

## AUTHIGENIC FELDSPARS IN CARBONATE ROCKS

MIRIAM KASTNER<sup>1</sup>, *Department of Geological Sciences,  
Harvard University, Cambridge, Massachusetts*

### ABSTRACT

Authigenic feldspars occur in both marine limestones and dolostones, and no correlation has been found between the amount of  $MgCO_3$  in the carbonate rocks and any chemical or physical properties of authigenic feldspars.

Optical and unit-cell parameters indicate that authigenic feldspars are highly ordered but not as ordered as low albites and microclines from low-grade metamorphic rocks and pegmatites. The albites contain less than 1 mole percent potassium and calcium and the microclines contain less than one mole percent sodium and calcium. Authigenic feldspars show no detectable cathodo-luminescence.

The composition of the carbonate inclusions that are present in all authigenic feldspars, is the same as that of the rock matrix.

Authigenic albite is far more abundant than authigenic microcline. In a few localities the two feldspars coexist, apparently in equilibrium as indicated by textural relations.

A mass balance between the maximum total percentage of authigenic feldspars and mica components in carbonates and the amount of fluid phase needed to provide the alkalis for the feldspars, suggests isochemical formation of authigenic feldspars. Calculations based on ion exchange and thermodynamic data from the literature show that the  $K/(K+Na)$  ratio in the fluid phase in equilibrium with both albite and microcline at 100°C is approximately equal to the  $K/(K+Na)$  ratio in sea water. Thus the chemical environment of formation of authigenic albite does not necessarily differ appreciably from the environment of authigenic microcline.

### INTRODUCTION

The feldspars are major constituents of arkoses and other sandstones, many shales, and are a minor constituent in other kinds of sediment. It is estimated that over 95 percent of feldspars in sedimentary rocks are detrital; the remainder are authigenic.<sup>2</sup>

Drian (1861) and Lory (1861) were the earliest to report an occurrence of feldspar of apparent sedimentary origin, in the Triassic dolostones from Roc Tourné, Modane, France. Since then the number of reports of authigenic feldspars have increased rapidly, though precise statements of mineralogical and chemical compositions have been scarce.

The physico-chemical conditions of authigenic feldspars must be inferred from a combination of careful descriptions and analyses of field assemblages as well as from experimental studies. In the past the descriptive approach has been pursued to a much greater extent than the experimental approach. However, there are extreme difficulties in the

<sup>1</sup> Present address: Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637.

<sup>2</sup> In this study "authigenic" is used in the sense of being formed *in situ* between sediment deposition and an established low metamorphic grade. Later introduction of hydrothermal or metasomatic fluids is excluded.

study of authigenic feldspars, which are mainly caused by (1) their low abundance (in most carbonate rocks studied, between 0.05 to 0.5 weight percent, and rarely up to 2 weight percent), (2) their very small dimensions, and (3) their frequent coexistence with detrital feldspars. This necessitates either a laborious mineral separation or the use of new criteria and techniques to distinguish between the authigenic and detrital feldspars. Furthermore, only a small amount of experimental data on the physico-chemical conditions of formation of authigenic feldspars is available, because of the difficulties in low temperature and low pressure experiments.

Distinctive differences in habit and twin laws between authigenic feldspars and feldspars from igneous and metamorphic rocks have attracted the attention of many investigators concerned mainly with the crystallographical and optical properties of authigenic feldspars. However, few petrologic details were included in the older studies. The recent detailed investigations of authigenic feldspars are those of Baskin (1956) and Reynolds (1963, 1965). Baskin (1956) reported some anomalous unit-cell parameters which suggested important differences between the properties of authigenic and other feldspars, and which could provide a clue to their geologic histories. Moreover, disagreements in the literature regarding the identification of the unusual twins, and inaccuracies in the chemical composition of authigenic feldspars because of bulk analyses, are numerous. In addition, reported optical and crystallographic properties of authigenic K-feldspars are inconsistent.

The purpose of the present study was to infer the physico-chemical environment of formation of authigenic feldspars by obtaining accurate and precise new data concerning the physical and chemical properties and comparing them with previous studies.

The decision to choose carbonate rocks for the initial study was made: (1) to limit the study to a relatively simple geochemical system (in contrast to shales or greywackes, for example); (2) because carbonate rocks were reported to carry both authigenic albites and authigenic K-feldspars. In contrast, mostly authigenic K-feldspars have been reported from shales and sandstones.

On the basis of mineral assemblages (that will be discussed below) the diagenetic origin of the feldspars from the Belt Series, North Michigan, and of the larger albites from Modane, France (Table 1) is in doubt. Nevertheless they are included in the tables.

The observations and results reported here and by Kastner and Waldbaum (1968)<sup>1</sup> explain discrepancies among previously reported results.

<sup>1</sup> The morphology and optical crystallography were discussed previously in detail by Kastner and Waldbaum (1968), and therefore will not be presented in this paper.

TABLE 1. PETROGRAPHY OF CARBONATE ROCKS CONTAINING AUTHIGENIC FELDSPARS

Locality	Formation and geological age	Rock type <sup>a</sup>	$\left( \frac{\text{calcite}}{\text{calcite} + \text{dolomite}} \right) \times 100$	Mole % MgCO <sub>3</sub> <sup>c</sup> In calcite ± 1.00% In dolomite ± 1.50%	Weight % insoluble residue	Mineralogy of insoluble residue	Non-detrital feldspar phase
M-46-GP Glacier Park, Montana	Altyn Fm., Late Precambrian	Micrite 95%	0	50.4	26.5	Quartz; K-feldspar; chlorite (Fe > Mg); illite; muscovite; black heavy minerals	Microcline
M-106-WP Waterton Park, Alberta	Waterton Fm., Late Precambrian	Micrite 95%	5	49.6	27.6	Quartz; K-feldspar; chlorite (Fe > Mg); biotite; black heavy minerals	Microcline
M-117-WP Waterton Park, Alberta	Waterton Fm., Late Precambrian	Micrite 80%	85 and 5	0.08	42.0	Quartz; K-feldspar; chlorite (Fe > Mg); muscovite; black heavy minerals	Microcline
M-131-WP Waterton Park, Alberta	Waterton Fm., Late Precambrian	Intramicticrite 95%	1		>60.0	Quartz; K-feldspar; chlorite (Fe > Mg); biotite; black heavy minerals	Microcline
M-201-NM Goose Lake, N. Michigan	Kona dolostone Huronian	Biotilitite	0	50.3	17.2	Quartz; K-feldspar; limonite; heavy minerals	Microcline
M-203-NM Goose Lake, N. Michigan	Kona dolostone Huronian	Biotilitite	0	50.4	15.8	Quartz; K-feldspar; limonite; chlorite	Microcline
M-251-GF Glens Falls, N.Y.	Trenton Fm., Ordovician	Biopelmicticrite 90%	99	0.54	6.4	Quartz; illite; chlorite; montmor- illonite; carbonaceous matter; K-feldspar; pyrite	Microcline
M-252-GF Glens Falls, N.Y.	Trenton Fm., Ordovician	Pelsparite 50% Biomicticrite 85%	97	0.72	14.4	Quartz; illite; chlorite; montmor- illonite; pyrite; carbonaceous matter; plagioclase	Albite

TABLE 1. (Continued)

Locality	Formation and geological age	Rock type <sup>a</sup>	$\left( \frac{\text{calcite}}{\text{calcite} + \text{dolomite}} \right) \times 100$	Mole % MgCO <sub>3</sub> <sup>b</sup> In calcite $\pm 1.00\%$ In dolomite $\pm 1.50\%$	Weight % insoluble residue	Mineralogy of insoluble residue	Non-detrital feldspar phase
M-256-GF Glens Falls, N.Y.	Trenton Fm. Ordovician	Fossiliferous pelsparite 55%	99	0.37	1.8	Quartz; chlorite illite; mixed-layered clay; pyrite; carbon- aceous matter; plagioclase	Albite
M-351-IR Rhodes, Greece	Eocene	Micrite 98%	98	0.25	3.5	Quartz; regular mixed-layered clay; (chlorite/vermiculite 1:1); pyrite; carbonaceous matter	Albite and microcline
M-355-IR Rhodes, Greece	Eocene	Micrite 98%	99	0.07	9.8	Quartz; regular mixed-layered clay; (chlorite/vermiculite 1:1); pyrite; carbonaceous matter	Albite and microcline
M-401-IC Ravdoukha, Crete	Triassic	Micrite 90%	40 <sup>d</sup>	50.4	4.5	Quartz; illite; carbonaceous matter	Albite
M-402-IC Ravdoukha, Crete	Triassic	Micrite 92%	1	50.4	5.5	Quartz; illite; carbonaceous matter	Albite
M-420-IC Liopetro, Crete <sup>e</sup>	Triassic or Cretaceous	Micrite	—	50.5	—	—	Albite
M-500-MF Modane, Savoie, France	Triassic	Diamicrite 70%	1	50.3	1.8	Pyrite; rutile; quartz; muscovite	Albite
M-501-MF Modane, France	Triassic	Diamicrite 45%	3	50.4	19.6	Phengite; pyrite rutile; quartz	Albite
M-654-OP Near Bellefontaine, Pa.	Trenton Fm. Ordovician	Biomicrite 65%	99	0.80	8.4	Quartz; illite; chlorite; mixed-layered clay; carbonaceous matter; pyrite; plagioclase; biotite	Albite

TABLE 1. (Continued)

Locality	Formation and geological age	Rock type <sup>a</sup>	$\left( \frac{\text{calcite}}{\text{calcite} + \text{dolomite}} \right) \times 100$	Mole % MgCO <sub>3</sub> <sup>b</sup>		Weight % insoluble residue	Mineralogy of insoluble residue	Non-detrital feldspar phase
				In calcite ± 1.00%	In dolomite ± 1.50%			
M-659-OP Near Bellefonte, Pa.	Trenton Fm. Ordovician	Partially recrystallized biomicrite 38%	100	0.87	3.5	Quartz; illite; chlorite; mixed-layered clay; pyrite; plagioclase; carbonaceous matter.	Albite	
M-659-OP Near Bellefonte, Pa.	Beekmantown Fm. Ordovician	Very fine grained sparite	0.5	50.5	5.2	Quartz; carbonaceous matter; pyrite; K-feldspar.	Microcline	
M-674-OP Pleasant Gap, Pa.	Valley View Fm. Ordovician	Biopelsparite 40%	100	0.05	1.2	Quartz; illite; mixed-layered clay; carbonaceous matter; pyrite	Albite	
M-682-OP Pleasant Gap, Pa.	Valentine (Lowville) Fm. Ordovician	Pelsparite and dismicrite 65%	96	0.08	0.3	Quartz; illite; mixed-layered clay; carbonaceous matter; plagioclase	Albite	
M-683-OP Pleasant Gap, Pa.	Valentine (Lowville) Fm. Ordovician	Pelsparite and dismicrite 68%	97	0.05	0.1	Quartz; illite; mixed-layered clay; (kaolinite); carbonaceous matter; plagioclase	Albite	
M-692-OP Avenann, Pa.	Beekmantown Fm. Ordovician	Pelmicrite 75%	96	0.59	2.8	Quartz; carbonaceous matter; pyrite; K-feldspar; illite; traces of mixed-layered clay	Microcline	
M-715-TD Tatum Dome, Miss.	Permian?	Rock salt	—	50.5	5.6	Anhydrite; dolomite; calcite; quartz	Albite	
M-739-PU	Paradox Fm.	Algal plate	—	—	5-10	Quartz; chert	Albite	

TABLE 1. (Continued)

Locality	Formation and geological age	Rock type <sup>a</sup>	$\left( \frac{\text{calcite}}{\text{calcite} + \text{dolomite}} \right) \times 100$	Mole % MgCO <sub>3</sub> <sup>c</sup> In calcite ± 1.00% In dolomite ± 1.50%	Weight % insoluble residue	Mineralogy of insoluble residue	Non-derital feldspar phase
Desert Creek Zone, Utah <sup>f</sup>	Pennsylvanian	limestone, micritic matrix	—	—	5-10	Quartz; chert	Albite
M-740-PU	Paradox Fm.	Algal plate limestone,					
Desert Creek Zone, Utah <sup>f</sup>	Pennsylvanian	micritic matrix	99	0.72	11.4	Quartz; K-feldspar; chlorite; mixed-layered clay; illite; carbonaceous matter; tourmaline	Albite
M-751-PU	Brazer Fm.	Intramictic and dismicritic	100	0.53	12.8	Quartz; K-feldspar; chlorite; mixed-layered clay; illite; carbonaceous matter	Albite and K-feldspar
Provo Canyon, Utah	Pennsylvanian						
M-752-PU	Brazer Fm.	Fossiliferous intramicritic					
Provo Canyon, Utah	Pennsylvanian						
M-1158-BW	Waterton Fm.	Micrite	1	50.1	60.0	Quartz; K-feldspar; chlorite; limonite	Microcline
Waterton Park, Alberta <sup>g</sup>	Late Precambrian	55%					
M-1159-BW	Waterton Fm.	Micrite	1	50.2	60.0	Quartz; K-feldspar; chlorite; limonite	Microcline
Waterton Park, Alberta <sup>g</sup>	Late Precambrian	55%					
M-15-JK	Dinwoody Fm.	Pelaspate	70	—	—	Quartz; K-feldspar; plagioclase; illite	Albite
Swift Creek, Wyoming	Triassic						
M-182-JK	Woodside Fm.	Pelaspate	80	—	—	Quartz; K-feldspar; illite	Albite
Fall Creek, Wyoming	Triassic						

<sup>a</sup> Folk's classification (1959). Percent micrite estimated from thin sections and given in brackets

<sup>b</sup> Estimated from thin sections with Alizarin Red S.

<sup>c</sup> Calculated from refined unit cell parameters.

<sup>d</sup> Dedolomitized.

<sup>e</sup> Not enough available for thin section.

<sup>f</sup> K. S. Deffeyes' samples and descriptions of rocks.

<sup>g</sup> Bashin's samples.

## LITHOLOGY

Authigenic feldspars in carbonate rocks ranging in age from late Precambrian to Eocene were studied. Samples of carbonate rocks, known to contain authigenic feldspars, were obtained from North American and from classical European localities. A few of Baskin's (1956) samples were also studied.

On the basis of microscopic examination of about 400 thin sections, 34 representative samples were chosen for the detailed study.

*Carbonate Matrix.* Authigenic feldspars occur with essentially equal development in both limestones and dolostones. In the 400 samples studied, almost all of which contain authigenic feldspar, micritic, pelmicritic, or biopelmicritic types are more abundant than other carbonate rock types, in approximate proportion to the representative samples shown in Table 1 (classification of Folk, 1959). Only a few are fine- to medium-grained or partially recrystallized carbonate rocks. This is in agreement with Reynolds' (1963) findings, but in sharp contrast to Carozzi's (1953) and Baskin's (1956) statement that authigenic feldspars occur most frequently in recrystallized and dolomitized carbonate rocks.

The carbonate rocks in which authigenic albites occur are colored medium light gray (N6<sup>1</sup>) to grayish black (N2); in contrast, the carbonate rocks in which authigenic K-feldspars occur are light gray (N7), pale brown (5YR 5/2), and grayish red purple (5RP 4/2).

The composition of the carbonate rocks ranges from pure calcitic limestone to stoichiometric dolomite. The relative amount of MgCO<sub>3</sub> in the carbonate rocks does not correlate with any physical or chemical properties of the authigenic feldspars. There is no genetic significance relating to feldspar formation in the presence of magnesium in the carbonates.

The Eocene limestone from Rhodes is the youngest carbonate now known to carry authigenic feldspars.

At many of the localities the rocks are structurally deformed on an outcrop scale. Stylolites, carbonate veins, and joint fillings are common. For example, in various carbonate rocks from Rhodes (Kastner and Waldbaum, 1968) and from Crete several generations of stylolites and carbonate veins intersect, and the authigenic feldspars are cut or even displaced by all of them, indicating that the feldspars crystallized before stylolitization or jointing and before any detectable deformation of the rock.

The authigenic feldspars are sparsely scattered in the carbonate rocks

<sup>1</sup> Geological Society of America (1963), Rock Color Chart.

and often not uniformly. They generally also do not show an increased concentration along bedding planes, veins, stylolites, or joints. However, Spencer (1925) observed that albite crystals in a limestone from Bengal are concentrated in zones parallel to the bedding planes. In samples from Modane, France,<sup>1</sup> some of the albite crystals (the larger ones) are associated with veins. However, the presence of phengite in sample M-501-MF and the textural relations between the large albite and phengite crystals indicate that these larger albites formed during metamorphism.

Where authigenic feldspars are found they are common in micrites, and also in pelmicrites, and biopelmicrites; in the latter two types of micrite the feldspars partially replace pellets and fossils. They are rare in sparry calcite cement, occurring, for example, in the samples from Glens Falls, New York (Table 1). In some rocks the feldspars partially replace pellets and also extend into the sparry calcite cement. The replacements of pellets and fossils are the strongest evidence for authigenesis of these feldspars; the replacement of cement, based on the composition and distribution of carbonate inclusions in the feldspars, is very strong evidence for post-lithification crystallization of these feldspars.

*Insoluble Residue.* Insoluble residues were extracted by dissolving rocks in 10 percent aqueous solution of Na-EDTA at pH 8.1 (Glover, 1961). Table 1 shows that samples containing authigenic feldspars have smaller amounts of insoluble residue than samples in which the diagenetic origin of the feldspars is in doubt. The meaning of this observed relation is not yet understood.

Spencer (1925) observed that in Bengal "limestone associated with the albite is usually free from argillaceous material, but some of the banded limestone contains albite crystals in the calcite material between the argillaceous layers." However, in this study, no correlation has been found between the total amount of insoluble residue and the composition or quantity of authigenic feldspar in the rocks studied.

In addition to authigenic feldspar and the authigenic quartz that is usually present, the most common phases of the insoluble residues are: detrital quartz, detrital feldspars, illite, montmorillonite, mixed-layered clays, micas, pyrite, and carbonaceous matter, as shown in Table 1. Kaolinite was detected in only one sample. Because of irregular variations in the major elements of anhedral feldspars and of the various clay minerals (and micas) present in the insoluble residues (Table 1), they are regarded as detrital phases; hence, they are not considered in the phase equilibrium relations. Illite, which is present in most of the carbonate rocks studied, is the clay mineral most likely to form authigenically from

<sup>1</sup> The Modane, France locality will be discussed in a separate paper.



an expandable clay in a marine diagenetic environment (Grim, 1951; Perry and Hower, 1970), providing that the lattice charge of the expandable clays is relatively high (Weaver, 1958a and b). Therefore, I assume that some of the illite may be authigenic.

On the basis of the above assumption, the following are the authigenic mineral assemblages found:

- 1) quartz-albite
- 2) quartz-microcline
- 3) quartz-albite-illite
- 4) quartz-microcline-illite
- 5) quartz-albite-microcline
- 6) quartz-albite-microcline-illite

The most prevalent assemblages are (1) and (3); and assemblages (5) and (6) have each been found in one locality.

#### CATHODO-LUMINESCENCE

*Experimental Method.* Uncovered thin sections and single crystals of feldspars, quartz, and carbonates were studied for their cathodo-luminescence, using the electron microprobe X-ray analyzer, Applied Research Laboratories (ARL-EMX), and a luminoscope (Nuclide Corporation) operated at a pressure of 10–40 microns with an electron beam potential of 10–18 kV. The electron beam excites luminescence in the visible spectrum that is due to impurity elements such as manganese and to defect structures such as electron traps.

*Feldspars.* None of the authigenic feldspars in this study show detectable characteristics luminescence. Smith and Stenstrom (1965) examined the cathodo-luminescence of feldspars from a variety of igneous rocks. All their feldspars showed either blue or red luminescence. They did not report any non-luminescing feldspars. This suggests that cathodo-luminescence in feldspars may be related to their different geological origin, and as such luminescence might be used as a criterion for distinguishing between authigenic and non-authigenic feldspars.

To verify this suggestion, the cathodo-luminescence properties of detrital feldspar grains and cores, that are present in many of the authigenic feldspar-bearing carbonate rocks, were compared with those of specimens from pegmatites and low-grade metamorphic rocks. The luminescence properties of some of these specimens are given in Table 2, and these results and those of Smith and Stenstrom (1965) may be summarized as follows:

- 1) authigenic feldspars in carbonate rocks show no characteristic luminescence.
- 2) albites from low-grade metamorphic rocks shown no characteristic luminescence.

TABLE 2. CATHODO-LUMINESCENCE OF FELDSPARS

- 
- 
1. Water-clear albite from pegmatite (Rutherford Mine, Amelia County, Virginia, U. S. A.): *yellowish-green luminescence*.
  2. Albite lamellae in amazonite from Rutherford pegmatite (above). Albite: *yellowish-green luminescence*; amazonite: *bright-blue luminescence*.
  3. Euhedral albite crystals with carbonaceous inclusions in Upper Cretaceous dolostone (Ravdoukra, Crete, Greece): *no luminescence*.
  4. Euhedral albite crystals with microcline rims and hourglass-structure of calcite and carbonaceous inclusions, in Eocene limestone (Asklipio, Rhodes, Greece): *no luminescence*.
  5. Euhedral albites with patchy zones of calcite and carbonaceous inclusions in Middle Ordovician Glens Falls limestone (Glens Falls, New York, U. S. A.): *no luminescence*.
  6. Euhedral microcline crystals with detrital K-feldspar cores in Middle Ordovician Glens Falls limestone (above). Euhedral microcline: *no luminescence*; detrital cores: *bright-blue luminescence*.
  7. Albite porphyroblasts containing helicitic carbonaceous inclusions in Cambrian quartz-albite-sericite-biotite-garnet schist (Hoosac Fm., Massachusetts, U. S. A.): *no luminescence*.
  8. Albite porphyroblasts containing helicitic carbonaceous inclusions in quartz-stilpnomelane-biotite-albite schist (Kitani, Tottori Pref., Japan): *no luminescence*.
- 

3) alkali feldspars from pegmatites and igneous rocks show distinctive cathodo-luminescence.

Luminescence has been shown to depend on defect structures and on the concentration and interaction of a variety of trace elements which act as activators, for example manganese (Köhler, 1940; Medlin, 1963a, b; Claffy and Ginther, 1959; and Long and Agrell, 1965). These activators are presumably present in varying amounts in nearly all geological environments. The absence of luminescence probably does not indicate that the necessary elements were unavailable during crystallization, but more likely that temperatures were too low for a sufficient amount of activators to be taken up by the feldspar structure. It is generally true that the concentration of impurity ions or atoms increases with temperature. The present study supports the suggestion of Smith and Stenstrom (1965) that cathodo-luminescence properties of minerals depend on the temperature of formation.

Experimental work is needed to find out which of the elements behave as activators and which as quenchers of luminescence, and to determine the minimum temperature required to incorporate these ions in the feldspar structure in sufficient concentrations to be detectable by luminescence.

The lack of cathodo-luminescence of authigenic feldspars is a distinctive characteristic, but the data in Table 2 indicate that this property it-

self does not provide a unique criterion for establishing the authigenesis of the euhedral feldspars in carbonate rocks, for the lack of luminescence is also characteristic of low-grade metamorphic rocks. But a combination of cathodo-luminescence and twinning can be used unmistakably to distinguish between authigenic and other feldspars.

#### ELECTRON MICROPROBE X-RAY ANALYSIS

*Experimental Method.* An Applied Research Laboratories EMX electron microprobe X-ray analyzer was used for the analyses of polished and carbon-coated thin sections and single crystals, mounted with cold epoxy resin. The analytical conditions were, accelerating potential: 20 kV; sample current:  $0.03 \mu\text{A}$ , beam size:  $1-3 \mu\text{m}$  in diameter. Counting was on the basis of fixed electron flux in the electron beam, instead of fixed time. The amount of drift was small, about 1.5 per cent during a period of 11 hours; if necessary the data were corrected assuming a linear variation of drift with time. In each of the crystals between five to ten points were analyzed, and each point was counted twice.

Thirteen analyzed synthetic and natural feldspars (prepared by Waldbaum, 1966) were carefully checked for inhomogeneities and used for the standard curves. The standards and the unknown authigenic feldspars were prepared and run under identical conditions. Standard curves for  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{Na}_2\text{O}$  are linear (Kastner, 1969). In addition, the feldspars were analyzed semiquantitatively for barium.<sup>1</sup> Corrections for background were not needed because of the identity of crystal structures and great similarity in composition of standards and the authigenic feldspars.

The precision varies between  $\pm 1.0$  to  $\pm 2.0$  percent of the values for  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$ ; and between  $\pm 1.5$  to  $\pm 2.5$  percent of the values for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Correction factors given by Smith and Ribbe (1966) were used to normalize the data for standards and unknown. Their correction factors were obtained for an accelerating potential of 15 kV instead of the 20 kV in this study, thus introducing a small systematic error. However, I assume that the given precisions are sufficient to include this small error.

The electron beam was swept across each of the analyzed authigenic feldspar grains several times, and across twin boundaries. The homogeneity and lack of zoning in authigenic feldspars indicated by optical microscopy was thereby confirmed.

*Feldspars.* Electron microprobe analyses of authigenic feldspars are given in Table 3. All the analyses give totals between 99 and 101 percent.

All authigenic feldspars that have been described are alkali feldspars, having compositions between  $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$  with less than 1 mole percent  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . The two "authigenic plagioclases" reported by Singewald and Milton (1929), and Tokay (1944) were identified on the basis of wet chemical analyses of samples which probably included detrital carbonate inclusions and detrital feldspars and so are not valid.

Authigenic feldspars contain less than 0.05 weight percent  $\text{BaO}$ , unlike most detrital K-feldspar cores and several detrital plagioclase cores, which do contain barium.

<sup>1</sup> Boron has not been detected in authigenic feldspars. The limit of detectability for boron is high, particularly for the relatively short counting times required for alkali feldspars analysis.

TABLE 3A. ELECTRON MICROPROBE ANALYSES OF AUTHIGENIC ALBITES IN WEIGHT PERCENT. AB., OR., AND AN. IN MOLE PERCENT

	Glens Falls, New York M-252-GF	Glens Falls, New York M-256-GF	Rhodes, Greece M-351-IR	Rhodes, Greece M-355-IR	Rav-doukha, Crete M-401-IC	Rav-doukha, Crete M-402-IC	Modane, France M-500-MF	Modane, France M-501-MF	Near Belle-fonte, Pa. M-654-OP
SiO <sub>2</sub>	n.d.	68.80	68.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al <sub>2</sub> O <sub>3</sub>	n.d.	19.70	19.85	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na <sub>2</sub> O	11.96	11.71	12.00	11.98	11.72	11.74	11.99	11.98	11.87
K <sub>2</sub> O	—	0.01	0.01	—	—	—	—	—	0.02
CaO	—	—	0.01	0.01	—	—	0.01	—	0.01
Total		100.21	99.87						
Ab		99.94	99.85						
Or		0.06	0.06						
An		—	0.09						

Near Belle-fonte, Pa. M-655-OP	Pleasant Gap, Pa. M-674-OP	Pleasant Gap, Pa. M-682-OP	Pleasant Gap, Pa. M-683-OP	Tatum Dome, Miss. M-715-TD	Desert Creek Zone, Utah M-739-PU	Desert Creek Zone, Utah M-740-PU	Provo Canyon, Utah M-751-PU	Provo Canyon, Utah M-752-PU	Albite, Theoretical Composition
n.d.	n.d.	67.80	68.20	68.30	n.d.	68.30	n.d.	68.50	68.73
n.d.	n.d.	19.82	19.48	20.00	n.d.	20.02	n.d.	19.99	19.44
11.80	11.89	11.86	12.01	11.90	11.92	11.81	11.76	11.97	11.83
0.01	0.02	0.01	0.02	—	0.02	0.01	—	0.01	—
0.01	—	—	—	—	—	—	—	—	—
		99.49	99.71	100.20		100.14		100.47	100.00
		99.94	99.89	100.00		99.94		99.94	100.00
		0.06	0.11	—		0.06		0.06	—
		—	—	—		—		—	—

Chemical analyses of feldspars frequently report the presence of small amounts of Sr, Ti, Fe, Pb, and H<sub>2</sub>O. The authigenic feldspars were not analyzed for these elements. Heier and Taylor (1959) showed that Sr is associated with Ba in K-feldspars. Hence it is suggested that authigenic feldspars likewise do not contain Sr. Probably at low to moderate temperatures the feldspar is unable to include Ti, Fe, and Pb in its structure. At present, the electron microprobe is the only suitable technique for reliable chemical analyses of authigenic feldspars. All other common chemical techniques require a clean mineral separation which is virtually impossible to obtain because of the presence of inclusions and detrital cores in authigenic feldspars.

TABLE 3B. ELECTRON MICROPROBE ANALYSES OF AUTHIGENIC MICROCLINES IN WEIGHT PERCENT. AB., OR., AND AN. IN MOLE PERCENT

	Water- ton Park, Alberta M-117- WP	Goose Lake, N. Michigan M-201- NM	Goose Lake, N. Michigan M-203- NM	Glens Falls, New York M-251- GF	Near Belle- fonte, Pa. M-659- PO	Axe- mann, Pa. M-692- OP	Water- ton Park, Alberta M-1158- BW	Micro- cline, The- oretical Compo- sition
SiO <sub>2</sub>	n.d.	64.80	64.70	64.90	64.80	65.00	n.d.	64.76
Al <sub>2</sub> O <sub>3</sub>	n.d.	18.65	18.60	18.45	18.94	18.72	n.d.	18.32
Na <sub>2</sub> O	0.04	0.10	0.10	0.10	0.10	0.05	0.05	—
K <sub>2</sub> O	16.90	17.02	16.98	16.90	16.96	16.94	16.92	16.92
CaO	0.03	0.01	—	—	—	0.01	0.03	—
Total		100.58	100.38	100.35	100.80	100.72		100.00
Ab		0.89	0.94	0.95	0.89	0.45		—
Or		99.01	99.06	99.05	99.11	99.45		100.00
An		0.10	—	—	—	0.10		—

The reported presence of H<sub>2</sub>O in feldspar analyses, ranging between 0.02–1.27 weight percent (Deer *et al.*, 1963), has been discussed by Smith and Ribbe (1966). They have suggested that the H<sub>2</sub>O may result either from alteration products or from the substitution of hydronium, (H<sub>3</sub>O)<sup>+</sup>, for alkalis. Liquid inclusions also may be responsible for some of the H<sub>2</sub>O. Alteration products and inclusions can easily be avoided in a careful microprobe analysis. If a significant substitution of hydronium for alkali metals has taken place relatively low values for alkalis should be obtained. Alkali metal values for authigenic feldspars in Table 3 do not suggest a notable substitution of this kind. According to Thompson and Waldbaum (1969) such an extensive substitution is not very likely in natural low-temperature feldspars coexisting with aqueous solutions of high pH.

The effect of carbonate inclusions and possibly of detrital feldspar cores on chemical analyses of authigenic feldspars, analyzed by Spencer (1925), Honess and Jeffries (1940), Jacob and Neher (1951), and Baskin (1956), indicates that this method is not valid for analyzing authigenic feldspars.

Non-authigenic low albites from pegmatites and other igneous rocks (without detrital cores and inclusions) have a higher content of potassium and calcium than authigenic albites; and non-authigenic microclines have a higher content of sodium and calcium than authigenic microclines, as

shown by Kracek and Neuvonen (1952), Emmons (1953), and Deer, Howie, and Zussman (1963). The low to moderate temperature of crystallization of authigenic feldspars accounts for their greater chemical purity.

One of the major conclusions of this study is that authigenic feldspars are homogeneous, stoichiometric end members of the alkali feldspar series. Authigenic albites contain more than 99 mole percent  $\text{NaAlSi}_3\text{O}_8$  and authigenic microclines contain more than 99 mole percent  $\text{KAlSi}_3\text{O}_8$ .

The homogeneity and lack of zoning in authigenic albite and microcline is shown in Figure 1; the conspicuous lack of K and Ca in authigenic albites and of Na and Ca in the authigenic microcline rim of sample M-355-IR, Rhodes, is shown in Figures 1 and 2. In addition to the homogeneity of both authigenic albite and authigenic microcline, these figures also show the sharp boundary between the two authigenic phases. This natural occurrence is the most chemically pure example of coexisting low albite and microcline known to the author. In contrast, the presence of Na in a K-feldspar detrital core and of Ca in a detrital plagioclase core are shown in Figures 3 and 4.

#### X-RAY CRYSTALLOGRAPHY

*Experimental Method.* Unit-cell parameters of authigenic feldspar crystals and their carbonate matrix were determined by least-square analysis of X-ray diffractometer data using the digital computer program of Burnham (1962) with three iterations for each set of data as described by Kastner and Waldbaum (1968, p. 1591).

The qualitative results of the X-ray diffraction analyses of the insoluble residues (which were extracted by dissolving the rock in a 10 percent aqueous solution of Na-EDTA at pH 8.1) are summarized in Table 1.

Each samples was mixed with the silicon internal standard and deposited on a glass slide. Ni-filtered copper radiation was used to obtain diffraction charts of the unglycolated and glycolated mounts at  $1^\circ 2\theta \text{ min}^{-1}$  in the range  $2^\circ$  to  $50^\circ$  with a chart speed of 1 inch per minute. Resolution of the  $3.54 \text{ \AA}$  (004) chlorite reflection and the  $3.58 \text{ \AA}$  (002) kaolinite reflection was obtained at  $0.25^\circ 2\theta \text{ min}^{-1}$ , as decribed by Biscaye (1965).

The accuracy of the refined unit-cell parameters in this study may be estimated by comparing data for Amelia albite and KCl-exchanged Amelia albite, (Kastner, 1969) with those of previous studies (Kastner and Waldbaum, 1968, Table 2; Luth and Suñé, 1970; Waldbaum and Robie, 1972, Table 1).

*Feldspars.* The separation and analysis of authigenic feldspars is difficult because detrital feldspars nearly always occur along with the authigenic feldspars in carbonate rocks. The detrital feldspars occur either as single grains or as cores. Their composition varies between alkali feldspars and sodium-rich plagioclases; their structural state varies between ordered and disordered.

Most albite crystals in these rocks show no evidence of detrital cores. Where detrital cores are present, they are the same minerals as found in

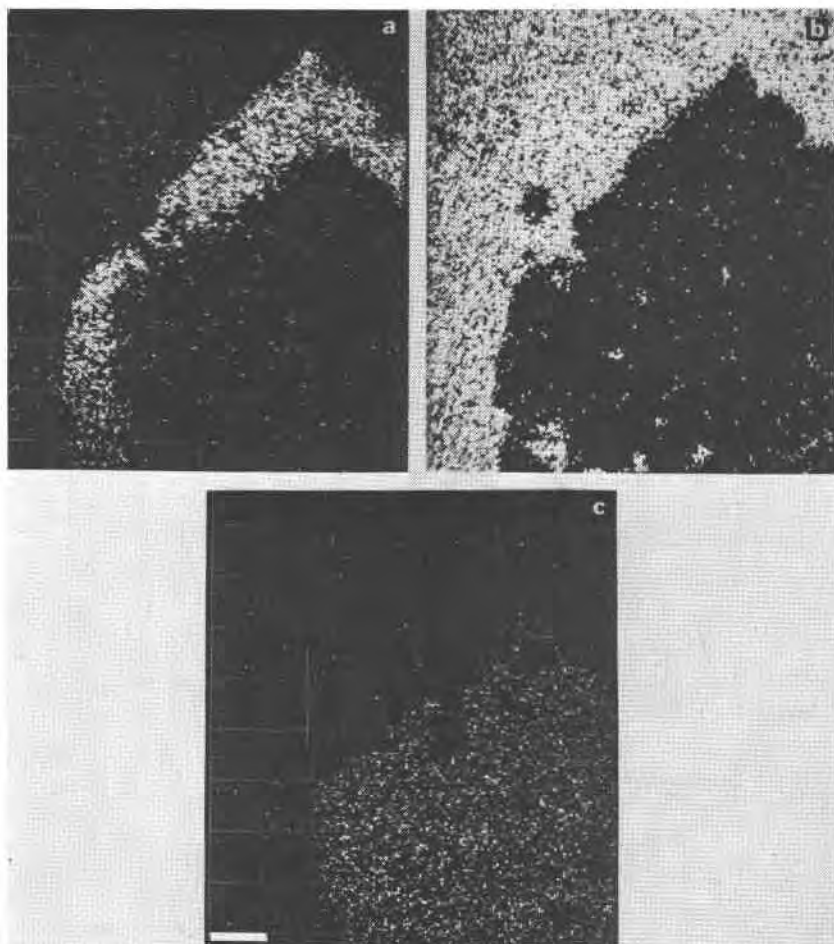


FIG. 1. Electron beam scanning photographs of upper portion of authigenic albite crystal with authigenic microcline rim, in thin section, sample M-355-1R, Rhodes.

- a) — $K\bar{K}$  X-ray image.
- b) — $Ca\bar{K}$  X-ray image.
- c) — $Na\bar{K}$  X-ray image of same area.

White line in lower left of Fig. 1c represents  $20\ \mu\text{m}$  for all photographs.

the matrix. Detrital cores of calcite, dolomite, quartz, K-feldspar and plagioclase have been identified with the electron probe (Figures 2, 3, and 4). A detrital core of pyrite was found in one occurrence from Glens Falls, N.Y. In contrast, however, most authigenic microcline crystals only grow around K-feldspar detrital cores; though this does not exclude the possibility of finding detrital cores of other compositions. Separate grains

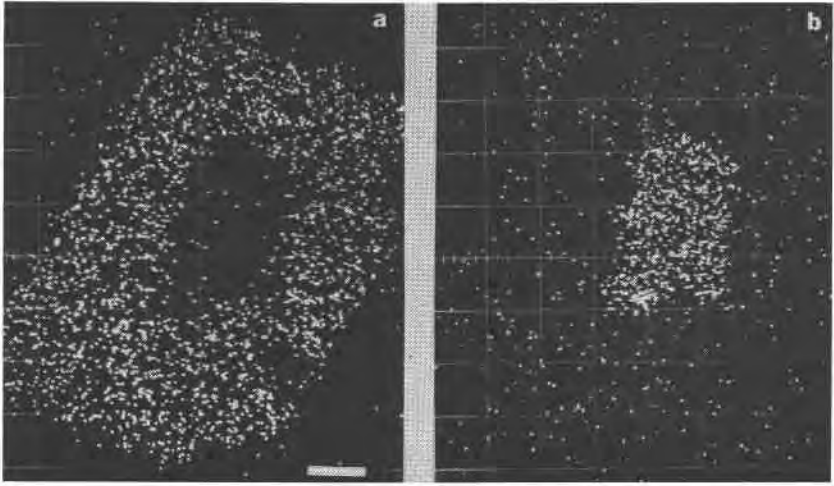


FIG. 2. Electron beam scanning photographs of authigenic albite and detrital K-feldspar core, sample M-752-PU, Utah.

- a) —Na<sub>K</sub>α X-ray image.  
b) —K<sub>K</sub>α X-ray image of same area.

White line in lower right of Fig. 2a represents 10 μm for both photographs.

of detrital K-feldspars have been observed in all rock specimens examined thus far. The presence of detrital feldspars interferes with and affects the quality of the X-ray reflections, and consequently affects also the refined unit-cell parameters, as discussed below.

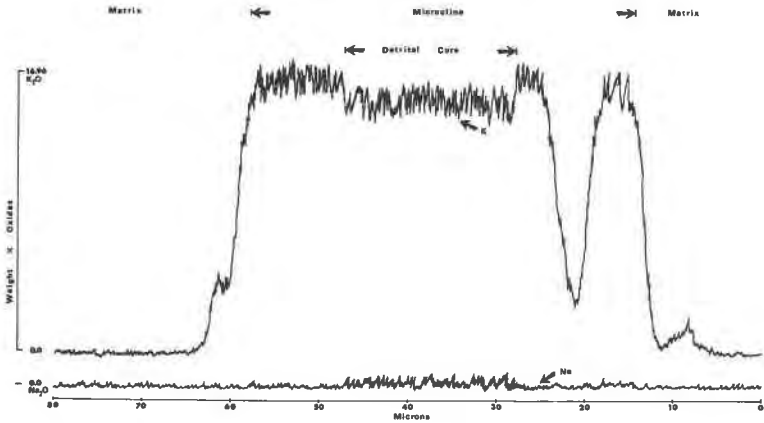


FIG. 3. Continuous electron beam scans for Na and K across limestone matrix, authigenic microcline overgrowth, and alkali feldspar detrital core, sample M-659-OP, Pennsylvania.



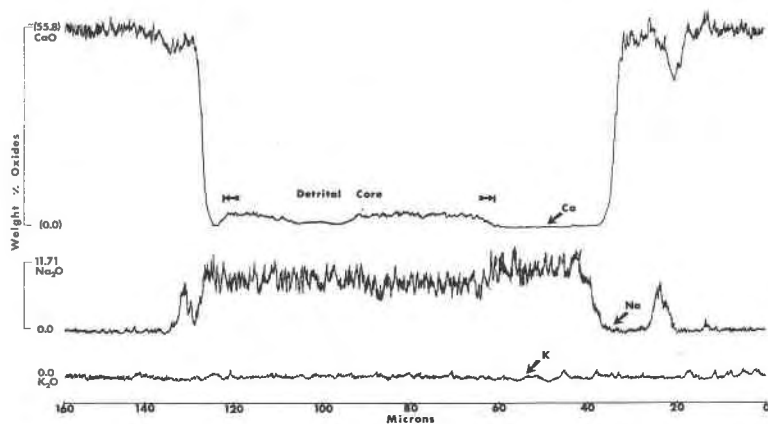


FIG. 4. Continuous electron beam scans for K, Na, and Ca across limestone matrix, authigenic albite overgrowth, and oligoclase detrital core, sample M-256-GF, Glens Falls, N.Y. Weight percent CaO, in brackets, denotes calculated values from X-ray analysis.

In this study, unit-cell parameters for authigenic feldspars without or with only a negligible amount of detrital cores were determined (Tables 4 and 5 and Figure 5). The effect on the refined unit-cell dimensions of mixing detrital and authigenic feldspars is shown in Table 6 and Figure 5. In Table 5, sample M-355-IR, from Rhodes, is the only authigenic microcline without detrital cores. It occurs as narrow microcline rims, 3 to 20  $\mu\text{m}$  wide, around relatively large authigenic albite crystals. (The largest crystals were 1.75 mm along  $a$ , 0.3 mm along  $b$ , and 1.5 mm along  $c$ ). Because of the large proportion of albite only a small number of microcline reflections could be obtained and used for the refinement. The other three microcline samples do include a few detrital K-feldspar cores.

The unit-cell parameters for authigenic albites and microclines in Tables 4 and 5 do not differ appreciably from previous determinations of low albites and microclines from non-sedimentary environments, as given in the bottom of Table 5 and Table 2, from Kastner and Waldbaum (1968). This conclusion however, is not in agreement with Baskin's data (1956), which indicate anomalously low cell dimensions for authigenic albites and microclines both from the same localities reexamined in the present study, and from other localities, as shown in Tables 4 and 5 and in Figure 5.

The results in Table 6 and Figure 5 show that determinations of the apparent unit-cell are affected appreciably by mixing authigenic and detrital feldspars. The limits of precision are slightly larger for the mixtures in Table 6 than of the purely authigenic feldspars of Table 4. The

TABLE 4. UNIT-CELL PARAMETERS OF PURELY AUTHIGENIC LOW-ALBITE. VALUES OF  $a$ ,  $b$ ,  $c$ , AND  $(d_{1\bar{1}\bar{1}} - d_{111})$  IN Å;  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha^*$  AND  $\gamma^*$  IN DEGREES;  $V$  (CELL VOLUME) IN Å<sup>3</sup>. UNCERTAINTIES (LEAST-SQUARE STANDARD ERRORS) ARE TABULATED NEXT TO EACH UNIT-CELL PARAMETER

Feldspar	Ref.	Lines <sup>a</sup>	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	$V$	$\alpha^*$	$\gamma^*$	$d_{1\bar{1}\bar{1}} - d_{111}$
M-256-GF Glens Falls, N. Y.	(1)	17	8.1301 (36)	12.7851 (30)	7.1578 (29)	94.216 (44)	116.658 (27)	87.805 (50)	663.11 (51)	86.383 (35)	90.342 (42)	0.1054
M-351-IR Rhodes, Greece	(1) (1a)	23	8.1380 (14)	12.7881 (13)	7.1571 (08)	94.229 (13)	116.605 (09)	87.807 (13)	664.14 (20)	86.367 (11)	90.337 (11)	0.1059
M-355-IR Rhodes, Greece	(1)	18	8.1367 (21)	12.7853 (18)	7.1583 (13)	94.170 (25)	116.610 (14)	87.813 (25)	664.03 (32)	86.431 (22)	90.360 (22)	0.1045
M-402-1C Kavdonkha, Crete	(1) (1a)	25	8.1365 (26)	12.7850 (18)	7.1560 (12)	94.227 (18)	116.597 (14)	87.789 (26)	663.81 (31)	86.378 (15)	90.358 (24)	0.1049
M-420-1C Lioptero, Crete	(1) (1a)	15	8.1345 (19)	12.7809 (15)	7.1561 (08)	94.206 (14)	116.581 (12)	87.818 (16)	663.55 (26)	86.387 (18)	90.337 (11)	0.1052
M-500-MF Modane, Savoie, France	(1)	25	8.1378 (16)	12.7769 (18)	7.1607 (14)	94.256 (16)	116.639 (13)	87.704 (17)	663.65 (29)	86.389 (14)	90.436 (15)	0.1032
M-501-MF Modane, France	(1)	23	8.1379 (17)	12.7752 (20)	7.1569 (10)	94.218 (17)	116.613 (09)	87.758 (17)	663.41 (23)	86.404 (13)	90.396 (13)	0.1017
M-682-OP Pleasant Gap, Pa.	(1)	11	8.1353 (19)	12.7761 (49)	7.1572 (10)	94.263 (26)	116.635 (10)	87.709 (28)	663.10 (29)	86.379 (18)	90.427 (21)	0.1035
M-751-PU Provo Canyon, Utah	(1)	10	8.1350 (89)	12.7845 (33)	7.1569 (57)	94.211 (73)	116.592 (56)	87.849 (69)	663.79 (99)	86.367 (60)	90.300 (56)	0.1060
Gelbhornstecke; Switzerland	(2)	8	8.125 (32)	12.757 (51)	7.149 (29)	94.267 (170)	116.700 (170)	87.817 (170)	660.14	86.321 (170)	90.300 (170)	0.1081
Gelbhornstecke; Switzerland	(2)	8	8.117 (32)	12.749 (51)	7.142 (29)	94.350 (170)	116.633 (170)	87.783 (170)	658.75	86.244 (170)	90.301 (170)	0.1105
Valentine Fm., Pa.	(2)	8	8.110	12.803	7.140	94.150	116.633	87.717	660.94	86.500	90.467	0.0976
Lowville Fm., Pa.	(2)	8	8.124	12.815	7.132	94.417	116.550	87.617	662.21	86.300	90.483	0.1063
Trochitenkalk, Göttingen, Germany	(2)	8	8.129	12.786	7.173	93.733	116.583	88.867	665.28	86.333	89.367	0.1312

<sup>a</sup> No. of lines in each chart

- (1) This study  
(1a) Kastner and Waldebaum (1968)  
(2) Baskin (1956)

TABLE 5. UNIT-CELL PARAMETERS OF AUTHIGENIC MICROCLINE. VALUES OF a, b, c, AND (d<sub>111</sub> - d<sub>112</sub>) IN Å; α, β, γ, α\*, β\*, γ\* AND γ\* IN DEGREES; V (CELL VOLUME) IN Å<sup>3</sup>. UNCERTAINTIES (LEAST-SQUARE STANDARD ERRORS) ARE TABULATED NEXT TO EACH UNIT-CELL PARAMETER

Feldspar	Ref.	Lines <sup>a</sup>	a	b	c	α	β	γ	V	α*	β*	γ*	d <sub>111</sub> - d <sub>112</sub>
M-201-NM Goose Lake, N. Michigan	(1)	21	8.5737 (54)	12.9669 (21)	7.2230 (30)	90.630 (25)	115.921 (25)	87.670 (27)	721.62 (73)	90.431 (25)	92.284 (26)	92.284 (26)	0.0787
M-355-JR K-rim, Rhodes, Greece	1	7	8.5839 (42)	12.9601 (54)	7.2178 (20)	90.593 (48)	115.881 (24)	87.722 (36)	721.84 (62)	90.447 (40)	92.245 (24)	92.245 (24)	~0.064
M-659-OP Near Bellefonte, Pa.	(1)	18	8.5852 (26)	12.9610 (14)	7.2212 (17)	90.537 (16)	115.956 (14)	87.984 (15)	722.01 (36)	90.384 (14)	91.981 (13)	91.981 (13)	0.0680
M-46-OP Glacier Park, Montana	(1)	13	8.5656 (72)	12.9632 (24)	7.2240 (41)	90.682 (33)	116.041 (34)	87.804 (31)	720.17 (1.04)	90.314 (28)	92.110 (26)	92.110 (26)	0.0685
Stonchenge Fm., Pa.	(2)	8.578 (34)	12.930 (52)	7.220 (29)	90.383 (170)	115.967 (170)	88.433 (170)	719.8	90.300 (170)	91.533 (170)	91.533 (170)	91.533 (170)	0.0632
Kona dolomite, Michigan	(2)	8.563 (34)	12.935 (52)	7.210 (29)	90.433 (170)	115.950 (170)	88.317 (170)	718.8	90.333 (170)	91.666 (170)	91.666 (170)	91.666 (170)	0.0776
Arbuckle Fm., Oklahoma	(2)	8.595 (34)	12.994 (52)	7.195 (29)	90.00	116.067 (170)	90.00	721.8	90.00	90.00	90.00	90.00	0.0
Pontisalk, Switzerland	(2)	8.571 (34)	12.941 (52)	7.229 (29)	90.650 (170)	115.950 (170)	87.650 (170)	720.4	90.417 (170)	92.300 (170)	92.300 (170)	92.300 (170)	0.0780
Fontisalk, Switzerland	(3)	8.5726	12.9618	7.2188	90.567	115.917	87.750	721.3	90.467	92.217	92.217	92.217	0.0780
<i>Non Authigenic microcline</i>													
Mean value <sup>b</sup>			8.5807	12.9662	7.2222	90.630	115.927	87.677	722.06	90.429	92.277	92.277	0.0787
Range of values <sup>b</sup>			8.5764	12.9610	7.2199	90.612	115.918	87.619	721.17	90.388	92.196	92.196	0.0746
			8.5840	12.9723	7.2238	90.653	115.947	87.747	722.79	90.454	92.330	92.330	0.0805

<sup>a</sup> No. of lines in each chart.

<sup>b</sup> Based on data by Kastner (1969), Orville (1967), and Waldbaum (1966).

(1) This study.

(2) Baskin (1956).

(3) Finney and Bailey (1964).

TABLE 6. UNIT-CELL PARAMETERS OF AUTHIGENIC FELDSPARS WITH DETRITAL FELDSPAR CORES. VALUES OF  $a$ ,  $b$ , AND  $c$  IN Å;  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha^*$  AND  $\gamma^*$  IN DEGREES;  $V$  (CELL VOLUME) IN Å<sup>3</sup>. UNCERTAINTIES (LEAST-SQUARE STANDARD ERRORS) ARE TABULATED NEXT TO EACH UNIT-CELL PARAMETER

Feldspar	Ref.	Lines <sup>a</sup>	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	$V$	$\alpha^*$	$\gamma^*$
<i>Authigenic NaAlSi<sub>3</sub>O<sub>8</sub></i>											
M-683-OP	(1)	10	8.1236 (530)	12.8222 (581)	7.1487 (102)	94.201 (425)	116.548 (318)	87.683 (407)	664.29 (3.85)	86.460 (283)	90.493 (270)
Pleasant Gap, Pa.											
M-715-TD	(1)	9	8.1416 (55)	12.7838 (25)	7.1482 (34)	94.156 (59)	116.588 (30)	87.884 (71)	663.55 (77)	86.411 (54)	90.289 (66)
Tatum Dome, Miss.											
M-715-TD	(1)	10	8.1413 (75)	12.7829 (36)	7.1519 (50)	94.082 (95)	116.611 (41)	87.925 (112)	663.75 (1.06)	86.473 (79)	90.278 (100)
Tatum Dome, Miss.											
M-740-FU	(1)	19	8.1418 (27)	12.7913 (15)	7.1503 (23)	94.183 (39)	116.621 (20)	88.013 (50)	663.95 (48)	86.316 (28)	90.128 (41)
Dessert Creek Zone, Utah											
<i>Authigenic KAlSi<sub>3</sub>O<sub>8</sub></i>											
M-106-WP	(1)	13	8.5748 (83)	12.9600 (55)	7.2137 (69)	90.741 (72)	115.922 (50)	87.853 (66)	720.48 (1.38)	90.219 (62)	92.027 (55)
Waterton Park, Alberta											
M-692-OP	(1)	17	8.5344 (124)	12.9703 (68)	7.2121 (110)	90.848 (109)	115.748 (93)	87.742 (103)	718.51 (2.50)	90.148 (95)	92.098 (87)
Axemann, Pa.											
M-1158-BW	(1)	12	8.6089 (33)	12.9663 (06)	7.1841 (24)	91.218 (09)	115.417 (19)	88.282 (18)	723.94 (63)	89.398 (10)	91.293 (18)
Waterton Park, Alberta											

<sup>a</sup> No. of lines in each chart.

(1) This study.

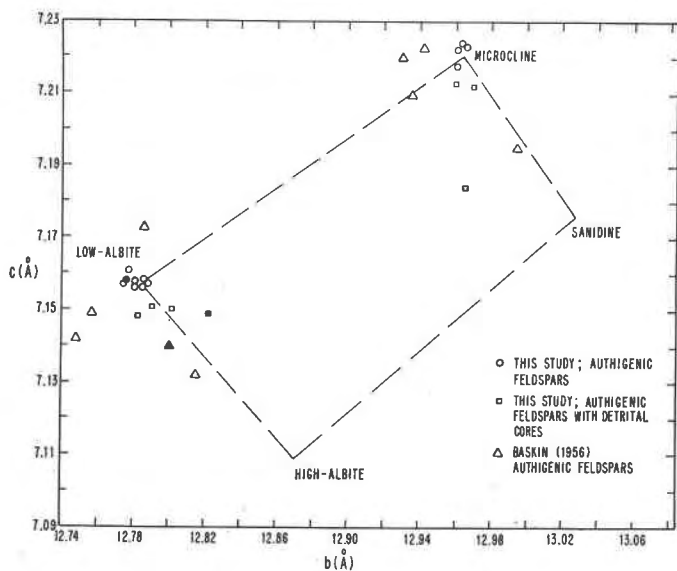


FIG. 5. Unit-cell parameters  $b$  and  $c$  of authigenic feldspars without and with detrital feldspar cores, in Tables 4, 6, and Table 2 in Kastner and Waldbaum (1968). Solid circle, square, and triangle denote values for albite from Valentine Fm., Pa., Tables 4 and 6. Dashed lines connect Stewart and Ribbe's (1969) values for cell parameters of alkali-feldspars end members.

mixing might be partially responsible for the very large limits of precision in Baskin's set of data. Both Baskin's data for authigenic albite, Valentine Fm., Pa. (Table 4), and present results for sample M-683-OP, a mixture of detrital and authigenic feldspars from the same formation and locality (Table 6), are anomalous for authigenic albite compared with unit-cell parameters of authigenic albite only, Valentine Fm. Pa., sample M-682-OP, Table 4, and with unit-cell parameters of authigenic albite from other localities given in Table 4.

These results do not support Martin's (1968) suggestion that Baskin's anomalous data might be typical for authigenic albite crystallized at low temperatures ( $100^{\circ}\text{C}$  or less) and incapable of recrystallization to the lowest structural state. In addition to a systematic error in Baskin's cell parameters, the most plausible explanation for the variance between his and present results is that Baskin might have studied mixtures of authigenic and detrital feldspars.

The extraordinary chemical purity and homogeneity of both authigenic albites and microclines has been confirmed by electron probe analyses given in Table 3. Because these authigenic feldspars are so chemically

pure, the  $d_{1\bar{3}1}-d_{131}$  reflections, which, in general, are measures of both chemical composition and Al-Si ordering (Orville, 1967; Waldbaum, 1966), can be used for these feldspars as a measure of Al-Si ordering alone.

The unit-cell parameters plotted in Figure 5 indicate that authigenic feldspars are highly-ordered low albites and microclines with respect to  $b$  and  $c$ , but the relatively low values of  $\alpha^*$  and  $\gamma^*$  of authigenic albites and microclines and the corresponding high values of  $d_{1\bar{3}1}-d_{131}$  of authigenic microclines, indicate that authigenic feldspars may be somewhat more disordered than pegmatitic triclinic alkali feldspars. Optic axial angles ( $2V$ ) which range between  $78^\circ$  and  $84^\circ$  for authigenic albites and between  $80^\circ-82^\circ$  for authigenic microclines, are in agreement with these results. Samples M-501-MF, Modane, France, in Table 4 and M-201-NM, Michigan, in Table 5 are exceptions. Their  $d_{1\bar{3}1}-d_{131}$  values are similar to values obtained from pegmatitic alkali feldspars. On the basis of the assemblages iron-rich chlorite-microcline the microclines of these two occurrences might have formed either in a low-grade metamorphic environment (Zen, 1960) or in a diagenetic environment, as discussed below.

The only albite of an intermediate degree of order, that is assumed to be authigenic, is that from Trochitenkalk (Lower Muschelkalk) at Göttingen described by Baskin (1956). All other reported data for authigenic albite are consistent with the present conclusions, i.e., that authigenic albites exhibit a high degree of order. In contrast, a few authigenic K-feldspars studied by Baskin (1956) are either monoclinic or disordered triclinic. Füchtbauer (1950, 1956), on the basis of optical measurements of authigenic feldspars from the Göttingen Muschelkalk, concluded that the authigenic feldspars that occur as overgrowths around detrital K-feldspars are monoclinic and probably inherited the Al/Si ordering of the detrital cores. But newly formed authigenic feldspars without detrital cores are triclinic.

The above observations on the samples studied here suggest that most, but perhaps not all, authigenic K-feldspars are highly-ordered and triclinic. More occurrences of authigenic K-feldspars should be studied with current techniques before conclusions can be reached regarding the ordering of authigenic K-feldspars.

Martin (1968) synthesized orthoclase but not microcline; under identical conditions he synthesized low-albite. In igneous, sedimentary, and metamorphic rocks most Na-feldspars are well-ordered albites, but most K-feldspars are monoclinic or disordered triclinic. The mechanism and kinetics of ordering of alkali-feldspars are not well enough understood to account for the measured differences between K- and Na-feldspars.

The unit-cell parameters of authigenic feldspars given in Tables 4 and

5, the triclinic morphology of authigenic microclines, (Baskin, 1956), and the absence of the typical transformation twins in these microclines (Baskin, 1956; Kastner, 1969) suggest that authigenic albites as well as some authigenic K-feldspars did not originally grow as highly disordered phases; they probably grew as ordered phases.

#### CRITERIA FOR AUTHIGENESIS

Eight major criteria distinguish the authigenic feldspars in carbonate rocks from those of igneous and medium to high-grade metamorphic rocks:

1. *Habit.* All authigenic feldspars are euhedral with pinacoidal faces. In addition, authigenic microclines have a triclinic morphology, unlike microclines from other geological environments which generally have a monoclinic morphology. (Bögild, 1910, 1924, described from Ivigtut the only other morphologically triclinic microcline).

2. *Textural Relationships.* As established by microscopy, authigenic feldspars replace fossils, cut across pellets, contain rock inclusions, and are cut and/or displaced by late epigenetic veins of calcite.

3. *Twinning.* Authigenic albites are either untwinned, twinned after the albite law as contact twins, or twinned after the X-Carlsbad law as penetration twins, each consisting of two individuals (Kastner and Wladbaum, 1968). Authigenic microclines are either untwinned, twinned after the albite and pericline laws as "fourlings" (Baskin, 1956), or after the Ala-A law (Folk, 1952). In this study no polysynthetic or cross-hatch twins have been observed in authigenic feldspars. They have been reported by Füchtbauer (1950), but only in overgrowth of similarly twinned feldspar cores.

4. *Inclusions.* Carbonate inclusions are present in all authigenic feldspars in carbonate rocks. The composition of the inclusions and the rock matrix are identical, as established by microprobe analysis and cathodoluminescence. Occasionally, a zonally-arranged pattern of inclusions or an inclusion hourglass structure is present.

5. *Al-Si Ordering.* Refined unit-cell parameters indicate that authigenic albites (and several authigenic microclines) are highly ordered but apparently not as ordered as albites (and microclines) from pegmatites.

6. *Optical Properties.* Table 7 shows that the optic axial angles ( $2V$ ) of authigenic albites are significantly larger than for low albites from other

TABLE 7. OPTIC AXIAL ANGLES ( $2V$ ) OF AUTHIGENIC FELDSPARS

Sample	Reference	$2V_{\gamma}$ meas.
<i>Albite</i>		
M-256-GF Glens Falls, N.Y.	(1)	$80.0 \pm 4.0$
M-351-IR Rhodes, Greece	(1, 1a)	$81.0 \pm 2.0$
M-501-MF Modane, France	(1)	$83.5 \pm 2.0$
M-683-OP Pleasant Gap, Pa.	(1)	$78.0 \pm 4.0$
M-751-PU Provo Canyon, Utah	(1)	$84.0 \pm 5.0$
Zweisimmen, Switzerland	(2)	$85.0 \pm 0.8$
St. Maurice, Switzerland	(2)	$88.5 \pm 0.4$
Bellefonte, Pa.	(3)	$70.0 \pm 5.0$
Göttingen, Germany	(4)	$90.0 \pm 5.0$
<i>Microcline</i>		
M-203-NM Goose Lake, N. Michigan	(1)	$81.0 \pm 5.0$
M-355-IR Rhodes, Greece	(1)	$> 80.0$
M-692-OP Axemann, Pa.	(1)	$82.0 \pm 5.0$
Arbuckle Fm, Oklahoma	(4)	50–55
Pontiskalk, Switzerland	(5)	$80.0 \pm 2.0$
Pontiskalk, Switzerland	(6)	77.0
Göttingen, Germany	(2a)	$43.0 \pm 0.5$

- (1) This study  
 (1a) Kastner and Waldbaum (1968)  
 (2) Füchtbauer (1948)  
 (2a) Füchtbauer (1950)  
 (3) Honess and Jeffries (1940)  
 (4) Baskin (1956)  
 (5) Perrenoud (1952)  
 (6) Finney and Bailey (1964)

geological environments (Füchtbauer, 1948, 1956; Schöner, 1960; Kastner and Waldbaum, 1968). The optic angles of our authigenic microclines are similar to those of microclines from other geological environments, although Füchtbauer (1950) reported angles of  $20^{\circ}$ – $40^{\circ}$  for a few authigenic microclines. The optic angles and the X-ray results of both albites and microclines are consistent with their Al-Si ordering.



7. *Composition.* Authigenic feldspars show extraordinary chemical purity. Both authigenic albite and microcline contain less than 1 mole percent  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . The albite contains less than 1 mole percent  $\text{KAlSi}_3\text{O}_8$  and the microcline contains less than 1 mole percent  $\text{NaAlSi}_3\text{O}_8$ . They are thus nearly end-member compositions of the alkali-feldspar series, homogeneous, and show no zoning.

8. *Cathodo-luminescence.* Authigenic feldspars show no detectable luminescence in contrast to bright luminescence of high-temperature igneous and metamorphic feldspars.

One criterion alone cannot be used for establishing the authigenic origin of authigenic feldspars. Nevertheless, a combination of twinning, chemical purity, and cathodo-luminescence can be used to distinguish unambiguously between authigenic feldspars and those from other geologic environments.

The main characteristics of authigenic versus detrital alkali feldspars are summarized in Table 8.

#### GEOCHEMICAL ENVIRONMENT AND ORIGIN OF AUTHIGENIC FELDSPARS IN CARBONATE ROCKS

*Clay (mica) Components.* The association of clay minerals with authigenic feldspars has been investigated. Table 1 shows the following: (1) Clay minerals associated with authigenic feldspars are: illite, montmorillonite, mixed-layered clays, and chlorite. (2) Illite is invariably present with authigenic albite, except for the Rhodian occurrence where the only coexisting potassium phase is microcline. (3) Most of the listed microclines coexist with both illite and chlorite, except for the microclines from Waterton Fm., Alberta, and from Kona dolostone, N. Michigan, which coexist with chlorite only. Montmorillonite and mixed-layered clays are considered to be detrital phases on the basis of the variations in their major elements as verified with the microprobe.

In addition to the abundance of detrital illites in sediments, illites are also known to form authigenically during diagenesis. Grim (1951) concluded that time is an important factor in the observed alteration of expandable clays to micas. Perry and Hower (1970) in their study of Pleistocene to Eocene shales from Gulf Coast oil wells concluded that with increasing depth the proportion of illite layers increases in illite/montmorillonite. Reynolds (1963), on the basis of the high content of 1M*d* illites in the upper Belt series, concluded that they are almost certainly authigenic. Hower, Hurley, Pinson, and Fairbairn (1963), on the basis of K-Ar ages also indicated diagenetic origin of illites. Considering

TABLE 8. MAIN CHARACTERISTICS OF AUTHIGENIC VERSUS DETRITAL ALKALI FELDSPARS

Feldspar	Petrography	Habit	Optics	Twinning	Cathodo- Luminescence	X-Ray	Alkalies	Inclusions
<b>Authigenic Albites</b>	Replacement of matrix	Euhedral	Significantly higher 2V than non-authi- genic low albites.	Untwinned, twinned after the albite law (no polysynthetic twins), or after the X-Carlsbad law.	Do not luminesce	Highly ordered	Ab. > 99 mole % Or. < 1 mole % An. < 1 mole %	Carbonate inclusions identical in composition to the matrix are always present.
<b>Detrital Albites</b>	Corners and edges rounded	A variety of habits and shapes	Significantly lower 2V than authigenic albites.	Untwinned or any possible twin law for albite.	Most do luminesce with varying in- tensities and colors.	Varying degrees of order.	Or. and An. > 1 mole %	No relation between composi- tion of inclusions (if present) and of matrix.
<b>Authigenic Microclines</b>	Replacement of matrix	Euhedral with triclinic morphology.	Similar to non- authigenic micro- clines.	Untwinned, twinned after the albite and pericline law as "fourlings" or after the Al <sub>2</sub> A law.	Do not luminesce	Highly ordered	Ab. < 1 mole % Or. > 99 mole % An. < 1 mole %	Carbonate inclusions identical in composition to the matrix are always present.
<b>Detrital Microclines</b>	Corners and edges rounded	A variety of habits and shapes, al- most always monoclinic morphology.	Similar to authi- genic microclines.	Untwinned; most often cross-hatch twins.	Most do luminesce with varying in- tensities and colors.	Varying degrees of order.	Ab. and An. > 1 mole %	No relation between composi- tion of inclusions (if present) and of matrix.

also similar observations by other investigators, it is suggested that probably some of the illites associated with authigenic feldspars are authigenic.

The tendency of authigenic feldspars to be associated with illite is explained in Figure 6, showing phases coexisting with quartz in the system  $\text{HAlO}_2\text{-NaAlO}_2\text{-KAlO}_2\text{-SiO}_2$ . The assemblages albite-illite, microcline-illite, albite-microcline, and albite-microcline-illite, are compatible. Moreover, in the system of Figure 6, K-feldspars are incompatible with clays other than illite (kaolinite, montmorillonite) as long as the illite and albite are compatible.

The small number of coexisting phases and the established chemical purity of the authigenic feldspars indicate that the feldspar assemblages studied most probably represent equilibrium assemblages, and that incompatibilities in the original detrital assemblages have been eliminated except for certain detrital cores shielded by their enclosing feldspar rims from further reaction.

The occurrence of microcline-illite-chlorite assemblages in the upper part of the Belt series, and of microcline-chlorite in Waterton Formation, Alberta, and in Kona dolostone, N. Michigan (quartz is always present), might be of low-grade metamorphic origin, for the following reasons: Reynolds (1963), and Maxwell and Hower (1967) investigated the illites

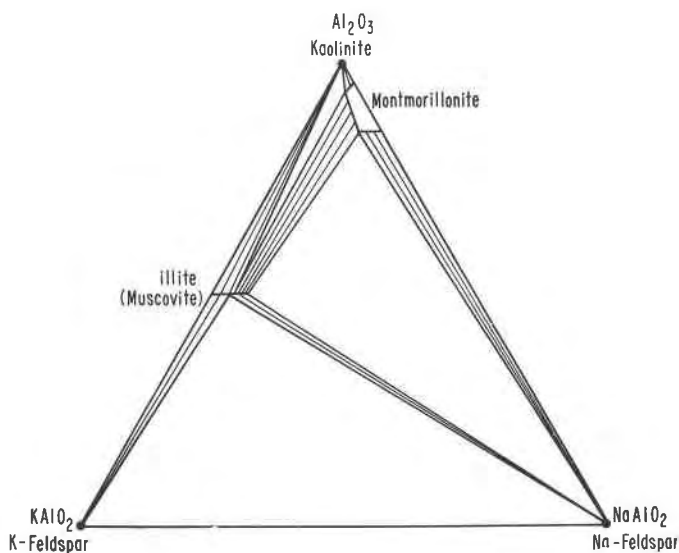


FIG. 6. A schematic diagram of the system  $\text{HAlO}_2\text{-NaAlO}_2\text{-KAlO}_2\text{-SiO}_2$  showing phases in equilibrium with quartz.

and microclines from the northern Rocky Mountains, Belt series. They observed a decrease in the ratio of 1M*d* to 2M polymorphs of illite with depth of burial. Based on Yoder and Eugster's (1955) experiments, they concluded that the increasing temperature and pressure with depth in the Belt series was responsible for the above transformation. Reynolds (1965) described an assemblage of microcline-illite-chlorite from the Cambrian, Ordovician, Silurian, and Devonian carbonate rocks from eastern N.Y. State and western Vermont. The similar abundance of microcline for the carbonates of all these ages from a given area led him to suggest that the microclines crystallized as a result of the Taconic and (in particular) the Acadian regional metamorphic and orogenic episodes.

As mentioned already, Zen (1960) in his study of the metamorphism of lower Paleozoic rocks in west-central Vermont, encountered the assemblage microcline-chlorite-muscovite-quartz. On the basis of an A-K-F(M) diagram he deduced the following: ". . . It is seen that chlorite in coexistence with potassic feldspar may be expected to show the highest Fe, Mg-Al ratio in the presence of muscovite; however, chlorite-potassic feldspar assemblages without muscovite may give even higher ratios . . ."

To test this idea, the microcline-chlorite assemblages from the Waterton and Kona dolostones and microcline-illite-chlorite assemblages from other carbonates in the Belt series were analyzed with the microprobe. The chlorites show high Fe, Mg-Al ratios. However, Füchtbauer and Goldschmidt (1959) in their study of the clays in the Zechstein formation reported an assemblage of illite Fe-rich chlorite K-feldspar, in which the K-feldspars are authigenic and the chlorite is presumably diagenetic. Diagenetic chlorites are well known from the literature; for example: Swindale and Fan (1967).

At present the differences in abundance of major and minor elements between diagenetic and metamorphic chlorites in specific assemblages is not known. Therefore the assignment of a diagenetic or metamorphic origin to a rock solely on the basis of the assemblages illite-Fe-rich chlorite-microcline and Fe-rich chlorite-microcline is ambiguous.

The division between diagenesis and metamorphism is arbitrary. The scarcity of diagenetic studies that contain detailed mineralogical analyses and chemical compositions of phases, and consequently the scant information about the mineralogical changes which take place between deposition and the established lowest metamorphic grade, make even this arbitrary division difficult.

*Occurrence of authigenic feldspars.* Authigenic feldspars are ubiquitous in carbonate rocks. In the past their abundance has gone unnoticed because

of the small dimensions of most of them (between 20–100  $\mu\text{m}$ ), and the fact that many are untwinned and could be mistaken for quartz in a rapid microscopic examination. The total amount of authigenic feldspars present in the rock samples studied is, at maximum, 2 weight percent, and generally less than 0.5 weight percent. Albite is far more abundant than microcline; most carbonate rocks sampled for this study as well as those previously investigated, contain albite only.

But there are important exceptions: Trümpy (1916) reported the presence of both sodic and potassic euhedral feldspars in Tertiary carbonates from Switzerland, and Füchtbauer (1950) observed albite, orthoclase, and microcline in the Triassic carbonates of Göttingen. In my study coexisting authigenic albite and microcline have been observed in two localities: (1) Pennsylvanian limestone, Provo Canyon, Utah, (sample M-752-PU, Table 1), in which authigenic albite and microcline have grown around detrital K-feldspar cores. (One grain had both albite and microcline overgrowths on opposite sides of a detrital K-feldspar core). Albites without cores are also abundant. The ratio authigenic albite/authigenic microcline is extremely high. (2) Eocene limestone, Rhodes, as shown in Figure 1. The inclusion hourglass structure in the albite, which indicates the direction of the most rapidly growing crystal faces (Kastner, 1970; Kastner and Waldbaum, 1968), continues into the microcline rim. Furthermore, the microcline rim which grew unevenly, is developed mainly along the most rapidly growing faces, as shown in Figure 1, and is frequently present only along these most rapidly growing faces, as shown in Figures 7 and 8a, b. The boundary between the albite and microcline is sharp. These textural relations convince me that the two feldspars crystallized continuously during the same diagenetic stage.

Authigenic albite grains are larger (70–120  $\mu\text{m}$ ) than those of authigenic microclines (40–80  $\mu\text{m}$ ). In those localities where the two coexist, albite is considerably more abundant than microcline. For example: the largest dimensions of albite from Rhodes are  $1.75 \times 0.3 \times 1.5$  mm, and the width of the unevenly distributed microcline rim ranges between 3–20  $\mu\text{m}$ . Microcline is present only as rims around the albites. These relative abundances and dimensions of authigenic albite and microcline were noted by Füchtbauer (1950) in his study of the Triassic carbonates from Göttingen.

As mentioned above, authigenic albites crystallize without reference to the composition of the detrital minerals in the matrix. In contrast, most authigenic microclines grow only where detrital K-feldspars are present. An explanation for the apparent dependence of authigenic microcline on detrital K-feldspars will be suggested below.

The stratigraphic distribution of authigenic albites and microclines in

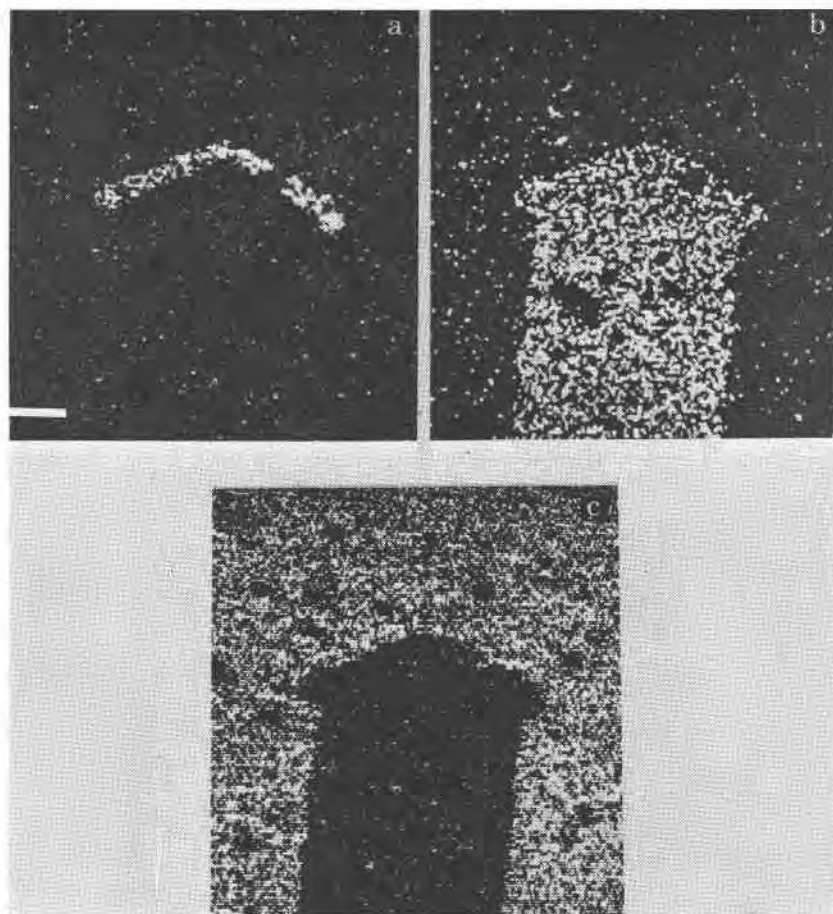


FIG. 7. Electron beam scanning photographs of upper portion of authigenic albite crystal with authigenic microcline rim only along the most rapidly growing faces, in thin section, sample M-355-IR, Rhodes.

- a) — $K_{K\alpha}$  X-ray image.
- b) — $Al_{K\alpha}$  X-ray image.
- c) — $Ca_{K\alpha}$  X-ray image, of same area.

White line in lower left of Fig. 7a represents 40 microns.

Ordovician carbonate rocks from the vicinity of State College, Pa., and from Glens Falls, N. Y., is a good example of the above relation between the composition of detrital cores and authigenic overgrowths, as summarized in Table 9. In both localities the lower part of the section contains almost exclusively detrital K-feldspars, with microcline overgrowths only around detrital K-feldspars, whereas the upper part con-

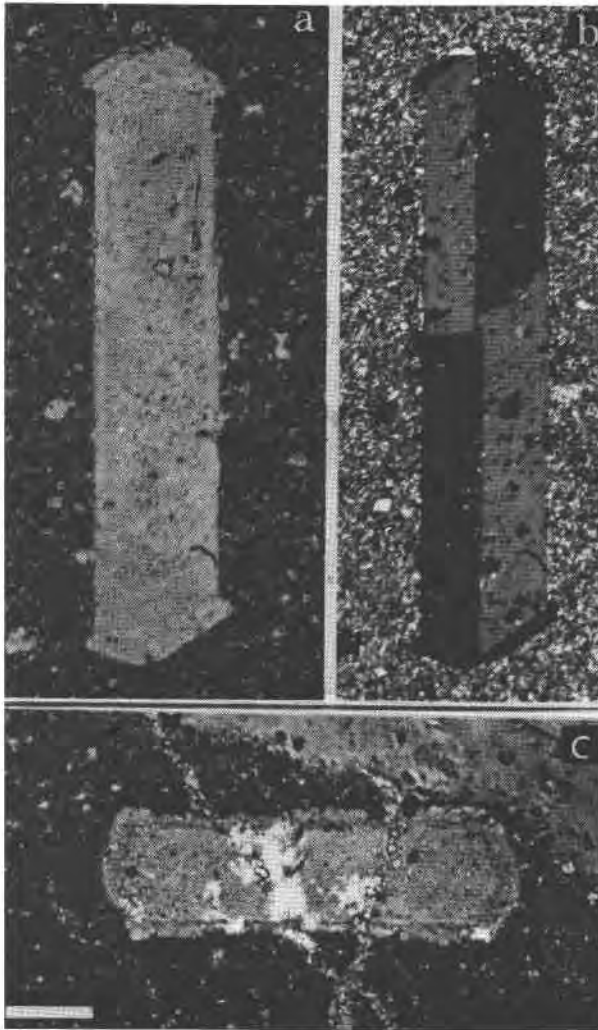


FIG. 8. Photomicrographs of authigenic albite crystals showing well developed authigenic microcline rims.

- a) Crystal from thin section M-355-IR, Rhodes, (plane polarized light).
- b) Same crystal (crossed polars).
- c) Crystal from edge of same thin section (plane polarized light).

Note calcite veins cut both the albite and the microcline in Fig. 8c, White line in lower left of 8c represents 0.1mm for all photomicrographs.

TABLE 9. AUTHIGENIC AND DETRITAL FELDSPARS IN ORDOVICIAN CARBONATE ROCKS FROM THE VICINITY OF STATE COLLEGE, PA., AND FROM GLENS FALLS, N.Y.

<i>Vicinity of State College, Pa.</i>				<i>Jointa Quarry, Glens Falls, N. Y.</i>		
Sample	Geologic Age	Formation	Authigenic Feldspar	Sample	Geologic Age	Authigenic Feldspar
M-655-OP	Middle Ordovician	Trenton limestone	Authigenic albite with and without plagioclase cores.	M-256-GF	Trenton Limestone? Middle Ordovician	Authigenic albite with and without plagioclase cores.
M-654-OP		Trenton limestone	Authigenic albite with and without plagioclase cores.	M-252-GF		Authigenic albite; plagioclase cores are rare.
M-683-OP		Valentine (Lowville) limestone	Authigenic albite; plagioclase cores are rare.	M-251-GF		Authigenic K-feldspars with K-feldspar cores.
M-682-OP		Valentine (Lowville) limestone	Authigenic albite; plagioclase cores are rare.			
M-674-OP		Valley View limestone	Authigenic albite without plagioclase cores.			
M-659-OP	Lower Ordovician Beekmantown Group	Nittany dolostone	Authigenic K-feldspar with K-feldspar cores.			
M-692-OP		Stonehenge limestone	Authigenic K-feldspars, with and some without K-feldspar cores.			

tains almost exclusively detrital plagioclase with authigenic albite overgrowths around detrital plagioclase, quartz and pyrite. At Glens Falls, N.Y., sample M-252-GF with albite overgrowths, is only 4 feet above sample M-251-GF, with microcline overgrowth. The very few samples studied do not provide sufficient evidence that the above abrupt mineralogical change is general throughout the area of the formation. However, if the relation proves to be general, early movements related to the Taconic orogeny might have been responsible for a change in source and composition of the detrital feldspars, and consequently of authigenic feldspar overgrowths. Further discussion and details are given in Kastner (1970b).

*Geochemical environment and diagenetic stage of the formation of authigenic feldspars.* In authigenesis of feldspars the following observations are important: (1) The total amount of authigenic feldspars present in car-



bonate rocks studied is very small. (2) Albite is the dominant authigenic feldspar phase in marine carbonate rocks. (3) The two alkali feldspar end members coexist, apparently in equilibrium. (4) Authigenic microcline forms only in the presence of an adequate source of potassium.

Clay minerals, varieties of free silica and, to some extent, detrital feldspars may provide the necessary silica and alumina for the crystallization of authigenic feldspars, and sea water or interstitial waters are the most important sources for the necessary alkalis (Kastner and Siever, 1968). Calculations based on maximum bulk percentage and dimensions of authigenic feldspars in carbonate rocks indicate that it is not essential to assume large amounts of water circulation in the sediment (Kastner, 1969). For example: the amount of sodium and potassium in 9 mm<sup>3</sup> of sea water is equivalent to the amount of sodium and potassium in an albite crystal 1 mm in diameter and in a microcline crystal 0.1 mm in diameter, respectively. This amount of water is equivalent to a sphere of 2.2 mm radius in a rock with 20 percent porosity (which is a very low value). Moreover, even on the basis of the assumption that clay minerals alone supply all the silica and alumina (which is unlikely), a mass balance between the average minimum amount of clay minerals and the maximum amount of authigenic feldspars present in carbonate rocks, indicates that authigenic feldspars in carbonates could form under isochemical conditions (Kastner and Siever, 1968; Kastner, 1969).

The compositions of interstitial waters of marine sediments, and some experimental evidence bearing on the required  $K/(K+Na)$  ratio of the fluid phase in equilibrium with two alkali feldspars at various temperatures have a bearing on authigenesis of feldspars, for they allow inferences on the chemical composition of the pore waters from which the feldspars precipitated.

In the literature several attempts have been made to estimate the alkali concentration of the fluid phase with which authigenic feldspars are stable. The results of Garrels and Howard (1959), Hemley (1959), and Hemley and Jones (1964), show that under near surface conditions, if the solution is saturated with respect to quartz, K-feldspar will be stable at  $[K^+]/[H^+] > 10^9-10^{10}$ . Orville (1963a) carried out similar calculations but his solutions were saturated with respect to amorphous silica instead of quartz. He concluded that K-feldspars will be stable at an approximately  $[K^+]/[H^+] = 10^5-10^6$ . In sea water this ratio is  $10^6$  assuming that the activity of potassium equals its concentration. Thus, K-feldspar could form from muscovite in sea water if saturated with respect to amorphous silica at essentially room temperature and a few atmospheres pressure. Hess had previously (1966) suggested that authigenic albites need (1)

either a system supersaturated with respect to amorphous silica (2) or higher temperature than 25°C (3) or a reduction in  $\mu\text{H}_2\text{O}$ .

Analyses of interstitial waters indicate that the  $[\text{K}^+]/[\text{H}^+]$  ratio never approaches the values  $10^9$  to  $10^{10}$  estimated by Garrels and Howard (1959). The highest K values are reported from subsurface brines of the chloride type which contain 50 to 1000 ppm K, (White, 1957); sea water contains 380 ppm K. Studies of the composition of interstitial waters of marine sediments by Siever, Beck, and Berner (1965) and Brooks, Presley, and Kaplan (1968) show that they are enriched in potassium and silica relative to sea water. Siever, Beck, and Berner (1965) attributed the enrichment of potassium to surface hydrolysis of K-feldspars and micas, and of silica to dissolution of diatoms. The amount of silica in interstitial waters is equal to or less than in equilibrium with amorphous silica.

The above measured, calculated, and experimental results are summarized below:

- (1) Mass balance between the maximum amount of authigenic feldspar and the minimum amount of clay minerals present in carbonates, and the amount of fluid necessary to convert the clays into feldspars indicates that authigenic feldspars can form under isochemical conditions.
- (2) K-feldspar could conceivably form from muscovite in sea water at essentially room temperature, if saturated with respect to amorphous silica.
- (3) Albite is more likely to form at temperatures higher than 25°C or in equilibrium with waters enriched in silica and alkalis relative to sea water.
- (4) Diagenetic processes are responsible for the enrichment of interstitial waters in potassium and silica relative to sea water.

The microcline rims around the albite crystals from Rhodes (samples M-351-IR and M-355-IR) are a clear indication of a change in physicochemical conditions during diagenesis, but does not necessarily imply a drastic change. The calcite veins which cut both the albite and microcline (Fig. 8c), and the fact that these veins are cut by later generations of veins and by stylolites, indicate that the earliest detectable changes which occurred in the consolidated rock are later than the formation of the microcline rim.

An abrupt change in crystallization from albite to microcline may have resulted from a nearly isothermal, isobaric change in the  $\text{K}/(\text{K}+\text{Na})$  ratio in the fluid phase, as shown in Figure 9, schematic isothermal isobaric ternary reciprocal phase diagram. Recent calculations by D. R. Waldbaum (personal communication) from thermodynamic data

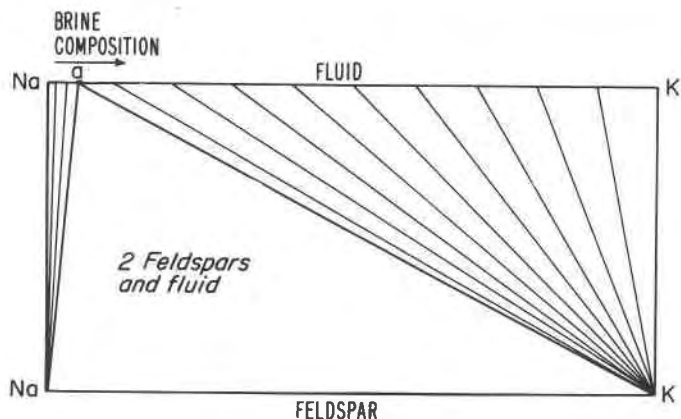


FIG. 9. Schematic isothermal isobaric ternary reciprocal phase diagram of equilibrium between alkali feldspars and fluid phase (at low T and P). Arrow denotes enrichment of potassium in fluid.

(Thompson and Waldbaum, 1967; Thompson and Waldbaum, 1968, Part I), which are based on Orville's (1963b) ion-exchange data, have shown that the ratio  $K/(K+Na)$  of a fluid phase in equilibrium with two alkali feldspars is about 0.03 at 100°C,<sup>1</sup> the ratio in sea water. This value is in agreement with Hemley's recent data (personal communication). A change from 0.02 to about 0.04 in the alkali ratio of the fluid phase during the late stages of feldspar growth would cause a discontinuous change in the composition of the feldspar that is in equilibrium with the fluid phase, as shown in the phase diagram, Figure 9. At point "a" of Figure 9 albite and microcline will coprecipitate.

Changes in alkali ratios could result from changes in pressure, temperature, or chemical composition, or appropriate combinations. Because of the obvious difficulties of changing pressure and temperature drastically during early diagenesis an isothermal, isobaric process is more likely. Such a change could take place by mixing the original fluid with a fluid enriched in potassium that originated from the dissolution of detrital K-feldspars and/or K-rich glass, during a previous diagenetic phase, or as a result of a relative depletion in sodium due to the earlier crystallization of albite.

In the above discussion it is not necessary to assume that K-feldspar and Na-feldspar are the most thermodynamically stable phases in the diagenetic environment, even if they are in ion-exchange equilibrium

<sup>1</sup> Thermodynamic data which are based on the sanidine-high albite solvus were used for the calculations and for the extrapolation. Thus, the value  $K/(K+Na)=0.03$  is an approximation.

with the fluid phase for this could be a metastable equilibrium. At the same time there are no compelling reasons to suggest that alkali feldspars could not crystallize as truly stable phases in diagenetic environments. Estimates of physicochemical conditions required for stability of alkali feldspars that show that they probably are stable at low to moderate temperatures and pressures have been given by Hess (1966), Orville (1963a), and Garrels and Christ (1965).

It is believed therefore that the microcline rim reflects changes that occurred at very early stages of diagenesis and reflects changes in the composition of the fluid phase coexisting with the feldspar. As noted above, this seemingly abrupt change can be accounted for by a continuous change in the  $K/(K+Na)$  ratio in the fluid.

The evidence presented here further indicates that the geochemical environment of formation of authigenic albite need not differ appreciably from the environment of authigenic K-feldspar as has been suggested in the literature.

On the basis of two observed and two reported occurrences of coexisting authigenic albite and microcline, it is further suggested that the  $K/(K+Na)$  ratio of interstitial waters responsible for the formation of authigenic feldspar in carbonate rocks, is on the Na-albite side of the phase diagram (to the left of point "a"), Figure 9, but very close to the  $K/(K+Na)$  ratio in equilibrium with two alkali feldspars. At temperatures in the range  $0^{\circ}$ – $100^{\circ}$ C. Under these conditions, as silica increases in solution by dissolution of free silica, albite will crystallize. An isochemical increase in temperature would shift the equilibrium ratio towards the K side, thus stabilizing the albite phase.

The formation of authigenic microcline depends on a supply of potassium adequate to increase the  $K/(K+Na)$  ratio. Partial dissolution of detrital K-feldspar is the most likely source of additional potassium; hence the close correlation between the occurrence of detrital K-feldspars and authigenic microclines.

Inasmuch as the formation of authigenic microcline depends also on an adequate supply of potassium, which might be provided from a previous diagenetic process, it is unlikely to be among the earliest diagenetic phases.

Authigenic albite might form either at lower temperatures (and preferably higher total alkali concentrations), or at higher temperatures (and lower total alkali concentrations). However, considering that under isochemical conditions the stability field of albite increases at higher temperatures; it is suggested that medium to high temperature diagenetic environments are more favorable for the formation of authigenic albite.

## ACKNOWLEDGEMENTS

This paper is based on part of a Ph.D. thesis submitted to Harvard University. I particularly want to thank Professor R. Siever for his continuous interest, kind assistance and advice throughout this research, and for his critical suggestions which led to the improvement of this manuscript, I am also grateful to Professors J. B. Thompson, Jr. and C. Klein for their kind assistance, discussions and suggestions during the research, to Dr. D. R. Waldbaum for numerous valuable and inspiring discussions. I wish to thank Professor F. McKim Swartz and Dr. W. J. Koch for their assistance in field work.

I am indebted to Professor W. L. Brown, University of Paris; Professor K. J. Deffeyes, Princeton University; Professor C. Frondel, Harvard University; Professor J. T. Iiyama, University of Paris; Dr. W. J. Koch, Shell Oil Company, Houston, Texas; Professor M. Miyakawa, Nagoya University, Professor Papastamatiou, University of Athens; Dr. J. Schlocker, U.S. Geological Survey, Menlo Park, California; Professor G. J. Wasserburg, California Institute of Technology, and Mrs. C. Bocquet, Institut Dolomieu, Grenoble, France, for providing rock and mineral specimens studied in this investigation. And to Mr. Campot, Mr. H. Thompson, and Mrs. N. Woodford, for technical assistance in microprobe, petrographic and chemical studies.

This research was supported by National Science Foundation Grants GA-571 and GA-12865. Additional financial support was also provided by the Department of Geological Sciences, Harvard University.

## REFERENCES CITED

- BASKIN, Y. (1956) A study of authigenic feldspars. *J. Geol.* **64**, 132-155.
- BISCAYE, P. E. (1965) Mineralogy and sedimentation of Recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geol. Soc. Amer. Bull.* **76**, 803-832.
- BÖGGILD, O. B. (1910) Ueber die Krystallform des Mikroklin. *Z. Kristallogr.* **48**, 466-472.
- (1924) On the labradorization of the feldspars. *Kgl. Danske Vidensk. Selsk. Math. Fys. Meddel.* **6**, 79 pp.
- BROOKS, R. R., B. J. PRESLEY, AND I. R. KAPLAN (1968) Trace elements in interstitial waters of marine sediments. *Geochim. Cosmochim. Acta* **32**, 397-414.
- BURNHAM, C. W. (1962) Lattice constant refinement. *Carnegie Inst. Wash. Year Book* **61**, 132-135.
- CAROZZI, A. V. (1953) Données micrographiques sur le Cretacé superieur helvetique. (Autochtone, nappes de Morcles et du Wildhorn). *Bull. Inst. Nat. Genevois* **56**, 1-76.
- CLAFFY, E. W., AND R. J. GINTHER (1959) Red-luminescing quartz. *Amer. Mineral.* **44**, 987-994.
- DALY, R. A. (1917) Low-temperature formation of alkaline feldspars in limestone. *Proc. U. S. Nat. Acad. Sci.* **3**, 659-665.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1963) *Rock Forming Minerals. Vol. 4: Framework silicates.* Longmans, Green and Co. Ltd., London, 435 pp.
- DRIAN, M. (1861) Notice sur les cristaux d'albite renfermés dans les calcaires magnesiens des environs de Modane. *Bull. Soc. Geol. France, Ser. 2*, **18**, 804-806.
- FINNEY, J. J., AND S. W. BAILEY (1964) Crystal structure of an authigenic maximum microcline. *Z. Kristallogr.* **119**, 413-436.
- FOLK, R. L. (1952) *Petrography and Petrology of the Lower Ordovician Beekmantown Carbonate Rocks in the Vicinity of State College, Pennsylvania.* Ph.D. Thesis, Pennsylvania State Univ.
- (1959) Practical petrographic classification of limestones. *Amer. Assoc. Petrol. Geol. Bull.* **43**, 1-38.

- FÜCHTBAUER, H. (1948) Einige Beobachtungen an authigenen Albiten. *Schweiz. Mineral. Petrogr. Mitt.* **28**, 709-716.
- (1950) Die nicht Karbonatischen Bestandteile des Göttinger Muschelkalkes mit besonderer Berücksichtigung der Mineralneubildungen. *Heidelberger Beitr. Mineral. Petrogr.* **2**, 235-254.
- (1956) Zur Entstehung und Optik authigener Feldspäte. *Neues Jahrb. Mineral. Monatsh.* **1**, 9-23.
- AND H. GOLDSCHMIDT (1959) Die Tonminerale der Zechsteinformation. *Beitr. Mineral. Petrogr.* **6**, 320-345.
- GARRELS, R. M., AND C. L. CHRIST (1965) *Solutions, minerals, and equilibria*. Harper and Row, New York, 450 pp.
- AND P. HOWARD (1959) Reactions of feldspar and mica with water at low temperatures and pressure. *6th Nat. Conf. Clays Clay Miner. Proc. Nat. Acad. Sci., Nat. Res. Council., Pap. No.* **156**, 68-88.
- GLOVER, E. D. (1961) Method of solution of calcareous materials using the complexing agent EDTA. *J. Sed. Petrology* **31**, 622-626.
- GRIM, R. E. (1953) *Clay Mineralogy*. McGraw-Hill, New York, 384 pp.
- HEIER, K. S., AND S. R. TAYLOR (1959) Distribution of Ca, Sr and Ba in southern Norwegian Pre-Cambrian alkali feldspars. *Geochim. Cosmochim. Acta* **17**, 286-304.
- HEMLEY, J. J. (1959) Some mineralogical equilibria in the system  $K_2O-Al_2O_3-SiO_2-H_2O$ . *Amer. J. Sci.* **257**, 241-270; **258**, 153.
- AND W. R. JONES (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. *Econ. Geol.* **59**, 538-569.
- HESS, P. (1966) Phase equilibria of some minerals in the  $K_2O-Na_2O-Al_2O_3-SiO_2-H_2O$  system at 25°C and 1 atmosphere. *Amer. J. Sci.* **264**, 289-309.
- HONESS, A. P. AND C. D. JEFFRIES (1940) Authigenic albite from Lowville limestone at Bellefonte, Pennsylvania. *J. Sed. Petrology* **10**, 12-18.
- HOWER, J., P. M. HURLEY, W. H. PINSON, AND H. W. FAIRBAIRN (1963) The dependence of K-Ar age on the mineralogy of various particle size ranges in a shale. *Geochim. Cosmochim. Acta* **27**, 405-410.
- KASTNER, M. (1969) *Authigenic Feldspars in Carbonate Rocks*. Ph.D. Thesis, Harvard University, 239 pp.
- KASTNER, M. (1970a) An inclusion hourglass pattern in synthetic gypsum. *Amer. Mineral.* **55**, 2128-2130.
- (1970b) Feldspars as provenance and physicochemical indicators (abstr.) *Geol. Soc. Amer. Abstr. Programs*, p. 591.
- AND R. SIEVER (1968) Origin of authigenic feldspars in carbonate rocks (abstr.) *Geol. Soc. Amer. Spec. Pap.* **121**, 155-156.
- AND D. R. WALDBAUM (1968) Authigenic albite from Rhodes. *Amer. Mineral.* **53**, 1579-1602.
- KÖHLER, A. (1940) Die Lumineszenz der Feldspäte mit Seltenen Erden. *Tschermak's Mineral. Petrogr. Mitt.* **52**, 273-275.
- LONG, J. V. P., AND S. O. ARGELL (1965) The cathodo luminescence of minerals in thin section. *Mineral. Mag.* **34**, 318-326.
- LORY, C. (1861) Comptes rendus d'une excursion géologique en Savoie. *Bull. Soc. Géol. France, Ser. 2*, **18**, 705-825.
- LUTH, W. C., AND F. QUEROL-SUNÉ (1970) An alkali feldspar series. *Contrib. Mineral. Petrology* **25**, 25-40.
- AND O. F. TUTTLE (1966) The alkali feldspar solvus in the system  $Na_2O-K_2O-Al_2O_3-SiO_2-H_2O$ . *Amer. Mineral.* **51**, 1359-1373.

- MARTIN, R. F. C. (1968) *Hydrothermal Synthesis of Low Albite, Orthoclase, and Non-stoichiometric Albite*. Ph.D. Thesis, Stanford University, 164 pp.
- MAXWELL, D. T., AND J. HOWER (1967) High-grade diagenesis and low-grade metamorphism of the illite in the Precambrian Belt Series. *Amer. Mineral.* **52**, 843-857.
- MEDLIN, W. L. (1963a) Emission centers in thermoluminescent calcite, dolomite, magnesite, aragonite, and anhydrite. *J. Opt. Soc. Amer.* **53**, 1276-1285.
- (1963b) Thermo-luminescence in quartz. *J. Chem. Phys.* **38**, 1132-1143.
- MEGAW, H. D. (1959) Order disorder in the feldspars. *Mineral. Mag.* **32**, 226-241.
- ORVILLE, P. M. (1963a) Is K-feldspar stable in a near-surface sedimentary environment (abstr.) *Geol. Soc. Amer. Spec. Pap.* **76**, 126.
- (1963b) Alkali ion exchange between vapor and feldspar phases. *Amer. J. Sci.* **261**, 201-237.
- (1967) Unit-cell parameters of the microcline-low albite and the sanidine-high albite solid solution series. *Amer. Mineral.* **52**, 55-86.
- PERRY, E., AND J. HOWER (1970) Burial diagenesis in Gulf Coast pelitic sediments. *Clays Clay Miner.* **18**, 165-177.
- PERRENOUD, J. P. (1952) Étude du feldspath potassique contenu dans le "Potiskalk" (Trias Valais). *Schweiz. Mineral. Petrog. Mitt.* **32**, 179-183.
- REYNOLDS, R. C. (1963) Potassium-rubidium ratios and polymorphism in illites and microclines from the clay size fractions of Proterozoic carbonate rocks. *Geochim. Cosmochim. Acta* **27**, 1097-1112.
- (1965) Diagenetic microcline formation in carbonate rocks. *Empire State Geogram, Geol. Surv. N. Y.* **3**, 1-4.
- SCHÖNER, H. (1960) Ueber die Verteilung und Neubildung der nichtkarbonatischen Mineralkomponenten der Oberkreider aus der Umgebung von Hannover. *Heidelberger Beitr. Mineral. Petrogr.* **7**, 76-103.
- SIEVER, R., K. C. BECK, AND R. A. BERNER (1965) Composition of interstitial waters of modern sediments. *J. Geol.* **73**, 39-73.
- SINGEWALD, J. T., JR., AND C. MILTON (1929) Authigenic feldspar in limestone at Glens Falls, New York. *Geol. Soc. Amer. Bull.* **40**, 463-468.
- SMITH, J. V., AND P. H. RIBBE (1966) X-ray emission microanalysis of rock-forming minerals III. Alkali feldspars. *J. Geol.* **74**, 197-217.
- AND R. C. STENSTROM (1965) Electron-excited luminescence as a petrologic tool. *J. Geol.* **73**, 627-635.
- SPENCER, E. (1925) Albite and other authigenic minerals in limestone from Bengal. *Mineral. Mag.* **20**, 365-381.
- STEWART, D. B., AND P. H. RIBBE (1969) Structural explanation for variations in cell parameters of alkali feldspar with Al/Si ordering. *Amer. J. Sci.* **267A**, 444-462.
- SWINDALE, L. D., AND POW-FOONG FAN (1967) Transformation of gibbsite to chlorite in ocean bottom sediments. *Science* **157**, 799-800.
- THOMPSON, J. B., JR., AND D. R. WALDBAUM (1967) Thermodynamic mixing properties of sanidine/high-albite crystalline solutions. (abstr.) *Trans. Amer. Geophys. Union* **48**, 230.
- AND —— (1968) Mixing properties of sanidine crystalline solutions: I. Calculations based on ion-exchange data. *Amer. Mineral.* **53**, 1965-1999.
- AND —— (1969) Mixing properties of sanidine crystalline solutions: III. Calculations based on two-phase data. *Amer. Mineral.* **54**, 811-838.
- TOKAY, M. (1944) Présence d'oligoclase basique-andésine authigène dans le Crétacé supérieur helvétique. *C. R. Soc. Phys. Geneve* **61**, 291-294.

- TRÜMPY, D. (1916) Geologische Untersuchungen in Westlichen Rhätikon. *Beitr. Geol. Karte Schweiz., No. 76 (N. S. 46), Pub. 2*, 83-111.
- WALDBAUM, D. R. (1966) *Calorimetric Investigation of the Alkali Feldspars*. Ph.D. Thesis, Harvard Univ., 247 pp.
- AND R. A. ROBIE (1972) Calorimetric investigation of Na-K mixing and polymorphism in the alkali feldspars. *Z. Kristallogr.* **134** (in press)
- WEAVER, C. E. (1958a) The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, chlorite, and volcanic material. *Amer. Mineral.* **43**, 839-861.
- (1958b) Geologic interpretation of argillaceous sediments, Part I. Origin and significance of clay minerals in sedimentary rocks. *Amer. Assoc. Petrol. Geol. Bull.* **42**, 254-271.
- WHITE, D. E. (1957) Magmatic, connate and metamorphic waters. *Geol. Soc. Amer. Bull.* **68**, 1659-1682.
- YODER, H. S., AND H. P. EUGSTER (1955) Synthetic and natural muscovites. *Geochim. Cosmochim. Acta* **7**, 225-280.
- ZEN, E-AN (1960) Metamorphism of lower Paleozoic rocks in the vicinity of the Taconic Range in west-central Vermont. *Amer. Mineral.* **45**, 129-175.

*Manuscript received, September 1, 1970; accepted for publication, March 30, 1971.*