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LOW TEMPERATURE FELDSPARS IN SEDIMENTARY ROCKS

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ABSTRACT. Authigenic feldspars form in many different kinds of sediments as well-crystallized grains of albite or K-feldspar, normally constituting only a small fraction of the rock. They are always very pure end-members, occurring either as homogeneous grains or more frequently as overgrowths around detrital cores of detrital feldspar, quartz, and non-silicates. Textural relations indicate growth in place by replacement; most have formed early after deposition. Albite is more abundant than K-feldspar in carbonate rocks, but the reverse is true for authigenic feldspars in sandstones, except for graywackes, in which albite dominates. Authigenic feldspars are associated with zeolites in some sandstones, in volcaniclastic rocks, or alkaline lake deposits. Authigenic feldspars occur in rocks of all ages, from Pleistocene to Precambrian, with some tendency for greater abundance in older rocks. Albites are triclinic euhedra that are frequently twinned. K-feldspars are triclinic or monoclinic, with various degrees of Al/Si ordering. Pure chemical composition, lack of cathodoluminescence, nature of twinning, and high positive $\delta^{18}O$ values are diagnostic of authigenic origin of feldspars. Thermodynamically stable assemblages in the system SiO_2–Al_2O_3–K_2O–Na_2O–H_2O, plus the addition of CO_2, CaO, MgO, and FeO, include feldspars, clay minerals, micas, carbonates, and several oxides and/or hydroxides. A kinetic analysis of the many geochemical processes accompanying shallow and deep burial leads to several geochemical models for authigenic feldspar formation that depend on the supply of dissolved silica, either from biogenic silica or from the hydrolysis of volcanic glass, and the supply of alkali metals, either from seawater or from detrital and diagenetic aluminosilicates. Aluminum is considered in most sedimentary environments to be present mainly in solid form, and in extremely low concentrations as dissolved species, except in some alkaline lakes. The preferred models are for isochemical change, for most petrographic evidence favors this origin. Some occurrences, however, must be analyzed in terms of exchange reservoir models.

INTRODUCTION

Alkali feldspar and quartz commonly occur authigenically as well-crystallized grains and overgrowths in many kinds of unmetamorphosed sedimentary rocks. This frequent low-temperature origin contrasts with almost all other rock-forming silicates that are normally of high temperature origin. The mafic silicates in particular rarely form as low-temperature authigenic minerals. Though authigenic quartz is far more common and abundant than authigenic alkali feldspars, it is increasingly apparent that the feldspars are much more widespread than generally has been thought, though they are only exceptionally a major constituent of the host rocks. Based on several hundred thin sections of limestones, sandstones, and shales of all types, and a literature survey, we estimate that approx 5 percent of all feldspars in continental sedimentary rocks are authigenic alkali feldspars. Reports of the Deep Sea Drilling Project suggest a similar proportion for sediments of the ocean basins.

The authigenic origin of much quartz matches its high stability in sedimentary environments. Its geological persistence is a function of its low solubility and rate of dissolution, related to being the thermodynamically stable phase of SiO_2 at low temperatures and pressures. But

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it seems less easy to explain the authigenic origin of feldspars, which seem not to form but to disappear in most sedimentary environments. During weathering, feldspars quickly alter to form clay minerals. In most aqueous sedimentary environments, feldspars are thermodynamically unstable with respect to clay minerals and the unsaturated solutions that surround them. At first sight, feldspars would appear to demand the higher temperatures and pressures of metamorphic and igneous environments for their formation. Here we try to deduce the geochemical and geological conditions under which feldspars form at the relatively low temperatures and pressures characteristic of unmetamorphosed sedimentary rocks.

Subsidiary questions are more specific. Are the geochemical conditions for feldspar formation diagnostic of particular, special geological conditions? Can authigenic feldspars be used as temperature indicators? How important are feldspars as sinks for the precipitation of Na and K in the sedimentary part of the crust? Finally, a broader question: can the study of feldspar authigenesis give additional insight into the general nature of diagenetic processes? We examine these questions in more detail below and attempt to answer them in this paper.

Authigenesis of feldspars results from either homogeneous precipitation from interstitial or formation waters or from the interaction of those waters and detrital and/or diagenetic aluminosilicates. The water composition is, of course, not an independent variable; it is derived from mineral-water reactions at all stages in the diagenetic history of a sedimentary rock pile. Balancing the relative importance of the silicate detritus deposited in various sedimentary environments versus the nature of the formation waters as decisive controls of feldspar authigenesis is one of our objectives. Detrital assemblages include feldspars, micas, mafic minerals, volcanic glasses, and clay minerals, all of which serve as potential donors of essential components for feldspar authigenesis. The composition and quantity of detritus are functions of provenance, differential weathering, sediment transport processes, and tectonism. Thus, large amounts of authigenic feldspars are more likely to be found in graywackes and volcaniclastics[1] associated with islands arcs, subduction zones, and marginal seas than in aluminous shales and pure quartz arenites associated with carbonate platform deposits, to give two extremes. Yet occasional authigenic feldspars are found in platform carbonate rocks, quartz arenites, and a wide variety of other rock types, so we must distinguish between occurrence and abundance.

A particular detrital assemblage may be transported into freshwater or saline lakes, alluvial plain deposits of continental basins, or a variety of marine environments. Although in each type of sedimentary depositional environment the course of diagenesis may differ, the authigenic feldspars that result may converge to similar compositions and textures.

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[1] We use the word volcaniclastic to include transported volcanogenic material, exclusive of lavas, ash flows, and other materials deposited in the immediate vicinity of the volcano.

For example, free silica is highly soluble and reactive opals and detrital aluminosilicates may be abundant components of both alkaline lakes and pelagic sediments, predisposing both to the early formation of authigenic feldspars, although at different rates. Given enough time and subsidence, non-marine sediments of cratonic basins might also pass through the physicochemical environment required for feldspar formation.

As a result of the interplay of so many variables, feldspars that form under a limited range of geochemical conditions may not be diagnostic of specific geological conditions, unless all the factors that influence sediment composition and texture are carefully evaluated. At the same time, there is hope that knowing the petrology and diagenetic history of the feldspars will contribute to deducing the whole-rock's history, for we are closer to specifying the range of conditions for feldspar nucleation and growth than for most other silicate or oxide components of sedimentary rocks.

The unmetamorphosed character of the host sediments and the properties of the feldspars themselves indicate a low to moderate temperature origin, that is, between 0° and about 300°C. One of the temperature dependent properties of the feldspars is their composition. Authigenic feldspars are almost the extremes of pure end members of the alkali feldspar series. The absence of cathodoluminescence indicates insufficient amounts of coprecipitated trace elements (activators), a function of low temperature. The crystal structure, including the high degree of Al/Si ordering of many authigenic feldspars, also indicates low to moderate temperatures of formation. But the temperature range, as yet imprecisely indicated by these properties alone, includes at its high end low-grade metamorphic and hydrothermal environments and at its low end sediments still in the cold regime of the ocean bottoms. The parameters that reflect low temperature origin will have to be determined much more sensitively and accurately than now possible to be reliable temperature indicators. In a later section we discuss oxygen isotope fractionation between coexisting authigenic feldspars and other minerals as a candidate for a geological thermometer.

The role of authigenic alkali feldspars in continental and nearshore sediments in the geochemical mass balances of Na and K is not large but may be of minor significance (Kastner, 1974). Authigenic feldspars in sediments deposited in the deep and marginal sea environments associated with subduction zones may be quantitatively more important. This is particularly so for the geochemical cycle of Na, because, as yet, there are insufficient proven sinks to balance the sources of Na in the oceans. We doubt that the feldspars alone will overcome the discrepancy but taking them into account may slightly ease the difficulty.

The examination of textural relations between authigenic feldspars and other components and/or deformational structures in a sedimentary rock has been found to be one of the most powerful and helpful methods for distinguishing between earlier and later diagenetic events; for example, triclinic overgrowths over monoclinic detrital grains or authigenic overgrowths around detrital or earlier authigenic feldspar. The detailed evaluation of these kinds of textural relations provides insight into the general nature of diagenetic processes. Deduction of the composition of the solutions in various fossil diagenetic environments can come from analysis of modern formation waters taken together with the history of precipitation of feldspars inferred from their diagenetic textures and those of other minerals, such as carbonates and quartz.

In sum, although authigenic feldspars are not quantitatively important as major textural components of sedimentary rocks, their presence in sediments is significant, because they provide important information about the general nature of diagenetic processes in a wide variety of sediments; they provide information about the composition of the formation waters from which they precipitated, and they may prove to be sensitive diagenetic temperature indicators. Of intrinsic interest, they offer the opportunity to study the purest, ordered alkali feldspars known.

REVIEW OF THE LITERATURE

Up to the middle of the 20th century, authigenic feldspars had received more attention than any other authigenic silicate. Drian (1861) was the first to report an occurrence of euhedral albite in a Triassic dolostone from Roc Tourné, Modane, France as an example of authigenic feldspar. Based on their nondirectional mode of dissemination throughout the rock, he concluded that they were not metamorphic feldspars but grew while the rock was still "in the process of formation." Lory (1861), who investigated the same locality, also concluded that these albites must have formed from aqueous solution at low temperatures prior to induration. But such revolutionary ideas for the time were not easily accepted. Lacroix (1897) inferred a hydrothermal origin for the same euhedral albites from Roc Tourné, though he was unable to locate a nearby igneous body that could have provided the hydrothermal solutions. The controversy over the origin of the euhedral albites from Roc Tourné is indicative of the difficulties and hesitations that confronted geologists in accepting the then new idea that feldspars can also form at low to moderate temperatures. The literature of the hundred years following the Roc Tourné discovery shows a gradual evolution from a belief that euhedral feldspars in sediments are metamorphic, to a belief that they are authigenic but very special and rare, to inference that they indicate marine environments, and finally in the last few years, to increasing awareness of their ubiquity in many different kinds of sedimentary rocks and environments.

First came the accumulation of much descriptive evidence for authigenesis, such as (1) their euhedral habit (Lory, 1861; Drian, 1861); (2) the peculiar "fourling" twinning (Rose, 1865); (3) the presence of zonally arranged carbonaceous inclusions parallel to crystallographic planes (Drian, 1861); (4) textural relations such as the replacement of fossils by feldspars (Lory, 1861); and (5) their random distribution in fine-grained rocks (Drian, 1861). The weight of the evidence finally convinced the dean of French petrographers, Cayeux (1903), that feldspars could form authigenically. For more than half a century, from 1861 to 1917, all reported occurrences of authigenic feldspars were from European Mesozoic and Eocene carbonate rocks, and most of them from Triassic carbonates. In 1917, Daly reported the first occurrence of authigenic K-feldspars outside Europe, in a Precambrian dolostone at Waterton Lake, Alberta, Canada.

The first authigenic K-feldspars to be discovered in sandstones were described by Reynolds (1929). Subsequently, authigenic feldspars have been observed and studied carefully in most sedimentary rock types: a variety of sandstones and marls (Tester and Atwater, 1934; Goldich, 1934; Heald, 1950; Berg, 1952), shales (Gruner and Theil, 1937; Weiss, 1954), ash beds (Deffeyes, 1959; Milton, and others, 1960; Hay, 1966; Sheppard and Gude, 1968, 1969), and evaporites (Schloker, personal commun.).

After metamorphic and hydrothermal origins for euhedral feldspars in sediments were abandoned in favor of an authigenic origin, the major geologic questions raised concerned the nature of their sedimentary origin. Did they form before, during, or after burial and lithification? What were the geochemical conditions of the sedimentary or diagenetic environment that favored their formation? Growth during deposition and before final consolidation was proposed by Drian (1861), Lory (1861, 1866a, b), and Von Foullon (1891). Grandjean (1909, 1910) even suggested that feldspars are at present crystallizing on the sea floor. Füchtbauer (1950), having observed both authigenic albite and K-feldspar in the Göttingen Muschelkalk and noting that the albites are distinctively larger than the K-feldspars, concluded that the albites grew before consolidation and the K-feldspars after. Growth during lithification in shallow marine environments was suggested by Berg (1952), and growth after lithification by De Lapparent (1918), Singewald and Milton (1929), Stringham (1940), Van Straaten (1948), Topkava (ms), Papastamatiou (1955), and Baskin (1956). These authors' conclusions were based mainly on textural observations, such as the replacement of fossils and oolites by feldspars. Textural evidence came from microscopic petrography, but much reasoning came from bulk chemical composition. Thus Daly (1917), on the basis of chemical composition, inferred an authigenic origin for up to 40 percent of the fine-grained feldspar found in the Precambrian of Alberta. It was only after the application of electron probe analysis to these rocks that it could be shown that most of the feldspar was detrital (Kastner, ms).

Optical and chemical analysis of separated authigenic crystals made it abundantly evident that authigenic feldspars were pure alkali feldspars with compositions between $KAlSi_3O_8$ and $NaAlSi_3O_8$, with up to 5 mole percent $CaAl_2Si_2O_8$.[2] More recently, electron probe analyses have shown authigenic feldspars of limestones to be homogeneous, stoichiometric end members of the alkali feldspar series (Kastner, 1971). The chemical purity of the authigenic feldspars and the high optic axial

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angles of authigenic albites were suggested by many authors to be indicators of low temperature origin, many agreeing with Daly's (1917) conclusion that they form at temperatures below 100°C.

Grandjean (1909) was the first to suggest that a marine environment is essential for authigenic feldspar formation, a suggestion that has been repeatedly advanced. Reynolds (1929), however, emphasized the importance of saline water, but not necessarily seawater, for the formation of authigenic feldspars. Later, Füchtbauer (1956) suggested that seawater supplies the sodium for the albites, but the potassium for K-feldspars is supplied from muscovite (illite). Kastner and Siever (1968) concluded that varieties of free silica, the clay minerals, and to some extent, detrital feldspars, supply the silica and alumina, whereas seawater or interstitial water is the major source for the alkali metals needed for the formation of authigenic feldspars.

The literature continues to grow as electron probe and scanning electron microscopic techniques are becoming widely used in sedimentary petrography. Additional information is now becoming available from isotopic analysis, both for radiometric ages and for oxygen isotope fractionation. This information is covered in the body of this paper.

More detailed reviews of parts of the literature are given by Boswell (1933), Baskin (1956), Hay (1966), and Kastner (ms and 1971).

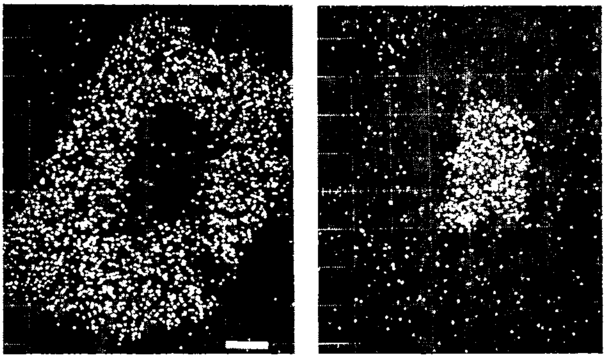
PETROGRAPHY AND GEOLOGIC OCCURRENCE

Feldspars are among the most common components of sedimentary rocks; analysis of petrographic studies of sands and sandstones of all ages gives an average of about 15 percent (Pettijohn, Potter, and Siever, 1972, p. 36). The average shale of Clarke (1924) has a calculated 30 percent feldspar; because of the fine grain size of these feldspars, most petrographic studies of shales report much less than the calculated value. Carbonate and other biologically and chemically precipitated sediments generally contain little feldspar — less than 2 percent.

Detrital feldspars, overwhelmingly those eroded from igneous and metamorphic rocks, constitute the great bulk of all feldspars in sediments. They typically show abraded edges and corners in grain sizes larger than about 0.1 mm diameter; the smaller grains are presumably too small to be significantly affected by physical wear during transportation. Detrital feldspars show all stages of weathering, from fresh looking to almost completely converted to kaolinite or other clay minerals. Chemical dissolution studies and electron microscopy that we report elsewhere show that almost all detrital feldspars, even the perfectly fresh appearing grains, have some incipient alteration along cleavage and other fractures, a conviction held long ago by C. W. Correns (personal commun.). Detrital feldspar grains range in size from fine clay to coarse sand and granules. Their chemical composition may lie anywhere in the stability

[2] There was one report of authigenic plagioclase with up to 20 percent anorthite (Singewald and Milton, 1929), but later analysis showed this to have been impure material.

PLATE 1



Electron beam scanning photograph of authigenic albite and detrital K-feldspar core, Pennsylvanian limestone, Utah. (A) $Na_{k\bar{\alpha}}$ image; (B) $K_{k\bar{\alpha}}$ image. White line in lower right of (A) represents 10μm for both photographs.

fields in the ternary system $NaAlSi_3O_8$–$KAlSi_3O_8$–$CaAl_2Si_2O_8$, but alkali-rich members predominate. The characteristics of detrital feldspars in sandstones and other sediments have been summarized recently by Pettijohn, Potter, and Siever (1972, p. 33-38) and Pettijohn (1974, p. 202-204).

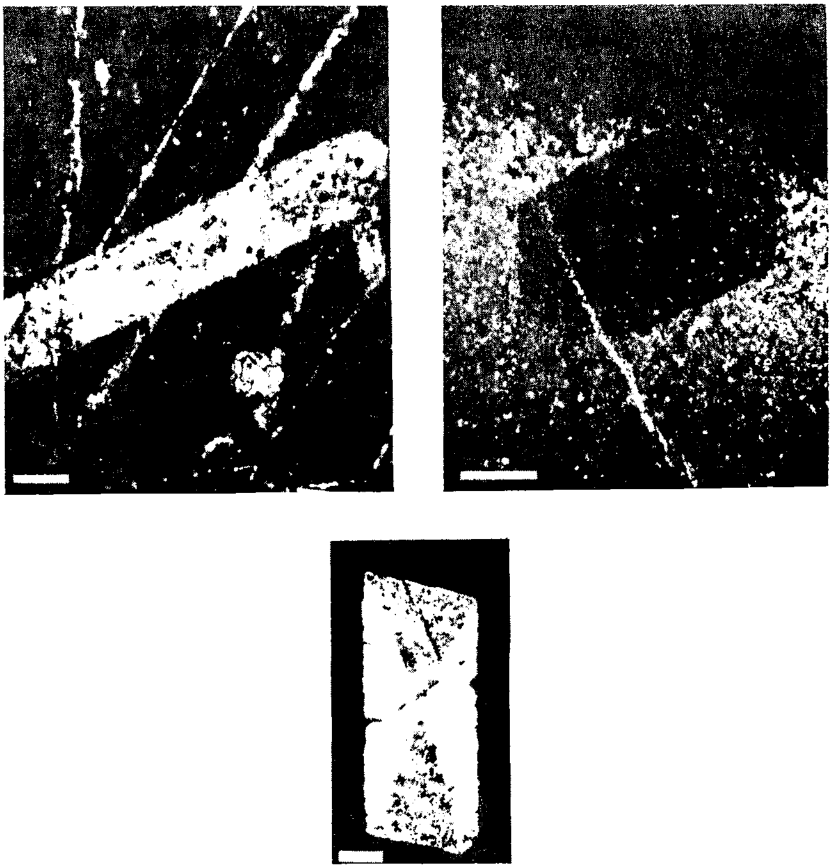
Authigenic feldspars, except in altered ash beds, are normally a small fraction of the feldspars in a rock, rarely more than a few percent and most commonly present only in trace amounts. This estimate is based mostly on our own observations and inferences from the literature, for few workers have made quantitative measurements. The authigenic feldspars occur as overgrowths around detrital cores and as newly formed crystals with no apparent preexisting core. Both types have well developed crystal faces, except in some ash beds, and show no evidence of weathering or alteration. Most grains fall within the silt grain size (2-60m). The most plausible explanation for the relatively few reports of authigenic feldspars in the literature is that it is easy to miss the small, mostly untwinned, grains in a cursory microscopic examination.

Several investigators have observed a correlation between the amount of detrital silicates, especially feldspars and to a lesser extent clay minerals, and the abundance of authigenic feldspars (Spencer, 1925; Odom, Hiatt, and Kramer, 1970). That correlation has not been observed by us for most of the approx 600 rock samples that we studied. Furthermore, the suggested correlation would imply that authigenic feldspars should be most abundant in shales, for they are the rocks that contain the most feldspars and clay minerals, yet our studies of shales fail to corroborate this expected abundance.

Authigenic albites are generally larger than authigenic K-feldspars (most albites are 40-100 μm in size, roughly equivalent to a 10 μm thick overgrowth on each side of a rectangular detrital core measuring 100 × 80 × 60 μm).

A large proportion of authigenic albites shows no evidence of detrital cores, although inclusions of the surrounding sediment are

PLATE 2

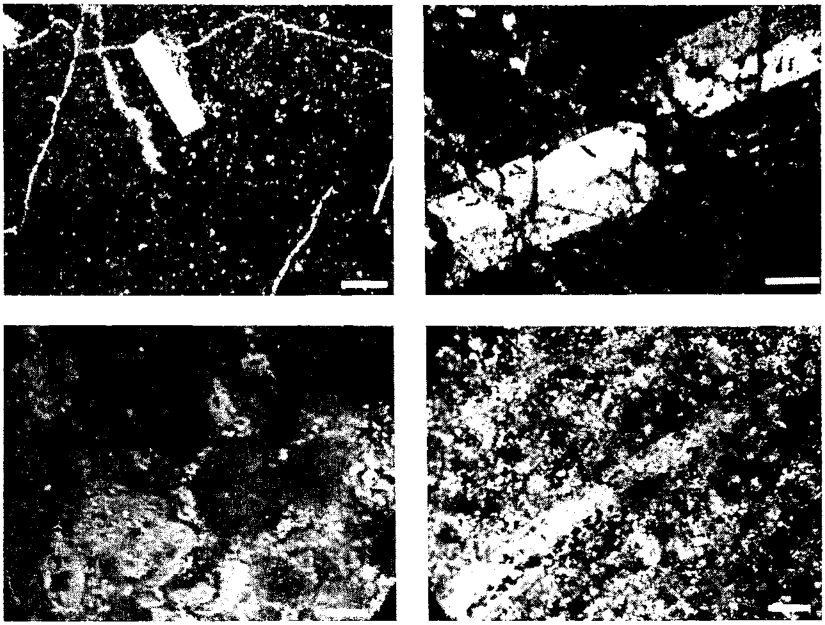


Photomicrographs of inclusion patterns in authigenic feldspars. (A) Carbonaceous inclusions zonally arranged parallel to crystal faces of authigenic albite crystal in Triassic dolostone, Crete. White line represents 0.3 mm. (B) Calcite inclusions zonally arranged parallel to crystal faces of authigenic albite crystal in Eocene limestone, Rhodes, Greece. White line represents 0.3 mm. (C) Hourglass structure of calcite, quartz, and carbonaceous matter inclusions in authigenic albite in Eocene limestone, Rhodes, Greece. White line represents 0.25 mm.

present; apparently they grew without preexisting nucleation centers. Where cores are present, they are of the same kinds of detrital or chemically precipitated minerals that are found elsewhere in the rock, including K-feldspars, quartz, and non-silicates such as calcite, dolomite, and, more unusually, pyrite (for example, pl. 1). In contrast, most authigenic K-feldspars, except those in ash beds, grow around detrital cores and most often around detrital K-feldspars.

Textural relations indicate that authigenic feldspars form in place and that replacement prevails rather than primary growth in unconsolidated highly porous sediment. The authigenic crystals are sparsely and randomly scattered in the rocks and generally do not show an

PLATE 3



Photomicrographs of authigenic albite crystals in thin sections (crossed polarizers). (A) Albite crystals in micritic Eocene limestone matrix, Rhodes, Greece (albite twin law). Note cross-cutting relations among albite, calcite veins (white), and styolites (black). White line represents 0.5 mm. (B) Albite crystal in Triassic micritic dolostone (X-Carlsbad twin law), Crete. Note displacement of albite by calcite vein. White line represents 0.5 mm. (C) Albite crystal in Ordovician pelsparite, Glen Falls, N.Y. Note euhedral albite replacing a pellet in lower left. Irregular grains (q) are detrital quartz grains. White line represents 30 μm. (D) Albite crystals in fine-grained Ordovician limestone, Pa. Note albite (black arrow) replaces fossil with carbonaceous matter that is also included in the authigenic albite. White line represents 50μm.

increased concentration along bedding planes, veins, or joints. Inclusions, which are common, are of the same detrital minerals found in the rock. The compatible composition of these inclusions and the rock detritus can be used for in-situ formation of the authigenic feldspar crystals versus mechanically redeposited ones, "second cycle" grains which may have incompatible composition of these inclusions. The distribution of these inclusions, which is either random or zonal parallel to crystal faces, or in an hourglass pattern (pl. 2) suggests growth rate histories (Kastner and Waldbaum, 1968; Kastner, ms).

In a number of rocks the textural relations make it possible to determine the relative sequence of events (pl. 3). Authigenic feldspars may infrequently act as a cement, binding framework grains of detrital feldspar, quartz, and other minerals; in some situations rendering the rock relatively impermeable at any early stage of diagenesis. In other rocks, authigenic feldspars may be found "floating" in a cement of different composition, such as carbonate cement in some arkoses; because the feldspars must have replaced the carbonate, they are post-cementation in age. In many sedimentary rocks, small-scale deformational or diagenetic structures, such as veinlets and stylolites, cut across the authigenic feldspars and indicate an upper bound to their age (pl. 3-A, -B). Authigenic feldspars in some dolostones have calcite inclusions, indicating a pre-dolomitization age. In many rocks, however, authigenic feldspars replace carbonate fossils and pellets (pl. 3-C, -D) and detrital silicates with no clear evidence bearing on the diagenetic stage in which authigenetic feldspars form. It would seem that the best way to get the age of an authigenic K-feldspar is to determine its $^{40}K/^{40}Ar$ age, but because of the common detrital K-feldspar cores, that analysis is difficult.

Authigenic feldspars in carbonate rocks.—In the generally pure carbonate rocks we have surveyed, the total amount of authigenic feldspars rarely exceeds 2 percent by weight. These carbonate rocks range from pure calcitic limestone to stoichiometric dolomite. Authigenic feldspars have been found (1) with about the same frequency in calcitic as in dolomitic carbonates; (2) more often in fine-grained rocks: micritic, pelmicritic, or biopelmicritic, than in medium to coarse-grained or recrystallized rocks; and (3) as replacements of pellets and fossils in these micritic rock types. Authigenic feldspars can be found as replacements of sparry calcite cements, although not common. Authigenic albite is by far more abundant than authigenic K-feldspar, even in the few localities where the two feldspars coexist. The albites are more abundant in dark gray, slightly carbonaceous limestones than in lighter colored, non-organic rich limestones. These albites may be intimately associated with organic matter as in the twinned crystals from an Eocene limestone from Rhodes (Kastner and Waldbaum, 1968), and from a Triassic dolostone from Crete (Kastner, ms and 1970). In the many carbonate rocks in which tectonic deformation associated with either mild vertical movements or regional orogenesis has resulted in fracturing and vein filling with either calcite or quartz, authigenic feldspars are invariably cut by these veins or displaced, indicating crystallization before deformational activity (pl. 3-A, -B). Stylolites almost always cut authigenic feldspars, suggesting that this type of pressure solution, a function of burial depth and time, postdates feldspar formation. Other textural and mineralogical characteristics of authigenic feldspars in carbonate rocks have been summarized by Kastner (1971).

Authigenic feldspars in sandstones.—Authigenic feldspars occur in all types of sandstones, mainly as overgrowths around detrital cores and occasionally as cement or newly formed crystals with no detectable detrital cores. Authigenic K-feldspars are relatively more abundant in most sandstones than authigenic albites; perhaps this is related to the greater abundance of detrital K-feldspar in most sandstones. Albite is the prevailing authigenic phase in graywackes and is both more frequently present and more abundant than in arkoses or quartz or lithic arenites. This seems to correlate with the ratio of detrital plagioclase to detrital K-feldspar and the Na/K ratio, both of which are larger in graywackes than in other sandstone types. The estimates of abundance of authigenic albites in graywackes are sometimes exaggerated by those who have noted the prominent occurrence of albitized feldspars in some low-grade greenschist graywackes, such as the Rensselaer grit of eastern New York State. As a great many ancient graywackes are in fact low-grade metamorphic rocks or high-grade diagenetic rocks of what has been called the anchimetamorphic facies (Kubler, 1967), the abundance of albites in the graywacke facies is an observation that relates the problems of original composition to both diagenesis and metamorphism.

We have observed that authigenic feldspar overgrowths in some quartz arenites, such as the Upper Cambrian Potsdam sandstone of New York State, have reciprocal relations with authigenic quartz overgrowths. Where the authigenic feldspar is abundant (more than a percent or two) authigenic quartz overgrowths are generally less common and the converse.

Füchtbauer (1964) pointed out that detrital feldspar/quartz ratios are strongly dependent on grain size. Odom, Hiatt, and Kramer (1970) reported that this relationship also holds in the Franconia Formation of Wisconsin, in which fine grained sandstones are much more feldspathic than coarse grained ones. The explanation for this effect lies in the greater comminution of feldspar grains during erosion and transport abrasion as compared with the harder and less easily cleaved quartz. Because most authigenic feldspars in sandstones are overgrowths on detrital grains, they make the grains larger, and so authigenesis tends to "restore" some of the grain that was lost by abrasion. A clear, positive correlation between large amounts of fine-grained detrital feldspars and greater amounts of authigenic overgrowths has, however, not been observed in most of the rocks studied by us.

Authigenic feldspars in sandstones are found in association with silicates other than quartz: zeolites and clay minerals. The zeolites most typically reported are analcime and clinoptilolite, but many others have been noted (Hay, 1966), particularly in volcaniclastic sediments. The feldspar-zeolite association is also found in marine and continental fine-grained sandstones with a high original component of volcanic glass, which was deposited by ash falls. The clay minerals associated with authigenic feldspars range from the kaolinites found in many arkoses, such as the Triassic of the Connecticut Valley, to illites, glauconites, chlorites, and smectites of other sandstone types. Kaolinite pseudomorphs of feldspar have been found in a number of sandstones. To our knowledge, no one has reported the occurrence of authigenic kaolinite and authigenic feldspar in textural equilibrium. Authigenic quartz is frequently found in association with both.

The most frequent association is of authigenic (1Md) and detrital illite and authigenic feldspar. Textural relations such as intergrowths and intimate association suggest chemical compatibility, as one would expect from thermodynamic relations in the Na_2O–K_2O–Al_2O_3–SiO_2 system. Chlorite is in frequent association with authigenic albites in graywackes.

Though, as noted above, organic matter in some limestones is intimately associated with authigenic feldspars, particularly with albite, there is no apparent relation between the two in organic-rich sandstones, either oil saturated sandstones or those rich in carbonaceous detritus, but there is no literature on the subject. Assessment of the relative ages of authigenesis of feldspar and oil infiltration in reservoir sandstones would help in the study of both.

Shales.—The scarcity of reports about authigenic feldspars in shales is not surprising, for the small grain size of the textural elements of shales makes it difficult to use the established criteria for authigenesis. Those who have reported authigenic feldspar in shale, such as Gruner and Theil (1937), relied primarily on chemical purity and secondarily on abundance in deducing an authigenic origin. In the absence of textural evidence, now supplied by scanning electron microscope analysis, an assignment of authigenic origin remains tentative. In a survey of a few typical varieties of ancient shales by electron microprobe we have found few authigenic feldspars. Where present, K-feldspar seems to predominate. The shales in which abundant authigenic feldspar is found, in some rocks well over 20 percent and up to 80 percent (Weiss, 1954; Gruner and Theil, 1937), are entire thin beds, overlain and underlain by "normal" shales with little or no feldspar. This distribution, together with the abnormal mineral composition, suggests a volcaniclastic origin. We believe many of these thin beds are ashfalls that have not been diagenetically altered in the usual way, that is, to bentonite or metabentonite.

Evaporites.—The only authigenic feldspars in evaporites known to us are authigenic albite overgrowths on plagioclase detrital cores in the cap rock of a salt dome in Mississippi (Schlocker, personal commun.; Kastner, ms). The presence of authigenic albite in this association should not be surprising, for there are ample raw materials for authigenesis in the insoluble residue materials of cap rocks. The overwhelming amount of sodium in this geochemical environment is the obvious determining factor that dictates albite composition. By analogy, we may expect authigenic K-feldspars to be characteristic of the far less common potassium-rich evaporites. The abundant authigenic albites of many Triassic carbonate rocks may be related to the hypersaline conditions inferred for their origin. Merino (1975a,b) also related the much greater abundance of authigenic albite in the Temblor Formation (Miocene) relative to the McAdams Formation (Eocene), Calif. to the higher concentration of the NaCl brines in the interstitial waters of the former.

Volcaniclastics.—Authigenic feldspars are major constituents of vitric marine and non-marine, silicic to intermediate tuffs and ash beds. Some feldspars are authigenic overgrowths around detrital silicates. Others replace detrital plagioclase grains. But most of the authigenic crystals, in particular in saline alkaline lacustrine environments, show no evidence of detrital cores; rather, they seem to be most frequently alteration or replacement products of phillipsite, erionite, clinoptilolite, and analcime,

PLATE 4

Euhedral and twinned authigenic K-feldspar crystals on the etched surface of basaltic glass, at the basalt/sediment interface, DSDP Site 322, Bellingshausen Abyssal Plain. White line represents 30μm.

and do not form directly from volcanic glass (Hay, 1966, 1968, 1970; Sheppard and Gude, 1968, 1969, 1973, 1974; and references therein).

Authigenic monclinic K-feldspar is by far more common than authigenic albite. Frequently, the authigenic K-feldspar has a high boron content (Sheppard and Gude, 1973, 1974). The boron analogue of albite, reedmergnerite, has been described from the Green River Formation, Utah (Milton, Axelrod, and Grimaldi, 1954).

In several localities, the authigenic feldspar forms almost monomineralic beds (Deffeyes, 1959; Moiola, 1964; Sheppard and Gude, 1968; Hay, 1966, 1968). A correlation between inferred alkalinity, salinity, and authigenic mineralogy has been indicated; authigenic feldspar correlates with the alkaline and hypersaline facies (Hay, 1966, 1970; Sheppard and Gude, 1968, 1973; Goodwin and Surdam, 1967; Surdam and Parker, 1972).

Pelagic sediments.—Authigenic K-feldspars have been described from Atlantic and Pacific Oceans volcaniclastic sediments and basalts, as euhedral or anhedral crystals replacing plagioclase (Mellis, 1952; Matthews, 1962, 1971; Bass and others, 1973; Stewart, Natland, and Glassley, 1973; Larson and others, 1974; Kelts and McKenzie, 1976) or volcanic glass (Lancelot, Hathaway, and Hollister, 1972; and pl. 4). They also form discrete euhedral crystals in volcaniclastic sediments (Donnelly and Nalli, 1973), in foraminifera chambers (Larson and others, 1974), and in porcelanite associated with volcaniclastic material (Kastner and Gieskes, 1976). In many the euhedral habit, chemical purity, composition of inclusions, absence of cathodoluminescence, and textural relations with the plagioclase crystals and volcanic glass that they replace suggest that they are authigenic. Nevertheless hydrothermal origin was suggested by Stewart, Natland, and Glassley (1973).

These K-feldspars occur at all depths in the sediments and have been described most frequently from upper Cretaceous volcaniclastic sediments of the Pacific, in particular in the coarser grain sized sections of these sediments (Kelts and McKenzie, 1976), which suggests a positive correlation between abundance of authigenic K-feldspar and porosity. Generally, they constitute a small fraction of the sediments and basalts. Kelts and McKenzie (1976), however, described layers with up to 60 percent K-feldspar in the basal volcaniclastic sediments of DSDP sites 315A and 316; these feldspars were identified as intermediate microcline. Mellis (1952) and Matthews (1962, 1971) identified the K-feldspars that replace plagioclase in dredged gabbro and tholeiite basalt from the western and eastern North Atlantic, respectively, as orthoclase; and Lancelot, Hathaway, and Hollister (1972) described sanidine replacing volcanic glass from DSDP site 105.

In deep-sea sediments, the coexistence of zeolites and K-feldspar has been reported only by Bass and others (1973) and Kelts and McKenzie (1976). But no obvious textural evidences that suggest a genetic relation between zeolites and K-feldspar have been observed as yet, and as shown in plate 4, K-feldspar also forms directly from vocanic glass.

At present, the only report of authigenic albite in pelagic sediments is from gypsum and dolomite-rich sediments associated with Late Miocene to Early Pliocene evaporites in the Mediterranean Sea, DSDP site 124, between 55 to 111 m depth (Kastner and Siever, 1972). The authigenic albites occur as overgrowths around detrital albite.

A summary of the relation of rock type to authigenic feldspar occurrence is given in table 1.

TABLE 1

Relation of rock type to feldspar occurrence

ROCK TYPE	FELDSPAR TYPES
Carbonates mainly in micrites, pelmicrites, and biopelmicrites	Na > K
Sandstones	K > Na
graywacke	Mainly Na
arkose	K > Na
lithic arenites	K > Na
Shales	K > Na
Volcaniclastics	Mainly K
Evaporites	Only Na reported.

Relative ages.—The youngest reported authigenic albites from the continents are from Eocene carbonate rocks, Rhodes, Greece (Drian, 1861; Von Foullon, 1891; Kastner, 1971) and from Miocene sandstones, California (Merino, 1975a,b). Recently, authigenic albites in Pliocene sediments from a Mediterranean DSDP core were described by Kastner and Siever (1972). The youngest known authigenic K-feldspar is the Late Pleistocene K-feldspar from Searle's Lake, Calif. (Smith, 1962). K-feldspars are a major constituent of thick non-marine Pliocene tuffaceous beds in the western United States.

Authigenic feldspars are abundant in more ancient rocks, particularly in Paleozoic and late Precambrian rocks. Cambrian and Ordovician examples have been noted frequently and seem to be more common than in later periods. Precambrian examples abound, many in sediments that have never been affected by metamorphism of greenschist or higher grade. Hay (1966) has argued that authigenic albite occurs most commonly in sedimentary and volcaniclastic rocks that have been buried more than 3300 m and that its occurrence tends to increase with increasing depth of burial. Basing his ideas on reports of authigenic K-feldspar occurrences in Europe and North America, he also suggested a decrease in amount of authigenic K-feldspars from the middle Paleozoic through the Mesozoic with a possible increase in the Triassic. This age correlation, if substantiated, may be related to another similar kind of correlation of age and mineralogy, that proposed by Weaver (1967) for the decrease in K-abundance in clay minerals after the late Paleozoic. Garrels, Mackenzie, and Siever (1971) have proposed a general diagenetic tendency to explain these tentative age-composition relations, rather than a non-uniformitarian change in seawater composition or land plant evolution.

An increase in abundance of all authigenic feldspars with geologic age is undoubted, but statistics are insufficient to describe the trend. Is the trend relatable to slow kinetics of feldspar authigenesis? Does it indicate that the fluid phase responsible for authigenesis needs long times to reach the required composition, thus suggesting that authigenic feldspars are late diagenetic products? The petrographic evidence militates against that conclusion. Or does it suggest that moderate temperature and pressure conditions are more favorable for the formation of authigenic feldspars? These alternative interpretations are discussed below.

CHEMICAL AND PHYSICAL CHARACTERISTICS

Habit and twinning.—(A) *Authigenic albite*: Crystals are transparent, translucent, or opaque, depending on the density of inclusions. Most crystals fall in the 60 to 120 μm range. The largest reported are those from some Triassic dolostones of Crete, 3.5 mm along *a*, 0.3 mm along *b*, 1.1 mm along *c*, (Kastner, ms).

Authigenic albites are triclinic euhedra. The most common well-developed crystal forms are {010}, {001}, {100}, $\{1\bar{3}0\}$, and $\{\bar{2}01\}$. Most crystals are tabular on (010) and a few on (001). Füchtbauer (1950) described both types from the Göttingen Muschelkalk, the albite-type and

PLATE 5

Photomicrograph of an authignic albite crystal with X-Carlsbad twins (fourling twins) in Triassic dolostone, Roc Tourné, Modane, France. White line represents 0.5 mm.

pericline-type, respectively. He noted that the albite-type crystals are twinned after the X-Carlsbad law, and the pericline-type after the simple albite law. This may not be universal, however. The authigenic albites from one limestone (Eocene, Rhodes), which are tabular on (010), have a similar morphology for both twin types (Kastner and Waldbaum, 1968). Some authigenic albites are twinned after the simple albite twin law (not polysynthetic twins). Many, perhaps most, authigenic albites are untwinned.

The unusual growth twins which appear as four-lings (pl. 5) are common in authigenic albites but have not been observed in igneous and metamorphic albites. The occurrence of this twin type is the basis for its use as a criterion for authigenesis (Kastner, 1971), though why such twins develop only at low to moderate temperatures remains conjectural. Fourling twins have been described in great detail from well developed euhedral transparent albite crystals in Triassic dolostones, Roc Tourné, Savoie, France, and thus are often called Roc Tourné twins (Drian, 1861; Rose, 1865; Lacroix, 1897; Füchtbauer, 1948; Donnelly, 1967; Kastner and Waldbaum, 1968). Rose (1865) suggested that the Roc Tourné twins are interpenetrating albite twins attached to each other by the Carlsbad law; Lacroix (1897) described them as a double twin on the albite law. Baskin (1956) used the term Roc Tourné for a combination of albite and Carlsbad twin laws. Kastner and Waldbaum (1968), based on plotting of axes on a stereographic projection, described the four-ling twins as two-unit penetration twins after the X-Carlsbad law with composition planes (010) and near (100). For a more detailed review of Roc Tourné twins, see Kastner and Waldbaum (1968) and Smith (1974, v. 2). Because of some confusion in the literature regarding the nature of this twin type, Smith (1974) has suggested that until single crystal measurements are available, Roc Tourné should be used only for the morphological habit and not in a specific sense.

(B) *Authigenic K-feldspar*: Authigenic K-feldspars are transparent or translucent. The largest authigenic microcline studied is about 100 μm, but most are much less than 40 μm. In described localities where authigenic albite and K-feldspars coexist, the albite crystals are larger than the K-feldspars (Trümpy, 1916; Füchtbauer, 1950; Kastner and Waldbaum, 1968; Kastner, ms and 1971).

Authigenic K-feldspars are either triclinic or monoclinic, with various degrees of Al/Si ordering. In general, in carbonate rocks most authigenic K-feldspars are triclinic (Baskin, 1956; Reynolds, 1965; Kastner, 1971), in sandstones and shales both triclinic and monoclinic (Reynolds, 1929; Weiss, 1954; Sáenz, 1963; Glover and Hosemann, 1967), and in altered ash beds, monoclinic (Sheppard and Gude, 1968, 1969). Examples of a few exceptions to the above generalization are the authigenic orthoclase crystals in chalks of the Paris Basin (Cayeux, 1903) and in the Lower Cambrian "Fucoid beds" of northwest Scotland (Swett, 1968). The triclinic authigenic feldspars are euhedral. The monoclinic ones are either euhedral, often with adularia-like habit with a narrow {010} form and a well developed {110} form (Lory, 1886a; Baskin, 1956; Füchtbauer, 1956), subhedral to euhedral (Sheppard and Gude, 1974), or anhedral (Hay and Moiola, 1963; Sheppard and Gude, 1968, 1969). According to Baskin (1956), the authigenic microclines have a unique habit arising from a combination of the {010}, {201}, {101}, and sometimes {001} crystal forms. This suggests that, unlike microclines in igneous rocks, these authigenic crystals originally crystallized as highly ordered triclinic crystals in the stability field of microcline and did not undergo a diffusive transformation from a monoclinic disordered state to a triclinic highly ordered state.

Authigenic microclines never show the typical cross-hatched twinning of microclines of igneous and metamorphic rocks. The nature of fourling twinning in authigenic microclines, uncommon in most rocks, is unclear. Baskin (1956) described it as a combination of albite and pericline twin laws. Smith (1974, v. 2), however, suggested that because of unusual angular relations of Baskin's X-ray photographs (1956, pl. 2-B), it is desirable to carry out further X-ray studies. Most authigenic K-feldspars are untwinned, whereas their detrital K-feldspar cores are often twinned. The extension of twin boundaries from the detrital cores to the authigenic overgrowth has been described from a few localities (Gilbert, 1949; Heald, 1950). In these occurrences, the structural state of the detrital core and the authigenic overgrowth are probably almost identical.

Almost all authigenic microclines and a high proportion of authigenic monoclinic K-feldspars grow around K-feldspar detrital cores. Detrital cores of other compositions have not been described frequently. In reports of some shales and ash beds with high concentrations of monoclinic authigenic K-feldspars, no detrital cores were described. That lack can be due to the very small dimensions of the crystals (2 to 5 μm) and the difficulties of finding detrital cores of less than 1 μm.

Authigenic K-feldspars also occur as cement (Berg, 1952) and as pseudomorphs after plagioclase, as in gabbro fragments from the northwestern Atlantic sea floor (Mellis, 1952) and in altered basalts from the eastern North Atlantic (Matthews, 1962, 1971).

Chemical composition and cathodoluminescence.—The electron microprobe is the technique of choice for reliable chemical analysis of authigenic feldspars. Other common chemical techniques applicable to bulk samples require clean mineral separation, which is virtually impossible to obtain because of the ubiquity of inclusions and/or the presence of detrital cores in authigenic feldspars. Electron microprobe analyses have shown that authigenic feldspars are extraordinarily pure albites and K-feldspars that could be taken as the best natural representatives of end members of the alkali feldspar series. The Ca previously reported in several bulk wet chemical analyses is present as carbonate inclusions (Kastner, 1971). Electron microprobe analysis was unable to detect Ba in authigenic K-feldspars. According to Heier and Taylor (1959), Sr in K-feldspars is associated with Ba. Therefore, we tentatively conclude that authigenic K-feldspars do not contain much Sr either. We assume that in growth at low temperatures, feldspar is unable to include Ti, Fe, and Pb in its structure.

The high chemical purity of authigenic feldspar most probably is responsible for the lack of luminescence when bombarded with an electron beam. Smith and Stenstrom (1965) examined the cathodoluminescence of feldspars from igneous and metamorphic rocks and concluded that both authigenic and low-grade metamorphic feldspars do not luminesce, implying that low as well as moderate temperature feldspars do not include enough activators, which are unknown as yet, for cathodoluminescence. It is generally true that the concentration of impurity ions or atoms increases with temperature, and this may be the major variable in luminescence.

Boron is the only quantitatively important impurity in authigenic feldspars. It may replace up to 1 percent of the aluminum in some authigenic K-feldspars from altered tuffs in saline alkaline lakes (Sheppard and Gude, 1968, 1969, 1973, 1974; Martin, 1971) and up to 100 percent of the aluminum in albite, forming a rare ordered end member. This is the boron feldspar, reedmergnerite, from the Green River Formation, Utah (Milton, Axelrod, and Grimaldi, 1954; Milton and others, 1960; Milton and Eugster, 1959). Eugster and McIver (1959) showed that a potassium–boron feldspar can also be synthesized. No natural occurrence of such a feldspar has been reported. Stern (1969) and Shaw and others (1963) reported no more than a few tens of ppm boron in nonauthigenic feldspars.

Authigenic buddingtonite, an ammonium feldspar with zeolitic water (theoretical formula $NH_4AlSi_3O_8 \cdot nH_2O$) has been described from a shale member of the Phosphoria Formation (Permian) of southeastern Idaho. The composition of various buddingtonite crystals ranges between

$Bd_{82}KF_{18}$ to $Bd_{13}KF_{87}$ (where Bd = buddingtonite and KF = K-feldspar) in the buddingtonite–K-feldspar series (Gulbrandsen, 1974). Gulbrandsen suggested that ammonia was derived from the decomposition of organic matter. The role of water in the structure is not as yet understood.

Oxygen isotopes.—Oxygen isotope values of authigenic feldspars and of alkali feldspars from granites and pegmatites and from metamorphic rocks are summarized in figure 1. The high positive $^{18}O/^{16}O$ ratios of authigenic feldspars are clearly diagnostic of their low temperature origin. Unfortunately, oxygen isotope fractionation between coexisting authigenic feldspars and carbonate minerals, ranging from -0.5 to $+1.4‰$ (Lawrence and Kastner, 1975), is too small for reliable geothermometry. But oxygen isotope differences between feldspar and quartz of authigenic origin, presumed on petrographic evidence to have been precipitated from the same pore waters, should prove to be a valuable measurement for geothermometry in diagenetic environments.

Optical parameters.—It is difficult to measure accurately optical properties of authigenic feldspars because of the small dimensions of most crystals, the presence of detrital cores, and twinning. Lack of continuity in optical properties between detrital cores and authigenic overgrowths results from differences in chemical composition and/or in degree of Al/Si disorder between the two domains. Refractive indices permit a fairly accurate estimate of relative Or/Ab content in authigenic alkali feldspars, because of their high chemical purity. Optical axial angles (2V) measurements of authigenic albites are significantly higher than those of low albites from igneous and metamorphic rocks (Füchtbauer, 1948, 1956; Schöner, 1960; Kastner, ms). Given the extraordinary purity of the authigenic albites, the high 2V values, ranging from 78° to 90° (Kastner, ms), suggest that the Al/Si distribution in these albites is not as highly ordered as in albites from pegmatites and metamorphic rocks. The optic axial angles of authigenic microclines, unlike those of authigenic albites, are not significantly higher than those of microclines from igneous and metamorphic rocks. All authigenic K-feldspars with adularia-like habit are

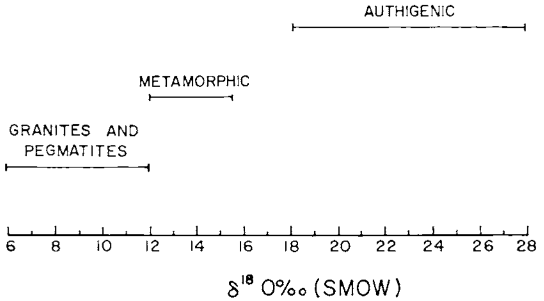


Fig. 1. $\delta^{18}O$ values of alkali feldspars: authigenic (Savin and Epstein, 1970; Lawrence and Kastner, 1975; Kastner and Clayton, unpub. data); granites and pegmatites and metamorphic (Taylor and Epstein, 1962; Garlick and Epstein, 1967; O'Neil, Shaw, and Flood, 1977).

optically monoclinic (Smith, 1974). For further discussion of optical properties, see Kastner (ms).

X-ray crystallography.—Authigenic feldspars with negligible amounts of detrital cores can be used for the determination of unit-cell parameters. An appreciable volume of detrital cores, which have variable compositions, has been shown to give diffraction patterns with a wide range of overlapping lines. This results in line broadening and loss of precision, making such feldspars poor for unit-cell parameter determination (Kastner, 1971). The unit-cell parameters of most authigenic feldspars are similar to those of pure low albites and K-feldspars from igneous and metamorphic rocks. Unit-cell parameters of alkali feldspars depend both on the Si/Al distribution in the tetrahedral sites and on the K/Na ratio. As authigenic feldspars are pure, homogeneous, end members of the alkali feldspar series, their unit-cell parameters depend only on the Si/Al distribution (table 2).

All authigenic albites show a high degree of ordering, but in contrast, authigenic K-feldspars are either highly ordered microcline, partially disordered adularia or orthoclase, or highly disordered sanidine. There seems to be a relationship to rock type; in carbonate rocks microcline, with an average abundance of trace amounts to 2 wt percent, predominates. In sandstones and shales, however, various degrees of Al/Si ordering of authigenic K-feldspars, from ordered microcline to sanidine, have been reported; the monoclinic polymorphs predominate in shales. The abundance of these authigenic K-feldspars ranges between 1 to 20 wt percent. Sanidine, from about 10 to more than 80 wt percent, is the most important polymorph in altered tuffaceous beds.

A positive correlation between the abundance of authigenic feldspars in the rock and their degree of Al/Si ordering strongly suggests a kinetic control on the order/disorder state of authigenic K-feldpars, for such a correlation would not be predicted from an equilibrium model. For example, Heald (1950) has reported abundant authigenic feldspar in Triassic arkoses of the Connecticut River Valley, and Weiss (1954) estimated an orthoclase content of as high as 80 percent in Ordovician shales and bentonitic tuffs from Minnesota. Sheppard and Gude (1968, 1969) described the ultimate in abundance, almost monomineralic beds of sanidine, the most disordered polymorph, from altered tuffs of the Barstow Formation and Lake Tecopa; similarly, Hay (1966, 1968) described almost monomineralic K-feldspar beds from altered tuffs in Searles Lake, Olduvai Gorge, and Lake Natron.

Highly disordered K-feldspars from altered rhyolitic tuffs have anomalous unit-cell parameters (Wright and Stewart, 1968). Sheppard and Gude (1969, 1973, 1974) have suggested these results from partial boron substitution for aluminum. This idea was confirmed experimentally by Martin (1971), who synthesized boron-bearing feldspars with 5.5, 8.1, and 9.7 percent B substitution for Al. He showed that the *a* and *c* parameters seem completely normal, but *b* is smaller. No end member boron K-feldspar has been described. Reedmergnerite, the boron analogue of

TABLE 2

Unit cell dimensions of authigenic and other feldspars

Type of Feldspar	a(Å)	b(Å)	c(Å)	α	β	γ	V(Å^3)	References
Authigenic microcline	8.5656(72)	12.9632(24)	7.2240(41)	90.682(33)	116.041(34)	87.804(31)	720.17(104)	Kastner (1971)
Authigenic microcline	8.5852(26)	12.9610(14)	7.2212(17)	90.537(16)	115.956(14)	87.984(15)	722.01(36)	Kastner (1971)
Hugo microcline	8.5891(34)	12.9628(38)	7.2230(15)	90.617(46)	115.952(33)	87.740(37)	722.52(29)	Orville (1967)
Authigenic sanidine with 5000 ppm B	8.592(3)	12.976(5)	7.164(3)	90	116.067(27	90	717.8(3)	Sheppard and Gude (1973)
Buddingtonite (ammonium feldspar)	8.804(3)	13.024(3)	7.183(1)	90	116.105(18)	90		Kimball and Megaw (1974)
Sanidine	8.6027(8)	13.0209(10)	7.1777(5)	90	116.010(7)	90	722.57(8)	Orville(1967)
Authigenic albite	8.1367(21)	12.7853(18)	7.1583(13)	94.170(25)	116.610(14)	87.813(25)	664.03(32)	Kastner (1971)
Authigenic albite	8.1345(19)	12.7809(15)	7.1561(8)	94.206(14)	116.581(12)	87.818(16)	663.55(26)	Kastner (1971)
Reedmergnerite	7.833(1)	12.360(2)	6.803(1)	93.308(12)	116.351(8)	92.055(14)		Appleman and Clark (1965)
Amelia albite	8.1414(16)	12.7836(20)	7.1571(11)	94.233(16)	116.592(12)	87.680(15)	664.25(25)	Waldbaum and Robie (1971)

albite, is isostructural with low albite; its unit-cell parameters are given in table 2. Buddingtonite, the authigenic ammonium feldspar from the Phosphoria Formation, southeastern Idaho, is monoclinic. The unit-cell parameters are summarized in table 2.

Criteria for authigenic origin and choice of analytical methods.—Crucial to the evaluation of the petrogenetic significance of authigenic feldspars is the reliable diagnosis of a given grain as authigenic and, beyond that, the determination of its mineralogical or chemical composition. The most serious problem is the difficulty with most methods, even with the most careful hand-picking of grains, of being sure that authigenic grains are not intimately mixed, as in overgrowths, with detrital feldspars. Our evaluation of relative reliability of various analytical methods is given in table 3.

The electron microprobe is the most appropriate for most rocks because it can be used for very small grains or overgrowths, unambiguously

TABLE 3

Analytical methods and criteria for authigenic origin of feldspars in sedimentary rocks, listed in order of decreasing reliability, assuming the possibility of separating a pure phase

Analytical Method	Criteria for Authigenic Origin	Remarks
Electron microprobe	High purity of end-member composition	For any size >1μ. High purity end members may also be found in low-grade metamorphic rocks and some pegmatites.
Optical petrography	Microscopic textures, such as overgrowths and twinning. Composition as determined by refractive indices and optic axial angle.	Good only for grains > 50μ.
Cathodoluminescence	No luminescence.	Good only for grains > 50μ(cathodoluminescence attached to microscope); >1μ (microprobe). Non-luminescing grains also found in low-grade metamorphic rocks.
Isotopic analysis	High positive $\delta^{18}O$ values.	Difficult to avoid contamination with detrital feldspars.
X-ray diffraction	Purity of composition.	Difficult to avoid contamination with detrital feldspars.
Bulk chemical analysis	High purity of end-member composition.	Difficult to avoid contamination with detrital feldspars and matrix inclusions.
Stain tests	Differential staining of detrital and authigenic feldspar.	Good only for grains > 50μ. Stains insensitive to small differences in composition between detrital cores and authigenic overgrowths, and strongly affected by preparation methods.

gives the chemical composition of the authigenic grain or overgrowth, and, in the scanning mode, presents a picture of the areal distribution of the elements that allows inference of textural relations as well as cathodoluminescence properties. Scanning electron microscopes equipped with X-ray energy dispersive systems have the advantage of direct visualization, but the disadvantage of giving only semi-quantitative compositions of non-polished samples. Optical petrography is excellent, particularly for textural relations, but is restricted to use with grains that are large enough (>50μm) to be resolved easily by the petrographic microscope and allow the determination of optical parameters. Cathodoluminescence is diagnostic of authigenic origin and also, often, of low grade metamorphic origin. As this method does not give feldspar composition other than implying the lack of certain impurities that stimulate, or the presence of those that quench luminescence, the distinction between detrital low-grade metamorphic cores and authigenic overgrowths requires an electron microprobe scan. It too is restricted to grains that can be seen with a petrographic microscope (unless the microprobe is being used).

Bulk chemical analysis, X-ray diffraction, and isotopic analyses, because of the normal impossibility of being sure that only a single phase—presumably authigenic — is present in the sample, tend to be in practice analyses of mixtures. When these methods are used, the samples should first be examined by the petrographic microscope, microprobe, and luminescence methods. Diffraction analysis is the only method available for determining order-disorder states but requires high-precision work, best done with single crystal methods, but large single crystals of authigenic feldspar are rare in sedimentary rocks. Isotopic analysis suffers from the same defects as bulk chemical analysis, that is, one needs pure material to calculate the value of the authigenic rim from an assumed value and given volume of the detrital core (Savin and Epstein, 1970). The few $\delta^{18}O$ analyses of authigenic feldspars that have been made thus far allow the distinction of authigenic from igneous and metamorphic grains. Stain tests are convenient as a rapid method for feldspar identification and as a check on routine microscopy, mainly for the distinction between K-feldspar and the plagioclases. Stains are not sensitive to differences in composition within each type but can, with care in the staining procedure, show the presence, for example, of albite overgrowths on K-feldspar.

THERMODYNAMICS OF FELDSPAR FORMATION AT LOW TEMPERATURE

Diagenetic reactions proceed almost exclusively through reaction at the interface between minerals and pore water, for at low temperatures solid state diffusion is so slow that even long geologic times are inadequate to accomplish bulk chemical change by that mechanism. Relating chemical analyses of the pore waters to the mineral phases present in the rocks is most frequently made by the assumption that the minerals are in equilibrium with the pore waters. Yet microscopic petrography and electron probe analysis show that in many sedimentary rocks, true equilibrium mineral assemblages do not exist, at least as measured by the yardstick of known thermochemical quantities. Rather, geologists have had recourse to "local equilibrium" assemblages of phases in close proximity — frequently in a volume of rock no larger than a few cubic millimeters — while other textural elements of the surrounding bulk of the rock may be far from equilibrium. In fact, many of these local domains may be little more than reacted "surfaces" which have barely diffused into three dimensions.

In this section, we treat the coexistence of phases with authigenic feldspars over any appropriate size domain over which we can, by textural evidence or proximity, more or less safely assume a "Gibbsian" equilibrium. In the section on geochemical models, we treat feldspar growth from a more realistic kinetic point of view.

The following minerals have been reported to coexist with authigenic feldspars: quartz, detrital feldspars of all compositions, kaolinite, illite, smectites of various compositions, chlorite, analcime, phillipsite, clinoptilolite, calcite, dolomite, gypsum, and halite. For the purpose of constructing phase diagrams, these minerals (except for gypsum and halite) are arranged in sequences of enrichment in cations of abundant elements (table 4).

We first consider assemblages in the sub-system SiO_2–Al_2O_3–K_2O–Na_2O–H_2O, after which we will evaluate the addition of CO_2, CaO, MgO, and FeO. In the subsystem, we may further simplify by observing that free

TABLE 4

Enrichment of feldspar and coexisting minerals in silica and other major elements; in order of increasing enrichment from top to bottom (most enriched)

Si	K	Na	Mg
Carbonate	Carbonate-Kaolinite-Chlorite	Carbonate-Kaolinite-Chlorite	Illite
Kaolinite			Smectite
	Smectite	Illite	
Chlorite			Dolomite
	Analcime		
		Smectite	
Analcime-Illite	Illite-Clinoptilolite-Phillipsite	Clinoptilolite-Phillipsite	Chlorite
Alkali Feldspar	K-Feldspar		
		Albite	
Smectite			
		Analcime	
Clinoptilolite			

silica, usually as quartz, is always present in rocks containing authigenic feldspar. Thus SiO_2 can be considered as saturated with respect to quartz, water as mobile, and we than plot phases of the relevant rocks in the ternary system Al_2O_3–$KAlO_2$–$NaAlO_2$. The most important reactions among the minerals in the subsystem are given in table 5. We assume the balancing cation for all reactions is normally HCO_3^-, but Cl^- or others may also be involved.

At the moderate temperatures characteristic of many low-grade metamorphic rocks in which quartz is always present, the compatibilities are of K-feldspar–albite–muscovite and albite–muscovite–pyrophyllite or albite–muscovite–paragonite (fig. 2E, F) with neither smectite nor zeolites present. Where smectite is present, typically in lower temperature (or younger) rocks, we believe, on the basis of observed mineral associations, that the compatibilities are K-feldspar–albite–illite, albite–illite–smectite, and smectite–illite (fig. 2D).

Mineral associations of rocks in which zeolites are present we believe to be K-feldspar–analcime–phillipsite, analcime–phillipsite–smectite, K-feldspar–analcime–clinoptilolite, analcime–clinoptilolite–smectite, analcime–K-feldspar–smectite, albite–K-feldspar–smectite, and smectite–illite–K-feldspar (fig. 2A, B, C). Unfortunately, not all these assemblages can be demonstrated to be in thermodynamic equilibrium, either as implied

TABLE 5

Some mineral reactions producing authigenic feldspar in the subsystem SiO_2–Al_2O_3–K_2O–Na_2O–H_2O

1. Kaolinite to Na- or K-feldspar:

$$Al_2Si_2O_5(OH)_4 + 2K^+ + 4\ (H_4SiO_4) \longrightarrow 2KAlSi_3O_8 + 9H_2O + 2H^+$$

$$Al_2Si_2O_5(OH)_4 + 2Na^+ + 4\ (H_4SiO_4) \longrightarrow 2NaAlSi_3O_8 + 9H_2O + 2H^+$$

2. Muscovite to K-feldspar:

$$KAl_2(AlSi_3)O_{10}(OH)_2 + 2K^+ + (H_4SiO_4) \longrightarrow 3KAlSi_3O_8 + 12H_2O + 2H^+$$

3. Na-Al Smectite to Na- or K-feldspar

$$Na(Al_5Mg)\ Si_{12}O_{30}(OH)_6 + 4Na^+ + 3(H_4SiO_4) \longrightarrow 5NaAlSi_3O_8 + 8H_2O + 2H^+ + Mg^{++}$$

$$Na(Al_5Mg)Si_{12}O_{30}(OH)_6 + 5K^+ + 3(H_4SiO_4) \longrightarrow 5KAlSi_3O_8 + 8H_2O + 2H^+ + Na^+ + Mg^{++}$$

4. Analcime to albite

$$Na(AlSi_2O_6)H_2O + H_4SiO_4 \longrightarrow NaAlSi_3O_8 + 3H_2O$$

5. Analcime to K-feldspar

$$Na(AlSi_2O_6).H_2O + H_4SiO_4 + K^+ \longrightarrow KAlSi_3O_8 + Na^+ + 3H_2O$$

6. Phillipsite to K-feldspar

$$(\tfrac{1}{2}Ca,Na,K)_5(Al_5Si_{11}O_{32}).10H_2O + 2K^+ + 4(H_4SiO_4) \longrightarrow 5KAlSi_3O_8 + Ca^{++} + Na^+ + 18H_2O$$

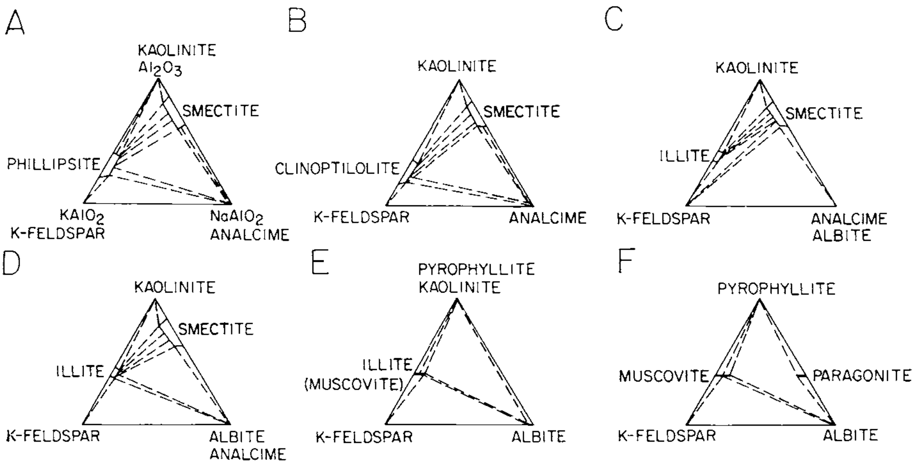


Fig. 2. Schematic diagram of the system Al_2O_3–$KAlO_2$–$NaAlO_2$, showing phases in equilibrium with quartz and other forms of free silica; (A) and (B): phases present are zeolites, clay minerals, and K-feldspar; (C) and (D): clay minerals and two feldspars; analcime might still be present; (E): two feldspars, muscovite (illite), and pyrophyllite (kaolinite); (F): two feldspars, muscovite, paragonite, and pyrophyllite.

by consistent and clear-cut petrographic evidence, or by calculation from thermochemical properties, which are not known sufficiently accurately. It is more likely that the zeolites — and perhaps even smectites — are kinetic intermediates; the free silica found in association with zeolites is often the metastable opaline silica (opal-A or -CT, Jones and Segnit, 1971) rather than quartz.

Another way to present the thermodynamic relations is by a combination diagram showing aqueous solutions in equilibrium with solid phases, with pH and activities of H_4SiO_4, Na^+, and K^+ as variables (Garrells and Christ, 1965). Unfortunately, there are no accurately determined values for the equilibrium solubilities of the zeolites and most natural smectites and illites, so that the boundaries between some fields are poorly known. Yet these diagrams are good guides to the properties of solutions that could be stable in diagenetic environments in which authigenic feldspars were precipitated, particularly when such diagrams are calculated for slightly elevated temperatures (for example, Helgeson, Brown, and Leeper, 1969, p. 16 and 19).

As can be seen from the combination diagrams for 0°C (figs. 3, 4), relatively high Na^+/H^+ or K^+/H^+ ratios coupled with high H_4SiO_4 activities are required for feldspar authigenesis. It is likely that non-equilibrium assemblages with authigenic feldspars form at values of these variables somewhat higher than the minima required for equilibrium. As has been noted frequently, the stability field for the feldspars is not far from seawater composition, if H_4SiO_4 activities are in equilibrium with amorphous silica. The range of interstitial water concentrations in many deep-sea sediments overlaps the feldspar field.

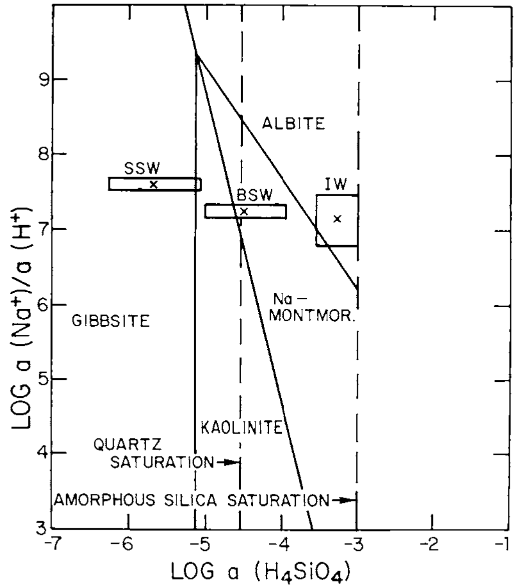


Fig. 3. Activity diagram for the system Na_2O–Al_2O_3–SiO_2–H_2O at 0°C, unit activity of water, and 1 atm (from Helgeson, Garrels, and Mackenzie, 1969, fig. 10). SSW = surface sea water, BSW = bottom sea water, IS = interstitial water.

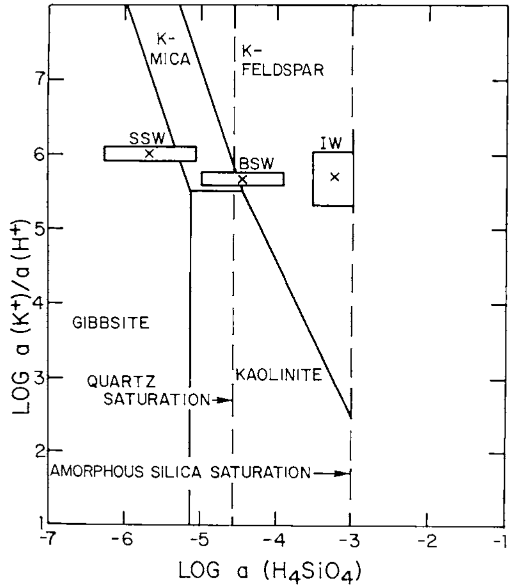


Fig. 4. Activity diagram for the system K_2O–Al_2O_3–SiO_2–H_2O at 0°, unit activity of water, and 1 atm (from Helgeson, Garrels, and Mackenzie, 1969, fig. 9).

The $K^+/(K^+ + Na^+)$ ratio of the solutions in equilibrium with either albite or K-feldspar is given by the schematic isothermal isobaric ternary reciprocal phase diagram (fig. 5). Calculations based on experimental data of Orville (1963), as discussed by Kastner (1971), show that at 100°C the $K^+/(K^+ + Na^+)$ ratio of a solution in equilibrium with two alkali feldspars is about 0.03, a value close to that of average seawater. White (1965) has plotted K^+/Na^+ ratios of hot spring and oilfield waters that are probably near equilibrium with alkali feldspars; they show values of about 0.03 to 0.04 for waters at 100°C.

The ternary reciprocal phase diagram (fig. 5) indicates that the geochemical environment of authigenic albite formation does not need to differ appreciably from the geochemical environment of authigenic K-feldspar formation. A continuous change in the $K^+/(K^+ + Na^+)$ ratio may cause an abrupt mineralogical change. Albite will be stabilized by an isochemical increase in temperature, which would shift the equilibrium $K^+/(K^+ + Na^+)$ ratio toward the K side. Thus, medium to higher temperature diagenetic environments are more favorable for the formation of authigenic albite.

Combination diagrams for various temperatures that have been calculated by Helgeson, Brown, and Leeper (1969), Helgeson, Garrels, and Mackenzie (1969), Helgeson (1971) show relatively unchanging stability fields of the feldspars for given K^+/H^+ or Na^+/H^+ ratios and H_4SiO_4 activities. This tells us that the geochemical controls for authigenic — or low-grade metamorphic — feldspars do not change much as the temperature increases. In fact, the thermodynamic data imply the possibility of feldspar formation even at room temperature, given the proper activities of alkali metals and silica in solution. Yet the experimental synthesis of authigenic feldspar at low temperature still eludes us.

In all the above discussions, we assume the conservation of Al in the solids; this assumption is amply justified by the extremely low solubility of aluminum species in the pH range 4 to 9 and the lack of significant amounts of dissolved Al in most natural waters in this pH range. Obviously, we would need to consider combination diagrams including the activities of either Al^{3+} or $Al(OH)_4^-$ for solutions of low or high pH. There is more to the matter than that, however, for the presence of authi-

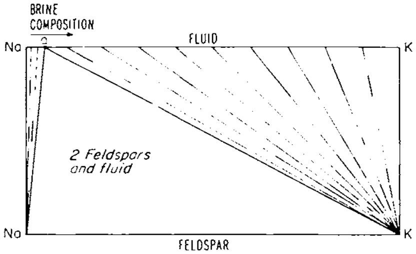


Fig. 5. Schematic isothermal isobaric ternary reciprocal phase diagram of equilibrium between alkali feldspars and fluid phase (at low T and P). Arrow denotes enrichment of potassium in fluid (Kastner, 1971, fig. 9).

genic feldspar overgrowths in some pure quartz arenites suggests aluminum mobility, just as does the occurrence of authigenic kaolinite in other quartz arenites. Aluminum may be carried in some ground-waters as stable complexes such as those described by Hem (1968), Hem and others (1973).

The addition of Ca to the subsystem discussed above adds anorthite as well as a calcium component of smectite and several zeolites. In addition, with CO_2 present as a mobile component, calcite is a phase. The most important reaction that needs to be considered is the reaction of an intermediate plagioclase to form albite, kaolinite or smectite, and calcite, essentially a disproportionation reaction:

$$(3NaAlSi_3O_8 \cdot 2CaAl_2Si_2O_8) + 4H^+ + 2CO_3^{--} + 2H_2O$$
$$\rightarrow 3NaAlSi_3O_8 + 2Al_2Si_2O_5(OH)_4 + 2CaCO_3$$

This reaction describes the alteration of the more unstable anorthite component of a detrital intermediate plagioclase to form kaolinite, releasing Ca^{++} (which combines with carbonate ion) and precipitating a pure albite. The association of authigenic albites and carbonate cements in many arkoses such as those of the Newark Series (Triassic) (Heald, 1956) is the consequence of this reaction.

The addition of (Fe,Mg) to the system allows us to include chlorite, the Mg component of smectites, and dolomite to the previously noted phases. We can, for example, write the reaction by which a nontronitic smectite decomposes to form albite, hematite, and dolomite:

$$2Na(Fe_4^{3+}Ca_{1.5}Mg_{1.5})(Si_{11.01}Al_{0.99})O_{30}(OH)_6 + 6HCO_3^- 20H_2O + 6H^+$$
$$\rightarrow 2NaAlSi_3O_8 + 16H_4SiO_4 + 4Fe_2O_3 + 3CaMg(CO_3)_2$$

This kind of reaction — essentially one in which nontronite is "weathered" to its components, which then reconstitute diagenetic precipitates — can be illustrated graphically in the quaternary systems Al_2O_3–$KAlO_2$–$NaAlO_2$–(Fe,Mg)O or Al_2O_3–$NaAlO_2$–CaO–(Fe,Mg)O as in figures 6A and B. We believe that the compatible mineral assemblages in this system are as shown for younger sedimentary rocks in which smectites are still characteristic, that is, rocks that are generally younger than about 200 m.y. As has been known for many years (see, for example, Grim, 1968;

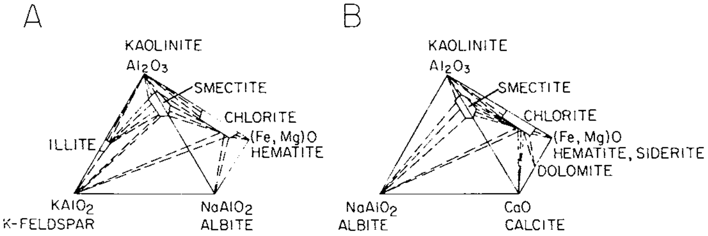


Fig. 6. (A) Schematic diagram of the system Al_2O_3–$KAlO_2$–$NaAlO_2$–(Fe,Mg)O; (B) The system Al_2O_3–$NaAlO_2$–CaO–(Fe,Mg)O.

Weaver, 1967), few middle and lower Paleozoic rocks and virtually no Precambrian rocks contain smectites (or zeolites). These older rocks would be characterized by the same system with the same joins, except for the absence of smectite. Tie lines between albite and kaolinite in figure 6A and between calcite/dolomite and kaolinite in figure 6B would be blocked by the illite–chlorite and feldspar–chlorite tie lines.

We have not shown compatibilities between zeolites and the other phases in these two quaternary systems, because neither the thermodynamic data nor consistent natural associations allow us to infer the geometry of an equilibrium diagram or even to be sure that, as noted earlier, the zeolites are truly thermodynamically stable between 10° to 150°C in this system.

GEOCHEMICAL MODELS FOR AUTHIGENIC FELDSPAR FORMATION

The thermodynamic information given in the previous section is the guide to the chemical conditions necessary for feldspar authigenesis. What is required at a minimum is for pore waters to become enriched sufficiently in K^+ and/or Na^+ relative to H^+ and H_4SiO_4 to convert solid aluminosilicates in the sediment to feldspar. To precipitate feldspars from solution requires in addition dissolved aluminum, presumably, in view of pH controls on aluminum speciation in solution, as $Al(OH)_4^-$. In this section, we suggest geochemical models that include the geological conditions that would make possible those mineral-pore water reactions critical for feldspar formation. We start with the simple models for isochemical transformation and follow with models that include mass transport of solution.

Isochemical models.—The major geologic information implying isochemical change is the petrographic evidence that we have presented previously for early authigenesis in relatively impermeable sediments. In addition to diffusion processes, we do not rule out entirely the possibility of slow mass transfer of solution during compaction, as waters from lower in the column are advected upward, but movement becomes sufficiently slow after initial compaction that it may be neglected. Supporting this conclusion are various mass balances we have made that show that redistribution of components present in the original sediment and trapped seawater can easily account for the quantity of feldspar we have observed.

The major components necessary for isochemical authigenesis, silica, alumina, and the alkali metals, are present in the variety of detrital and chemical components of the average marine sediment and some continental ones as well. Silica can be supplied by the dissolution of diatom frustules, radiolarian tests, sponge spicules, and silicoflagellates. It may also be released by the dissolution and alteration of volcanic glass, clay minerals, zeolites, and detrital alkali or plagioclase feldspars. Aluminum can be released to solution by all the above and possibly also small amounts from biogenic silica surfaces. The pore waters themselves, particularly trapped seawater, can be an important contributor of Na, less so of K; particularly, if pore waters bathe evaporite minerals such as halite and sylvite, they will be greatly enriched in alkali metals. Kinsman (1970) has shown that release of alkali metal cations occurs when aragonite inverts to calcite. This small additional source of alkali metals in the pore waters may contribute to the formation of authigenic feldspars in some shelf carbonates.

Because of the obvious difficulties of changing pressure and temperature drastically during early diagenesis, we assume an isothermal, isobaric process for most occurrences. This assumption may not be valid for processes occurring in high-heat flow areas, such as the Salton Sea of California, but we believe that most of the sedimentary rocks in which authigenic feldspars are found indicate normal geothermal gradients and characteristic average sedimentation rates for the various sedimentological environments. Considering hiatuses in sedimentation and the slow subsidence characteristic of many sedimentary basins, a typical overall rate might lie in the range 10 to 100 m per m.y., which would imply burial for periods of about 16 to 160 m.y. for a rise in temperature of 50°C and a corresponding pressure rise of about 370 bars. That temperature increase may assume importance for the reactions we consider, but the pressure increase proves negligible. Decrease in temperature and pressure accompanying uplift and erosion is not considered, because there is no evidence that would suggest that authigenic feldspars are formed in that milieu.

The first model, the most common and probably the simplest, is for early diagenetic formation of authigenic albite in a marine carbonate rock or mudstone (fig. 7). Starting with seawater trapped in an average marine sediment that contains a mixture of detrital clay minerals and silicates from crystalline rocks as well as biogenic carbonate, silica, and

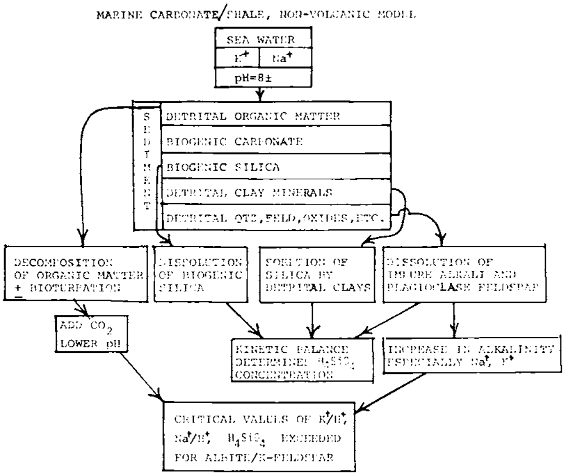


Fig. 7. Marine carbonate/shale, non-volcanic model for early diagenetic formation of authigenic feldspars in marine carbonate rock or mudstone.

organic matter, the assemblage reacts as follows: the decomposition of organic matter, bacterially and by metazoan bioturbation, may result in a temporary or permanent increase in P_{CO_2}, and so a slight decrease in pH, as organic matter, is oxidized by respiratory processes. If the sediment is relatively impermeable and the degradation is primarily bacterial, the CO_2 pressure may remain slightly elevated; if on the other hand, bioturbation by metazoans is extensive, the sediment will be equilibrated with the overlying seawater, and there will be only the most transitory decrease in pH.

Biogenic silica, opal-A, will start to dissolve at rates that are predictable on the basis of various experiments on diatomaceous and radiolarian sediments and cultured diatoms (Hurd, 1972, 1973; Hurd and Theyer, 1975; Kastner, Keene, and Gieskes, 1977; and Stein and Siever, 1976). Those experiments, as well as compositions of interstitial waters in diatomaceous sediments, indicate a rise in the concentrations of H_4SiO_4 to levels that may approach saturation with respect to amorphous silica. At the same time, detrital high temperature alkali and plagioclase feldspars may continue to dissolve slowly, for most early pore waters — as seawater is — are in the stability fields of various clay minerals rather than feldspar. Even when the waters approach compositions that would be in equilibrium with pure albite or K-feldspar, they would still be unsaturated with respect to the impure and therefore more soluble intermediate feldspar phases. The slow dissolution of detrital feldspar would not raise the concentration of H_4SiO_4 appreciably in comparison to release by dissolution of biogenic silica nor Na^+ in comparison to the high concentration of that element, 0.47M, in normal seawater. But as judged by K^+ content of interstitial waters, the K^+ content may increase.

As the H_4SiO_4 concentration increases, the detrital clays may sorb it in significant quantities depending on pH and cation activities (Siever and Woodford, 1973). Yet another factor that controls the concentration of H_4SiO_4 is the series of diagenetic transformations of opal-A to opal-CT and to chalcedony and quartz. Though we do not yet have a reliable value for the solubility of opal-CT, it is clear that it must be between opal-A and quartz or chalcedony, about $10^{-2.7}$ M and $10^{-4.0}$ M, respectively, at 25°C. The net concentration of H_4SiO_4 is the balance between these four rates of release and uptake. Initially the rate of biogenic silica release is relatively fast compared to detrital feldspar dissolution. The sorption of silica by clays is relatively fast at first but is quickly limited by the saturation of the free surface of the clays. In comparison to the above reaction rates, depending on the geochemical environment, the rates of opal-CT and quartz formation are medium to very slow, on the order of 5 to 50 m.y. (Kastner, Keene, and Gieskes, 1977; Keene, ms).

The relative amounts of different kinds of clay minerals and their sorptive capacities for H_4SiO_4, in relation to the abundance of biogenic silica, whose dissolution supplies H_4SiO_4, strongly affect the course of diagenesis. If there is insufficient clay surface in the sediment to keep the dissolved silica levels below supersaturation with respect to feldspar formation, the first condition for feldspar authigenesis is met. If, on the other hand, the amount of sorptive clay is large in comparison to the quantity of biogenic silica that releases silica, H_4SiO_4 levels may not rise enough to permit feldspar formation.

It is appropriate here to consider the combination diagrams for the Na_2O– and $K_2O–SiO_2–Al_2O_3–H_2O$ systems at 0°C as calculated by Helgeson, Garrels, and Mackenzie (1969) shown in figures 3 and 4. Shown on the diagrams are fields for surface seawater and some enriched bottom and interstitial waters of sediments rich in diatom debris (Siever, Beck, and Berner, 1965; Hurd, 1972, 1973). From these diagrams, it can be seen that bottom seawater values are outside the albite field, but some interstitial waters are sufficiently supersaturated that it is not at all unlikely for albite to form starting almost as soon as the sediment is buried, given sufficiently high H_4SiO_4 concentrations. A similar situation obtains for the combination diagram for K-phases. But here even bottom seawater values are into the K-feldspar field. It is apparent that if these diagrams are correct, little or no change in K^+/H^+ or Na^+/H^+ ratio of bottom seawater is required. Assuming that aluminum is present, the sole control needed is the concentration of H_4SiO_4. We may then project the ideal conditions for the appearance of authigenic albite in a sediment, assuming that metastable zeolite formation does not take place: a sediment without too much clay (which would sorb too much silica) but an abundance of biogenic silica. Some clay is necessary to supply the aluminosilicate raw material. Though either a sandstone or carbonate rock would do, sandstones are not associated with appreciable biogenic silica, or they are too diluted by rapid rates of sand accumulation. Thus we are left with carbonates as the most fertile ground, and that indeed is the case; the most and best authigenic feldspars are found in limestones. It is now clear why the average non-marine sediment is a poor place for early diagenetic authigenic feldspar. There is little silica to supply the needed H_4SiO_4 concentrations.

Of course, not all the dissolved silica need be supplied by diatoms, radiolarians, and sponges. Volcaniclastic debris, particularly the mafic glasses, hydrolyze quickly in water to produce high concentrations of dissolved silica. This brings us to the volcaniclastic models, both marine and non-marine (figs. 8 and 9). In the marine model, the trapped seawater reacts with a mixture of volcaniclastic material and pelagic clay and/or carbonate. In this situation, the rate of release of silica may not be as rapid as that from biogenic silica, but the release of K^+ may drive up the K^+/H^+ ratio sufficiently to bring the water well into the K-feldspar stability field. Though Na^+ and K^+ may be taken up by the hydrolyzing glass as it converts to smectite and/or zeolite, at low temperatures the effect is small and would alter the Na^+/H^+ ratio only negligibly. At low temperatures, basaltic glass may even take up K^+. Thus we have some explanation of why K-feldspars are more common in non-zeolitic or in analcime-rich volcaniclastic sediments. What is critical for feldspar authigenesis in this environment is the ratio of volcaniclastic to pelagic

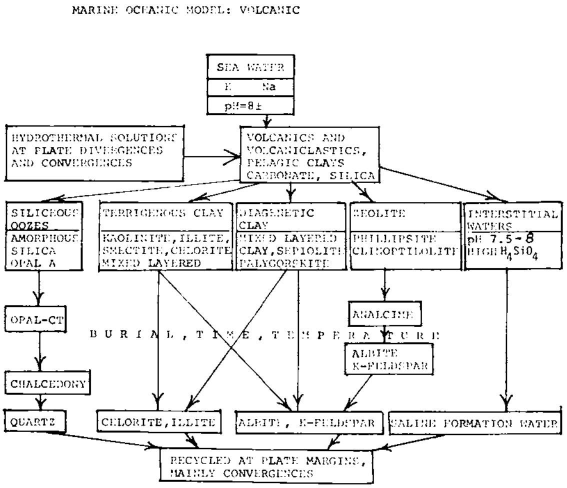


Fig. 8. Marine oceanic, volcanic model for diagenetic formation of authigenic feldspars.

clay. If there is much pelagic clay, the concentrations of H_4SiO_4 may be held too low by sorption, depending on the mineralogy of the clays. To the extent that volcaniclastic material is mixed with biogenic silica, the conditions for feldspar authigenesis are improved. Accompanying or preceding feldspar formation — and sometimes instead of it — are zeolites and smectites. In sediments older than about 200 m.y., zeolites and smectites are rarely found, and we may infer that there has been further alteration to an illite–chlorite–feldspar assemblage.

Formation of chert may interfere with feldspar authigenesis. If dissolved silica concentrations are sufficiently high that opal-CT nucleates, the growth of opal-CT lepispheres may be sufficiently rapid (Kastner, Keene, and Gieskes, 1977) that H_4SiO_4 concentrations may be held too low to promote feldspar nucleation. One thing seems to be true from examination of both ancient sediments on the continental platforms and those drilled by the DSDP: there is no reported association between chert and authigenic feldspar unless volcanic material is also present (Kastner, 1976; Kastner and Gieskes, 1976); the volcanic material may be the source for some of the aluminum necessary for authigenic feldspar formation, in this high silica environment.

The non-marine volcaniclastic model differs mainly in the chemistry of water that is trapped as pore water. The chemical composition of rivers, lakes, and ground waters in terrains in which volcaniclastic sediments are laid down is highly variable, but the H_4SiO_4 concentrations tend to be higher than normal. The cation composition is highly variable, depending on the chemical composition of the volcanics. Observations made on alteration of volcaniclastics are mainly on sediments that were deposited in lakes (Sheppard and Gude, 1968, 1969; Hay, 1966, 1970;

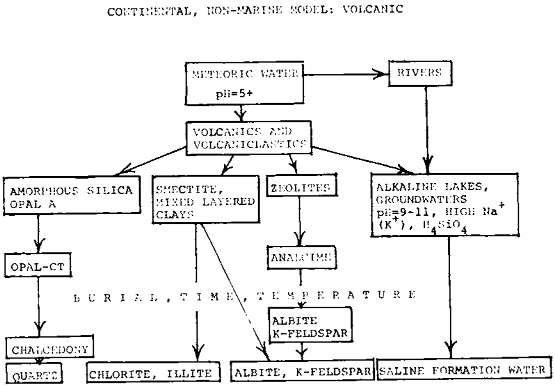


Fig. 9. Continental, non-marine, volcanic model for diagenetic formation of authigenic feldspars.

Surdam and Parker, 1972); alluvial deposits have not been investigated as much. Reactions of lake-derived waters with volcaniclastic debris give relatively high pH values, high silica concentrations, and relatively high Na^+ and K^+ activities. Some of these high values may be in part from moderate evaporite conditions that are typical of many playa and other interior drainage lakes where volcaniclastics have been mapped.

Just as in the marine model, the glasses may alter first — or exclusively — to zeolites and/or smectites. Later alteration moves the assemblage, as it does in the marine case, to feldspar and illite–chlorite. In this environment, the precipitation of opal-CT and chert seems to accompany the transformation from zeolite to feldspar, and there is no absence of association such as is common in the non-volcaniclastic marine sequence. The proportion of K^+/Na^+ depends on the composition of the volcanics but also on the differential reaction of waters with respect to the two alkali metal cations: the K^+/Na^+ ratio increases after basalt-water reaction if the water is high in Na (Mottl, Corr, and Holland, 1974). This, as we noted earlier, accounts for the much greater abundance of authigenic K-feldspar than albite in volcaniclastic sediments.

We may follow the course of alteration of volcaniclastics by means of the series of phase diagrams shown in figure 2. The initial alteration of glass is the formation of smectite and zeolites, here shown as assemblages of phillipsite and smectite (fig. 2A). The silica polymorph found at this stage is opal-A. After about 5 to 50 m.y., the assemblage converts to that shown in figure 2B, in which the authigenic K-feldspar has formed and is compatible with zeolites such as clinoptilolite and analcime, the silica polymorph being opal-CT. From this stage, the rock may progress to a feldspar-smectite assemblage without zeolite (fig. 2C), in which the silica polymorph is opal-CT and/or chalcedony. It is possible that the sediment may move directly from the phillipsite–smectite assemblage without feldspar to the feldspar assemblage without zeolite. After the passage of about 100 m.y., the assemblage converts to that shown in figure 2D, in which feldspars are associated with both smectite and illite, the silica polymorphs being both opal-CT and microcrystalline quartz. As the formation gets buried more deeply and gets older, it moves to the final, most stable assemblage (fig. 2E): feldspar, illite, quartz, and smectite being absent. Whether this transition represents increasing temperature attendant on burial or mainly time, we are not sure. But there are many formations with this final assemblage whose precursors seem to be volcaniclastics that have never been buried very deeply. The appearance of paragonite does seem to be due to an increase in temperature and the development of true low-grade metamorphic rocks, the phases of which are as shown in figure 2F.

If there is any significant amount of Fe or Mg, chlorite formation will accompany some stage in the evolution of feldspar. The evidence seems to be that chlorite may form in association with authigenic feldspars in volcaniclastic rocks, for example in lithic graywackes derived from andesite detritus, at a stage when zeolites have already disappeared but before illite has formed, so that the association is chlorite–smectite. The chlorite–smectite assemblage later gives way to chlorite–illite. This association of chlorites with authigenic feldspars is probably not too common, because the andesitic graywackes generally have too much detrital clay, which by sorption of later chemical reaction buffers the silica at levels below that necessary for feldspar formation. In this environment, too, it is not likely that evaporites will be nearby in the stratigraphic section, and so Na^+ and K^+ activities cannot rise too high.

We believe that some well known authigenic feldspar occurrences, in which feldspar is a large proportion of the rock, such as the Waterton Formation (Precambrian) and the Glenwood shale (Ordovician), are diagenetically altered volcaniclastic deposits. They may have been deposited as ash beds — either aeolian- or water-laid — which early went through the smectite–zeolite stage and then converted to feldspar–illite–chlorite. The high proportion of K-feldspar may imply a more silicic composition to the volcanic glasses that altered; less of the Fe, Mg, and Ca components as well as a high Si/Al ratio would limit the amounts of illite and chlorite. These compositional factors might account for the residual smectite found in some early Paleozoic ash beds.

In summary, we give an eaxmple of a possible history of authigenic feldspar in a limestone:

1. An original sediment of micritic marine limestone consisting of 90 percent carbonate, 5 percent biogenic silica, and 5 percent terrigenous detritus, including smectite (kaolinite), illite, quartz, and feldspar. The sediment has been deposited in shallow (~20 m) normal seawater at a mean temperature of 15° to 20°C. The initial porosity is about 60 to 70 percent, and the interstitial water is similar to the overlying seawater, with the exception that H_4SiO_4 concentrations are slightly elevated, to about $10^{-3.6}$ M.

2. Burial proceeds with constant submergence at a rate of 10 m/m.y. In the first few million years, the major changes are a decrease in porosity

as a result of compaction, some minor cementation, and slow minor changes in interstitial water composition as dissolution of biogenic silica increases H_4SiO_4 concentration, some K^+ and Na^+ is fixed by sorption by smectite, and the more calcic plagioclase detrital grains continue to dissolve very slowly. After initial compaction and advection, the water has become virtually static, except for diffusional communication.

3. After 50 m.y., the temperature has increased to about 35°C, the pressure to about 115 bars, and the porosity has decreased to 35 percent. The concentration of H_4SiO_4 has increased to $10^{-2.6}$ M, pH has stayed in the range 7.8 to 8.0, and the $K^+/(K^+ + Na^+)$ ratio has decreased to 0.02 from its original seawater value of about 0.03. The water composition is now well supersaturated with respect to albite, and as the temperature has risen, nucleation of albite by conversion of detrital clays has started. If, however, the $K^+/(K^+ + Na^+)$ ratio has increased above 0.03 due to preferential Na^+ adsorption by smectite, K-feldspar instead of albite will form.

4. As precipitation of albite slowly continues, the pore water becomes depleted in Na^+, and if enough H_4SiO_4 and aluminosilicate detritus are available to continue feldspar growth, the $K^+/(K^+ + Na^+)$ ratio may increase back to 0.03, at which point both microcline and albite coprecipitate.

5. The depletion of the fluid with respect to either alkali metals or H_4SiO_4 ends the process, as the solution becomes saturated or undersaturated, and further precipitation ceases. The total amount of authigenic feldspars formed is small and is controlled by the amount and composition of interstitial water due to sediment-seawater interaction.

The above isochemical models are appropriate for most but certainly not all the early authigenic feldspar occurrences in sedimentary rocks, which in turn probably account for the majority of all the authigenic feldspar occurrences in sedimentary rocks. For many feldspars, particularly those formed later in a rock history or those that might be termed premetamorphic, we infer models that involve mass transfer of solution.

Exchange reservoir models.—The major difference between isochemical models and mass transfer or exchange reservoir models is the movement of fluids from one reservoir to another, involving substitution or mixing of two fluids of different composition. Permeability is a prerequisite, and so sandstones and porous carbonate rocks are the most likely candidates. All the components, solid and liquid, are as before, but they may not all be in the host rock. One of the most obvious possibilities is transport of a brine from formation waters of evaporite sections. The rate of feldspar formation is dependent on the flow rate of the solution as well as its chemical composition. Its chemical composition is dependent on its original composition (sea, meteoric, or hydrothermal water) and the mineralogy of the beds through which it has passed.

The first case we consider is the invasion of meteoric waters from above. Starting out as rain waters that have filtered through a soil zone, they tend to be of very low ionic strength and somewhat acidic; the pH usually is between 5 and 6, or even lower. What are the kinds of sedimentary rocks that would bring such waters up to feldspar saturation when they pass through them? Rain water flowing through a diatomaceous earth, for example, might become enriched in H_4SiO_4, but its pH, Na^+, and K^+ contents would not be increased appreciably, certainly not enough to bring it to the necessary Na^+/H^+ or K^+/H^+ ratios. A variety of silica phases will precipitate from such a water, but it is doubtful that authigenic feldspars would form. An evaporite formation would, on the other hand, supply the alkali metals but not the silica. Volcaniclastics, however, would seem to satisfy all the requirements: H_4SiO_4, Na^+, K^+, and increase in pH. As we have seen, this is the nonmarine volcaniclastic model. If the permeability of the volcaniclastic beds is high enough, but not so high that the flow rates are too rapid to enrich the solution, the water may flow through without precipitating feldspar (or zeolite or smectite) and enter another bed below. If that bed is one with suitable nucleation sites, for example detrital feldspars in a sandstone, feldspar authigenesis may begin. This might be at a very late stage in the diagenesis of sandstone, which might lie below an unconformity separating it from the overlying volcaniclastics. This model can include meteoric water infiltration of an ancient rock section which has been uplifted and eroded following orogeny. Or it might be like the Pliocene volcaniclastics overlying the Pennsylvanian sections of the western great plains. Still another case would be the temporary meteoric invasion of a recently deposited coastal plain sediment which has been subjected to numerous marine transgressions and regressions.

Mixing of different fluids could also accomplish the critical solution compositions. If a water were to pass first through an evaporite sequence, from which it would pick up Na^+ and/or K^+, and then traverse a siliceous sediment such as a diatomite, the solution might become saturated with respect to feldspar. Evaporite-silica associations are known from environments such as Lake Magadi in Africa, where magadiite, a sodium silicate, is the precursor of chert (Eugster, 1967). Waters that leach the magadiite of Na^+ also carry much dissolved silica and might be expected to precipitate albite, if there is a source of aluminum, such as clay minerals in underlying sediments. But marine evaporites and siliceous sediments are not commonly associated and so cannot be looked to as a combined source for feldspar components.

On a coastal plain, mixing takes place along the border between meteoric water flowing down dip and seawaters in the deeper submerged portions. If the meteoric water were to have picked up appreciable H_4SiO_4 on its way down, the mixing zone would increase its Na^+ and K^+ content. But, to the extent that such mixing takes place, the Na^+ and K^+ of seawater are diluted ,and as we have seen, in seawater they are at or below the minimum for feldspar formation. The dilution and the low pH of the meteoric waters make fluid mixing in this environment unlikely as a mechanism for feldspar authigenesis.

As noted in our review of the earlier literature, the most venerable hypothesis for feldspar authigenesis is upward percolation of hydrothermal fluids, which then may mix with preexisting formation waters. In modern times, Heald (1956) has described authigenic feldspars in the Newark Series of Connecticut and Massachusetts that he believes, on the basis of petrographic evidence, are related to hydrothermal waters generated by mafic intrusions at depth, even though the normal hydrothermal indicators are absent. There is now little doubt that meteoric waters move downward, interact with an intrusive body at depth, such as Yellowstone Park, and convect upward carrying high concentrations of H_4SiO_4, Na^+, and K^+. When such waters move into arkosic sediments, where there are abundant nuclei for feldspar overgrowths and relatively little clay to act as sorbent for H_4SiO_4, we may expect the results that Heald observed.

Though one might expect the hydrothermal solutions permeating sediments overlying spreading mid-ocean ridges to produce feldspar, the only evidence for feldspar growth is in greenstone-greenschist facies rocks altered from basalts, rather than the overlying unmetamorphosed sediments (Melson, Thompson, and van Andel, 1968). But the sediments at mid-ocean ridges are thin and discontinuous. Farther from the ridges, a greater thickness of sediment might be affected by slow invasion of hydrothermal waters from still hot basalt below, resulting in much higher levels of H_4SiO_4 in interstitial waters. Unfortunately, there are not enough interstitial water analyses of sediments on ridge flanks to check this possibility.

Another pore water movement that might result in altered composition is slow flow through a semi-permeable shale formation (Bredehoeft and others, 1963). When water of a given ionic strength is forced through a semipermeable membrane, ion hindrance will result, producing on the upflow side of the membrane a brine that would be enriched in alkali metals without change in pH. If H_4SiO_4 concentrations were high enough, the raising of Na^+/H^+ and K^+/H^+ ratios might move the solution into the feldspar field. Though this mechanism has been proposed for a long time for the origin of some concentrated formation waters, to our knowledge no occurrences of authigenic feldspar have been noted that were or could be clearly related to such effects.

We have not stressed the importance of molecular diffusion in transport of solute and thus of changing a pore water's composition. The slowness of molecular diffusion at the relatively low temperature characteristic of most of the sedimentary rocks that contain authigenic feldspars, and the relatively great distances such diffusion would have to overcome, make it an unattractive alternative except for the relatively permeable, uncompacted top few hundred meters of a freshly deposited sedimentary sequence. As the rock becomes lithified and permeability decreases by cementation — or conversion of argillaceous rock fragments to clay matrix in a graywacke — the effective diffusion coefficients become even smaller, perhaps by as much as several orders of magnitude. That effect more than compensates for the increase in diffusion coefficients with the slight increase in temperature attendant on moderate burial. Diffusion cannot be neglected for the higher temperatures of deeply buried sections, particularly those subjected to greater than normal heating in orogenic belts. In such sections, typified by many ancient graywacke belts, diffusion irons out local differences, but there is no chemical or petrographic evidence of any systematic gradients in Na^+ or K^+ that might be generated by diffusion gradients from below.

The ultimate choice that must be made between isochemical models and exchange reservoir models should be based on the analysis of the particular geologic situation. Evidence of restriction to certain stratigraphic horizons might suggest local — therefore isochemical — control. On the other hand, nearby sources of feldspar components such as evaporites and homogeneous distributions within the assumed flow distance may imply exchange. Our estimate is that most of the occurrences we have reviewed would fit into the isochemical models with little or no mass transfer necessary over long distances.

We also believe that temperature is not the most important consideration for feldspar authigenesis. Nothing we have seen in distribution patterns suggests a minimum depth of burial that would correspond to minimum geothermal heating before authigenesis can occur. And there are so many occurrences in demonstrably "cool" environments, such as the relatively young sediments of the ocean floors drilled by the DSDP, that we find low temperature no bar to feldspar nucleation or crystal growth. There is, however, little question that some feldspars have grown at temperatures higher than "normal," perhaps well over 150°C. Diagenesis and metamorphism are a continuum, and the higher the temperature the faster we can expect nucleation and crystal growth. The temperature may have its most important effect in switching feldspars from K-feldspar to albite, as the temperature determines the invariant point on the ternary reciprocal of feldspar solids and solutions (Kastner, 1971).

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