Clays and Clay Minerals, Vol. 34, No. 4, 483–487, 1986.

K/Ar SYSTEMATICS OF BENTONITE AND SHALE IN A CONTACT METAMORPHIC ZONE, CERRILLOS, NEW MEXICO[1]

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Abstract—To test the ability of illitic clay minerals to retain argon, K/Ar ages were measured on grain-size separates from the Cretaceous Mancos Shale and associated bentonites that have been transformed into K-bentonite near the contact with a large Tertiary igneous stock. The ages of size separates of illite/smectite from the K-bentonite nearest the contact were internally concordant and matched the hornblende K/Ar age of the stock. In contrast, K/Ar data from clay size fractions from shales adjacent to each K-bentonite were internally discordant with measured ages that were much greater than the age of the intrusion. Thus, significant radiogenic argon was retained by fine-grained detrital illite, even in shale samples very near the igneous contact. These results are convincing evidence that illitic clay minerals are excellent K/Ar clocks under conditions prevailing in sedimentary and diagenetic environments.

Key Words—Age dating, Bentonite, Contact metamorphism, Illite, Illite/smectite, K/Ar ages.

INTRODUCTION

In recent years, the diagenesis of clastic sedimentary rocks and its effect on petroleum reservoir properties have become topics of extensive research (Stalder, 1973; Seemann, 1979; van Wijhe *et al.,* 1980). Numerous studies have attempted to relate K/Ar ages measured on illitic clay to the redistribution of potassium and radiogenic argon in deeply buried shales and bentonites and to the timing of the growth of pore-fill diagenetic clays in sandstones (Weaver and Wampler, 1970; Perry, 1974; Sommer, 1975; Aronson and Hower, 1976; Hoffman *et al.,* 1976; Hoffman, 1979; Clauer, 1981; Bonhomme *et al.,* 1983; Aronson and Burtner, 1983; Law, 1983; Burtner and Aronson, 1984; Lee, 1984). Several of these studies contain internally consistent and concordant results that suggest that the K/Ar illite clock is appropriate for the temperature-pressure conditions affecting most sedimentary rocks that have not undergone heating beyond that of burial metamorphism. Nonetheless, skepticism exists that such fine-grained clays are able to retain radiogenic argon quantitatively over geologic time even at low temperatures. This study addresses that problem.

One approach to determine the extent to which radiogenic argon is retained by clay minerals is to determine experimentally the diffusion coefficient of Ar in illite at elevated temperatures where the diffusion rate is high enough to be measured and then extrapolate the data to lower temperatures. Such a laboratory approach is impractical for clay minerals because of their instability at high temperatures (see Giletti, 1974). Another approach, the one applied here, is based on analyses of naturally occurring samples whose thermal histories are well known. For example, Bonhomme *et al.* (1983) argued that the concordance of measured K/Ar ages of 185–196 m.y. for six size fractions of illite separated from the silicified wall rock of a hydrothermal ore deposit, including the <0.2-μm fraction, indicated that 1 *M* illite reliably registered the time of ore deposition. The present study evaluated argon retentivity of illite and interstratified illite/smectite (I/S) by dating size separates of these minerals in K-bentonite (meta-bentonite) beds and their enclosing shales from a contact metamorphic zone surrounding a 5-km-wide Tertiary stock at Cerrillos, New Mexico.

GENERAL GEOLOGY

In the Cerrillos mining district, mineralizing solutions have been related to the emplacement of a Tertiary stock into the Cretaceous Mancos Shale. The composite intrusion was emplaced during Oligocene time and consists of an earlier hornblende monzonite and a later pyroxene-bearing monzonite (Disbrow and Stoll, 1957).

The Mancos Shale was deposited about 110–82 m.y. ago and spans the Early–Late Cretaceous boundary (Cobban, 1972; Obradovich and Cobban, 1975). Nadeau (1980) and Nadeau and Reynolds (1981) studied the effect of contact metamorphism by the Cerrillos stock on the clay mineralogy of shales and bentonites within the Mancos Shale. Using an estimated temperature of 750°C for the emplacement of the stock, they found that clay minerals in bentonite beds and adjacent shales generally are more illitic closer to the stock. Clay minerals in bentonites at some distance from the stock (i.e., 20 km) are smectite, but near the stock they are

[1] Contribution No. 158 of the Department of Geological Sciences, Case Western Reserve University.

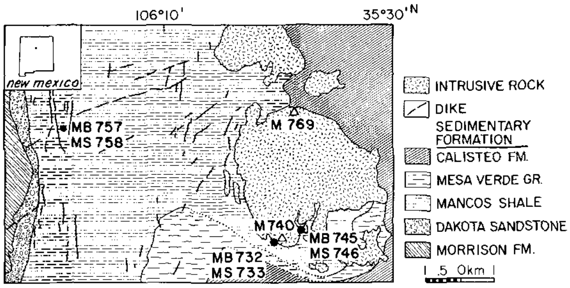

Figure 1. Simplified geological map of the study area showing sample locations. Solid circles are Mancos bentonite-shale sample pairs. Open triangles are Cerrillos pluton samples.

ordered I/S with 65–90% illite layers. Nadeau and Reynolds (1981) interpreted the illitic (potassium) bentonites to have formed from smectitic bentonites in response to the contact metamorphism.

SAMPLES

K_2O and Ar were measured on three sets of bentonite and adjacent shale pairs and two samples of the composite igneous pluton. All samples were collected by Nadeau and Reynolds; sample localities are shown on the geological map of Figure 1. Bentonite-shale pair MB732-MS733 was collected 1.5 m from the contact of the sedimentary rock with the outer phase of the composite stock, which itself was collected nearby as sample M740. Post-intrusive structural distortion of the Mancos at the intrusive contact allows the possibility that these near-contact samples could have been initially as far away as 10 m from the contact (personal communication, R. C. Reynolds, Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire, 1985). An additional sample of the pluton, M769, was taken from the opposite side of the stock. Sample-pair MB745-MS746 was collected from a large roof pendant of the Mancos Shale projecting into the stock. Sample-pair MB757-MS758 was collected about 7 km from the stock.

EXPERIMENTAL METHODS

Clay-size fractions for X-ray powder diffraction (XRD) and K/Ar determinations were obtained by gently crushing the samples in a mortar, followed by mild ultrasonic disaggregation. The submicrometer size fractions were obtained by using a Sharples super centrifuge. The grain sizes recovered are thought to represent those actually present in the bentonite and shales.

K_2O and Ar measurements were made on several clay-size separates from each of the bentonites and adjacent shales and on hornblende and whole rock samples of the stock. K_2O analyses were made with a flame photometer on acid solutions of beads fused in lithium metaborate. Typically, 100 mg of the clay samples were analyzed for Ar; none were pre-baked. Ar was analyzed using an MS10 mass spectrometer equipped with an on-line, multi-loaded extraction system and a bulb-pipeted ^{38}Ar tracer calibrated by the LP-6 interlaboratory standard at 19.3×10^{-10} mole/g of radiogenic argon ($^{40}Ar^*$). Typically, about 80–30% of the extracted argon was radiogenic, which enabled a precise measurement of the radiogenic argon ($^{40}Ar^*$). Potassium decay constants used in this study were those proposed by Steiger and Jäger (1977). The uncertainty in each age analysis is estimated to be 4%; however, the relative uncertainty between samples is only about 2% because of the similar processes and standard solutions utilized for all samples.

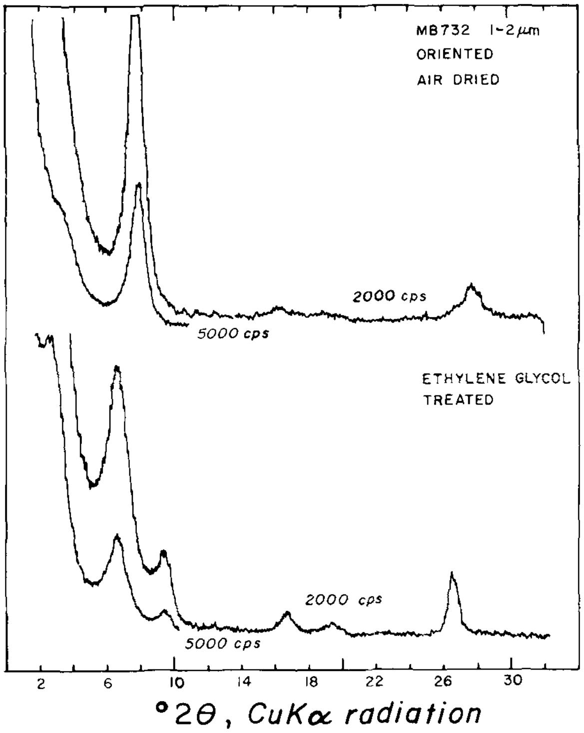

Figure 2. X-ray powder diffractograms of air-dried and ethylene glycol-saturated clay fraction (1–2-μm fraction) of sample MB732.

RESULTS

Petrology of the igneous samples

Sample M740, from the earlier intrusive phase of the stock adjacent to the contact, is a monzonite porphyry with 75% trachytic groundmass. Feldspar phenocrysts are intensely altered to a coarse illite with petrographically observable pleochroism; however, hornblende phenocrysts are unaltered. Sample M769, from the later intrusive phase, is holocrystalline and composed almost completely of less extensively illitized feldspar (iso-orthoclase) and pyroxene.

Table 1. Clay mineralogy of bentonites and shales studied.

Sample	Thickness of bentonite (cm)	Mineralogy[1]	Illite layers in illite/smectite (%)[2]
MB732	20	I/S, Chl	65–75
MS733		I, I/S, Chl	65–85
MB745	8	I(?), I/S, Chl	85–100
MS746		I, I/S, K, Chl	95–100
MB757	2	I/S, K, Chl	45–75
MS758		I, I/S, K, Chl	52

[1] I/S = illite/smectite mixed-layer clay; I = discrete illite; Chl = chlorite; K = kaolinite, ? = questionable.
[2] After Reynolds and Hower (1970).

Clay mineralogy of bentonites and shales

Table 1 lists the clay mineralogy of all bentonites and shales examined. Figure 2 shows the XRD pattern of the 1–2-μm fraction of sample MB732 and is typical of all such samples examined.

K/Ar data

Hart (1964) showed that hornblende is an excellent K/Ar clock that is resistant to secondary argon loss. The relatively small Cerrillos pluton was emplaced at a shallow level and would have quickly cooled below hornblende's K/Ar blocking temperature, estimated by Jäger (1979) at about 500°C. Three K/Ar analyses of a pure separate of unaltered hornblende from sample M740 were in good agreement at an age of 28.9 ± 1.0 m.y. (Table 2) and, therefore, we accept this as the age of the emplacement of the pluton.

K/Ar analyses were also made on whole rock samples M740 and M769, to test the effect of the illite alteration of the feldspars. This extensively developed illite contains much of the potassium in these rocks. The whole rock analyses yielded ages of 27.1 ± 1.3 and 28.5 ± 1.6 m.y. (Table 2) that are concordant and in close agreement with the 28.9 ± 1.0 m.y. measured age of the unaltered hornblende from sample M740. Thus, the alteration of the feldspar appears to have been a deuteric reaction at about the time of intrusion, and the illite alteration product was argon retentive.

Four size fractions of sample MB732, the 20-cm thick bentonite at the contact, were analyzed for K_2O and Ar. The measured ages are between 27.9 to 29.8 m.y. (Table 3) for all size separates, including the <0.1-μm fraction. The mean value of the four ages of I/S is 28.7 ± 1.0 m.y., in close agreement with the age (28.9 ± 1.0 m.y.) of the intrusion estimated from the hornblende. These data strongly suggest that, even for the <0.1-μm particles, I/S is an excellent K/Ar clock if it is not subsequently reheated.

The pattern of measured ages for size fractions of sample MS733, the shale member of the sample-pair collected at the contact, is markedly different from that of the bentonite member of the sample-pair. The ages range from 119 to 91 m.y. for three separates varying downward in size from 0.5 to <0.1 μm (Table 3). These ages are close to, or greater than, the age of deposition of the Mancos Shale and are much greater than the age of intrusion. That a considerable portion of radiogenic argon was not degassed from the detrital illite (or I/S) under this secondary heating for a sample within only a few meters of a large monzonite intrusion is further indication that submicrometer-size illitic grains strongly retain radiogenic argon.

The age vs. grain size pattern for the three size separates from each of the other two shale samples, MS758 and MS746, is similar to that observed for sample

Table 2. K/Ar ages of igneous samples.

Sample	K_2O (%)	Age (m.y.)	Radiogenic argon (%)
Trachytic monzonite M740			
Hornblende 1	1.66	27.8 ± 1.4	74.1
Hornblende 2	1.73	29.8 ± 1.5	73.4
Hornblende 3	1.70	29.0 ± 1.5	74.0
Whole rock	4.60	27.1 ± 1.3	58.0
Monzonite M769			
Whole rock	4.00	28.5 ± 1.6	38.5

Table 3. K/Ar ages of three pairs of bentonites and shales.

Sample	Size (μm)	K_2O (%)	Age (m.y.)	Radiogenic argon (%)
Bentonite MB732	1–2	3.58	29.5 ± 1.7	37.0
	1–2[1]	3.87	29.8 ± 1.7	34.1
	0.5–1	3.82	28.0 ± 1.6	35.7
	0.1–0.2	3.83	29.7 ± 1.8	30.8
	<0.1	3.92	27.7 ± 1.7	27.7
Shale MS733	0.2–0.5	4.39	118.8 ± 5.7	66.8
	0.1–0.2	4.47	98.3 ± 4.7	71.1
	<0.1	3.78	91.4 ± 4.3	86.1
Bentonite MB745	1–2	3.51	97.8 ± 4.6	84.6
	0.5–1	4.53	69.0 ± 3.2	87.8
	0.2–0.5	4.67	62.8 ± 3.0	76.0
	0.1–0.2	4.99	46.6 ± 2.3	56.8
	<0.1	4.84	44.1 ± 2.2	59.4
Shale MS746	>2	2.45	139.1 ± 6.7	87.0
	0.2–0.5	5.15	79.4 ± 3.6	86.8
	0.1–0.2	5.85	63.3 ± 2.9	84.6
	<0.1	5.67	60.5 ± 2.8	79.5
Bentonite MB757	1–2	3.24	31.5 ± 1.6	56.2
	0.5–1	3.50	36.8 ± 1.8	73.1
	0.2–0.5	3.85	36.1 ± 1.8	68.3
	0.1–0.2	3.81	31.4 ± 1.5	68.9
	<0.1	3.59	36.2 ± 1.8	60.2
Shale MS758	>2	0.80	136.3 ± 6.6	68.0
	0.2–0.5	3.47	81.0 ± 3.9	78.8
	0.1–0.2	3.75	68.6 ± 3.2	79.7
	<0.1	3.70	62.3 ± 3.0	72.2

[1] Repeated run after treated with diluted HCl for 30 min at 70°C.

MS733. All samples show internally discordant measured ages, older than that of the intrusion and decreasing with grain size (Table 3).

The 2-cm-thick bentonite (sample MB757) was collected 7 km from the exposed contact, in a region where several thin dikes occur. It produced ages that vary irregularly with grain size from 31 to 37 m.y., all of which are greater than the age of the stock. The meaning of these ages is not clear. They may be due to contamination by detrital I/S that could have occurred either during sedimentation or during sample collection (the thinness of this bentonite makes it difficult to avoid tiny amounts of contamination from the adjacent shale). Alternatively, the thin dikes in this region may have affected the bentonite, and they may be older than the main stock. Also, some of the illite in the bentonite may have formed during an earlier stage of diagenesis unrelated to heating by the intrusion.

Bentonite sample MB745 was collected from an 8-cm-thick bed in the major roof pendant of the stock. Its measured age pattern of highly discordant ages, in which coarser grain-size separates gave older ages, is anomalous compared to the other two bentonites and is similar to that observed in the three shales. In addition, the measured ages (98 to 44 m.y.) of the sample are considerably greater than the stock. The measured age pattern suggests that sample MB745 either may not be a bentonite or, if so, was highly contaminated during its initial deposition.

SUMMARY AND CONCLUSIONS

The I/S in the bentonite at the contact with the Cerrillos pluton originated when the bentonite and the enclosing shale were intruded by the Tertiary stock. The internally concordant K/Ar ages obtained for several size fractions (ranging to <0.1 μm) of the I/S from the K-bentonite at the contact, and their agreement with the age of the stock as determined by K/Ar on hornblende, indicate I/S retains radiogenic argon, if it is not subsequently reheated. The fact that feldspar in the stock is highly altered to illite or sericite, yet whole rock K/Ar ages agree with the hornblende age, also supports this contention because such results indicate the extensive illite alteration of the pluton was late stage (deuteric) in origin and that this illite is argon retentive. With respect to K/Ar ages obtained from shale at the contact, the internally discordant ages with grain size in which all size fractions have ages much older than the stock (as old as 120 m.y.) indicate that a significant proportion of the radiogenic argon in the detrital illitic clays was retained even when they were strongly heated.

Together, these results are strong evidence that illite and I/S are excellent K/Ar clocks that can monitor the timing of post-depositional processes during which these phases either undergo diagenetic or burial metamorphic transformation, or actually grow anew.

ACKNOWLEDGMENTS

We are grateful to P. H. Nadeau and R. C. Reynolds for supplying the samples examined in this study and for the geological and mineralogical background obtained in their original study. We thank S. P. Altaner, R. L. Burtner, and D. R. Pevear for their critical reviews and F. A. Mumpton for careful editorial review. We also thank Linda Abel for preparing the figures. We are extremely grateful for a long and close association with John Hower who initiated, encouraged, and greatly influenced our K/Ar research on the illite clays at Case Western Reserve University. Financial support for this study was provided by NSF grant EAR-79-20064 (J. L. Aronson). M. Lee is grateful to S. M. Savin for providing a research assistantship from the OCE-76-83902 grant during the course of this study.

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(Received 11 May 1984; accepted 10 February 1986; Ms. 1370)