DISTRIBUTION AND ORIGIN OF ANALCIME IN MARGINAL LACUSTRINE MUDSTONES OF THE GREEN RIVER FORMATION, SOUTH-CENTRAL UINTA BASIN, UTAH

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Abstract—X-Ray powder diffraction and thin section analyses indicate that marginal lacustrine mudstones of the Green River Formation in the south-central Uinta basin, Utah, contain abundant analcime. The analcime has a low Si/Al ratio (<2.31) and occurs as very fine grained disseminated crystals and, to a lesser extent, as coarser-grained pore-filling cement. Analcime-rich mudstones and associated sandstones, siltstones, and carbonates lack volcanic detritus and zeolites other than analcime, thus making it difficult to support the concept that the analcime formed from precursor zeolites derived from volcanic glass altered in saline, alkaline-lake water. Abundant dolomite, syneresis cracks, and the absence of freshwater pelecypods and gastropods suggest that the lake (Lake Uinta) was moderately saline and alkaline. The restricted illite-illite/smectite clay mineral suite in the analcime-rich mudstones suggests that detrital clays significantly altered in a moderately saline and alkaline environment, thereby providing a source of Si and Al for the formation of analcime.

Red mudstones contain twice as much analcime as green mudstones (14 vs. 7 wt. %). Green mudstones have a clay mineral suite consisting of illite (44 wt. %), mixed-layer illite/smectite (35 wt. %), smectite (12 wt. %), and minor kaolinite (4 wt. %) and chlorite (5 wt. %), whereas red mudstones have a more restricted clay mineral suite consisting of illite (68 wt. %) and mixed-layer illite/smectite (26 wt. %) with very minor smectite, chlorite, and kaolinite. Periodic minor fluctuations in lake level probably exposed large areas of shallow lacustrine-interdistributary green mud. Evaporative pumping on the exposed mud-flats concentrated the moderately saline and alkaline-lake water, thereby producing Na-rich brines that enhanced the formation of analcime by accelerating the alteration of detrital clays and, perhaps, other minerals. Oxidation of iron from altered iron-bearing minerals stained the analcime-rich mud red with iron hydroxide or oxide (perhaps hematite). The overall reaction from green to red mud (mudstones) was probably: detrital phyllosilicates + Na-brine + iron-bearing minerals + oxygen → analcime + iron hydroxide or iron oxide.

Key Words—Analcime, Diagenesis, Illite/smectite, Mudstone, X-ray powder diffraction, Zeolite.

INTRODUCTION

Analcime, a sodium zeolite having an ideal structural formula of $Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$, is a common authigenic silicate mineral in sediments and sedimentary rocks. It occurs in numerous geologic settings: (1) saline, alkaline lake deposits, (2) saline, alkaline soils, (3) marine sediments, (4) deposits formed by percolating water in open hydrologic systems, (5) burial diagenesis deposits, and (6) hydrothermal alteration deposits (Hay, 1977, 1978; Sheppard, 1973). Saline, alkaline-lake deposits are the most common and well-documented of these occurrences (Surdam, 1977; Surdam and Sheppard, 1978). Most modern and ancient analcime-bearing lacustrine deposits contain abundant tuffaceous material. The combination of highly reactive volcanic detritus (particularly glass) with saline, alkaline solutions is considered ideal for the formation of analcime and other zeolites. Analcime, however, does not form directly from glass (Surdam and Sheppard, 1978); rather, it forms from alteration products of glass by the reactions: silicic glass + saline, alkaline-lake water → precursor mineral + saline, alkaline-lake water → analcime (Surdam and Parker, 1972). Alkali

zeolites are the most widely-reported precursors of analcime in modern lakes and ancient lacustrine deposits (Surdam and Sheppard, 1978). The reaction of alkali zeolite to analcime is favored by an increase in salinity and alkalinity because an increase in these parameters decreases the activity of water and the Si/Al ratio and increases the Na^+/H^+ ratio, all of which favor the formation of analcime (Surdam and Sheppard, 1978). In addition to alkali zeolites, gels (Surdam and Eugster, 1976) and clay minerals (Brobst and Tucker, 1973) derived from glass have been proposed as precursors for analcime in saline, alkaline lakes. Analcime has altered to potassium feldspar in the presence of highly saline and alkaline solutions (Surdam and Sheppard, 1978).

Some saline, alkaline-lake deposits that contain analcime lack significant volcanic detritus (Sheppard, 1971). Van Houten (1962), Hay (1966), Sheppard (1971), and Wu (1970) have proposed that analcime may precipitate directly from saline, alkaline-lake water. Others have suggested that analcime may form as a product of the alteration of detrital clays in saline, alkaline lakes (Keller, 1952; Hay and Moiola, 1963; Pipkin, 1967; Hay, 1970; Hay and Guldman, 1986).

Table 1. Reported occurrences of analcime in the Green River Formation.

Reference	Location; stratigraphic interval	Lithology	Proposed origin
Dyni (1976)	Utah; Parachute Creek Mbr.	oil shale, claystone	(not specified)
Cole and Picard (1978)	Utah, Colorado; Parachute Creek Mbr.	oil shale, tuff, marlstone	silicic glass or clay → zeolite precursor → analcime
Bradley (1929)	Utah, Colorado, Wyoming; upper Green River Formation	oil shale, tuff	dissolution products of silicic glass + salts in lake → analcime
Brobst and Tucker (1974)	Colorado; Parachute Creek Mbr.	oil shale, tuff	silicic glass → precursor clays and zeolites → analcime
Brobst and Tucker (1973)	Colorado; Parachute Creek Mbr.	oil shale, tuff, marlstone	silicic glass → precursor clays and zeolites → analcime; and from alteration products of detrital clays
Hosterman and Dyni (1972)	Colorado; Parachute Creek and Evacuation Creek Mbrs.	oil shale, tuffaceous sandstone	(not specified)
Smith and Milton (1966)	Colorado	oil shale	nepheline and halloysite → analcime
Desborough (1975)	Colorado; Parachute Creek Mbr., Wyoming; Wilkins Peak and Tipton Shale Mbrs.	tuff	(not specified)
Goodwin (1973)	Wyoming	tuff	silicic glass → alkali zeolites → analcime
Surdam and Parker (1972)	Wyoming	tuff	silicic glass → alkali zeolites → analcime
Roehler (1972)	Wyoming; Laney Mbr.	oil shale, tuff, tuffaceous sandstone	silicic glass → montmorillonite clinoptilolite and mordenite → analcime
Goodwin and Surdam (1967)	Wyoming; Tipton Shale Mbr.	tuff	silicic glass → alkali zeolites → analcime
Iijima and Hay (1968)	Wyoming; upper Wilkins Peak Mbr., upper Tipton Shale Mbr., Laney Mbr.	tuff	silicic glass → precursor zeolite → analcime
Ratterman and Surdam (1981)	Wyoming; Laney Mbr.	tuff	silicic glass → precursor zeolite + upwelling Na-carbonate brine → analcime

X-ray powder diffraction (XRD) analyses of marginal lacustrine rocks of the Green River Formation (Eocene) in the south-central Uinta basin, Utah (Figure 1), performed as part of a study of depositional environments, revealed the presence of abundant analcime in red and green marginal-lacustrine mudstones (Remy and Ferrell, 1987). Although analcime is a common accessory mineral in the Green River Formation, a review of reported occurrences of analcime in the formation (Table 1) shows that: (1) most reported analcime occurs in tuffs or oil shales, not mudstones, (2) analcime had not previously been reported in marginal lacustrine rocks of the south-central Uinta basin, and (3) most researchers argue that analcime in the formation formed by the reactions: silicic glass → precursor zeolite → analcime. Our field and laboratory analyses, however, and the published thin-section analyses of Jacob (1969), Banks (1981), and Pitman *et al.* (1982) indicate that the Green River Formation in the south-central Uinta basin does not contain zeolites other than analcime and received, at most, only minor volcanic detritus. The purpose of the present study was: (1) to describe the occurrence, mineralogy, and distribution of analcime-bearing mudstones and related rocks

of the south-central Uinta basin, and (2) to test the hypothesis that the analcime was derived from detrital clays and not from precursor zeolites derived from silicic vitric material.

MATERIALS AND METHODS

Marginal lacustrine mudstones and associated sandstones, siltstones, and carbonates were examined in outcrops in Nine Mile Canyon and its tributaries and along the Roan Cliffs in the south-central Uinta basin (Figure 1). The study section includes the carbonate marker unit of Ryder *et al.* (1976), which marks the base of the main body of the Green River Formation, the entire delta facies of Bradley (1931), and the lower half of the Parachute Creek Member (as defined by Cashion and Donnell, 1974). The top of the study section was defined by the Horse Bench Sandstone of the Parachute Creek Member. Fifteen stratigraphic sections totaling nearly 3500 m were measured by one of us (R.R.R.) to determine the color, thickness, grain size, sedimentary structures, nature of bounding surfaces, geometry, and fossil content of red and green mudstones, sandstones, siltstones, and carbonates.

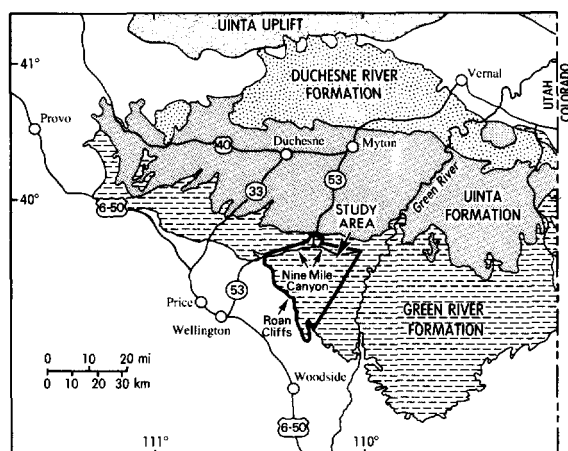Thin sections of mudstones, sandstones, siltstones,

Figure 1.   Map showing location of Green River Formation outcrop and study area in Uinta basin of northeastern Utah. (Base map modified from Fouch *et al.*, 1976.)

Figure 2.   Relationship between position of analcime 639 peak (in °2θ for CuKα radiation) and Si/Al ratio and composition of analcime. Also shown is mean Si/Al ratio and composition of analcime in marginal lacustrine mudstones of Green River Formation. (Modified from Coombs and Whetten, 1967.)

and carbonates were examined to determine the mineralogy and texture of the rocks and to study the texture and distribution of analcime. Several mudstones were examined with a JEOL T300 scanning electron microscope equipped with an attached energy-dispersive X-ray analyzer to examine the grain size and morphology of analcime. XRD analyses using a Philips APD 3520 X-ray diffractometer and monochromatic CuKα radiation and theta-compensating slits were conducted to determine the mineralogy of bulk rock and clay-size fractions of mudstones, and to determine the Si/Al ratio of the analcime. The bulk mineralogical composition of 76 mudstones, carbonates, siltstones, and sandstones was determined by XRD using the quantitative procedure described by Cook *et al.* (1975). Their mineral factors for calcite, dolomite, quartz, potassium feldspar, plagioclase, and analcime were used in the quantitative analysis, except for the following modifications: calcite window, 29.25°–29.85°2θ; calcite intensity factor, 1.92; dolomite window, 30.75°–31.25°2θ; dolomite intensity factor, 2.00; potassium feldspar intensity factor, 1.50; plagioclase intensity factor, 1.50. A new category to represent the total clay mineral wt. % was created with a window from 19.50°–20.10°2θ and an intensity factor of 20.00. The bulk rock XRD patterns were used to identify minerals excluded from the computer analysis. Conventional techniques (Schultz, 1964) were employed to estimate semiquantitatively the clay mineral compositions of 17 red and green mudstones from the Green River Formation and one red shale from the underlying Colton Formation.

The mean Si/Al ratio of analcime in 41 mudstone samples was determined by employing the technique of Saha (1959, 1961) and the calibration curve of Coombs and Whetten (1967). The technique is based
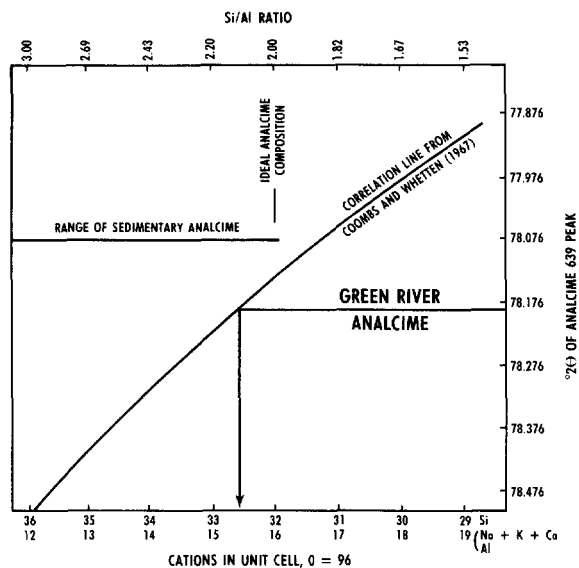
on the observation that the position of the analcime 639 peak (as determined by XRD) shifts toward higher degrees 2θ as the Si/Al ratio of analcime increases (Figure 2). The standard technique was modified by using the position of the quartz 203 peak (68.13°2θ), rather than the position of the silicon 331 peak (76.376°2θ) as an internal standard. The correlation curve of Coombs and Whetten (1967) was used to convert the position of the analcime 639 peak to the Si/Al ratio of the analcime (Figure 2). Electron microprobe analyses of 16 analcime crystals from three different samples using a JEOL JXA733 electron microprobe were made to determine the composition and Si/Al ratio of analcime, using a modified Bence-Albee procedure and Amelia albite and Kakanui hornblende as standards (Ferrell and Carpenter, 1989).

RESULTS

Field observations

The Eocene Green River Formation of the south-central Uinta basin consists of 700–800 m of clastic-rich marginal-lacustrine rocks of the informal carbonate marker unit of Ryder *et al.* (1976) and the delta facies of Bradley (1931) overlain by 300–400 m of finer-grained open-lacustrine deposits of the Parachute Creek Member (Remy, 1989a). The marginal-lacustrine rocks were deposited in a large fluvial-deltaic complex along the southern shore of Eocene Lake Uinta (Jacob, 1969; Remy, 1989a, 1989b). According to
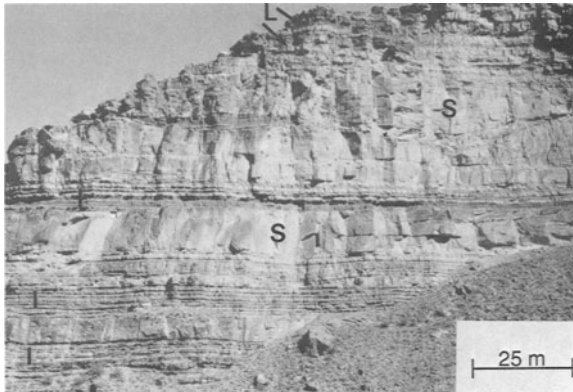
Figure 3. Typical exposure of marginal lacustrine rocks of Green River Formation in south-central Uinta basin. Note thick fluvial-deltaic sandstones (S) with erosive bases and lateral accretion bedding, interbedded sandstones and mudstones (I) (mudstones are recessed rocks in the photo) of interdeltaic origin, and limestones (L) deposited in lake-margin carbonate-flats.
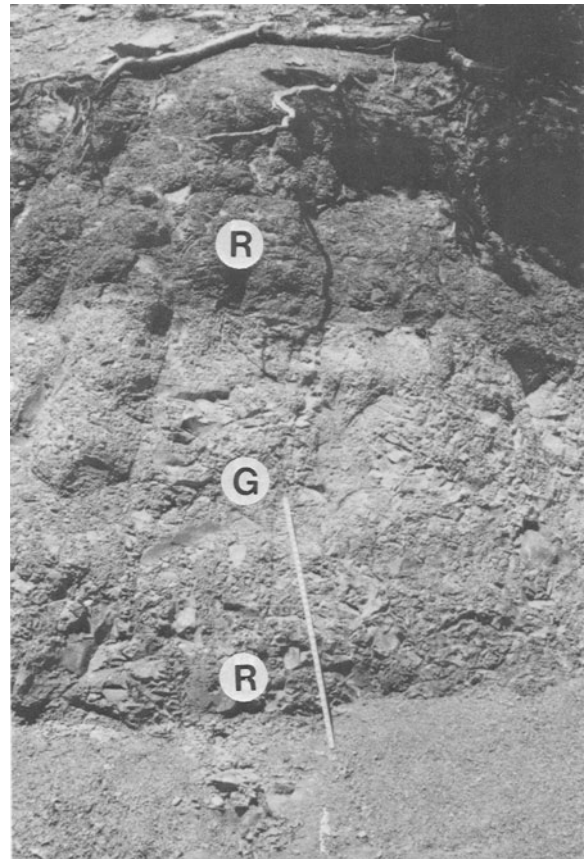

Figure 4. Typical exposure of red (R) and green (G) mudstones. Contacts between mudstones of different color vary from sharp (upper contact in photo) to gradational (lower contact). The rocks are characteristically structureless and weather into piles of millimeter- to centimeter-size angular fragments. Jacob staff (1.5 m) for scale.

the depositional model of Ryder *et al.* (1976), the marginal lacustrine rocks consist of thick (>5 m) fluvial-deltaic lenticular sandstones, thinner (<5 m) sandstones, siltstones, and red and green mudstones deposited in the interdeltaic environment, and limestones (particularly ostracode- and oolite-grainstones and stromatolites) deposited in lake-margin carbonate-flats (Figure 3). Because it had no outlet, Lake Uinta underwent frequent fluctuations in depth and shoreline position (Ryder *et al.,* 1976). According to Johnson (1985), following an initial freshwater stage Lake Uinta became gradually more saline through time. The marginal lacustrine rocks are overlain by open-lacustrine fine-grained carbonate (including minor oil shale), mudstone, siltstone, and minor sandstone of the Parachute Creek Member deposited during a major transgression of the lake. Tuffs are absent in the lower marginal-lacustrine part of the formation, but are moderately abundant in the transgressive upper part of the formation (personal field observation). Fouch *et al.* (1976), Franczyk *et al.* (1989), and Remy (1989a) described the stratigraphy, lithologies, and depositional environments of the study area.

The color of the mudstone changes systematically from red and purple to greenish gray and grayish green to dark gray and brown (Ryder *et al.,* 1976). Red and purple mudstones occur in the alluvial and subaerially exposed marginal lacustrine environments, grayish green and greenish gray mudstones were deposited in shallow lacustrine-interdistributary mudflats, and the generally finer-grained and commonly organic-rich dark gray and brown mudstones were deposited in the open lacustrine environment. Contacts between mudstones of different color are sharp to gradational (Figure 4), and color mottling is common (personal field observation). Red mudstones are absent from the transgressive upper third of the formation.

Most mudstones are slightly silty to very silty (personal field observation). Silty mudstones are commonly gradational with siltstones and sandstones, whereas finer-grained carbonate-rich mudstones are commonly gradational with limestones and dolostones. Mudstone beds range from a few centimeters to a few meters thick and are commonly truncated by lenticular sandstones and siltstones. Mud cracks are the only common sedimentary structure in mudstones. Mud cracks in green mudstones are commonly filled with ostracodes. Root casts, burrows, and other sedimentary structures are rare. The rocks also generally lack fine laminations or fissility and cannot be classified as shales. Shales are common only within the carbonate
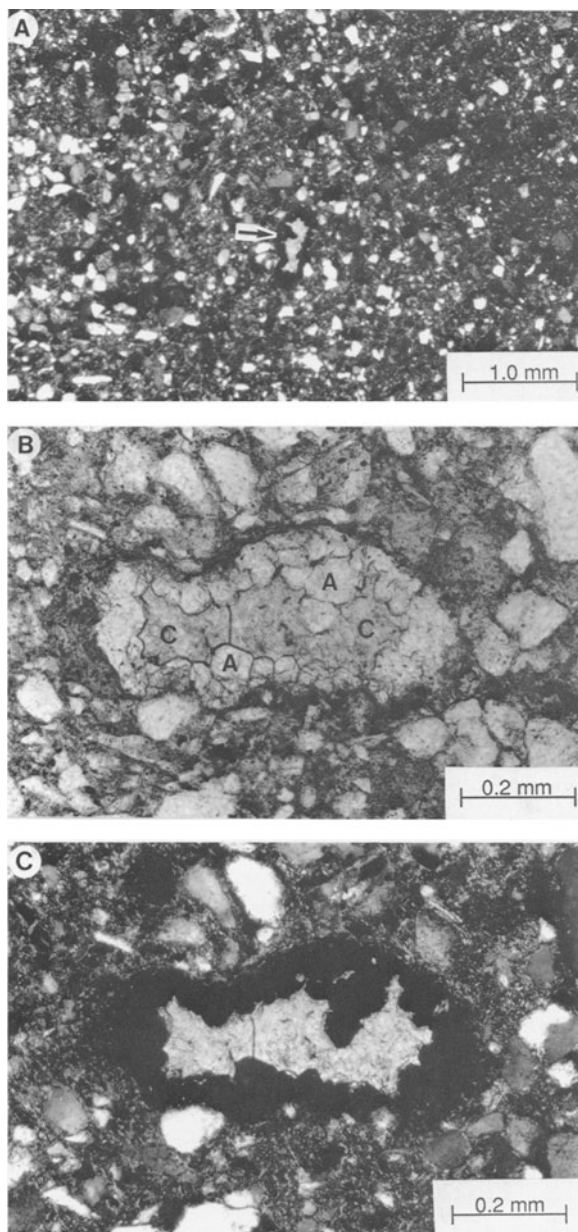
Figure 5. Photomicrographs of analcime-bearing green mudstone (sample NMC18-1B). A. Low-magnification view in crossed polars showing detrital quartz and feldspar (large grains) in matrix of phyllosilicates, carbonates, and analcime. Arrow points to void lined by analcime (black) and filled with calcite (white). See Table 3 for mineralogical composition of this sample. B and C. Close-up views of analcime-lined void indicated in A, in plane polarized light (B) and crossed polars (C). Analcime (A) crystals are clear, equant, and nearly isotropic. Center of void is filled with calcite (C). The dark fine grained material surrounding the former void is composed of phyllosilicates.

marker unit, which occurs at the base of the main body of the formation. Most mudstone beds characteristically weather into piles of centimeter- to millimeter-size, angular, equidimensional fragments (Figure 4). Green mudstone is commonly thickly to thinly interbedded with limestone and locally contains ostracodes, whereas red mudstone lacks ostracodes and rarely coexists with limestone.

Thin section petrography

Mudstones consist of varying proportions of silt-size quartz, feldspar, and micas in a fine-grained matrix of phyllosilicates, carbonates, and analcime (Figure 5A). Petrographic examination of the mudstones supports the field observation that the rocks are generally massive and structureless. In thin section, silt is generally evenly disseminated in the rock, and burrows, root casts, and other sedimentary structures are rare. Only the finest-grained clay-rich mudstones exhibit alignment of clay minerals and micas. In places, voids are lined by analcime crystals (Figures 5B and 5C). These relatively coarse-grained analcime crystals are equant, clear, and nearly isotropic. Analcime-lined voids are commonly filled with calcite. XRD analyses (see below) show that red and green mudstones contain, on average, 14 and 7 wt. % analcime, respectively. Pore-lining analcime, however, never constitutes more than a small percentage of a sample, indicating that most of the analcime in the mudstones is very fine grained and disseminated. Scanning electron microscope (SEM) analyses of several mudstones show that the analcime is too fine grained to be readily observable under SEM.

From SEMs of sandstones from the Sunnyside tar sand deposit, which is in the southern part of the study area along the Roan Cliffs (Figure 1), Pollastro and Schenk (1986) identified unspecified amounts of analcime, chabazite, and erionite. XRD and thin section analyses of sandstones of the study area, however, failed to reveal the presence of any zeolites, including analcime. Whether the zeolites reported by Pollastro and Schenk (1986) are unique to the Sunnyside tar sands or occur in amounts too small to be detected by routine XRD analyses and are too fine grained to be identified in thin section is unknown.

In addition to mudstones and sandstones, several dozen siltstones, carbonates, and tuffs were examined in thin section for the presence of zeolites and volcanic detritus. Tuffs are the only rocks other than mudstones that contain discernible analcime. Except for tuffs and a few sandstones in the transgressive upper part of the formation (Parachute Creek Member), volcanic glass, volcanic rock fragments, volcanic glass pseudomorphs, concentrations of hornblende, augite, or other heavy minerals, volcanic quartz, or any other evidence for volcanic detritus were not found in rocks of the study area.

Table 2. Average mineralogical composition of major lithologies by X-ray powder diffraction.

| Lithology | Mean weight percent | | | | | | | Number of samples |
	Calcite	Dolomite	Quartz	Potassium feldspar	Plagioclase	Analcime	Clay	
Sandstone	13	4	47	12	22	0	2	3
Siltstone	5	7	43	9	16	3	17	17
Limestone	54	30	7	1	5	1	2	5
Dolostone	19	65	6	2	2	1	5	9
Dark mudstone	10	14	26	4	11	9	26	5
Green mudstone	15	10	24	4	8	7	32	18
Red mudstone	5	6	30	5	10	14	30	19

Mineralogy of mudstones, sandstones, siltstones, and carbonates

Bulk mineralogy. Table 2 lists the average mineralogy of sandstone, siltstone, limestone, dolostone, dark mudstone, green mudstone, and red mudstone as determined by XRD analysis. Sandstone and siltstone contain >60 wt. % quartz and feldspar, as determined by XRD analysis. The distinction between sandstone and siltstone is based on mean grain size. Carbonates (limestones and dolostones) are rocks containing >60 wt. % calcite + dolomite. Limestones contain more calcite than dolomite, whereas dolostones contain more dolomite than calcite. Mudstones are fine-grained, non-laminated rocks that contain variable proportions of detrital silt-size and some sand-size quartz and feldspar, detrital and authigenic(?) phyllosilicates, and authigenic carbonates and analcime. As herein defined, mudstones do not contain more than 60 wt. % carbonates or more than 60 wt. % quartz + feldspar.

Table 3 lists the bulk mineralogy of 42 mudstones. The mudstones are divided into three color groups for purposes of mineralogical comparison: (1) dark mudstones, which include medium to dark green, gray, and brown mudstones, (2) green mudstones, which include various shades of light green, gray, and greenish gray mudstones, and (3) red mudstones, which include both purple and red mudstones. All three mudstone types contain abundant quartz, feldspar, and clay minerals of presumed detrital origin. Red mudstones are analcime-rich (14 wt. %) and contain minor calcite and dolomite, whereas the green and dark mudstones are relatively analcime-poor (7 and 9 wt. %, respectively) and carbonate-rich. A single red shale sample from the underlying, mainly fluvial, Colton Formation was found to be devoid of analcime. Mineralogical differences within the three mudstone categories are moderate (Table 3). Red mudstones contain 0.5–23 wt. % analcime, and the green mudstones contain 0–17 wt. % analcime. Several red mudstones mineralogically resemble the green and gray mudstones, and several green mudstones mineralogically resemble the red mudstones. Mudstones are mineralogically gradational with siltstones, limestones, and dolostones.

The fine-grained to very fine grained sandstones consist of quartz (47 wt. %), feldspar (34 wt. %), calcite (13 wt. %), and minor dolomite and clay. The siltstones are also feldspar-rich and contain relatively abundant clay (17 wt. %) and minor dolomite, calcite, and analcime. Thin section analyses indicated that the carbonates occurred principally as intergranular cements. The XRD analyses support the petrographic analyses of Banks (1981), Pitman *et al.* (1982), and Dickinson *et al.* (1986) who suggested that these feldspar-rich clastic sediments were derived chiefly from granitic gneissic basement rocks exposed in the Laramide San Luis uplift of south-central Colorado.

Limestones in the study area are mainly ostracode- and oolite-grainstones, stromatolites, and micrites. Mineralogically, these rocks are composed of calcite (54 wt. %) and dolomite (30 wt. %), subordinate quartz and feldspar, and very minor analcime (1 wt. %) and clay minerals. The dolostones consist of dolomite (65 wt. %), subordinate calcite (19 wt. %), and minor quartz, feldspar, analcime (1 wt. %), and clay minerals. Petrographically, the dolostones are of two types: (1) fine-grained laminated and commonly organic-rich rocks deposited in the open lacustrine environment, and (2) dolomitized marginal-lacustrine ostracode- and oolite-grainstones, stromatolites, and micrites.

Analyses of two tuffs from the Parachute Creek Member show that the rocks contain >20 wt. % analcime. In addition to analcime, one of the analyzed tuffs contains abundant plagioclase (43 wt. %) and subordinate quartz (20 wt. %) and clay minerals (10 wt. %), whereas the other tuff contains abundant calcite (52 wt. %) and subordinate quartz (4 wt. %), potassium feldspar (5 wt. %), plagioclase (1 wt. %), and clay minerals (14 wt. %).

In summary, except for a few tuffs, the greatest concentrations of analcime are in marginal lacustrine mudstones. Red mudstone contains twice as much analcime as green mudstone (14 vs. 7 wt. %), and analcime was the only zeolite detected in the rocks.

Clay mineralogy. The clay mineral content of 33 mudstones was examined by means of XRD analysis. The quality of nearly half (15) of the XRD patterns was too poor to use because abundant clay-size analcime interfered with the orientation of the clay flakes. Results

Table 3.   Mineralogical composition of mudstones as determined by X-ray powder diffraction analysis.

Lithology and sample no.	Calcite	Dolomite	Quartz	Potassium feldspar	Plagioclase	Analcime	Clay
Dark mudstone							
1-8-1	0	48	16	4	13	1	18
1-11-1	26	7	23	4	12	tr	28
3-13-2	6	11	40	6	13	11	13
11-23	4	7	27	3	8	2	49
3-6	13	0	22	3	11	30	21
Green mudstone							
WUB2	17	2	25	2	3	0	51
1-3-1	0	1	18	4	5	2	70
Top MS1	20	8	16	4	5	3	44
CSD	31	23	12	0	11	4	19
NMC10-1B	3	4	35	4	11	8	35
4-12-1B	43	11	7	0	4	11	24
IC5	5	0	26	4	8	17	40
1-34-1B	19	13	29	8	9	4	18
9-79B	5	0	26	6	14	17	32
9-97	11	3	37	5	14	9	21
9-164	8	47	16	3	5	4	17
7-49-2	6	11	34	5	10	6	28
7-109-1	15	32	20	11	4	0	18
14-9	1	4	30	6	19	12	28
NMC6	25	6	21	4	10	8	26
11-16	27	7	25	2	5	3	31
11-30	21	11	18	3	8	2	37
9-10B	4	0	35	6	9	13	33
Red mudstone							
1-36-1	4	0	43	5	9	18	21
1-72-1	2	9	39	7	12	8	23
NMC10-1A	2	4	25	0	6	14	49
NMC18-1A	1	1	37	7	5	3	46
1-34-1A	3	0	31	5	11	23	27
BPR5	8	18	31	5	11	11	16
BPR6	tr	16	39	5	11	10	19
NMC14-1	4	0	42	5	13	13	23
3-16-1	5	9	26	4	6	20	30
3-14-2	0	12	19	4	8	16	41
3-8-1	2	9	28	5	13	18	25
3-12-1A	1	0	26	0	11	20	42
4-2-1A	14	0	35	7	15	11	18
9-79A	7	0	27	7	15	17	27
BMS1-6	10	19	36	3	6	11	15
BMS1-1	5	13	24	5	8	13	32
Below MS9	10	0	29	5	14	16	26
7-61-1	5	1	22	2	5	1	64
9-10A	12	0	23	5	8	16	36

from the 17 useable analyses are presented in Table 4. The clay mineral fraction of red and green mudstones in the Green River Formation is dominated by illite and illite/smectite. The red mudstones contain minor chlorite (1 wt. %) and smectite (5 wt. %), whereas the green mudstones contain a more abundant accessory suite of clay minerals consisting of kaolinite (4 wt. %), chlorite (5 wt. %), and smectite (12 wt. %). XRD analysis of a red shale from the underlying Colton Formation indicates that these shales contain illite/smectite (69 wt. %), kaolinite (15 wt. %), and illite (16 wt. %).

Composition of analcime

Analcime has an ideal structural formula of $Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$ and an ideal Si/Al ratio of 2.0. The structural formula and Si/Al ratio of natural analcime, however, varies widely. Analcime crystals from tuffs in the Green River Formation of Wyoming exhibit a range of Si/Al ratios from 1.95 to 2.90 (Iijima and Hay, 1968). The Si/Al ratio of analcime is an important parameter, because it provides information on the conditions under which the analcime formed (Saha, 1961; Coombs and Whetten, 1967; Iijima and Hay, 1968;

Table 4. Comparison of clay mineralogy of red and green mudstone.

Lithology	Statistics	Weight percent					Number of samples
		Kaolinite	Chlorite	Illite	Smectite	Mixed-layer illite/smectite	
Green mudstone	Mean	4	5	44	12	35	10
	Range	0–13	0–19	0–85	0–65	5–76	
	Standard deviation	6	6	21	24	26	
Red mudstone	Mean	trace	1	68	5	26	7
	Range	0–2	0–4	38–82	0–21	18–51	
	Standard deviation	1	2	19	8	5	

Mariner and Surdam, 1970; Boles, 1971; Goodwin, 1973; Surdam, 1977).

According to electron microprobe analyses, analcime in marginal lacustrine mudstones of the study area has an average Si/Al ratio of 2.30 (Tables 5 and 6; Figure 6). The Si/Al ratio of analcime as determined by the position of the analcime 639 XRD peak is 2.10 (Table 6; Figure 2). Both analytical techniques thereby indicate that the analcime is a low-silica variety relative to the range of Si/Al ratios exhibited by natural analcime. The difference between the Si/Al ratio of analcime as determined by electron microprobe and XRD analysis is probably statistically significant given the small standard deviations of the results of the analyses (Table 6). Goodwin (1973) also found that microprobe analyses yielded higher Si/Al ratios than the XRD method. He argued that XRD is probably the more accurate of the two analytical techniques because it is insensitive to mineral impurities in analcime, whereas microprobe analyses may include minute inclusions of quartz or noncrystalline silica, thereby overestimating the amount of silica in analcime. The reason for the difference in the Si/Al ratio of Green River Formation analcime in the study area as determined by the two analytical techniques could not be assessed.

DISCUSSION

Origin of analcime

Evidence analcime was not derived from volcanic glass. Most researchers have suggested that analcime in the Green River Formation formed by the reactions: silicic glass + saline, alkaline-lake water → precursor mineral (generally an alkali zeolite) + saline, alkaline-lake water → analcime (Table 1). Two lines of evidence, however, strongly suggest that analcime in marginal lacustrine mudstones of the south-central Uinta basin did not form from precursor zeolites derived from vitric material. (1) XRD and thin section analyses show that analcime is the only zeolite in the rocks. (2) There is no trace of the large quantities of volcanic material required to produce the analcime detected in the mudstones. Thin section analyses of Jacob (1969), Banks (1981), and Pitman *et al.* (1982) support the conclusion of this study (*vide supra*) that the lower two-thirds of

the study section contains, at most, only a very minor amount of volcanic detritus. Whereas volcanic glass is highly unstable and probably would not have survived in the moderately saline and alkaline water of Lake Uinta, other types of volcanic detritus such as volcanic quartz, volcanic rock fragments, hornblende, and augite are relatively stable. Field and thin section analyses indicate that volcanic detritus in the form of augite and hornblende concentrations in sandstones and as discrete tuffs occur only in the upper third of the study section in the Parachute Creek Member, indicating that such material could and did survive in the saline and alkaline environment of Lake Uinta. Moreover, red mudstones from the lower part of the study section

Table 5. Chemical composition and Si/Al ratio of analcime determined by electron microprobe analysis.

Sample no.[1] and analysis no.	Oxide weight percent[2]			Si/Al ratio
	SiO_2	Al_2O_3	Na_2O	
4-2-1A				
1	61.87	23.98	14.15	2.19
2	62.50	24.12	13.38	2.19
3	64.11	23.23	12.66	2.33
4	62.42	23.60	13.98	2.24
5	63.82	23.78	12.40	2.28
6	61.45	24.03	14.52	2.17
NMC10-1A				
7	62.42	23.52	14.06	2.25
8	64.51	23.23	12.26	2.36
9	62.58	23.50	13.92	2.26
10	68.24	24.83	6.92	2.33
11	65.06	23.29	11.65	2.37
BPR6				
12	64.40	23.05	12.55	2.37
13	64.05	22.47	13.48	2.41
14	63.70	23.50	12.80	2.30
15	64.05	22.21	13.74	2.45
16	63.20	22.80	14.00	2.35

[1] Each analysis is from a different analcime crystal. The locations of analyses 1, 2, 3 in sample 4-2-1A and 14, 15, 16 in sample BPR6 are shown on back-scattered electron photomicrographs of Figure 6. The mineralogical composition of samples 4-2-1A, NMC10-1A, and BPR6 are shown in Table 3.

[2] Oxide weight percentages recalculated to 100, excluding water. Other oxides account for <3 wt. % of total oxides in analcime.

Table 6. Comparison of Si/Al ratio and structural formulae of analcime determined by electron microprobe analysis and d-value of analcime 639 peak.

	Si/Al ratio			
Analytical technique	Mean	Standard deviation	Structural formula of analcime	Number of samples
Electron microprobe	2.30	0.08	$Na_{14.5}Al_{14.5}Si_{33.5}O_{96} \cdot nH_2O$	16
d-value of analcime 639 peak	2.10	0.07	$Na_{15.4}Al_{15.4}Si_{32.6}O_{96} \cdot nH_2O$	41

contain more analcime than the green and dark mudstones from the relatively tuff-rich upper section, indicating that the distribution of analcime was not controlled by the distribution of volcanic detritus. We conclude, therefore, that: (1) the absence of significant amounts of volcanic detritus in most of the study section is due to non-deposition of this material rather than post-depositional removal, and (2) the analcime in the study section was not derived from precursor zeolites derived from volcanic glass.

Evidence analcime was derived from alteration of detrital clays. Some researchers have suggested that analcime may have formed as an alteration product of clays deposited in a saline, alkaline lake (Keller, 1952; Hay and Moiola, 1963; Pipkin, 1967; Hay, 1970; Hay and Guldman, 1986). Detrital clay minerals are known to react extensively in a saline, alkaline environment (Hay and Moiola, 1963; Hay, 1966; Brobst and Tucker, 1973; Hay and Guldman, 1986). The clay mineralogy of the Green River Formation has been examined by several researchers. In the Tipton Shale Member of the Green River Formation in Wyoming, Tank (1969) found a correlation between lithology and clay mineral suite: analcime-rich tuffs contained only illite, coarser clastics contained chlorite and illite, and montmorillonite-rich tuffs and oil shales contained montmorillonite- and illite-dominated clay suites. Brobst and Tucker (1973) examined the mineralogy of oil shales, marlstones, and tuffs of the Parachute Creek Member in the Piceance Creek basin by XRD and found that oil shales and marlstones contained minor illite and that tuffs contained minor illite and chlorite. They attributed the absence of abundant clay minerals in the fine-grained rocks to the destruction of detrital clays in the alkaline lake environment.

Saline lakes commonly exhibit a salinity gradient with the freshest water occurring near the lake margin and the denser, more saline water in the lake center, which is often also a topographic low (Eugster and Hardie, 1978). Tuffs deposited in saline, alkaline lakes commonly exhibit a zonal arrangement of authigenic minerals that reflect these lateral salinity gradients (Surdam, 1977; Eugster and Hardie, 1978). These mineral zonations are well-documented in modern and ancient lake deposits (Sheppard and Gude, 1968, 1969), including the Green River Formation (Surdam and Parker, 1972), and consist of a peripheral zone of un-

altered glass succeeded basinward by zones of alkali zeolites, analcime, and potassium feldspar at the basin center. Carbonates in saline, alkaline lakes exhibit salinity-controlled zonations, with calcite occurring near lake margins and dolomite occurring in lake centers (figure 11 of Dyni, 1976). Clay minerals in the Green River Formation also appear to exhibit salinity-controlled zonations. Dyni (1976) and Hosterman and Dyni (1972) examined the mineralogy of oil shales, marlstones, and tuffs of the Parachute Creek Member in Indian Canyon, which is west of the present study area in the Uinta basin, and in the Piceance Creek basin, respectively, and found that rocks deposited in the fluvial or freshwater lacustrine environments contain kaolinite, illite, mixed-layer clays, and smectite (montmorillonite), rocks deposited in nearshore fresh to moderately saline environments contain illite and smectite (montmorillonite), and offshore lacustrine environments contain only illite. The hypersaline depocenter of the Piceance Creek basin is nearly devoid of clay minerals due to dissolution in highly saline and alkaline fluids (Dyni, 1985). The hypothesis that detrital clay minerals undergo extensive alteration in a saline, alkaline environment is supported by analyses of smectite and illite in the Green River Formation, which suggest that the minerals have undergone extensive alteration (Dyni, 1985). The clay mineral suite of mudstones of the study area (Table 4) resembles the restricted illite-illite/smectite suite of Dyni (1976, 1985) and Hosterman and Dyni (1972).

Because the freshwater fluvial equivalents to the analcime-rich mudstones of the study area have been removed by erosion, it is impossible to determine whether a clay mineral zonation like that described above ever existed in the study area. Shales deposited in fluvial environments, however, occur in the underlying Colton and North Horn Formations and in the Flagstaff Member of the Green River Formation. Petrographic analyses of Stanley and Collinson (1979), Pitman et al. (1982), and Dickinson et al. (1986) show that the Colton and Green River Formations in the Uinta basin received feldspathic sediment derived principally from basement rocks. The North Horn Formation was derived from several sources (Dickinson et al., 1986), including the basement rocks which became the principal sediment source for the overlying Colton and Green River Formations. The fact that these rocks were derived, at least in part, from the same

source area suggests that they probably had roughly similar clay mineral suites at the time of deposition. XRD analysis of a red shale from the Colton Formation indicates that these shales contain more illite/smecite (69 wt. %) and kaolinite (15 wt. %) and less illite (16 wt. %) than either red or green mudstones of the Green River Formation. According to Fouch *et al.* (1987), shales of the North Horn Formation and the Flagstaff Member of the Green River Formation, which underlie the Colton Formation, contain small to moderate amounts of illite, kaolinite, chlorite, and illite/smectite. In other words, shales deposited in the predominantly freshwater environments of the Colton and North Horn Formations and the Flagstaff Member of the Green River Formation contain a wide variety of clay minerals, whereas the red and green mudstones of the main body of the Green River Formation contain a restricted illite-illite/smectite clay suite. Moreover, the fact that red and green mudstones contain different clay mineral suites despite the fact that they presumably originally had similar detrital clay minerals strongly suggests that clays underwent post-depositional alteration. These observations suggest that detrital kaolinite and chlorite, and perhaps illite/smectite and smectite may have been altered to illite, and perhaps also dissolved, in ancient Lake Uinta.

Evidence for saline, alkaline conditions. Analcime in marginal lacustrine mudstones of the south-central Uinta basin exhibits a low Si/Al ratio. According to Boles (1971) and Surdam (1977), analcime inherits the Si/Al ratio of its zeolite precursor. Evidence discussed above, however, strongly suggests that the analcime did not form from a zeolite precursor. Coombs and Whetten (1967) argued that silica-rich analcimes formed by reaction of acid volcanic ash with saline water, silica-poor analcimes formed either by direct chemical precipitation or by reaction of clay minerals with waters of high alkalinity, and analcimes formed during burial metamorphism have an intermediate Si/Al ratio. Others have stated that an increase in salinity (Iijima and Hay, 1968) or pH (Mariner and Surdam, 1970; Goodwin, 1973) of solutions in contact with an analcime precursor mineral causes a decrease in the Si/Al ratio of the resulting analcime. The presence of low-silica analcime in the study area therefore suggests that the analcime formed from clay or other non-zeolite precursors in contact with saline and alkaline fluids.

Several observations suggest that Lake Uinta was at least moderately saline and alkaline during deposition of the analcime-rich mudstones. (1) Except for the carbonate marker unit, which occurs at the bottom of the main body of the formation, the Green River Formation in the south-central Uinta basin generally lacks freshwater gastropods and pelecypods. (2) Dolomite is a common mineral in mudstones, dolostones, and oil shales of the study section. Dolomite forms in high pH
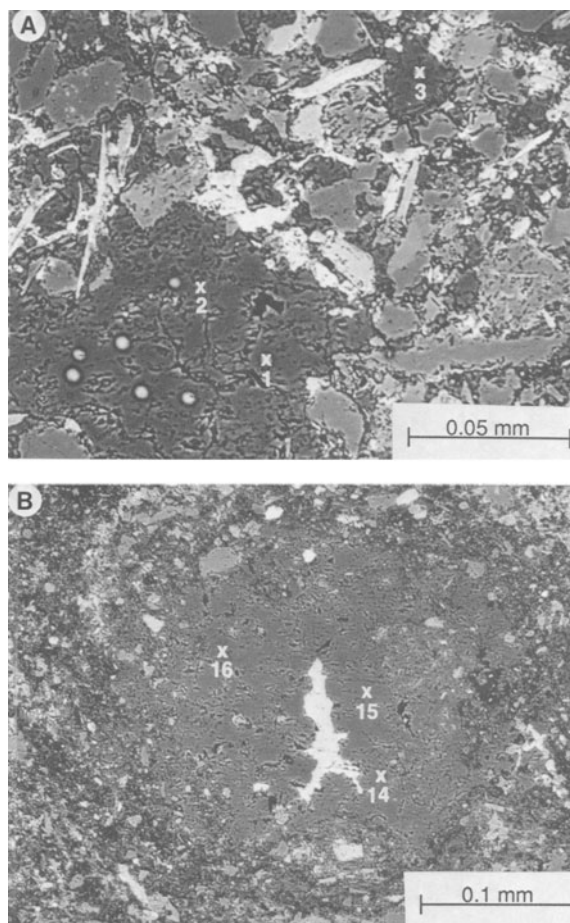

Figure 6.   Back-scattered electron micrographs showing several analcime crystals analyzed by electron microprobe. Results of analyses of spots 1, 2, and 3 on A and spots 14, 15, and 16 on B are presented in Table 5.

and alkaline lakes (Kelts and Hsü, 1978) and generally does not precipitate in freshwater lakes (Jones and Bowser, 1978). (3) Syneresis cracks are moderately abundant in the lower half of the study section, but are very abundant in the upper half of the study section. Syneresis cracks are believed to be produced by the subaqueous shrinkage of clays, due either to clay flocculation or salinity-induced changes in volume of certain clay minerals (Collinson and Thompson, 1982). The upward increase in abundace of syneresis cracks in the study section thereby suggests that the lake underwent an increase in salinity. Johnson (1985) indicated that following an initial freshwater phase, Lake Uinta became gradually more saline through time, ultimately resulting in the precipitation of nahcolite and halite during the final stages of the lake. The saline, alkaline-lake waters of Lake Uinta facilitated the formation of analcime by altering clay, and perhaps other minerals, thereby releasing Si and Al, and by providing Na for the formation of analcime.
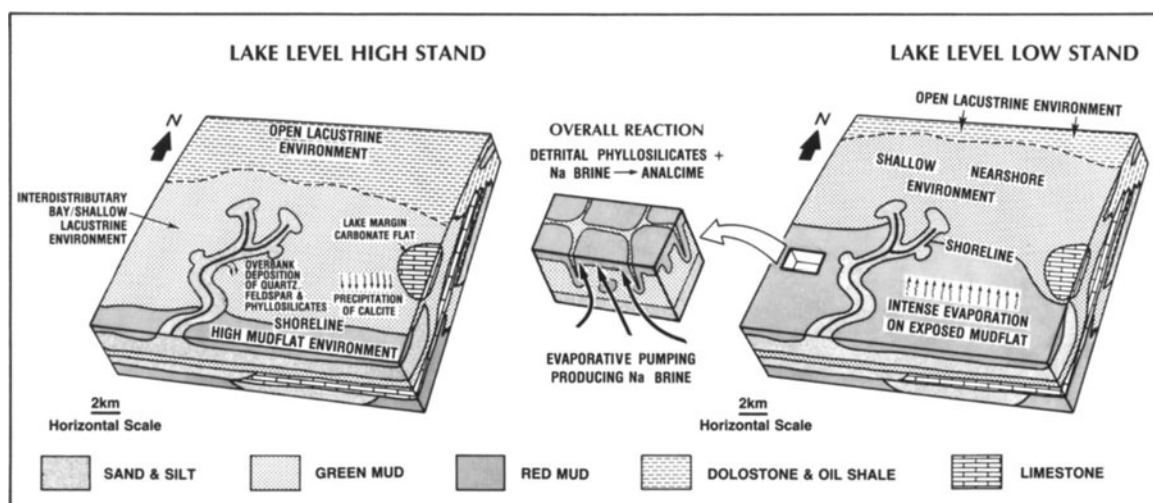
Figure 7. Geochemical-sedimentological model showing origin of analcime-rich red mudstones along southern shore of Eocene Lake Uinta. During lake-level high-stands, detrital quartz, feldspar, and phyllosilicates, authigenic carbonates, and minor analcime derived from phyllosilicates altered in moderately saline, alkaline-lake water accumulated in the interdistributary bay and shallow lacustrine environments. During lake-level low-stands intense evaporation on exposed mudflats produced Na-rich brines which facilitated formation of analcime by enhancing alteration of phyllosilicates and serving as a concentrated source of Na for analcime. Alteration of iron-bearing minerals produced iron hydroxide or oxide (perhaps hematite) which stained the analcime-rich mud red. Horizontal scale is approximate.

Although the salinity and alkalinity of the lake at the time of analcime formation cannot be measured directly, two observations suggest that the lake was only moderately saline and alkaline. (1) No halite or other evaporite minerals have been reported in the study section. (2) In highly saline and alkaline environments analcime has altered to potassium feldspar (Surdam and Sheppard, 1978). The absence of evidence for conversion of analcime to potassium feldspar in mudstones of the study area indicates that the salinity and alkalinity were not high enough to favor such a reaction.

Origin of mineralogical difference between red and green mudstones

Red mudstones contain much more analcime and less kaolinite, chlorite, and smectite than green and dark mudstones. Red mudstones are common in the alluvial and marginal lacustrine environments of the lake. Because it had no outlet, the depth and shoreline position of Lake Uinta oscillated nearly continuously (Ryder et al., 1976). During low stands of the lake, parts of the shallow lacustrine-interdistributary environment were exposed, leading to the formation of extensive mudflats where clay clasts, mud cracks, and red coloration were produced in the fine-grained sediment (green mud). Intense evaporation on the surface of exposed fine-grained sediment causes evaporative pumping (Hsü and Siegenthaler, 1969), a process by which loss of fluids at the surface of the sediment by evaporation causes capillary draw of fluids upward

through the sediment. Given enough time, evaporative pumping produces a brine within the sediment and an efflorescent crust at the surface (Eugster and Hardie, 1978). Surdam and Stanley (1979), Smoot (1978), and Ryder et al. (1976) postulated that evaporative pumping produced Mg-rich brines which dolomitized much of the shallow lacustrine carbonates deposited along the shores of the Green River Formation lakes. Sodium is one of the most abundant ions in saline and saline, alkaline lakes (Eugster and Hardie, 1978). Therefore, the brines produced by evaporative pumping were presumably rich in sodium as well as magnesium. We postulate that subaerial exposure of shallow lacustrine-interdistributary fine-grained sediments led to evaporative pumping on the exposed mudflats, thereby concentrating the moderately saline and alkaline lake water (Figure 7). The resulting Na-Mg-carbonate brine facilitated the formation of analcime by accelerating the alteration of detrital clays, and perhaps other minerals, and by providing a source of abundant sodium. Alteration of iron-bearing minerals released iron, which oxidized, thereby producing an iron hydroxide or iron oxide (perhaps hematite) which stained the originally greenish mud red. Our model is similar to that of Hay (1970), who suggested that analcime and other minerals were formed in Pleistocene alluvial deposits of Olduvai Gorge, Tanzania, by reaction of detrital clays with sodium carbonate solutions concentrated at the land surface by evapotranspiration.

The argument that clays in the red mudstones underwent more alteration than clays in green mudstones is

supported by XRD analyses (Table 4), which show that green mudstones have a more extensive accessory clay mineral suite than red mudstones. Red mudstones contain more illite and less illite/smectite than green mudstones, suggesting that illite/smectite was altered to illite.

The overall reaction from green, analcime-poor mud (mudstone) to red, analcime-rich mud (mudstone) was: detrital clays + Na-Mg brine produced by evaporative pumping + iron-bearing minerals + oxygen → analcime + iron oxide or iron hydroxide. Whether the analcime directly replaced clay minerals or formed from the Si and Al released from altering clays is uncertain; however, the presence of minor pore-lining analcime (Figures 5B and 5C) indicates that at least some of the analcime precipitated in pores. Most of the analcime occurs as very fine grained crystals that probably precipitated in the micropores between clays and other constituents of the fine-grained mudstones.

SUMMARY AND CONCLUSIONS

1. Marginal lacustrine red and green mudstones in the Green River Formation of the south-central Uinta basin contain, on average, 14 wt. % and 7 wt. % analcime, respectively. The analcime has a low Si/Al ratio (<2.31) and occurs as very fine grained disseminated crystals and, to a lesser extent, as coarser-grained pore-filling cement.

2. The lack of volcanic detritus and zeolites other than analcime strongly suggests that the analcime was derived from a precursor other than an alkali zeolite derived from volcanic glass. The restricted illite-illite/smectite clay mineral suite of the mudstones, differences between the clay mineral suites of red and green mudstones, and evidence for moderately saline and alkaline-lake water suggest that detrital clays altered in saline, alkaline Lake Uinta were the precursors to the analcime.

3. Frequent minor fluctuations in lake level periodically exposed shallow lacustrine-interdistributary greenish mud composed of authigenic carbonates, minor authigenic analcime, and detrital phyllosilicates and silt. Evaporative pumping caused by intense evaporation on the exposed mudflats produced Na-carbonate brines, which enhanced the formation of analcime by accelerating the destruction of detrital clays, thereby releasing Si and Al for analcime formation, and by serving as a concentrated source of Na (Figure 7). Iron was oxidized, staining the mud red with iron hyroxide or oxide (perhaps hematite). The overall reaction from green to red mudstones was: detrital phyllosilicates + Na-brine + iron-bearing minerals + oxygen → analcime + iron hydroxide or iron oxide.

ACKNOWLEDGMENTS

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