ISOTOPIC RECORDS IN DETRITAL AND AUTHIGENIC FELDSPARS IN SEDIMENTARY ROCKS

Gunter FAURE
Department of Geological Sciences
The Ohio State University, Columbus, Ohio 43210 (USA)

When igneous and metamorphic rocks are exposed to chemical weathering at or near the surface of the earth, the minerals they contain decompose at different rates in accordance with Bowen's Reaction Series (Goldich, 1938). Consequently, quartz, muscovite and K-feldspar, which are more resistant to weathering than the ferromagnesian minerals and the plagioclase feldspars, may be incorporated into the solid weathering products. These contain, in addition, certain accessory minerals which also resist weathering: zircon, magnetite, ilmenite, spinel, garnet, tourmaline, sphene, etc. The grains of resistant minerals are concentrated by running water in deposits of sand and gravel which may become lithified into sandstones and conglomerates.

Geologists have traditionally used the presence of certain resistant minerals in sandstones to identify the sources from which the minerals originated. For example, purple zircons called hyacinth occur only in rocks of Archean age because the color results from radiation damage caused by the decay of U, Th and their unstable daughters (Poldervaart, 1955). Other resistant minerals that are derived from specific source rocks include diamonds, native Pt-group elements, glaucophane, certain kinds of garnets, tourmaline, spinel, and others.

Zircon is especially useful as an indicator of its provenance because it is not only highly resistant to chemical weathering and mechanical abrasion, but can also be dated by the isotopic U-Th-Pb method and by the fission-track method (Hurford et al., 1984). The technique for dating zircons by the isotopic U-Pb method has been refined such that small numbers of grains selected on the basis of color, shape and magnetic susceptibility can be dated (Gaudette et al., 1981). Even fragments of single zircon grains have been dated successfully by conventional wet chemical methods by Schärer and Allègre (1982), Gariepy et al. (1984) and by others, whereas Froude et al. (1983) used an ion microprobe called SHRIMP to identify 4.1 to 4.2 Ga detrital zircons from the Mt. Narryer quartzite in the Archean Yilgarn Block of Western Australia.

In this chapter we focus attention on the alkali feldspars which occur in sedimentary rocks both as detrital grains and as authigenic minerals or as authigenic overgrowths on detrital grains. The alkali feldspars are not only common constituents of sedimentary rocks, but also contain different kinds of isotopic records from which useful information about their provenance and about the geologic history of their host rocks can be derived.

THE OCCURRENCE OF FELDSPAR

Detrital Feldspars in Sedimentary Rocks

The feldspars are the most abundant group of minerals in the crust of the earth because they occur in most igneous and high-grade metamorphic rocks. They are aluminosilicates of Na, K, Ca and Ba, but also contain many other cations including Rb, Sr, Pb and even NH_4^+ (Gulbrandsen, 1974). The mineralogy of the feldspars is presented in textbooks and in specialized monographs by Barth (1969), Smith (1974), and Ribbe (1983).

Feldspar is a common constituent of many sand and gravel deposits and occurs as a detrital mineral in sandstones and conglomerates that formed by lithification of such deposits (Pettijohn, 1963). In addition, detrital feldspar occurs in unsorted weathering products, including till and soil, and has also been reported in deep-sea sediment from the South Pacific Ocean by Peterson and Goldberg (1962) who concluded that the feldspar in deep sea sediment was derived from volcanic centers on the ocean floor.

Detrital feldspar in terrigenous sediment tends to be enriched in K-feldspar compared to plagioclase because it is more resistant to chemical weathering and because plagioclase grains break along twinning planes more readily than do grains of K-feldspar (Pittman, 1969; Haldorsen, 1978). For example, Taylor and Faure (1981) reported that the ratio of K-feldspar to plagioclase in Wisconsinan till of Ohio and Indiana (U.S.A.) increases with increasing grain size and that the Rb/Sr ratios of these size fractions increase similarly. The same authors later observed the same relationships in Neogene till of the Transantarctic Mountains (Faure and Taylor, 1981; Faure et al., 1983).

The difference in the relative susceptibilities to chemical weathering of K-feldspar and plagioclase has led to suggestions that their abundances in detrital sedimentary rocks indicate paleoclimatic conditions (Todd, 1968) or reflect the advent of land plants during the Silurian Period (Basu, 1981). However, a study by James et al. (1981) of feldspar weathering in Holocene stream deposits did not support Todd's proposal because they found that plagioclase (Ab 80-95) is more altered than K-feldspar regardless of climatic conditions. Moreover, Basu's hypothesis was challenged by Graustein and Velbel (1981) because K-uptake by plant roots does not necessarily accelerate weathering of K-feldspar in soil and because of the absence of evidence that the K-feldspar/plagioclase ratios of all kinds of sandstones actually decreased during the Silurian Period when plants began to grow on land.

When detrital feldspar grains in sediment are buried, they may decompose as a result of diagenetic reactions with connate water. This process was called "burial metamorphism" by Aronson and Hower (1976) who demonstrated that the increase in the illite/smectite ratio with depth in Tertiary sediment deposited at the mouth of the

Mississippi River coincides with a decrease in the abundance of K-feldspar. They concluded from this evidence that K-feldspar was dissolving and that the K ions entered interlayer sites of smectite causing it to be converted to illite. Similarly, Land and Milliken (1981) demonstrated that plagioclase is converted to albite and that the abundance of K-feldspar decreases with depth in the sandstones of the Frio Formation (Oligocene) in Brazoria County (Texas). Gold (1987) reported similar observations from a study of Miocene sandstones in Louisiana.

Authigenic Feldspar in Sedimentary Rocks

It has been known for a surprisingly long time that many sedimentary rocks contain small amounts of authigenic feldspar (Drian, 1861). Both albite and the K-feldspar adularia occur in many sandstones, siltstones, shales, limestones, dolomites, and evaporites as authigenic constituents that formed at low temperature by reactions involving aqueous solutions (Füchtbauer, 1956; Kastner and Siever, 1979). The existence of authigenic feldspar in unmetamorphozed sedimentary rocks was somewhat controversial because of difficulties in distinguishing it from detrital feldspar by optical methods or by X-ray diffraction (Wright, 1968). In addition, it was by no means obvious how feldspars, which crystallize at high temperatures in igneous and metamorphic rocks, can also form by chemical reactions involving aqueous solutions at low temperatures.

The stability of the feldspars in contact with aqueous solutions is now explained by means of activity diagrams based on thermodynamics and the Law of Mass Action (Helgeson, 1972). Such diagrams were used by Kastner and Siever (1979) to demonstrate that bottom seawater and interstitial water in marine sediment may be supersaturated with respect to K-feldspar and may even reach saturation with respect to amorphous Si. In addition, albite and amorphous Si may also form from interstitial water, which explains why adularia and albite may coexist in equilibrium with secondary quartz in sedimentary rocks of marine origin.

However, the Ca-feldspar anorthite cannot form in this way because calcite precipitates before the activity of Ca increases sufficiently to be in equilibrium with anorthite (Bowers et al., 1984). The instability of anorthite in contact with natural solutions explains the observation by Land and Milliken (1981) that detrital plagioclase in the Frio Formation of Texas was progressively converted to albite with increasing depth. The Ca released by the decomposition of plagioclase subsequently precipitated as a carbonate cement.

The activity diagrams also indicate that detrital feldspar grains may be stabilized when they are emersed in solutions having the required activities of K, Na, H and H_4SiO_4. In such environments, secondary overgrowths of authigenic albite or adularia may form on detrital feldspar grains. Such overgrowths are common in the Permo-Triassic sandstones of England and elsewhere (Waugh, 1978). The presence of both detrital and authigenic feldspars in the same rock greatly enriches the isotopic record that is available for study, provided that the two varieties can be separated from each other. A method for separating overgrowths of secondary quartz, developed by Lee and Savin (1985), was used successfully by Girard et al. (1988) to separate diagenetic feldspar from its detrital substrate. In addition, Hearn (1987) proposed a quantitative technique to determine the abundances of authigenic and detrital feldspar in mineral concentrates using cathode luminescence and a scanning electron microscope.

Feldspar in Hydrothermal Deposits and in Volcanic Ash

Adularia is a common constituent of hydrothermal veins associated with granitic intrusives. It occurs in the quartz-fluorite veins of Europe (Pivec, 1973; Lippolt et al., 1985), is associated with calcite and zeolite in veins on the Lizard Peninsula of Cornwall, England (Halliday and Mitchell, 1976), and has been reported from veins in the geothermal areas of New Zealand (Steiner, 1970; Blattner, 1975). The occurrence of adularia in active geothermal systems is especially important because the temperature and chemical composition of the solution from which it is forming can be studied directly. Adularia has also been reported from spilites on the Iberian Peninsula of Europe (Munhà et al., 1980) and from the Precambrian basement rocks of Ohio (Bass, 1960; Faure and Barbis, 1983; Mensing and Faure, 1983). Additional occurrences of adularia in hydrothermal vein deposits were discussed by Bass and Ferrara (1969) and by Cerny and Chapman (1986).

Feldspar crystals of igneous origin occur also in deposits of volcanic ash and in bentonites derived from them. In addition, such deposits may contain cogenetic zircon, biotite, and plagioclase all which are datable by precise isotopic methods. Such dates reflect the time of crystallization and rapid cooling of the minerals and commonly indicate the time of deposition of the ash layers. Dates derived from phenocrystic minerals of bentonites are good estimates of the depositional ages of the sedimentary rocks with which they are interbedded and therefore help to define the geologic time scale (Odin, 1982; Baadsgaard and Lerbekmo, 1983; Baadsgaard et al., 1988; Yanagi et al., 1988). However, bentonites may be altered by hot brines which may cause conversion of smectite to illite and resetting of the isotopic dates derivable from the clay minerals (Elliott and Aronson, 1987). Evidence for the presence of brines derived from the isotope record of authigenic K-feldspar in Cambrian carbonate rocks was reported by Hearn and Sutter (1985) and by Hearn et al. (1987).

Finally, we mention the unexpected discovery of <u>spherules</u> of almost pure K-feldspar in the basal laminae of sediment deposited during the transition from the Cretaceous to the Tertiary periods at Caravaca, Spain (Smit and Klaver, 1981). These spherules may have formed from a melt that resulted from the impact of an asteroid on the earth. The spherules are very K-rich (K/K+Na = 0.99), but contain opaque inclusions with high concentrations of Cr, Ni, Co, As and Sb. The feldspar occurs in the form of crystal-lites radiating from the opaque inclusions. Sanidine spherules have also been found in K-T boundary layers in the Pacific Ocean (Kyte and Rasmussen, 1982), as well as in Colorado and New Mexico (Izett, 1987). However, spherules extracted from this layer in Umbria (Italy) are rich in siderophile elements (Smit and Kyte, 1984) and the origin of the different kinds of spherules in the boundary layers remains controversial (Cisowski, 1988; Montanari, 1986).

PROVENANCE DATING OF DETRITAL FELDSPAR

Detrital feldspar grains in sedimentary rocks crystallized at the time of formation of the igneous or high-grade metamorphic rocks from which they originated. Their ages therefore reflect events in the geologic history of their source rocks and may be used to identify their provenance. Feldspars are potentially datable by several isotopic methods including the Rb-Sr, K-Ar, K-Ca, $^{40}Ar/^{39}Ar$, and the common Pb method (Faure, 1986). Each of these relies on the validity of assumptions pertaining to the relevant parent-daughter decay schemes. However, when these methods are used to date detrital feldspar grains from a sedimentary rock, additional assumptions about the geology of the source area and about the state of preservation of the feldspar come into play. These assumptions include:

1. All feldspar grains recovered from a specific stratigraphic interval originated from the same source rocks which had a specific crystallization age.
2. The parent-daughter decay schemes in the feldspar grains were not disturbed as a result of chemical weathering of the source rocks or during transport of the feldspar grains to the site of deposition.
3. The feldspar grains were not altered during diagenesis (burial metamorphism) or by later interaction with circulating brines.
4. Overgrowths of authigenic feldspar are either not present or were removed prior to analysis for isotopic dating.

These assumptions are rarely, if ever, completely satisfied. In many cases, detrital feldspar grains in sedimentary rocks are mixtures derived from source rocks having different ages. The grains are commonly altered to kaolinite or illite as a result of weathering or during diagenesis after deposition, and they may contain overgrowths of authigenic feldspar or may be completely reconstituted to adularia or secondary albite by reactions with brines after diagenesis. These difficulties significantly restrict the use of detrital feldspar in sedimentary rocks for studies of their provenance.

For this reason, isotopic dating of detrital muscovite is an attractive alternative because this mineral is more resistant to alteration than K-feldspar and has higher concentrations of K and Rb than most feldspars. In addition, muscovite is somewhat easier to recover in pure form from sedimentary rocks because of its distinctive grain shape and larger grain size than detrital feldspar (Heller et al., 1985).

The intrinsic limitations on dating feldspar by isotopic methods are:

1. Most K-feldspars have low Rb/Sr ratios (< 1.0) because Sr is captured in place of K whereas Rb is only admitted by growing crystals of microcline or orthoclase. As a result, the amount of radiogenic ^{87}Sr in K-feldspars is low compared to muscovite, which increases the uncertainty of dates derived from them.
2. When mixtures of detrital feldspar grains, derived from sources having different ages, are dated by the Rb-Sr method they do not form proper Rb-Sr isochrons and dates derived from the slopes of linear data arrays have no real time significance.
3. K-feldspar does not retain radiogenic ^{40}Ar quantitatively, except volcanic sanidine in tuff beds or bentonites. Therefore, K-Ar dates of detrital feldspar underestimate the crystallization age.
4. Mixtures of detrital feldspars derived from sources having different ages yield intermediate K-Ar dates which reflect the proportions of mixing and have no real time significance.

In spite of the limitations on isotopic dating of detrital feldspar, useful information was obtained by Heller et al. (1985) from K-feldspar in sandstones of the Eocene Tyee Formation in Oregon (U.S.A.) and by Szabo and Faure (1987) who dated feldspar from the Berea Sandstone (Lower Carboniferous) of Ohio. In addition, Patterson and Tatsumoto (1964) interpreted the isotope compositions of Pb in detrital feldspars extracted from beach and river sands in North America.

Detrital feldspar in <u>till</u> is especially well-suited for dating by the Rb-Sr method because the feldspar grains are commonly less altered than they are in sandstones. Moreover, the preferential grinding of plagioclase relative to K-feldspar causes differences in the Rb/Sr ratios of the feldspar in the sand-size fractions of till (Faure and Taylor, 1981; Faure et al., 1983).

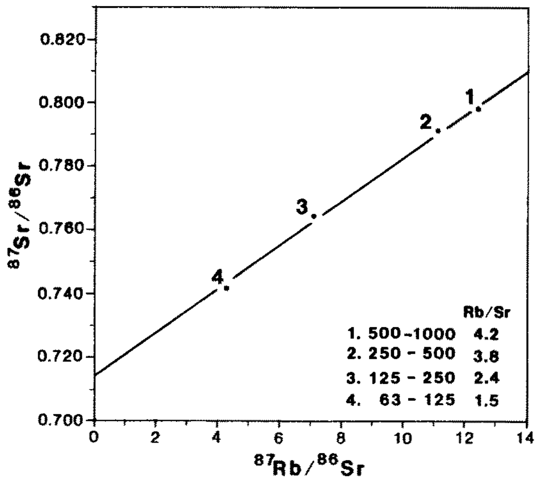

Figure 1: Size fractions of feldspar-quartz concentrates of till from the summit plateau of the Wisconsin Range in the Transantarctic Mountains. The slope of the line yields a date of 480 ± 21 Ma which is characteristic of the granitic basement rocks of the region. The Rb/Sr ratios decrease with decreasing grain diameters because of preferential grinding of plagioclase by the ice sheet (Faure et al., 1983)

An example of feldspar dating by the Rb-Sr method is the study by Faure et al. (1983) of till from the summit plateau of the Wisconsin Range in the Transantarctic Mountains (Mercer, 1968). A sample of this till was sieved into four size fractions between 63 μm and 1000 μm. These fractions were cleaned ultrasonically in dilute HCl and demineralized water for about 8 hours, followed by removal of ferromagnesian minerals on a magnetic separator. The resulting feldspar-quartz concentrates were analyzed for dating by the Rb-Sr method. The results form four colinear points on the Rb-Sr isochron diagram in figure 1. The slope of the line yields a date of 480 ± 21 Ma ($\lambda\ ^{87}Rb = 1.42 \times 10^{-11}\ y^{-1}$) and the initial $^{87}Sr/^{86}Sr$ ratio is 0.7144 ± 0.0030. Faure et al. (1983) concluded from these results that the feldspar in this till sample had originated from the local granitic basement rocks which are known to have crystallized during the Ross Orogeny in Cambro-Ordovician time. Therefore, this till may have been deposited by an ice cap that formed on the Wisconsin Range plateau, as originally proposed by Mercer (1968). The apparent absence of a component of Precambrian feldspar in this till means that it was probably not formed by ice which originated on the East Antarctic craton which contains granulite gneisses of Archean age (Grew and Manton, 1979).

A component of Precambrian feldspar is present in till studied by Faure and Taylor (1981) from Mt. Tuatara along the Byrd Glacier in the Transantarctic Mountains. Feldspar fractions at this locality yielded a date of 1100 $\pm$ 69 Ma which is the result of mixing of grains derived from the local granitic basement (about 500 Ma) and from the East Antarctic craton (about 2500 Ma). The presence of Precambrian feldspar in till deposited by the Byrd Glacier is consistent with the fact that it drains a large area of the ice-covered interior of East Antarctica.

THERMOCHRONOMETRY OF DETRITAL MICROCLINE

When detrital feldspar grains derived from granitic rocks of uniform age are buried after deposition, they may be reheated sufficiently to lose some of the radiogenic ^{40}Ar that had formed by decay of ^{40}K since they cooled through their closure temperature of about 130°C. Therefore, the K-Ar dates of detrital feldspar in sedimentary rocks may decrease with increasing depth in a core or with increasing age of their sedimentary host rocks. This tendency may be counteracted by the fact that feldspar derived from the top portion of a granite batholith may have older K-Ar ages than feldspar which originated from deeper levels in the batholith because the top of the batholith cooled through the closing temperature of microcline before the interior did. Consequently, the K-Ar dates of detrital feldspar released during the erosion of such a batholith may increase with the stratigraphic age of their sedimentary host.

The loss of radiogenic ^{40}Ar from K-feldspar grains caused by diffusion in response to heating can be revealed by the $^{40}Ar/^{39}Ar$ age spectrum obtained by stepwise release of Ar at increasing temperatures (Faure, 1986). An example of such a study is the work of Harrison and Bé (1983) who obtained $^{40}Ar/^{39}Ar$ age spectra for detrital microcline concentrates from drill cores of Tertiary sandstones in the San Joaquin Valley of central California (U.S.A.). The spectra derived from eleven samples yielded plateau dates that averaged about 78 Ma, whereas the fission-track dates of detrital zircons from the same cores yielded 83 Ma (Briggs et al., 1981). These dates refere to the age of the igneous rocks in the adjacent Tehachapi and Sierra Nevada Ranges from which the sediment originated. The dates represent the time elapsed since microcline and zircon cooled through their respective blocking temperatures when radiogenic ^{40}Ar and fission tracks began to accumulate.

The $^{40}Ar/^{39}Ar$ ratios of the very first gas released by the microclines yielded fictiteous dates of about 65 Ma which are attributable to loss of ^{40}Ar during slow cooling of the granitic pluton. However, the microcline recovered from the greatest depth of 6200 m lost additional radiogenic ^{40}Ar amounting to 18%, presumably caused by geothermal heating. Harrison and Bé (1983) used Fick's second law of diffusion to show that the observed loss of ^{40}Ar could have been caused by heating the perthitic microcline to 160°C starting at 200 ka in the past. However, the ^{40}Ar loss can also be attributed to heating for a longer period of time as a result of increasing depth of burial. If the geothermal gradient was about 30°C/km, the temperature to which the microcline was heated would have increased steadily to its present observed value of 157°C. The loss of ^{40}Ar caused by diffusion under these conditions would also amount to about 18%. Therefore, the $^{40}Ar/^{39}Ar$ method of dating detrital microcline provides not only a provenance date but can, under favorable circumstances, also reveal evidence regarding its thermal history.

OXYGEN ISOTOPE COMPOSITIONS OF DETRITAL AND AUTHIGENIC FELDSPARS

Authigenic feldspars which formed in sedimentary rocks from aqueous solutions at low temperatures may be enriched in ^{18}O compared to detrital feldspar of igneous origin (Savin and Epstein, 1970; Lawrence and Kastner, 1975). Therefore, the isotope composition of O can be used to distinguish between authigenic and detrital feldspars that may coexist in a sedimentary rock. In addition, the $\delta^{18}O$ values of cogenetic secondary quartz and authigenic feldspar can be used to determine both the $\delta^{18}O$ value of the water and the temperature of isotope equilibration using experimentally determined fractionation equations (Friedman and O'Neil, 1977).

The temperature-dependence of the isotope fractionation factors is expressed by equations of the form (Faure, 1986):

$$1000\ln\alpha^{1}_{2} = \frac{A \times 10^{6}}{T^{2}} \quad B \tag{1}$$

where α^{1}_{2} is the fractionation factor of O in phases 1 and 2, A and B are experimentally determined constants, and T is the temperature in Kelvins. For albite (or K-feldspar), equation 1 takes the form (Matsuhisa et al., 1979):

$$1000\ln\alpha^{f}_{w} = \frac{1.59 \times 10^{6}}{T^{2}} \quad 1.16 \tag{2}$$

and for quartz:

$$1000\ln\alpha^{q}_{w} = \frac{3.34 \times 10^{6}}{T^{2}} \quad 3.31 \tag{3}$$

Equations 2 and 3 can be combined by making use of the approximation that:

$$1000 \ln \alpha^1_2 = \delta_1 - \delta_2 \quad (4)$$

Therefore, the fractionation of O isotopes between feldspar and quartz in equilibrium with water of the same isotope composition at the same temperature is:

$$\delta^{18}O_q - \delta^{18}O_f = \frac{1.75 \times 10^6}{T^2} \quad 2.15 \quad (5)$$

However, this possibility has not yet been realized partly because it is difficult to separate overgrowths of quartz and feldspar from their substrates.

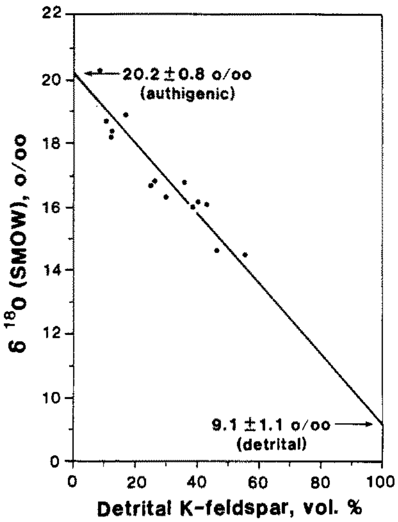

Figure 2: Relationship between $\delta^{18}O$ values of concentrates of authigenic K-feldspar overgrowths and the abundance of residual detrital K-feldspar in three arkoses from Angola. The concentrations of detrital feldspar were estimated by point counting based on cathodoluminescence. The extrapolated $\delta^{18}O$ values apply to the pure authigenic and detrital feldspar components (Girard et al., 1988)

Authigenic overgrowths of adularia were successfully concentrated by Girard et al. (1988) from Lower Cretaceous arkose in Angola, southwest Africa, and the $\delta^{18}O$ values and K-Ar dates of the concentrates were measured. The results indicated that both parameters varied linearly with the abundance of detrital K-feldspar remaining in the concentrates. The O data in figure 2 were extrapolated to the pure end-members whose $\delta^{18}O$ are +20.2 ± 0.8 permil for the authigenic feldspar and +9.1 ± 1.1 permil for the detrital component. The K-Ar dates of the two feldspar components were similarly resolved into 98 ± 16 Ma for the authigenic feldspar and 516 ± 26 Ma for the detrital component. These dates indicate that the authigenic overgrowths formed during the Cretaceous Period about 50 Ma after deposition. The detrital feldspar probably originated from granitic basement rocks which participated in the Pan-African event in Cambro-Ordovician time.

The average $\delta^{18}O$ value of the authigenic feldspar overgrowths can be used to calculate the $\delta^{18}O$ of the water from which they precipitated, assuming a temperature of 145 ± 4°C, which is the homogenization temperature of fluid inclusions in these overgrowths. The result obtained by Girard et al. (1988) is that the $\delta^{18}O$ value of the water was between +5.7 and +8.9 permil (SMOW). Evidently, the water was strongly enriched in ^{18}O compared to meteoric water or seawater, either as a result of prior evaporation at the surface or because of isotope exchange with oxygen-bearing minerals at elevated temperatures. In either case, the brines did not evolve in situ but invaded the rocks after deposition and caused the precipitation of feldspar overgrowths.

ISOTOPIC RECORDS OF AUTHIGENIC FELDSPAR

Authigenic K-feldspar and albite are common but minor constituents of many sedimentary rocks. These minerals can form on the bottom of the oceans, in which case they record both the time of sedimentation and the $\delta^{18}O$ or temperature of the water from which they formed. However, authigenic feldspar may also form after sediment deposition during diagenesis or by reactions caused by circulating brines. In such cases, the ages of the feldspars postdate the time of deposition, and their O isotope compositions depend on the $\delta^{18}O$ of the connate water or circulating brines and on the temperature at the time the reactions took place. Migrating brines may also cause the formation of adularia in igneous or metamorphic rocks at unconformities along which the primary feldspars may have been altered to clay minerals when the rocks were exposed to weathering. The dates derived from such authigenic feldspars also postdate the age of the basement rocks and may approach the time of brine alteration.

Authigenic sanidine in nearly monomineralic layers in the St. Peter Sandstone of Wisconsin was first dated by the K-Ar method by Krueger and Woodard (1972) and more recently by Marshall et al. (1986). The latter reported discordant K-Ca and K-Ar dates for two samples of 443 $\pm$ 12 and 403 $\pm$ 16 Ma (K-Ca) and 402 $\pm$ 13 and 377 $\pm$ 13 Ma (K-Ar), respectively. Information reviewed by Marshall et al. (1986) indicates that the St. Peter Sandstone (Middle Ordovician) is older than about 454 Ma. Consequently, even the K-Ca dates are younger than the depositional age of the rocks, and this indicates that the sanidine is not syngenetic but is either late diagenetic or epigenetic in origin. This is a very significant result because dates derived from such authigenic feldspar <u>cannot</u> be used to constrain the geologic timescale. In addition, Marshall et al. (1986) used the apparent loss of radiogenic ^{40}Ar from the two sanidines (about 8.4%) to show that Ar diffuses significantly faster at low temperatures than expected from an extrapolation of experimental data obtained at high temperatures.

The presence of authigenic feldspar in the crystalline basement rocks of Ohio (U.S.A.) was first indicated by Faure and Barbis (1983). They reported that whole-rock samples of granitic gneiss taken up to 6.5 meters below the unconformity yielded an anomalously low Rb-Sr isochron date of 699 $\pm$ 16 Ma, whereas samples from greater depth confirmed the Grenville age of these rocks with a date of 1173 $\pm$ 41 Ma. Subsequently, Mensing and Faure (1983) demonstrated by cathode luminescence that the feldspars below the unconformity contained both secondary low-temperature feldspar (adularia) and residual primary feldspar, whereas the feldspar more than 6.5 meters below the former erosion surface was composed only of microcline. The mixed adularia-microcline feldspars yielded a date of only 599 $\pm$ 69 Ma compared to 1162 $\pm$ 11 Ma for the unaltered microclines, in good agreement with the whole-rock date obtained by Faure and Barbis (1983). Mensing and Faure (1983) regarded the line formed by the microclines in figure 3 as an isochron but interpreted the adularia-microcline array as a mixing-line. Therefore, they concluded that the adularia is younger than the date indicated by the slope of this line.

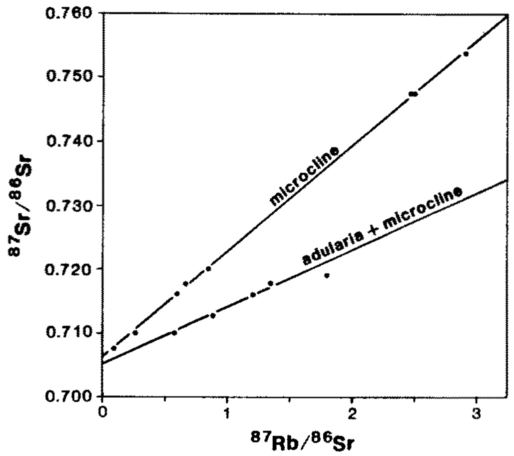

Figure 3: Rb-Sr dating of feldspars in granitic basement rocks of Ohio, U.S.A.. The microclines form an isochron yielding an age of 1168 ± 11 Ma consistent with the Grenville age of these rocks. However, the adularia + microcline concentrates, taken within 6.4 meters of the unconformity which separates the basement from the overlying Paleozoic sedimentary rocks, is a mixing line. Therefore, the age of the adularia is <u>less</u> than the 599 ± 69 Ma date indicated by its slope (Mensing and Faure, 1983)

The $\delta^{18}O$ of the feldspars from the Ohio basement rocks were increased as a result of the formation of adularia in such a way that $\delta^{18}O$ correlates positively with K and negatively with Na concentrations (Shieh and Mensing, 1986). Apparently, the exchange of O isotopes was accompanied by the replacement of Na by K ions in the feldspar. In addition, MacIntyre (1986) reported that K-Ar dates of the same feldspar concentrates increase with depth in the upper portion of the core from about 370 to 420 Ma. However, the unaltered microcline 6.4 meters below the unconformity yielded K-Ar dates between 750 to 850 Ma which are consistent with K-Ar dates of biotites from the Precambrian basement of Ohio, if allowance is made for the loss of radiogenic ^{40}Ar from the microcline by diffusion at low temperature (Bass, 1960; Lidiak et al., 1966).

EVIDENCE FOR HYDROTHERMAL BRINES IN THE APPALACHIANS

The isotopic records preserved by the adularia in the basement rocks of Ohio point to the invasion of hot saline solutions in Late Paleozoic time which affected not only the basement rocks but interacted also with the sedimentary rocks of Early Paleozoic age that overlie them. For example, Grant et al. (1984) reported that glauconite from the Lower Silurian Brassfield Formation of Ohio and Indiana yielded Rb-Sr and K-Ar dates of 370 $\pm$ 11 Ma and 362 $\pm$ 6 Ma, respectively. These dates are younger than the stratigraphic age of the Brassfield Formation, but they coincide with the K-Ar dates of the adularia in the underlying basement (MacIntyre, 1986). The dates also agree with Rb-Sr and K-Ar age determinations by Grant et al. (1984) of glauconites from the Davis Formation (Upper Cambrian) in the "Viburnum Trend" of Missouri which is famous for its Mississippi-Valley type Pb-Zn deposits. Evidently, the ages of the glauconites in Ohio, Indiana, and Missouri may have been reset by brines which participated in the deposition of galena and sphalerite of the ore deposits in Missouri.

Evidence for the circulation of hot brines in the Paleozoic rocks of the southern Appalachian Mountains was reported by Elliott and Aronson (1987). They obtained K-Ar dates for authigenic clay (1-2μm and <0.125μm) from Middle Ordovician bentonites ranging from 256 to 313 Ma, which they attributed to the illitization of smectite by brines driven out of the Appalachian Basin during the Alleghanian Orogeny in Late Carboniferous to Permian time. Although their dates are younger than those of Grant et al. (1984), Elliott and Aronson (1987), nevertheless, associated the illitization of bentonites with the formation of Mississippi-Valley type Pb-Zn deposits.

Another line of evidence for the presence of hot brines arises from $^{40}Ar/^{39}Ar$ dating of K-feldspar from marine carbonate rocks of Early Paleozoic age in the southern Appalachian Mountains (U.S.A.). Hearn and Sutter (1985) and Hearn et al. (1987) obtained $^{40}Ar/^{39}Ar$ partial-release spectra of detrital feldspars with authigenic overgrowths from several Cambrian formations in Pennsylvania, Maryland, Virginia, and Tennessee. They dated the detrital feldspars with their overgrowths and also the detrital feldspars alone, after removing the overgrowths by leaching with 5% HF. The age of the authigenic component (A_0) was then calculated for each incremental step by the equation:

$$A_t = A_0 M_0 + A_c (1-M_0) \qquad (6)$$

where A_t is the apparent age of the total sample, A_c is the apparent age of the core, and M_0 is the mass fraction of the authigenic overgrowths. Values of A_t and A_c were calculated by standard methods from the $^{40}Ar/^{39}Ar$ ratios of gas released at increasing temperatures and M_0 was determined by a modal analysis in which the total area of feldspar grains was compared to the area of the grains displaying cathode luminescence. Authigenic feldspars do not luminesce because they lack the trace elements that cause cathode luminescence.

The results reported by Hearn et al. (1987) indicate plateau dates ranging from 278 to 315 Ma for the authigenic feldspars. These dates are within the late Carboniferous-Early Permian Periods and agree with the K-Ar dates of illitization of Ordovician bentonites in the same area reported by Elliott and Aronson (1987). Hearn et al. (1987) demonstrated that the formation of authigenic K-feldspar required the introduction of K-bearing brines. In addition, a study of fluid inclusions within the overgrowths indicated homogenization temperatures between 100 to 200°C and salinities of 18 to 21 weight percent NaCl equivalent. These results are similar to conclusions derived from fluid inclusions of Pb-Zn deposits in the southern Appalachian States. Therefore, Hearn et al. (1987) suggested that the authigenic feldspar and the Pb-Zn deposits were probably formed by the same brines in late Paleozoic time. Moreover, the brine migration was apparently a regional phenomenon associated with the tectonic activity that accompanied the Alleghanian orogeny.

The concordant results reported by Elliott and Aronson (1987) and Hearn et al. (1987) apply to the southern and central Appalachian Mountains, whereas Grant et al. (1984) studied material from the midwestern region of the U.S.A., including Ohio, Indiana, Kentucky and Missouri. Therefore, the reequilibration of the Rb-Sr decay schemes in glauconite by brines in the midwest may have *preceded* the alteration of bentonites and the formation of authigenic feldspar in the southern Appalachian Mountains. Consequently, the so-called Mississippi-Valley type Pb-Zn deposits may have formed during a lengthy interval of time that lasted from the Early Devonian to the Early Permian Periods.

SUMMARY

Detrital as well as authigenic alkali feldspars are common constituents of sedimentary rocks. They can be dated by different isotopic decay schemes including the K-Ar, $^{40}Ar/^{39}Ar$, K-Ca, Rb-Sr and the Pb-Pb methods. In addition, the O isotope composition of authigenic feldspars can be used to determine the temperature of isotope equilibration or the isotope composition of the water with which they equilibrated.

The examples considered in this chapter include the provenance determination of detrital feldspar in Neogene till of the Transantarctic Mountains, the thermal history of detrital microclines in Tertiary sandstones in the San Joaquin Valley of California, as well as the origin of detrital feldspar and the subsequent formation of overgrowths of adularia in an arkose in Angola in southwest Africa. The late diagenetic or post diagenetic origin of authigenic feldspar in Angola applies also to authigenic sanidine layers in the Middle Ordovician St. Peter Sandstone of Wisconsin. Consequently, dates derived from authigenic feldspar cannot be used to construct the geologic timescale, unless it can be shown that the feldspar is *syngenetic* or *early diagenetic* in origin.

Authigenic feldspar in the crystalline basement rocks of Ohio shows evidence of brine migration during the Devonian Period. The same brines also appear to have altered glauconite in the early

Paleozoic rocks of Ohio and Indiana and in the Pb-Zn deposits of Missouri. However, studies of authigenic feldspar and bentonites in the southern Appalachians indicate that the Pb-Zn deposits in the region formed later in Carboniferous to early Permian time.

The studies cited in this chapter illustrate the broad range of important geologic problems that can be addressed by isotopic studies of feldspar in sedimentary rocks. Now that the potential of this line of research has been demonstrated, the field is wide open for much additional research.

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