Authigenic Potassium Feldspar in Cambrian Carbonates: Evidence of Alleghanian Brine Migration

Abstract. *The shallow-water limestones and dolostones of the Conococheague Limestone (Upper Cambrian) of western Maryland contain large amounts of authigenic potassium feldspar. The presence of halite daughter crystals in breached fluid inclusions, low whole-rock ratios of chlorine to bromine, and thermochemical data suggest that the potassium feldspar formed at low temperature by the reaction of connate brines with intercalated siliciclastic debris. Analyses of argon age spectra indicate that the authigenic feldspar probably formed during Late Pennsylvanian to Early Permian time. These results may indicate mobilization and migration of connate brines brought about by Alleghanian folding. The widespread occurrence of authigenic potassium feldspar in Cambrian and Ordovician carbonate rocks throughout the Appalachians suggests that this may have occurred throughout the entire basin.*

Numerous occurrences of abundant authigenic potassium feldspar (K-feldspar) in Lower Paleozoic strata of the U.S. mid-continent region and the Appalachian Basin have been described during the past 50 years (*1-4*). Authigenic K-feldspar is a characteristic component of the Cambrian-Ordovician rocks that formed on the east-facing shelf of the proto-Atlantic Ocean (*5*). The common association of authigenic K-feldspar with dolomitized sequences of tidal-flat carbonates has led some investigators to suggest that the feldspar was a product of early diagenesis involving potassium-rich brines (*6*). However, results of $^{40}Ar/^{39}Ar$ age-spectrum analyses of authigenic K-feldspar from the Cambrian Conococheague Limestone of western Maryland indicate that the feldspar formed at least 200 million years after the deposition of these sediments.

The thinly interbedded limestones and dolostones of the Conococheague Limestone are characteristic of the platform carbonate rocks of Cambrian and Ordovician age that are exposed along the entire length of the Appalachian Basin. These rocks exhibit a variety of features typical of lagoonal–tidal flat complexes: flat and wavy lamination, thin bedding, mudcracks, evaporite casts and molds, and stromatolites (*7*). Samples of subfacies members of the Conococheague were collected from outcrops approximately 10 miles west of Hagerstown, Maryland. Optical, x-ray, and scanning-electron-microscope analyses show K-feldspar and quartz to be the primary silicate minerals in these rocks. Minor amounts of muscovite and chlorite are present, plus a suite of heavy minerals including pyrite, siderite, zircon, monazite, titanium oxide, and apatite (*8*). This mineral assemblage suggests that crystalline rocks of the craton were the source of the detrital material. The pyrite and siderite are secondary in origin and are thought to reflect reducing conditions created by the decomposition of stromatolitic algae.

Authigenic K-feldspar is distinguished petrographically by its lack of luminescence under an electron beam. It occurs both as overgrowths on grains of detrital K-feldspar, and more extensively as a fine-grained matrix (Fig. 1). The two modes of occurrence generally parallel primary sedimentary structures. Grains of detrital K-feldspar with authigenic overgrowths (Fig. 1, A and B) are concentrated in limestone interbeds, which are primarily peloidal carbonate sand. The matrix-forming K-feldspar (Fig. 1, C and D) is associated with the finer-grained dolostone interbeds, where it surrounds rhombs of dolomite. This K-feldspar is most likely an alteration product of siliciclastic mud. Total K-feldspar in the various subfacies of the Conococheague ranges from 7 to 25 percent by weight (Table 1). Estimates based on cathodoluminescence images indicate that 40 to 50 percent of the K-feldspar in limestone interbeds and at least 75 percent in the dolostone interbeds are authigenic.

Analysis of x-ray diffractograms indicates that both the fine-grained matrix K-feldspar and the K-feldspar overgrowths are predominantly orthoclase, whereas the detrital igneous K-feldspar is a mixture of orthoclase and microcline (*9*). Optical measurements of axial angle on authigenic overgrowths made by spindle-stage techniques (*10*) indicate that

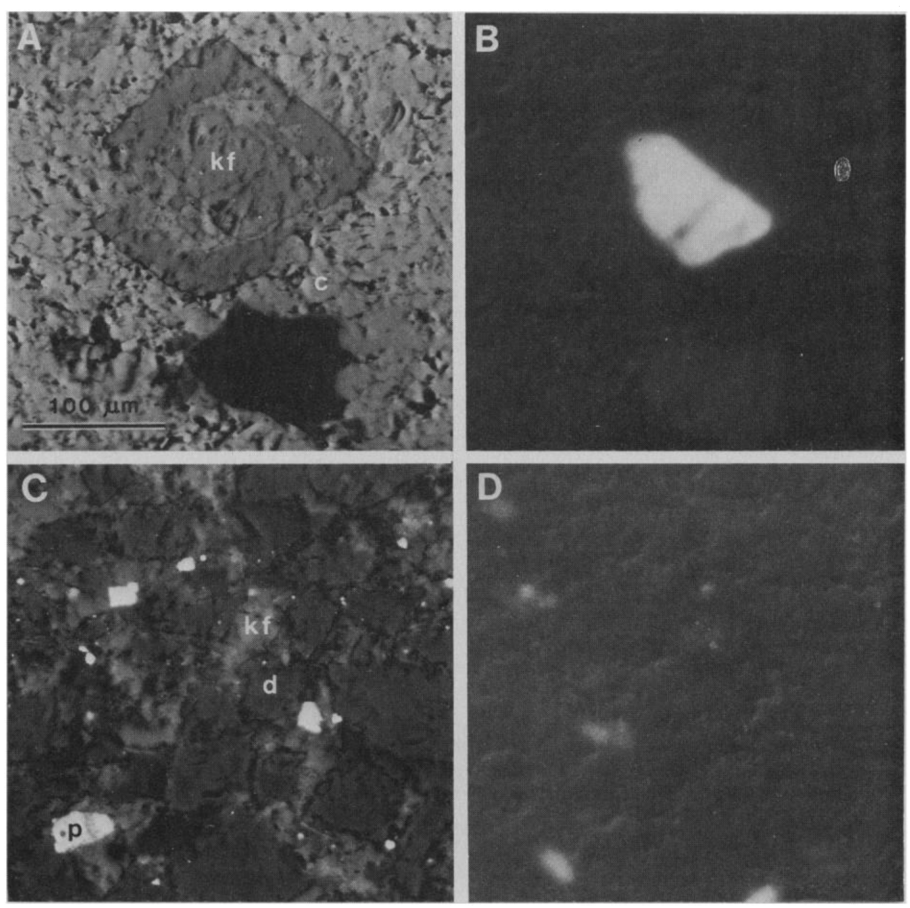

Fig. 1. Scanning electron micrographs of authigenic K-feldspar in the Conococheague Limestone. (A) Backscattered electron image of detrital grain of K-feldspar (kf) with authigenic overgrowth in matrix of calcite (c). (B) Cathodoluminescence image of grain in (A), showing luminescing detrital core and nonluminescing authigenic overgrowth. (C) Backscattered electron image of fine-grained matrix K-feldspar and grains of dolomite (d) and pyrite (p). (D) Cathodoluminescence image of field in (C), showing general lack of luminescence of matrix K-feldspar.

the aluminum-silicon ordering of the authigenic K-feldspar is relatively low, with $(t_1o + t_1m) \approx 0.75$ (*11*).

Authigenic K-feldspar is characteristically pure in comparison to igneous varieties (*12, 13*). Although in these rocks (Table 2) its composition is closer to the pure end-member composition than most igneous K-feldspar, the authigenic K-feldspar in both limestone and dolostone interbeds contains significant amounts of impurities (*13, 14*). Bulk samples show significantly higher ratios of potassium to rubidium and to barium than the normal range of values for igneous K-feldspar, indicating significant depletion of rubidium and barium (Table 1). Apparently, the inclusion of cations other than potassium in the K-feldspar structure is much less pronounced when growth occurs at low temperatures. The high chemical purity of authigenic K-feldspar and the consequent absence of activator ions are probably responsible for the lack of luminescence under an electron beam (*13*).

Pure mineral separates of K-feldspar from the Conococheague Limestone were analysed by the $^{40}Ar/^{39}Ar$ age-spectrum technique (*15–17*). First, a $^{40}Ar/^{39}Ar$ age spectrum was generated from a sample of detrital K-feldspar cores with

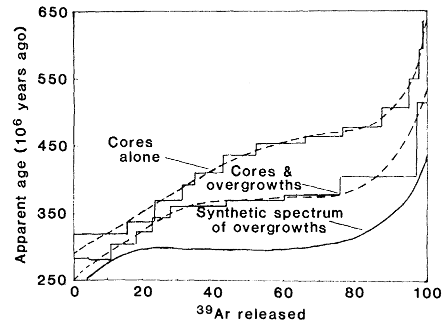

Fig. 2. Experimental $^{40}Ar/^{39}Ar$ age spectra for detrital K-feldspar grains with overgrowths and detrital grains whose overgrowths have been removed by acid dissolution (step-like patterns), and generalized age spectra for each (smooth dashed curves). A synthetic age spectrum for the authigenic overgrowths alone (solid curve) was obtained by subtracting one generalized age spectrum from the other.

authigenic overgrowths, and then the overgrowths were removed by dissolution in a 5 percent solution of hydrofluoric acid and a second $^{40}Ar/^{39}Ar$ age-spectrum analysis was performed (Fig. 2). To obtain an approximate $^{40}Ar/^{39}Ar$ age spectrum for the authigenic overgrowths, a smooth curve was fitted to both of the experimentally produced age spectra and the "cores-and-overgrowths" curve subtracted from the "cores alone" curve (Fig. 2). The resulting synthetic curve is an approximation of the age spectrum that would result from the analysis of authigenic overgrowths if such a sample could be analyzed.

Several conclusions can be drawn from the age spectra (Fig. 2). (i) The two experimentally produced age spectra indicate that the detrital K-feldspar retains at least a small portion of its predepositional history. Since the core K-feldspar fragments are partly orthoclase, the age spectrum indicates that the Conococheague was not heated after deposition above about 250°C; above this temperature monoclinic K-feldspar would be expected to lose all of its accumulated radiogenic ^{40}Ar (*18–20*). This conclusion is consistent with temperatures from conodont-alteration indices in the area (*21*) and depth-of-burial estimates for these sediments at 10 km or less (*22*). (ii) The estimated age spectrum for the authigenic overgrowths shows a plateau about 300 million years ago, indicating that the authigenic K-feldspar most probably grew during the Pennsylvanian Period (*23*). (iii) The combined $^{40}Ar/^{39}Ar$ age spectra indicate that the uplift and cooling history of these sediments is rather simple, a conclusion supported by paleomagnetic data and the regional geology.

The conclusion that the authigenic K-feldspar grew during the Pennsylvanian is consistent with reports of low-temperature secondary magnetization showing Late Carboniferous pole positions in early to middle Paleozoic rocks of the Central Appalachians (*24, 25*). This Carboniferous magnetization is carried by magnetite and is not due to the thermal resetting of detrital magnetite; rather it results from the chemical precipitation of a secondary magnetite component that was contemporaneous with folding (that is, during the Carboniferous).

Several lines of evidence suggest that authigenic K-feldspar in the Conococheague Limestone formed because of the presence of hypersaline brines. The presence of halite daughter crystals in some breached fluid inclusions (Fig. 3) indicates that these rocks contained interstitial brines saturated with NaCl. Defining the exact origin of these brines is difficult. However, a relatively simple scenario involving the generation of a connate brine in a sabkha-like environment and its subsequent entrainment and burial appears to be consistent with other evidence.

In addition to the numerous sedimentary structures, indicating tidal-flat deposition, mudcracks and evaporite casts

Table 1. Analyses of subfacies samples from the Conococheague Limestone. Subfacies are described by Reinhardt and Hardie (*7*).

Subfacies	Potassium (% bulk)	K-feldspar (%)	K/Rb	K/Ba	Chlorine (ppm)	Bromine (ppm)	Cl/Br
Mud-cracked dolomitic laminite	3.56	24	741	115	160	1.4	114
Prism-cracked cryptalgal laminite	1.24	8	564	90	90	0.9	100
Rippled ribbon-rock: dolostone interbed	3.68	25	650	225	190	1.6	119
Limestone interbed	1.10	7	680	130	170	1.3	131
Algal limestone	1.17	8	585	117	80	1.4	57
Crossbedded oolite or calcarenite	1.07	7	535	10	90	1.4	66

Table 2. Electron microprobe analyses of authigenic and detrital potassium feldspar in the Conococheague Limestone. (Averages are based on analyses of 10 grains.)

Sample	Percent (by weight)						
	SiO_2	Al_2O_3	K_2O	CaO	Na_2O	BaO	Total
Detrital, in limestone interbeds	63.93	18.55	15.64	0.65	0.61	0.39	99.77
Authigenic overgrowths, in limestone interbeds	64.15	18.82	15.89	0.81	0.14	0.10	99.72
Detrital, in dolostone interbeds	65.20	18.64	15.04	0.57	0.48	0.44	100.35
Authigenic "matrix," in dolostone interbeds	64.15	18.14	14.96	0.55	0.19	0.21	98.20

and molds provide evidence of a sabkha-like environment for the Lower-Paleozoic carbonate rocks in the central Appalachian Basin (*26*). Brines could have been generated in such an environment through simple evaporative reflux. Brines produced from the evaporation of seawater should have Cl/Br ratios ranging from 182 to 70 during the initial stages of halite precipitation (*27*). The whole-rock Cl/Br ratios for the Conococheague (Table 1) are more consistent with a brine produced in this manner than a brine derived from the dissolution of evaporites by meteoric water, which would be expected to have a higher Cl/Br ratio.

The presence of a brine of sabkha origin is also consistent with thermochemical data on the growth of K-feldspar. The data of Helgeson (*28*) indicate that a brine in equilibrium with both K-feldspar and albite should have a K/Na activity ratio of 0.18 at 300°C and 0.06 at 200°C; extrapolation to 100°C yields an equilibrium ratio of 0.02. Solutions with K/Na activity ratios higher than the value for a given temperature would be saturated with respect to K-feldspar. The evaporation of seawater should produce a brine with a K/Na activity ratio of 0.02 at the first point of gypsum precipitation, and ratios of 0.04 to 0.17 during the first stages of halite precipitation (*27*). In contrast, a brine derived from a halite-rich evaporite body should have a K/Na activity ratio less than or equal to the seawater value of 0.02. Since the maximum temperature experienced by the Conococheague Limestone was probably between 200° and 250°C (*21*), the growth of K-feldspar in a brine supersaturated with halite is quite reasonable; K-feldspar growth at temperatures below 100°C would have been possible in weaker brines.

Although K-feldspar growth appears possible thermodynamically, mass balance calculations indicate that the feldspar could not have formed isochemically, but required the flux of potassium-bearing fluids through the rocks. A typical dolostone interbed in the Conococheague contains approximately 25 percent K-feldspar by weight (Table 1). Cathodoluminescence images indicate that at least 75 percent of this K-feldspar is authigenic. Thus, a cubic centimeter of dolostone contains approximately 80 mg of authigenic potassium. If we assume an initial sediment porosity of 70 percent and a pore water supersaturated with halite, there would be less than 12 mg of dissolved potassium per cubic centimeter available for diagenetic reactions. Even if the initial siliciclastic mud was

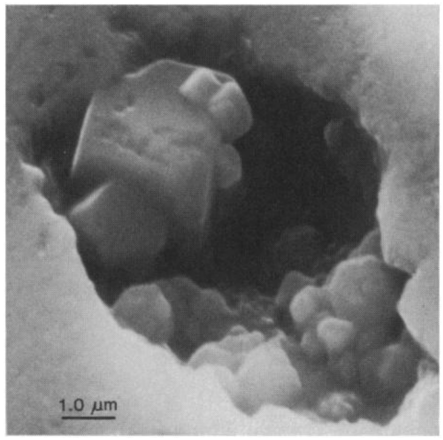

Fig. 3. Scanning electron micrograph of halite daughter crystal in breached fluid inclusion cavity.

pure illite, there would not be sufficient potassium present for the authigenic K-feldspar to have formed isochemically. Rather, feldspar growth had to involve the flux of multiple pore volumes of potassium-bearing fluids through the sediments. This fact, plus the Late Pennsylvanian to Early Permian timing indicated by the age-spectrum analyses, strongly suggest that the K-feldspar in the Conococheague Limestone was formed by the migration of connate brines that were mobilized by Alleghanian tectonism.

Far from being a geologic rarity, authigenic K-feldspar is a common constituent of Lower Paleozoic strata along the entire length of the Appalachian Basin. In addition to occurrences in Newfoundland, New York, and Pennsylvania (*5*), abundant authigenic K-feldspar has also been found by one of us (P.P.H.) in Cambrian carbonate rocks from Vermont, Virginia, and Tennessee. The results of this study raise the possibility that Alleghanian folding was responsible for the mobilization of brines in Lower Paleozoic carbonate rocks throughout the Appalachians and may have important implications for research on oil and gas migration pathways and the genesis of brine-derived stratiform ore deposits.

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9. Monoclinic and triclinic K-feldspars were distinguished by the x-ray diffraction criteria of J. R. Goldsmith and F. Laves [*Geochim. Cosmochim. Acta* **5**, 1 (1954)]; the presence of a single (131) reflection indicated the presence of monoclinic K-feldspar, whereas the presence of a $(131)-(1\bar{3}1)$ doublet indicated the presence of triclinic K-feldspar. Diffractrograms of insoluble residues of dolostone interbeds showed only a single (131) reflection, indicative of monoclinic K-feldspar. Diffractograms of separates of detrital K-feldspar with overgrowths showed a single (131) monoclinic reflection flanked by less intense triclinic (131) and $(1\bar{3}1)$ reflections. Diffractograms of detrital grains whose overgrowths had been removed by dissolution in dilute HF also showed monoclinic and triclinic reflections, but the intensity of the monoclinic reflection was substantially reduced.
10. Axial angle measurements provided by Glen Izett, using techniques described by R. E. Wilcox and G. A. Izett [*Am. Mineral.* **53**, 269 (1968)].
11. The optic axial angle $2V_x$ provides a precise estimate of ordering of aluminum and silicon in the tetrahedral sites of K-feldspar [S. C. Su, F. D. Bloss, P. H. Ribbe, *Am. Mineral.* **69**, 440 (1984)]. The $(t_1o + t_1m)$ parameter was estimated graphically from Su's $2V_x$ measurements.
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29. The assistance of J. Gillison, B. Johnson, and C. Palmer in performing chemical analyses is gratefully acknowledged. We also thank J. Reinhardt for helpful discussion and field assistance and B. Dalrymple, B. Jones, and B. Cecil for constructive comments on the manuscript. Authorized by the director of the U.S. Geological Survey.

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