006	0.207	.006	16.00	3.96	0.2	5.2	94.5	.2
Hakone 1	.000	8.274	.000	7.629	.076	3.809	.005	0.160	.000	15.98	3.97	0.0	4.0	95.8	.1
Hakone 3	.000	8.210	.000	7.701	.084	3.834	.010	0.111	.000	15.99	3.95	0.0	2.8	96.9	.3
Miyake 99	0.003	8.225	0.000	7.690	0.080	3.819	0.003	0.130	0.000	16.00	3.95	0.0	3.3	96.7	0.1

TABLE 2—X-RAY EMISSION ANALYSIS OF PLAGIOCLASE FELDSPARS

SPECIMEN	WEIGHT PER CENT ELEMENTS											WEIGHT PER CENT OXIDES									
	Si	Ti	Al^{I}*	Al^{II}†	Fe	Sr	Ca^{I}	Ca^{II}	K	Na	P	SiO_2	TiO_2	$Al_2^{II}O_3$	Fe_2O_3	SrO	$Ca^{I}O$	K_2O	Na_2O	P_2O_5	Total
E1	32.56	0.00	10.31	10.52	0.00	0.00	0.00	0.00	0.04	8.77	0.11	69.7	0.0	19.9	0.0	0.0	0.0	0.0	11.8	0.3	101.7
E30	32.05	0.00	10.29	10.50	0.00	0.01	0.03	0.03	0.08	8.61	0.09	68.6	0.0	19.8	0.0	0.0	0.0	0.1	11.6	0.2	100.3
Amelia (KN)	32.10	0.00	10.11	10.32	0.00	0.00	0.01	0.01	0.11	8.71	0.00	68.7	0.0	19.5	0.0	0.0	0.0	0.1	11.7	0.0	100.0
Monteagle Township	31.20	0.00	10.65	10.84	0.11	0.01	1.10	1.10	0.18	8.03	0.01	66.7	0.0	20.5	0.2	0.0	1.5	0.2	10.8	0.0	99.9
Haddam	31.30	N.d.	10.90	11.09	N.d.	N.d.	1.27	1.28	N.d.	8.02	N.d.	45.6	N.d.	21.0	N.d.	N.d.	1.8	N.d.	10.8	....	99.2+
Villeneuve	30.89	0.00	10.94	11.13	0.02	0.01	1.40	1.40	0.13	7.86	0.01	66.0	0.0	21.0	0.0	0.0	1.9	0.2	10.6	0.0	99.7
BM1940, 27	30.95	0.00	11.11	11.30	0.03	0.03	1.42	1.44	0.09	7.65	Trace	66.2	0.0	21.4	0.0	0.0	1.9	0.1	10.3	0.0	99.9
E2	31.04	0.00	11.16	11.35	0.03	0.02	1.59	1.50	0.05	7.88	0.00	66.4	0.0	21.4	0.0	0.0	2.2	0.1	10.6	0.0	100.7
Monteagle Valley	......	0.00	......	......	0.13	0.04	......	1.78	0.17	7.64	0.01	....	0.0	......	0.2	0.0	....	0.2	10.3	0.0	....
F4	30.36	0.00	11.60	11.78	0.00	0.02	2.16	2.30	0.18	7.19	0.00	64.9	0.0	22.3	0.0	0.0	3.0	0.2	9.7	0.0	100.1
E3	30.28	0.00	11.62	11.79	0.05	0.02	2.25	2.23	0.13	7.32	0.00	64.8	0.0	22.3	0.1	0.0	3.1	0.2	9.9	0.0	100.4
81822 (KN)	30.45	0.00	11.59	11.76	0.03	0.06	2.44	2.45	0.28	7.14	0.01	65.1	0.0	22.2	0.0	0.1	3.4	0.3	9.6	0.0	100.7
E32	29.76	0.00	11.56	11.73	0.03	0.05	2.45	2.45	0.55	7.02	0.01	63.7	0.0	22.2	0.0	0.1	3.4	0.7	9.5	0.0	99.6
E5	29.40	0.00	11.95	12.12	0.06	0.02	2.86	2.80	0.20	6.74	0.00	62.8	0.0	22.9	0.1	0.0	4.0	0.2	9.1	0.0	99.1
80165 (KN)	29.83	0.00	12.15	12.31	0.03	0.03	3.24	3.10	0.50	6.78	0.01	63.8	0.0	23.3	0.0	0.0	4.5	0.6	9.1	0.0	99.3
97490 (KN)	28.81	0.00	12.51	12.66	0.05	0.13	4.00	4.06	0.49	6.00	0.00	61.7	0.0	23.9	0.1	0.2	5.6	0.6	8.1	0.0	100.2
Howie 2270	28.35	0.00	12.50	12.65	0.09	0.08	4.16	4.23	0.40	5.80	Trace	60.6	0.0	23.9	0.1	0.1	5.8	0.5	7.8	0.0	98.8
Lambert RB561	28.68	0.00	12.84	12.98	0.09	0.08	4.45	4.38	0.08	6.03	0.01	61.4	0.0	24.5	0.0	N.d.	6.2	0.1	8.1	0.0	100.3+
Lambert RB579	28.50	0.00	12.94	13.08	0.06	0.10	4.50	4.45	0.23	5.98	0.01	61.0	0.0	24.7	0.1	0.1	6.3	0.1	8.1	0.0	100.4
Howie S347	28.55	0.00	13.11	13.25	0.08	0.06	4.76	4.84	0.24	5.76	0.01	61.0	0.0	25.0	0.1	0.1	6.7	0.3	7.8	0.0	101.0
SK4145	28.02	0.02	12.85	12.98	0.36	0.06	5.26	5.14	0.38	5.34	Trace	59.9	0.0	24.5	0.5	0.1	7.3	0.5	7.2	0.0	100.0
SK4272	27.55	0.03	13.28	13.41	0.35	0.05	5.52	5.55	0.30	5.16	Trace	58.9	0.1	25.3	0.5	0.1	7.7	0.4	7.0	0.0	100.0
Howie 4642A	27.55	0.00	13.68	13.80	0.05	0.02	5.90	5.96	0.25	4.89	0.04	58.9	0.0	26.1	0.1	0.0	8.2	0.3	6.6	0.1	100.3
E9	26.15	0.00	14.66	14.76	0.09	0.07	7.14	6.89	0.38	4.18	0.00	55.9	0.0	27.9	0.1	0.1	9.9	0.5	5.6	0.0	100.0
EH201	25.78	0.04	14.82	14.91	0.35	0.05	7.80	7.30	0.27	4.14	Trace	55.1	0.1	28.2	0.5	0.1	10.9	0.3	5.6	0.0	100.8
EH20	25.91	0.04	14.82	14.91	0.32	0.04	7.80	7.56	0.26	4.02	0.00	55.4	0.1	28.2	0.5	0.0	10.9	0.3	5.4	0.0	100.8
E13	25.49	0.00	15.31	15.40	0.06	0.06	7.89	8.00	0.07	3.75	0.02	54.5	0.0	29.1	0.1	0.1	11.0	0.1	5.1	0.0	100.0
E12	25.40	0.00	15.39	15.48	0.13	0.06	8.16	7.95	0.05	3.76	0.01	54.3	0.0	29.2	0.2	0.1	11.4	0.1	5.1	0.0	100.4
E16	25.20	0.01	15.61	15.69	0.03	0.07	8.35	8.50	0.09	3.51	Trace	53.9	0.0	29.6	0.0	0.1	11.7	0.1	4.7	0.0	100.1
E14	25.32	0.00	15.78	15.86	0.18	0.08	8.51	8.20	0.05	3.64	Trace	54.1	0.0	30.0	0.2	0.1	11.9	0.1	4.9	0.0	101.3
Clear Lake	24.75	0.03	15.54	15.61	0.35	0.05	9.07	9.00	0.10	3.13	0.00	52.9	0.1	29.5	0.5	0.1	12.7	0.1	4.2	0.0	100.1
Crystal Bay (KN)	......	0.02	......	......	0.29	0.00	......	10.13	0.05	2.42	0.00	....	0.0	......	0.4	0.0	....	0.1	3.3	0.0	....
E23	23.31	0.00	16.87	16.93	0.13	0.07	10.50	10.38	0.00	2.32	Trace	49.8	0.0	32.0	0.2	0.1	14.7	0.0	3.1	0.0	99.9
7510 (KN)	23.16	0.02	16.97	17.02	0.15	0.04	10.93	10.88	0.16	2.06	Trace	49.5	0.0	32.2	0.2	0.0	15.3	0.2	2.8	0.0	100.2
H92	22.18	0.02	17.37	17.42	0.53	0.03	11.75	11.68	0.04	1.69	N.d.	47.4	0.0	32.9	0.8	0.0	16.4	0.0	2.3	N.d.	99.8
G98	21.95	0.02	17.37	17.41	0.50	0.03	11.95	11.54	0.03	1.76	N.d.	46.9	0.0	32.9	0.7	0.0	16.7	0.0	2.4	N.d.	99.6
EB18 (KN)	22.04	0.00	17.73	17.76	0.29	0.01	12.24	12.20	0.06	1.28	0.00	47.1	0.0	33.6	0.4	0.0	17.1	0.1	1.7	0.0	100.0
Juvinas	21.55	N.d.	18.08	18.11	N.d.	N.d.	12.91	13.05	0.02	0.60	N.d.	46.0	N.d.	34.2	N.d.	N.d.	18.1	0.0	0.8	N.d.	99.0
Anorthite (Japan)	21.02	0.00	18.46	18.48	0.49	0.04	13.46	13.58	N.d.	0.43	N.d.	45.0	0.0	34.9	0.7	0.0	18.8	N.d.	0.6	N.d.	100
Hakone 1	20.91	0.00	18.51	18.52	0.38	0.03	13.72	13.75	0.00	0.33	Trace	44.7	0.0	35.0	0.5	0.0	19.2	0.0	0.4	0.0	99
Hakone 3	20.70	0.00	18.64	18.65	0.42	0.08	13.78	13.80	0.00	0.23	Trace	44.2	0.0	35.2	0.6	0.1	19.3	0.0	0.3	0.0	99.
Miyake 99	20.80	0.00	18.67	18.68	0.40	0.03	13.86	13.70	0.00	0.27	0.01	44.5	0.0	35.3	0.6	0.0	19.4	0.0	0.4	0.0	100.2
An_0 glass	33.35	0.00	10.78	10.99	0.03	0.00	0.0	0.0	0.01	4.95	0.00	71.3	0.0	20.8	0.0	0.0	0	0.0	6.7	0.0	98.8
An_{10} glass	32.59	0.00	11.88	12.07	0.06	0.00	1.54	1.59	0.01	4.20	N.d.	69.7	0.0	22.8	0.1	0.0	2.2	0.0	5.7	N.d.	100.5
An_{20} glass	30.84	0.00	12.82	12.99	0.05	0.00	3.08	3.10	N.d.	4.44	N.d.	66.0	0.0	24.5	0.1	0.0	4.3	0.0	6.0	N.d.	100.9
An_{30} glass	28.98	0.00	13.38	13.53	0.05	0.00	4.57	4.56	N.d.	4.69	N.d.	62.0	0.0	25.6	0.1	0.0	6.4	0.0	6.3	N.d.	100.4
An_{40} glass	27.20	0.00	14.06	14.18	0.02	0.00	6.05	6.04	N.d.	5.01	N.d.	58.2	0.0	26.8	0.0	0.0	8.5	0.0	6.8	N.d.	100.3
An_{50} glass	26.00	0.00	14.84	14.94	0.06	0.00	7.42	7.50	0.01	4.26	N.d.	55.6	0.0	28.2	0.1	0.0	10.4	0.0	5.7	N.d.	100.0
An_{60} glass	24.50	0.00	15.78	15.86	0.05	0.00	8.92	8.85	N.d.	3.38	N.d.	52.4	0.0	30.0	0.1	0.0	12.5	0.0	4.6	N.d.	99.6
An_{70} glass	23.55	0.00	16.62	16.68	0.05	0.00	10.32	10.27	N.d.	2.51	N.d.	50.4	0.0	31 5	0.1	0.0	14.4	0.0	3.4	N.d.	99.8
An_{80} glass	22.49	0.00	17.52	17.56	0.03	0.00	11.66	11.64	N.d.	1.60	N.d.	48.1	0.0	33.2	0.0	0.0	16.3	0.0	2.2	N.d.	99.8
An_{90} glass	21.20	0.00	18.52	18.54	0.03	0.00	13.07	13.07	N.d.	0.78	N.d.	45.4	0.0	35.0	0.0	0.0	18.3	0.0	1.1	N.d.	99.8
An_{100} glass	20.20	0.00	19.38	19.38	0.02	0.01	(14.41)	14.37	0.00	(0.00)	0.00	43.2	0.0	36.6	0.0	0.0	20.2	0.0	0.0	0.0	100.0

* Al^{I} using calibration curve that joins the data for synthetic albite and anorthite.

† Al^{II} using calibration curve that passes through synthetic anorthite and uses the factors of table 3, *a*, of Part III.

‡ $Si_{calc} = 3(Na+K) + 2(Ca+Sr)$.

§ $\Delta_1 = (Si+Ti+P) - Si_{calc}$.

‖ $Al_{calc} = (Na+K) + 2(Ca+Sr)$.

\# $\Delta_2 = (Al+Fe) - Al_{calc}$.

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