Clays and Clay Minerals, Vol. 47, No. 3, 286–296, 1999.

THE KINETICS OF THE SMECTITE TO ILLITE TRANSFORMATION IN CRETACEOUS BENTONITES, CERRO NEGRO, NEW MEXICO

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Abstract—The thermal effects, as well as the survivability and origins of microorganisms in Cretaceous rocks, are evaluated from the timing and extent of the smectite to illite transformation in Cretaceous bentonites collected from cores outside the thermal aureole of the Pliocene Cerro Negro volcanic neck. Overall, randomly ordered mixed-layered illite-smectite (I-S) is the predominant clay mineral in these bentonites, and the K-Ar ages of I-S range from 36 to 48 Ma (21 analyses, two additional analyses were outside this range). Increased temperature from burial is thought to be the primary factor forming I-S in these bentonites. Kinetic model calculations of the smectite to illite transformation are also consistent with I-S formed by burial without any appreciable thermal effects due to the emplacement of Cerro Negro. In a core angled toward Cerro Negro, the percentages of illite layers in I-S from the bentonite closest to Cerro Negro are slightly higher (32–37%) than in most other bentonites in this study. The K-Ar ages of the closest I-S are slightly younger as a group (38–43 Ma; Average = 41 Ma; N = 4) than those of I-S further from Cerro Negro in the same core (41–48 Ma; Average = 44 Ma; N = 6). A small amount of illite in this I-S may have formed by heat from the emplacement of Cerro Negro, but most illite formed from burial. Vitrinite reflectance, however, appears to record the effects of heating from Cerro Negro better than I-S. Tentatively, the temperature of this heat pulse, based on vitrinite data alone, ranged from 100 to 125°C and this is most evident in the CNAR core. The upper temperature, 125°C, approximates the sterilization temperatures for most microorganisms, and these temperatures probably reduced a significant portion of the microbial population. Thermophiles may have survived the increased temperatures from the combined effects of burial and the intrusion of Cerro Negro.

Key Words—Bentonite, Cerro Negro, Cretaceous, Illite, I-S, K-Ar, Kinetics, Microorganisms, New Mexico, Smectite.

INTRODUCTION

Studies combining mineralogic and chronologic data and mathematical models were successful in increasing the understanding of the formation of diagenetic illite-smectite (I-S) in argillaceous rocks. These results were also useful in studying the thermal histories of sedimentary basins (*e.g.*, Hoffman and Hower, 1979; Pollastro, 1993; Huang *et al.*, 1993; Altaner and Ylagan, 1997). The stacking order of I-S was used to constrain the maximum temperature of burial, whereas the age of I-S signified the time of maximum temperature due to burial (*e.g.*, Hoffman and Hower, 1979; Elliott *et al.*, 1991; Pollastro, 1993). The timing of basin-wide fluid migrations and petroleum generation and migration was inferred from the K-Ar ages of I-S and diagenetic illite (*e.g.*, Lee *et al.*, 1989; Barnes *et al.*, 1992). The mechanism(s) by which smectite transforms to I-S remains an open question and this mechanism may vary in different types of argillaceous rocks (Boles and Franks, 1979; Bethke and Altaner, 1986; Eberl *et al.*, 1990; Altaner and Ylagan, 1997).

Under burial diagenetic temperatures <150°C, I-S retains radiogenically produced Ar (*i.e.*, $^{*40}Ar$), and conventional K-Ar ages of I-S are interpreted as mean, or time-integrated, ages of illitization (Aronson and Hower, 1976). The duration of the transformation was estimated in several studies through mathematical models employing Arrhenius rate law expressions describing the kinetics of this transformation (Pytte and Reynolds, 1989; Elliott *et al.*, 1991; Velde and Vasseur, 1992; Elliott and Matisoff, 1996). The ability to derive both time and temperature of maximum heating makes diagenetic I-S a useful mineral for burial and basin history reconstructions. Of note, Dong *et al.* (1995) found that the $^{40}Ar/^{39}Ar$ total gas age of a diagenetic illite was concordant with the conventional K-Ar age measured for that same illite, showing the potential of Ar-Ar methods to provide precise ages of I-S. The application of the ^{40}Ar-^{39}Ar step-heating technique to I-S has also the potential to provide accurate ages of both detrital and diagenetic end-members of binary mixtures of muscovite and diagenetic I-S. This technique can potentially lead to improved age determinations of diagenetic illite in shales (Onstott *et al.*, 1997).

This study is part of a thorough evaluation of the thermal history and the geomicrobiology of the Cretaceous rocks intruded by Cerro Negro 3.39 Ma. An

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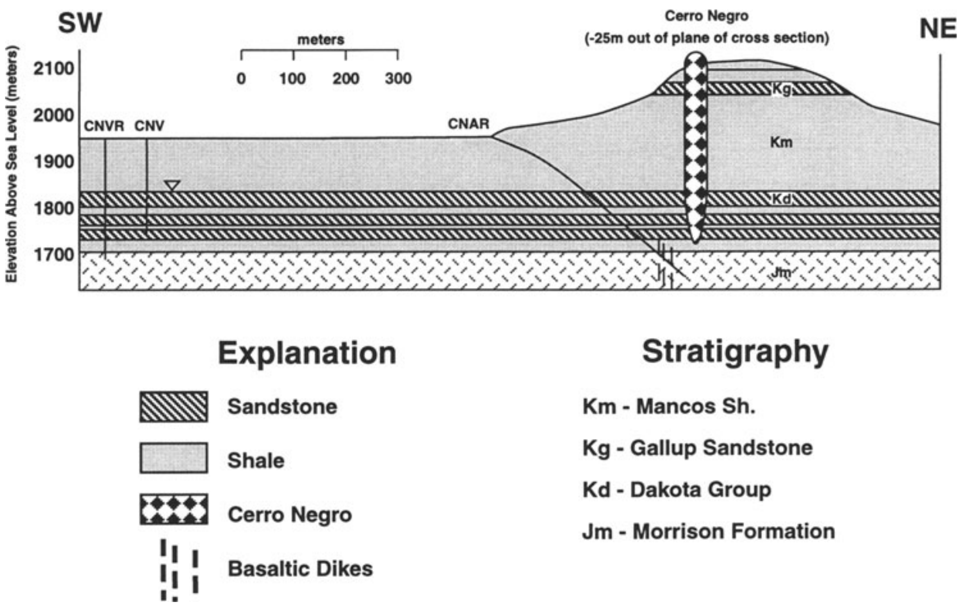

Figure 1. Geologic cross section of Cerro Negro showing Cretaceous Dakota Group and Mancos Shale, Cerro Negro, and the locations of three wells (modified after Frederickson *et al.*, 1997). The main vent of Cerro Negro is out of the plane of cross section by 25.

original goal was to constrain the maximum temperatures caused by heat from Cerro Negro by studying the timing and extent of the smectite to illite transformation. Such maximum temperature could be related to the origins and survivability of microorganisms described by Frederickson *et al.* (1997) and Krumholz *et al.* (1997) in these Cretaceous rocks. Where the temperatures derived from the emplacement of Cerro Negro were sufficiently high to have sterilized these rocks ($\geq$125°C), then microorganisms found in adjacent strata must post-date the intrusion and must have been transported into these rocks by groundwater flow. Alternatively, if the rocks sampled never reached sufficiently high temperatures to kill microorganisms, then the *in situ* microorganisms may be endemic to these strata.

Geologic Setting and Methods

Three wells (CNV, CNVR, and CNAR) were drilled through Cretaceous rocks belonging to the Dakota Group and Mancos Shale in proximity to Cerro Negro (Figure 1). Two of these wells reached the Jurassic Morrison Formation. The depositional ages of the Cretaceous strata studied herein span from 88 to 93 Ma. The details regarding the drilling and collection of cores were described by P.E. Long and J.K. Frederickson (unpubl. data, 1995) and Frederickson *et al.* (1997). The $^{40}Ar/^{39}$ Ar plateau age of Cerro Negro is 3.39 ± 0.02 Ma; the evolution and chronology of the volcanic necks in the Rio Puerco Valley were summarized by Hallett (1994) and Hallett *et al.* (1997). Thin basaltic dikes transect the CNAR core in the lower Dakota Group and Morrison Formation (Figure 1). The thicknesses of these dikes range from 0.2 to 1 m. Abundant bentonites are found in the shale members of the Dakota Group and in the Mancos Shale at Cerro Negro and throughout the Western Interior Basin (McGookey, 1972).

Burial curves for Cretaceous formations at Cerro Negro were constructed by using "Subside! A Basin Analysis Program" (Wilkerson and Hsui, 1989). This program is a backstripping method that includes decompaction and sediment removal corrections (see Sclater and Christie, 1980, for equations and derivations). The stratigraphic sequence (thickness data) for the Cerro Negro region was used to derive these burial curves (Baars *et al.*, 1988). The thickness of Tertiary sediments that may have overlain Cerro Negro is uncertain, therefore a burial curve was constructed without significant unconformities that best fit the time-temperature history of these rocks in proximity to Cerro Negro. The uplift and erosion history are less well constrained than burial and are based primarily on regional tectonic events, the level of erosion at present, and the level of erosion at the time of emplacement of Cerro Negro. The burial curves for the Oak Canyon Shale Member of the Dakota Group and the Mancos Shale at Cerro Negro are shown in Figure 2. These burial curves were used to derive Lopatin time-temperature index (TTI) values (Waples, 1980). Calculated vitrinite values and maximum temperatures were estimated from the TTI using the nomographs for Easy %Ro of Sweeney and Burnham (1990). In terms of the estimation of Ro from TTI, the Easy %Ro method is

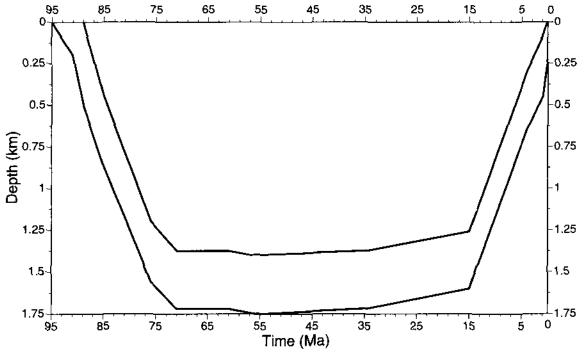

Figure 2. Burial curves for Mancos Shale and Oak Canyon Member sediments at Cerro Negro. The upper curve describes the burial of the Mancos Shale and the lower curve describes the burial of the Oak Canyon Member. Cretaceous rocks were buried progressively deeper during the late Cretaceous Period and into the early Tertiary Period as a result of the Laramide Orogeny. Uplift to present depths began slowly at 55 Ma and increased markedly at 15 Ma. Cerro Negro later intruded these strata 3.4 Ma ago (Hallett *et al.*, 1997).

similar to the Lopatin method; the Easy %Ro method, however, considers the rates of heating by different geologic processes (*e.g.*, hydrothermal heating, basinal burial).

Twenty to thirty grams of each bentonite sample were soaked overnight in deionized water and then treated at 50°C to remove carbonate, organic carbon, and iron oxides following the methods of Jackson (1979). These treatments leave I-S Na-saturated but do not have adverse effects on the K-Ar systematics of I-S (*e.g.*, Elliott and Aronson, 1987; Lee *et al.*, 1989). Sand and silt (>20 μm), coarse clay (2–20 μm), and clay (<2 μm) size fractions were obtained by timed settling and centrifugation. Submicron fractions were obtained by centrifugation. The clay minerals were identified using a Philips Model 12045 X-ray Diffractometer equipped with the MDI Databox. Air-dried, glycol-solvated, and heated (550°C) oriented clay mineral separates were analyzed on glass slides from 2 to 32 °2θ at 1 °2θ/min with CuKα X-radiation with a graphite monochromator. The stacking order of illite layers in I-S was determined by the procedures of Hower (1981). The 002(10 Å)/003(17 Å) mixed-layer peak was used to quantify the percentage of illite layers in I-S (Reynolds and Hower, 1970). To relate the measured positions of this peak to percentages of illite layers in I-S, a "best fit" curve was constructed through points plotted from the percentage of illite layers *versus* the 002(10 Å)/003(17 Å) peak position data listed in Table 7.3 of Moore and Reynolds (1989). Uncertainties were also estimated from this "best fit" curve by noting the distances between the "best fit" curve and the points used to construct it (Moore and Reynolds, 1989). The uncertainties range from <5% illite layers for I-S with <20% illite layers to ±5% illite layers for I-S with >20% illite layers. The clay mineralogy, stacking order of I-S, percentages of illite layers in I-S, and bentonite depths measured from the tops of cores are presented in Table 1.

Powdered samples of I-S for Ar isotopic analyses and K analyses were weighed on a Sartorius microbalance. The sample sizes for these analyses ranged from 50 to 130 mg for Ar isotopic analyses and 9 to 13 mg for K. Potassium was determined by atomic absorption spectrophotometry. I-S samples were dissolved in a 10:1 $HF:HClO_4$ mixture and then heated to dryness. The resultant perchlorate salts of major elements were diluted with a mixture of nitric acid (0.25 M), LiCl (0.025 M), and CsCl (0.0025 M). The absorption by K was measured from this diluted solution and the concentration of K was determined by comparing the measured absorption to a calibration curve developed from a series of reference solutions having known K concentrations. The mean of four analyses of the diluted solution was used to calculate the K content reported for each sample.

For the Ar isotopic analyses, each I-S sample was fused in a resistance heater after introduction of a known amount of ^{38}Ar into the extraction line. Two U-tube traps, each featuring an inner finger containing liquid O_2 within an outer U-tube surrounded by liquid N_2, were used sequentially to remove water and CO_2 before the extracted gases reacted with heated Ti. These traps were effective in removing water and CO_2 and retained only a negligible amount of Ar. The weight after vacuum drying was used for subsequent age calculations. The LP-6 Biotite interlaboratory reference sample was analyzed twice for its radiogenic Ar content (*i.e.*, $*^{40}Ar$). The amounts of $*^{40}Ar$ measured from LP-6 were 19.14 and 19.28 nmol g^{-1}, and these values were very close to the accepted value of 19.30 nmol g^{-1} (Odin, 1982). Further details regarding the K and Ar analyses are in Edenfield (1998).

Three mathematical models were used to simulate the smectite to illite transformation in the Mancos Shale and the Oak Canyon Member (*i.e.*, Pytte, 1982; Velde and Vasseur, 1992; Huang *et al.*, 1993). Each model features a different expression to describe the kinetics of the transformation. The burial curves (Figure 2) and a pore water K concentration of 200 ppm were used in all three models (Altaner, 1985); the additional parameters as well as the applications of these models to diverse geologic settings were described by Elliott and Matisoff (1996). Two types of simulations were employed for each of the three models. The first employed a constant geothermal gradient of either 25°C km^{-1} or 35°C km^{-1}. The second employed a constant geothermal gradient from the date of deposition to 4 Ma (approximately the time of intrusion of Cerro Negro) followed by a higher geothermal gradient (75°C km^{-1} or 105°C km^{-1}) for the last 4 Ma to present. This latter scenario describes hypothetical and

https://doi.org/10.1346/CCMN.1999.0470304 Published online by Cambridge University Press

Table 1. Clay mineralogy and percentage of illite layers in I-S.

Well, formation	Measured depth[1] (m)	Size fraction (μm)	Clay mineralogy	I in I-S (%)
CNAR, Mancos Sh.	95.79–95.97	<2	I-S (random), kaolinite	<2
CNAR, Whitewater Arroyo Sh.	307.70–307.77	<2	kaolinite, I-S (random)	45 ± 5
CNAR, Whitewater Arroyo Sh.	307.70–307.77	<0.25	I-S (random), kaolinite	32 ± 5
CNAR, Whitewater Arroyo Sh.	313.32–313.35	<2	I-S (random), kaolinite	19 ± 5
CNAR, Whitewater Arroyo Sh.	313.32–313.35	1–2	I-S (random), kaolinite	20 ± 5
CNAR, Whitewater Arroyo Sh.	313.32–313.35	<0.25	I-S (random), kaolinite	10 ± <5
CNAR, Oak Canyon Member	407.16–407.31	<2	I-S (random), kaolinite	4 ± <5
CNAR, Oak Canyon Member	420.73–420.90	<2	I-S (random), kaolinite	33 ± 5
CNAR, Oak Canyon Member	420.73–420.90	<0.25	I-S (random), kaolinite	26 ± 5
CNAR, Oak Canyon Member	441.31–441.34	<2	I-S (random), kaolinite	37 ± 5
CNAR, Oak Canyon Member	441.31–441.34	<0.25	I-S (random), kaol (tr.)	32 ± 5
CNV, Whitewater Arroyo Sh.	142.3–143.6	<2	I-S (random), kaolinite	14 ± <5
CNV, Whitewater Arroyo Sh.	148.4–150.0	<2	kaolinite, I-S (random)	13 ± <5
CNV, Oak Canyon Member	202.2	<2	I-S (random), kaolinite	30 ± 5
CNV, Oak Canyon Member	202.2	<0.25	I-S (random), kaolinite	20 ± 5
CNVR, Oak Canyon Member	202.75–203.25	<2	I-S (random), kaolinite	23 ± 5
CNVR, Oak Canyon Member	202.75–203.25	1–2	I-S (random), kaolinite	26 ± 5
CNVR, Oak Canyon Member	202.75–203.25	<0.25	I-S (random), kaolinite	26 ± 5
CNVR, Oak Canyon Member	226.30–226.32	<2	I-S (random), kaolinite	35 ± 5
CNVR, Oak Canyon Member	226.30–226.32	1–2	I-S (random), kaolinite	45 ± 5
CNVR, Oak Canyon Member	226.30–226.32	<0.25	I-S (random)	20 ± 5
CNVR, Oak Canyon Member	226.50–226.52	<2	I-S (random)	6 ± <5
CNVR, Oak Canyon Member	226.52–226.56	<2	I-S (random)	8 ± <5
CNVR, Oak Canyon Member	226.65–226.68	<2	I-S (random)	8 ± <5
CNVR, Oak Canyon Member	226.72–226.76	<2	I-S (random)	13 ± <5
CNVR, Oak Canyon Member	226.80–226.82	<2	I-S (random)	18 ± <5
CNVR, Oak Canyon Member	226.82–226.84	<2	I-S (random), kaol (tr.)	18 ± <5
CNVR, Oak Canyon Member	227.38–227.40	<2	I-S (random), kaolinite	7 ± <5

[1] For CNAR, depths are those measured from top of core.

maximum heating derived from the emplacement of Cerro Negro.

Vitrinite reflectances (VRo) were measured on kerogen prepared by standard techniques. Kerogen was isolated by sink-float at 1.8 g ml^{-1}. In these cores, the kerogen type was vitrinite derived from "woody" plant precursors. Twenty reflectance points were measured on each sample using rotational polarization. Partially oxidized organic matter, inertinite, and weathered vitrinite were not measured. Vitrinite reflectance data were measured by Carbon Consultants International, Murphysboro, Illinois under contract to Pacific Northwest National Laboratory.

RESULTS

Clay mineralogy

Randomly ordered I-S is the predominant clay mineral in these bentonites although kaolinite is a minor phase in many of the clay fractions (Table 1). The percentage of illite layers in I-S ranges from <2% (essentially smectite) to 45%. In the CNV well, three bentonites were collected, two from the Whitewater Arroyo Shale at 142.3–143.6 m and at 148.4–150.0 m, a third from the Oak Canyon Member at 202.2 m (Table 1; Figure 3a). The percentage of illite layers in I-S is slightly higher in the deeper Oak Canyon Member, to 30%, than in Whitewater Arroyo Shale (Table 1; Figure 3a). I-S of the <0.25 μm-fraction of the deepest bentonite has a smaller percentage of illite layers (20%) than the <2 μm-fraction (30%). As shown below, the K-Ar ages of these two size fractions of this I-S are essentially equal.

In well CNVR, two bentonites were collected from the Oak Canyon Member, at 202.75–203.25 m and at 226.30–226.84 m (basal contact at 227.10 m), and a shale was collected at 227.38–227.40 m (Table 1; Figure 3a). The percentage of illite layers in I-S from the highest bentonite (202.75–203.25 m) in this core was 26%. Seven subsamples were collected from the thick bentonite at 226.30–227.10 m, and the percentages of illite in I-S range from a high of 45% in the uppermost bentonite subsample (226.30–226.32 m) to 6–8% illite in I-S in the three subsamples collected from the interior of this thick bentonite at 226.50–226.68 m. The percentages of illite layers in I-S increase again toward the basal contact of this bentonite to 18% at 226.82–226.84 m, still nearly 30 cm above the basal contact at 227.10 m. The deepest sample (227.38–227.40 m) is a clayey-silty shale in which the percentage of illite in I-S is 7%.

Six bentonites were collected from the angled well, CNAR (Figure 1; Table 1). The depths of the benton-

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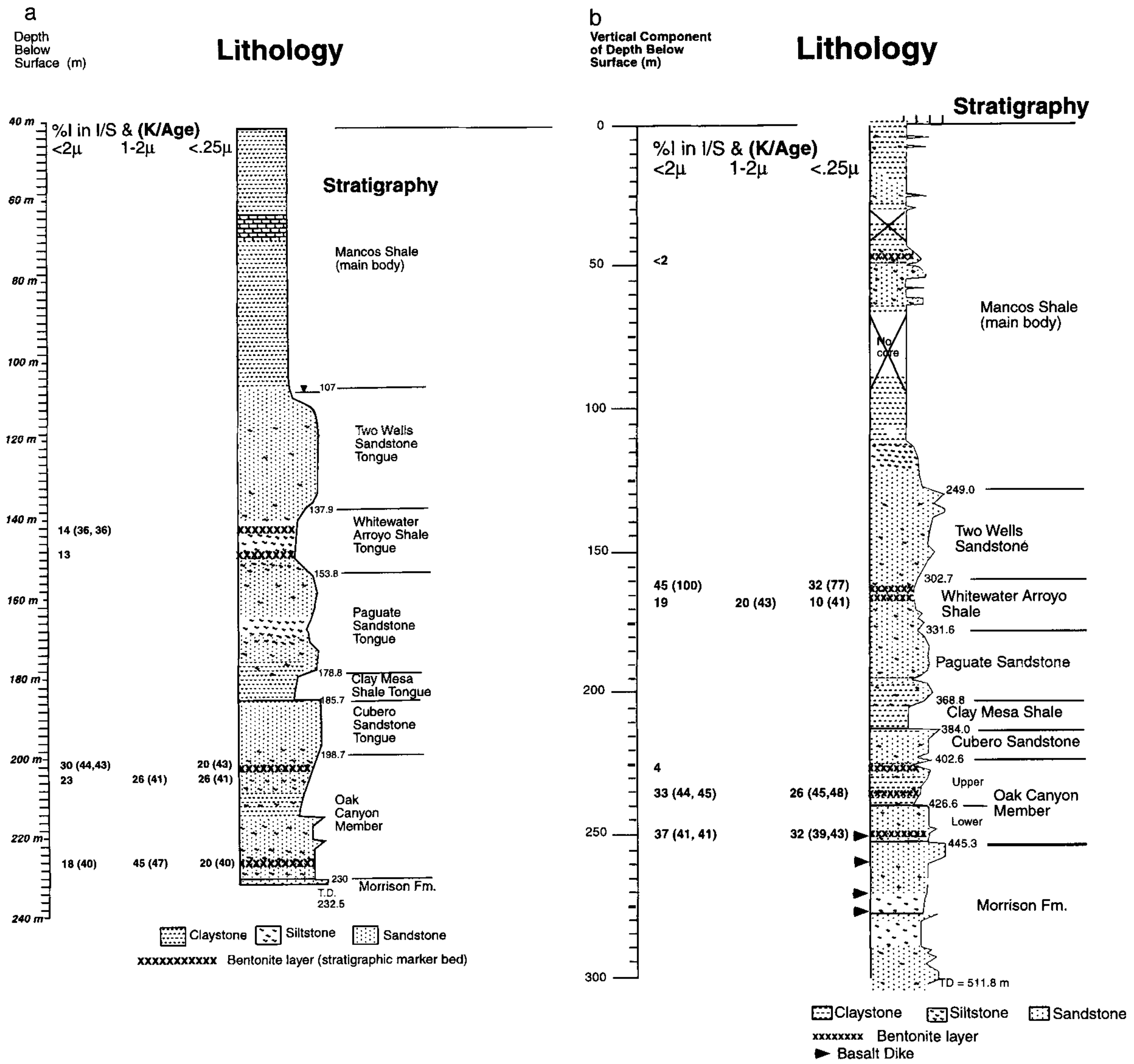

Figure 3. Stratigraphic descriptions of wells CNV, CNVR (Figure 3a), and CNAR (Figure 3b) showing the Mancos Shale, Dakota Group, the percentage of illite layers in I-S and the K-Ar ages of I-S. Note, the K-Ar ages of I-S are in parentheses. Sections drawn are from lithologic descriptions from P.E. Long and J.K. Frederickson (unpubl. data, 1995). In Figure 3a, the vertical depth is the same as the measured depths of bentonite samples. In Figure 3b, the depths of bentonites measured from the top of the core are shown to the right of the stratigraphic column, and they differ from the vertical depth components on the left edge. Arrowheads in Figure 3b denote the locations of basaltic dikes.

ites were measured from the top of the well and ranged from 95.79 to 441.31 m. The measured depths from the top of this angled well and the derived vertical components of these measured depths are both shown in Figure 3b. The bentonites collected in both of the vertical holes (CNV, CNVR) and the angled hole (CNAR) were at similar vertical depths enabling comparison of clay mineral data (*e.g.*, percentage of illite layers in I-S) and K-Ar ages of I-S from bentonites collected from all three cores. As in CNV and CNVR, randomly ordered I-S is the predominant clay mineral in the bentonites from CNAR; minor amounts of kaolinite were found in most clay fractions. The I-S range from nearly pure smectite at 407.16–407.31 m to 45% illite layers in I-S at 307.70–307.77 m (Table 1). Except for the kaolinite-rich bentonite at 307.70 m which arguably contains detrital I-S as discussed below, the I-S from the deepest bentonite (441.31–441.34 m) has the highest percentage of illite layers (32–37%). This bentonite is closest to Cerro Negro and a few meters from basalt dikes lower in this core (Figure 3b).

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Table 2. K-Ar age data of I-S.

Well, formation	Measured depth[1] (m)	Size fraction (μm)	I in I-S (%)	% K (wt. %)	*^{40}Ar (%)	*^{40}Ar (pmol g^{-1})	K-Ar age (Ma)
CNAR, Whitewater Arroyo Sh.	307.70–307.77	<2	45	1.95	68.5	348.1	100 ± 2
CNAR, Whitewater Arroyo Sh.	307.70–307.77	<0.25	32	2.52	69.5	343.4	77 ± 1
CNAR, Whitewater Arroyo Sh.	313.32–313.35	1–2	20	2.17	75.6	165.0	43 ± 1
CNAR, Whitewater Arroyo Sh.	313.32–313.35	<0.25	10	2.21	65.9	158.7	41 ± 1
CNAR, Oak Canyon Member	420.73–420.90	<2	33	2.62	67.8	221.9	44 ± 1
CNAR, Oak Canyon Member	420.73–420.90	<2	33	2.72	80.1	216.0	45 ± 1
CNAR, Oak Canyon Member	420.73–420.90	<0.25	26	2.57	75.5	205.7	45 ± 1
CNAR, Oak Canyon Member	420.73–420.90	<0.25	26	2.41	80.1	202.9	48 ± 1
CNAR, Oak Canyon Member	441.31–441.34	<2	37	3.36	53.6	245.5	41 ± 1
CNAR, Oak Canyon Member	441.31–441.34	<2	37	3.42	69.9	246.7	41 ± 1
CNAR, Oak Canyon Member	441.31–441.34	<0.25	32	3.14	75.2	213.9	39 ± 1
CNAR, Oak Canyon Member	441.31–441.34	<0.25	32	2.84	77.3	214.6	43 ± 1
CNV, Whitewater Arroyo Sh.	142.3–143.6	<2	14	1.56	26.4	105.2	36 ± 2
CNV, Whitewater Arroyo Sh.	142.3–143.6	<2	14	1.56	43.5	105.0	36 ± 1
CNV, Oak Canyon Member	202.2	<2	30	2.69	43.9	208.4	44 ± 1
CNV, Oak Canyon Member	202.2	<2	30	2.69	41.3	202.2	43 ± 1
CNV, Oak Canyon Member	202.2	<0.25	20	2.50	67.4	188.6	43 ± 1
CNVR, Oak Canyon Member	202.75–203.25	1–2	26	2.83	72.4	204.1	41 ± 1
CNVR, Oak Canyon Member	202.75–203.25	<0.25	26	2.39	56.5	169.7	41 ± 1
CNVR, Oak Canyon Member	226.30–226.32	1–2	45	3.60	78	297.9	41 ± 1
CNVR, Oak Canyon Member	226.30–226.32	<0.25	20	3.02	74.4	213.9	40 ± 1
CNVR, Oak Canyon Member	226.82–226.84	<2	18	2.81	56.8	198.0	40 ± 1
CNVR, Oak Canyon Member	226.82–226.84	<2	18	2.81	66.7	195.8	40 ± 1

[1] For CNAR, depths are those measured from top of core.

K-Ar ages

The K-Ar ages of I-S range from 36 to 48 Ma except for two anomalous old ages (77 Ma and 100 Ma) for two size fractions of the same bentonite at 307.70–307.77 m from the CNAR core (Table 2). The anomalous K-Ar ages and the high percentages of illite (32% and 45%) in I-S indicate that this bentonite contains a significant amount of detrital I-S, implying a secondary or reworked bentonite (*e.g.*, Jeans *et al.*, 1982). For the bentonite closest to the neck at 441.31–441.34 m, the K-Ar ages range from 39 to 43 Ma (Mean = 41 Ma, N = 4). The K-Ar ages of the other I-S samples from CNAR range from 41 to 48 Ma (Mean = 44 Ma, N = 6).

In the CNVR core, the ages of I-S range from 40 to 47 Ma (Table 2; Figure 3a). The one age at 47 Ma appears anomalous, and the sample also has a higher percentage of illite layers (45%). Ages of all other I-S range from 40 to 41 Ma. The older age and the higher percentage of illite layers in I-S indicate the presence of small amounts of detrital illite in the coarse fraction (1–2 μm) while the age of the finest fraction (<0.25 μm) is similar to the K-Ar ages of I-S measured from this thick bentonite. In the CNV core, the K-Ar ages of I-S range from 36 to 43 Ma.

Mathematical models

The ages and percentages of illite calculated from the mathematical models are shown in Table 3. As in previous efforts using these models, the calculated percentages of illite are taken to represent the percentages of illite layers in I-S (*e.g.*, Altaner, 1985; Elliott and Matisoff, 1996). The calculated percentages of illite layers in I-S for a geothermal gradient of 25°C km^{-1} are 43% (Mancos Shale) and 54% (Oak Canyon Member) by using the model of Velde and Vasseur (1992), 25% (Mancos Shale) and 49% (Oak Canyon Member) by the model of Huang *et al.* (1993) and from 20% (Mancos Shale) and 38% (Oak Canyon Member) by the model of Pytte (1982). Of the three models used, the results from the model of Pytte compare most favorably to the measured percentages of illite layers in I-S derived from X-ray diffraction data (XRD) (Table 1). Percentages were also calculated with a higher geothermal gradient (35°C km^{-1}) resulting in much higher percentages than those measured from XRD. The calculated ages were older than the measured K-Ar ages regardless of the model used.

The effect of heating by the Cerro Negro intrusion was simulated by increasing the geothermal gradient by 50°C km^{-1} or 70°C km^{-1} for the last 4 Ma. Two sets of simulations were employed: one with a geothermal gradient of 25°C km^{-1} increased to 75°C km^{-1} for the last 4 Ma; one using a geothermal gradient of 35°C km^{-1} increased to 105°C km^{-1} for the last 4 Ma. From the burial curve, the maximum temperatures of the Oak Canyon Member at 4 Ma are 72°C and 91°C, using the high geothermal gradients respectively (75°C km^{-1} or 105°C km^{-1}) and a surface temperature of 25°C (Figure 2). This duration (4 Ma) and extremely

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Table 3. Calculated ages of illite by three models.

Model	Formation	GTG (°C km⁻¹)	Calculated illite[2] (%)	Calculated ages of illite (Ma)
Velde and Vasseur (1992)	Mancos Sh.	25	43	53
		35	57	61
		25/75[1]	43	53
		35/105[1]	57	61
	Oak Canyon	25	54	59
		35	63	67
		25/75[1]	54	59
		35/105[1]	63	67
Pytte (1982)	Mancos Sh.	25	20	51
		35	47	58
		25/75[1]	20	51
		35/105[1]	47	58
	Oak Canyon	25	38	56
		35	66	66
		25/75[1]	38	55
		35/105[1]	67	65
Huang *et al.* (1993)	Mancos Sh.	25	25	49
		35	63	56
		25/75[1]	25	49
		35/105[1]	63	56
	Oak Canyon	25	49	53
		35	87	65
		25/75[1]	50	52
		35/105[1]	88	65

[1] Signifies increased geothermal gradient for the last 4 Ma. These models calculate the amount of illite from the loss of smectite.

[2] The percent illite is taken to be equivalent to the percent illite layers in I-S.

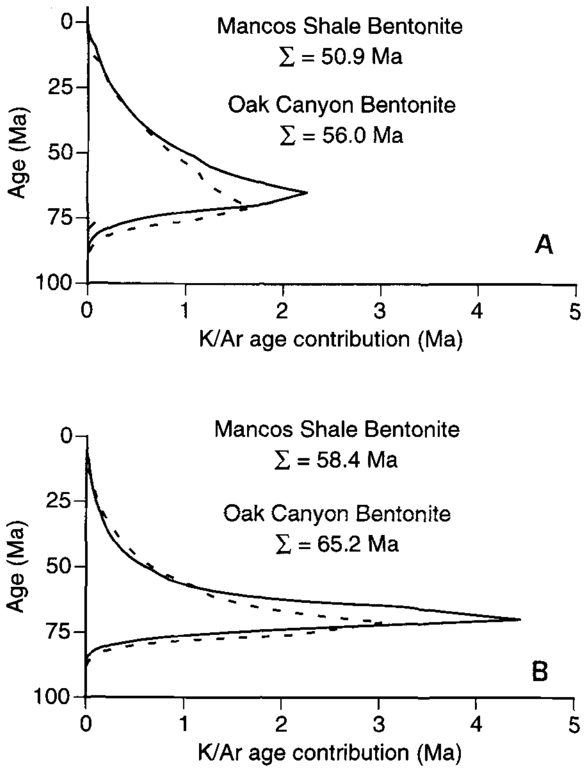

Figure 4. The contributions to the K-Ar age as a function of geologic time by the model of Pytte. The calculated mean ages of illitization (Σ) are those given for both the Mancos Shale (dashed lines) and Oak Canyon Members (solid lines) using the model of Pytte (1982) in Table 3. Figure 4a shows results using a 25°C km⁻¹ geothermal gradient. Figure 4b shows results using the highest geothermal gradient (35°C km⁻¹ increased to 105°C km⁻¹ 4 Ma ago) and using the model of Pytte (1982). Time step is 1 Ma.

high geothermal gradients comprise a hypothetical maximum time and temperature history of increased heat flow from Cerro Negro. Even with these higher geothermal gradients over the longest possible time of 4 Ma for a K pore fluid concentration of 200 ppm, there was virtually no additional formation of illite (Table 3). Higher K pore water concentrations combined with a high geothermal gradient would result in an increase in the amount of illite layers formed in I-S in a short period of time. For example, at the Salton Sea, Elliott and Matisoff (1996) demonstrated that I-S with as low as 20% illite layers can be transformed completely to illite under a high geothermal gradient (75°C km⁻¹) in the presence of high K pore water concentrations (3200 ppm) in ~20,000 years.

The ages of illite calculated by these models range from 49 Ma (Mancos Shale) to 67 Ma (Oak Canyon Member), whereas the measured K-Ar ages range from 36 to 48 Ma in Table 2 (Whitewater Arroyo Member and Oak Canyon Member) excluding the two anomalous ages. As a group, the calculated ages are <5 to 15 Ma older than the oldest measured ages of I-S. The results for the Oak Canyon Member using the models of Pytte (56 Ma) and Huang *et al.* (53 Ma) with a geothermal gradient of 25°C km⁻¹ are closest to the measured K-Ar ages for I-S. The ages of illite calculated by these models with high geothermal gradients for the last 4 Ma are not appreciably younger than the ages calculated with a constant, lower, geothermal gradient (*i.e.*, 25°C km⁻¹ or 35°C km⁻¹). Consequently, these model simulations show that an increase in geothermal gradient during the past 4 Ma resulted in little or no additional formation of illite.

The models, however, provided insight regarding the duration of the transformation and the time at which illite should have formed rapidly. The contribution to the calculated mean age of illitization at each time step is shown for the Oak Canyon and Mancos Shale bentonites in Figure 4a and 4b. By the model of Pytte, for geothermal gradients of either 25 or 35°C km⁻¹, illite formation would have peaked at ~70 Ma. This is when these Cretaceous rocks first approached their maximum depth according to the burial history. Since the initial rates at 70 Ma would be greater under the higher geothermal gradient (35°C km⁻¹), relatively more illite would have formed early to produce the

https://doi.org/10.1346/CCMN.1999.0470304 Published online by Cambridge University Press

Table 4. Vitrinite reflectance values.

Well	Formation	Measured depth (m)	Vitrinite reflectance, VRo (%)
CNAR	Mancos Shale	92.9	1.141
	Whitewater Arroyo Sh.	293.9	1.024
	Oak Canyon Member	402.9	1.129
	Oak Canyon Member	424.6	1.054
	Oak Canyon Member	441.7	1.166
CNV	Whitewater Arroyo Sh.	151.2	0.825
	Oak Canyon Member	197.0	0.947
CNVR	Oak Canyon Member	206.5	1.046
	Oak Canyon Member	224.9	0.908
	Oak Canyon Member	229.9	0.930

sharper peaks seen in Figure 4b, and the mean ages are thus greater. Similarly, the mean ages for the Oak Canyon Member are older because the initial rate of illite formation would have been greater than in the Mancos Shale (Table 3).

DISCUSSION

The combined clay mineral, K-Ar, and mathematical model results present convincing evidence that illite formed primarily by increased temperature in response to burial during the Cretaceous and early Tertiary periods when these rocks were most deeply buried (Figure 2). The emplacement of Cerro Negro was not the major cause of illite formation in these Cretaceous bentonites. In angled core CNAR, the deepest bentonite had slightly higher percentages of illite layers in I-S and the K-Ar ages of I-S were slightly younger relative to the other I-S from nearby bentonites in that well. These differences are only slightly greater than the estimated ranges of analytical error. It is possible that a small amount of younger illite was formed by the flux of heat and fluids resulting from the emplacement of Cerro Negro. Such a radial flux of heat was not represented by the kinetic models. Alternatively, this small amount of illite may have formed from additional heat supplied by the nearby basaltic dikes (Figures 1 and 3b). Otherwise, burial explains sufficiently the formation and ages of illite in bentonites collected from these cores, especially those further from Cerro Negro.

The Cretaceous Dakota Group rocks were buried to a maximum depth of 1.75 km and heated to a maximum burial temperature of 60–70°C assuming the geothermal gradient was 25°C km^{-1} and the ambient surface temperature was 20–25°C. The presence of randomly ordered I-S is consistent with this burial and heating (*e.g.*, Hoffman and Hower, 1979). The K-Ar ages of I-S range from 36 to 48 Ma (Table 2), and these mean ages of I-S correspond approximately to the mid-point (~45 Ma) of the period of deep burial extending from the late Cretaceous Period (75 Ma) to ~15 Ma (Figure 2). If illite in I-S formed via a dissolution-reprecipitation scheme or by Ostwald ripening at maximum burial temperatures (*e.g.*, Boles and Franks, 1979; Eberl *et al.*, 1990), then one might expect ages of illite to be closer to the time of uplift (15 Ma) provided the K-Ar age of I-S dates the incorporation of K into the interlayer following complete dissolution of K and removal of Ar from all previously formed illite. Since the measured K-Ar ages of illite in I-S are roughly in the mid-point of the period of deep burial and the measured percentages of illite layers in I-S are not large, it is plausible to suggest instead that the K-Ar ages reflect a mean age of illite formation via transformation (*e.g.*, Aronson and Hower, 1976).

The transformation was simulated best using the model from Pytte (1982) employing the burial curves in Figure 2. The kinetic expression (Pytte, 1982; Pytte and Reynolds, 1989) also best simulated the smectite to illite transformation in Cretaceous bentonites in the Denver Basin (Elliott *et al.*, 1991). As in the Denver Basin, the Cretaceous rocks at Cerro Negro were buried deeply for a prolonged duration. It is possible that a high-order kinetic expression with K concentrations ~200 ppm in pore waters, typically used in conjunction with the model of Pytte (1982), best describes the transformation(s) having a prolonged duration while lower-order kinetic expressions using higher concentrations of K (~3200 ppm) better describe the transformation in burial settings having a shorter duration, such as the Salton Sea or the Gulf Coast (Huang *et al.*, 1993; Elliott and Matisoff, 1996). If a higher order kinetic expression (Pytte, 1982) is eventually found to simulate more cases of prolonged burial such as Cerro Negro or Denver Basin, then the model results should be generally useful to indicate the important parameters forming illite in such settings. For now, the agreement of the model results with the measured data can be used to indicate that burial was sufficient to form the bulk of illite found in these bentonites.

Outside the thermal aureole, the migration of heat generated from the emplacement of Cerro Negro was recorded better by vitrinite reflectance (VRo) than by the ages and extent of the smectite to illite transformation. VRo increases toward Cerro Negro from 0.825–1.166% within the formations sampled from these cores (Table 4) to 2–2.5% within the aureole itself (P.E. Long and J.K. Frederickson, unpubl. data, 1995). Outside the aureole, the lowest and the highest measured VRo values correspond to TTI values of ~6 (VRo = 0.8%) and 20 (VRo = 1.1%) using a basinal burial rate model and Easy %Ro (Sweeney and Burnham, 1990). The TTI values derived from the measured VRo are greater than TTI values calculated for the base of the Mancos Shale (TTI = 2.1) and for the base of the Oak Canyon Member (TTI = 3.9) using the method of Lopatin and the burial curves in Figure 2 (Waples, 1980). The measured VRo values (0.8–

1.16%) are also greater than VRo (0.68% and 0.75%) derived from the calculated TTI values (2.1 and 3.9) using a basinal burial rate model and Easy %Ro (Sweeney and Burnham, 1990). By application of the Lopatin-type TTI analysis, burial alone could not have produced the high measured VRo values (0.8–1.1%) seen outside the aureole, particularly for CNAR whose measured VRo increased toward Cerro Negro. The VRo values measured from CNAR are likely due to heat from burial and the emplacement of Cerro Negro. For CNV and CNVR, however, the difference between the calculated VRo and the measured VRo might reflect an increased regional thermal gradient caused by increased volcanic activity associated with the Mount Taylor flow, the Mesa Prieta and Mesa Chivato trachyte flows, and the emplacement of volcanic necks just prior to and younger than Cerro Negro (Hallett *et al.*, 1997).

The percentages of illite layers in I-S also do not reflect the combined effects of heat from burial and the emplacement of Cerro Negro. TTI values of ~6 and 20, derived from the measured VRo of 0.8–1.1%, also correspond to a range of illite layers in I-S from 20 to 60% (Waples, 1980). These estimated percentages are higher than the range of measured percentages of illite layers (10–45%) in I-S in this study. Additionally, the measured percentage of illite layers did not increase significantly toward Cerro Negro with the exception of the bentonite closest to Cerro Negro (Table 1). Consequently, the overall thermal-maturity level reflected by the clay mineralogy of the bentonites is less than the thermal maturity reflected by vitrinite. The differences in temperature indicated by vitrinite reflectance *versus* the measured percentages of illite in I-S is enigmatic though not unique (*e.g.*, Velde and Lanson, 1993). At Cerro Negro, this phenomenon may be attributed to the retardation of the progressive formation of I-S by one or some combination of the following: the presence of K-poor pore fluids, a high silica content derived from the adjacent sandstones and shales (Abercrombie *et al.*, 1994), limited availability of K^+ by diffusion into thick bentonites (Altaner *et al.*, 1984; Altaner, 1989), and heating in the absence of fluids. The effects of diffusion of K^+ is observed best in the thick bentonite, in core CNVR at 226.3–227.1 m, where the percentage of illite layers ranges from 6–8% in the interior to 45% at the contacts with the adjacent shale. Diffusion of K^+ from the upper and lower contacts apparently limited the progressive formation of I-S.

In CNAR, the flow of heat from Cerro Negro is also reflected better by VRo than by the formation of I-S, and this flow is certainly capable of sterilizing rocks within the metamorphic aureole as suggested by the high VRo of 2–2.5% indicative of $T_{max} > 125°C$. Outside the aureole, the heat from burial over 60 Ma is believed to have produced VRo between 0.68–0.75%, and heat from the emplacement of Cerro Negro and other nearby volcanic activity is proposed to have increased VRo to 0.8–1.1% in a time period of <3 Ma. Using the nomograph of Sweeney and Burnham (1990, their Figure 5) and measured VRo's, these rocks are tentatively projected as heated between 100–125°C, significantly reducing microbial populations. Thermophiles, however, may have survived these temperatures.

Lastly, although significant amounts of illite were not formed outside the metamorphic aureole because of the emplacement of Cerro Negro, the formation of illite in shales in proximity to intrusions is documented elsewhere in the Western Interior Basin (*e.g.*, Nadeau and Reynolds, 1981; Pytte, 1982; Pytte and Reynolds, 1989). For example, diagenetic illite was formed in shales and bentonites more than 1 km away from the Cerrillos Intrusion (Nadeau and Reynolds, 1981). Pytte (1982), however, noted a local and sharp decrease in percentage of illite layers in I-S from nearly pure illite within late Cretaceous Pierre Shales adjacent to the Walsenburg Dike to I-S with only 20% illite layers a few meters from the dike. The gradient in percent illite in I-S *versus* distance from an intrusion is clearly related to the size and geometry of the intrusion as expected from standard thermal models (*e.g.*, Carslaw and Jager, 1986). The Cerrillos Intrusion is ~1 km in radius whereas the Walsenburg dike is 8.5 m in width (Nadeau and Reynolds, 1981; Pytte, 1982). Cerro Negro is ~50 m in diameter at the surface, and the thermal aureole is not clearly delineated but likely extends ~100–150 m (P.E. Long and J.K. Frederickson, unpubl. data, 1995). In addition, it is possible that Cerro Negro is smaller in diameter at depth (Figure 1). Given these considerations and by comparison to the Cerrillos Intrusion and the Walsenburg Dike, it is unlikely that significant amounts of illite in I-S would form in the bentonites at distances >100 m from Cerro Negro.

CONCLUSIONS

K-Ar ages, clay mineral data, and mathematical model simulations indicate that the emplacement of Cerro Negro did not cause appreciable amounts of new illite to be formed in the Cretaceous bentonites outside the aureole. Using the models of Waples (1980) and Sweeney and Burnham (1990), the VRo values of 0.825–1.166% indicate that the bentonites were exposed to higher temperatures than indicated by percent illite in I-S, and these VRo values are higher than VRo values expected from burial alone. Thus, in this case, the timing and extent of the smectite to illite transformation at Cerro Negro reflects prolonged effects of burial, whereas VRo values record the combined heat effects from burial and from emplacement of Cerro Negro. Tentatively, heat from Cerro Negro probably led to significant reduction in microbial populations for some distance outside the metamorphic aureole presumably to the deepest depths of CNAR whereas thermophiles may have survived the combined heat derived from both burial and the emplacement of Cerro Negro.

ACKNOWLEDGMENTS

This study was supported by subcontract 300614-A-F8 from the Subsurface Science Program (F. Wobber, Program Manager) of the Department of Energy through Pacific Northwest National Laboratory (PNNL) to Case Western Reserve University (G. Matisoff) and to Georgia State University (W.C. Elliott). PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy. The Chancellor's Initiative Fund at Georgia State University contributed salary support for Edenfield. The authors thank T.C. Onstott, S.P. Altaner, W.H. Hudnall, and S. Guggenheim for their comments.

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(Received 2 March 1998; accepted 30 September; Ms. 98-030)