THE AMERICAN MINERALOGIST, VOL. 50, MAY–JUNE, 1965

MONTMORILLONITE PSEUDOMORPHIC AFTER PLAGIOCLASE IN A PORPHYRY COPPER DEPOSIT[1]

ROBERT O. FOURNIER, *U. S. Geological Survey, Washington, D. C.*

INTRODUCTION

Plagioclase is completely altered to montmorillonite in some portions of a hydrothermally altered porphyritic rock located in the Liberty Pit porphyry copper mine near Ely, Nevada. In these places the altered rock is easily crumbled in one's hand and perfect pseudomorphs of montmorillonite after plagioclase can readily be picked out of the debris. In view of the high purity of this montmorillonite as compared to most montmorillonite, it was decided to investigate this material to see where it lay in the montmorillonite-beidellite group and to examine various determinative techniques in the light of the composition. The material described in this paper was collected from near the bottom of the northwest corner of the Liberty Pit at about 103,300N, 101,500E and 6500 feet elevation.

The host rock initially was a monzonite or quartz monzonite with euhedral phenocrysts of sodic plagioclase, orthoclase, and hornblende set in an aplitic groundmass composed mainly of quartz and orthoclase. In the montmorillonite-bearing rock orthoclase is unaltered, hornblende alters to biotite and chlorite, and plagioclase altered mainly to montmorillonite. In some places mixtures of montmorillonite, 2M muscovite, and kaolinite are found after plagioclase. However, where appreciable muscovite or kaolinite is present, pseudomorphs of clay after plagioclase are not preserved when the rock is crumbled. Pyrite, chalcopyrite and molybdenite grains are disseminated throughout the rock and the following kinds of veins are common: a) calcite, b) calcite plus quartz plus montmorillonite, c) montmorillonite, d) chabazite plus stillbite.

SEPARATION OF MATERIAL FOR ANALYSIS

Two rock samples, about 15 feet apart, were collected and pseudomorphs of montmorillonite after plagioclase were hand picked from each sample. The montmorillonite picked from rock sample 1 was disaggregated in water with the aid of an ultrasonic vibrator. This was followed by separation of the fine-grained montmorillonite from coarser-grained impurities by differential rates of settling. The clay which settled within 6 hours in a water column 15 inches tall was discarded and the remaining suspended material was removed from the water, dried at room tempera-

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[1] Publication authorized by the Director, U. S. Geological Survey.

ture and analyzed. Samples 1a and 1b in Table 1 are duplicate separations.

Hand-picked montmorillonite from sample 2 was ground in a mullite mortar and pestle, dispersed by vigorous stirring in bromoform of specific gravity 2.3, and finally centrifuged to remove heavy impurities from the sample. Samples 2a and 2b in Table 1 are duplicate separations by this process.

Sample 3, vein montmorillonite, is from a coating in a fracture which cut rock sample 2. The montmorillonite was scraped from the rock and further cleaned by hand-picking impurities from the sample with the aid of a binocular microscope.

ANALYTICAL METHODS AND RESULTS

The montmorillonite samples were analyzed by methods described by Shapiro and Brannock (1962). The results are shown in Table 1. The distribution of elements among possible lattice sites within the generally accepted montmorillonite framework was estimated by the method described by Kelley (1955). In addition to the assumptions made by Kelley, the following assumptions were employed here:

1) After subtracting enough iron to combine with all the sulfur in the sample to form pyrite, all the remaining iron is present in the ferric state and this iron substitutes for aluminum in octahedral position. 2) All potassium is present as muscovite impurity and appropriate silica and alumina are assigned to muscovite. 3) Magnesium occurs in octahedral

TABLE 1. CHEMICAL ANALYSES OF MONTMORILLONITE[1]

Sample	Weight per cent				
	1a	1b	2a	2b	3
SiO_2	50.0	50.1	51.7	50.4	51.0
Al_2O_3	21.6	22.0	20.2	21.0	20.0
Total iron as Fe_2O_3	.83	.83	.77	.83	.60
MgO	3.3	3.1	3.4	3.5	3.4
CaO	2.3	2.3	2.5	2.3	2.4
Na_2O	.06	.06	.09	.07	.10
K_2O	.60	.52	.84	.60	.36
H_2O^-	12.8	13.2	13.0	14.2	14.3
H_2O^+	8.0	7.8	7.4	7.2	7.3
Aqua regia soluble S as SO_4	.07	.04	.09	.06	.10
Sum	99.56	99.95	99.99	100.16	99.56

[1] Analyses by Paul Elmore, Samuel Botts, Gillison Chloe, Lowell Artis and H. Smith, U. S. Geological Survey.

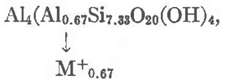
position only to the extent that the sum of Al^{3+}, Fe^{3+}, and Mg^{2+} equals 4 cations per unit cell containing 20 oxygens and 4 OH^-.

All other magnesium is assigned to exchangeable interlayer positions. The importance of magnesium as an exchangeable cation in montmorillonite has been discussed by other workers including Kelley (1945), Foster (1951) and Osthaus (1955).

Table 2 shows the calculated distribution of cations in lattice positions for each sample as well as those for ideal montmorillonite and beidellite. In sample 1 about 41 per cent of the charge deficiency originates in the tetrahedral layers and the remaining 59 per cent in the octahedral layer. Approximately 17 per cent of the magnesium is assigned to interlayered sites. Samples 2 and 3 are very similar; 26 to 27 per cent of the charge deficiency is in the tetrahedral layers and 9 to 10 per cent of the magnesium is in interlayer positions.

As a check on the calculated quantities of cations in interlayered positions, the exchangeable cations were analyzed after being leached from 1 gram portions of each sample by base exchange with lithium chloride. The base exchange was accomplished for each sample by washing and filtering 4 successive times each with 30 ml of 3M lithium chloride solution. The filtrates were made up to known volumes and Ca^{2+} and Mg^{2+} were determined by versine titration and Na^+ and K^+ were determined by flame photometry[1]. Corrections were made for impurities of these constituents in the initial LiCl solution. The filtrate also was analyzed for alumina and silica. No alumina was found and only insignificant amounts of silica were present, less than 0.002 moles per 100 gram sample. The analyses of the exchangeable cations in the filtrate are shown in Table 3 along with the quantities of exchangeable cations predicted from the calculated distribution of cations tabulated in Table 2. There is very good agreement between the predicted and measured values and the analytical precision does not warrant a recalculation of the distribution of all cations in lattice positions to give complete agreement with measured values of exchangeable cations.

After correcting for silica and alumina in hypothetical muscovite impurity, the Si:Al atomic ratios in the montmorillonite samples 1, 2, and 3 are, respectively, 4.06:2; 4.49:2; and 4.46:2, as compared to 3:2 for ideal beidellite.



$$\begin{array}{c} Al_4(Al_{0.67}Si_{7.33}O_{20}(OH)_4, \\ \downarrow \\ M^{+}_{0.67} \end{array}$$

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[1] Foster (1951) used a similar technique, using 1N NH_4Cl to leach cations from montmorillonite by base exchange. Exchangeable magnesium and other cations were then directly determined and these values were used as a basis for calculating the distribution of rations in the lattice.

TABLE 2. CALCULATED DISTRIBUTION OF CATIONS IN LATTICE POSITIONS

	Sample 1 Average 1a and 1b		Sample 2 Average 2a and 2b		Sample 3		Ideal Montmorillonite		Ideal Beidellite	
Tetrahedral	Si 7.564	net charge	Si 7.726	net charge	Si 7.748	net charge	Si 8.00	net charge	Si 7.33	net charge
	Al .436	− .436	Al .274	− .274	Al .252	−.252	Al 0	0	Al .67	−.67
	8.000		8.000		8.000		8.00		8.00	
Octahedral	Al 3.284		Al 3.170		Al 3.213		Al 3.33		Al 4.00	
	Fe .095		Fe .091		Fe .066		Fe 0		Fe 0	
	Mg .621	− .621	Mg .739	− .739	Mg .721	−.721	Mg .67	−.67	Mg 0	0
	4.000	−1.057	4.000	−1.013	4.000	−.973	4.00	−.67	4.00	−.67
Interlayer	Mg .132		Mg .083		Mg .070		Mg 0		Mg 0	
	Ca .389	+1.060	Ca .411	+1.013	Ca .401	+.972	Ca .335	+.67	Ca .335	+.67
	Na .018		Na .025		Na .030		Na 0		Na 0	

and 4.8:2 for ideal montmorillonite,

$$\underset{\displaystyle M^{+}_{0.67}}{\underset{\downarrow}{Al_{3.33}Mg_{0.67}}}(Si_8O_{20}(OH)_4$$

OPTICAL, X-RAY, DIFFERENTIAL THERMAL AND DENSITY INVESTIGATION

No differences could be detected in the respective optical, *x*-ray, and differential thermal analysis (DTA) characteristics among the montmorillonites in the three rock samples. Individual grains are about 2 microns in maximum dimension, and the indices of refraction are $\alpha = 1.489 \pm .002$ and $\gamma = 1.517 \pm .002$. The bulk density of eight pseudomorphs of montmorillonite after plagioclase ranged from 2.040 to 2.125 and averaged 2.095. An *x*-ray diffractometer pattern is shown in Fig. 1 and a DTA pattern in Fig. 2.

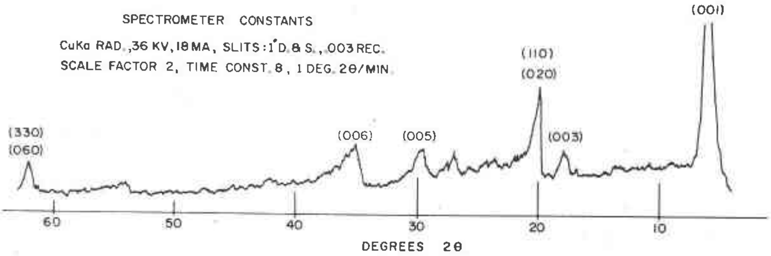

FIG. 1. *X*-ray diffractometer pattern of montmorillonite pseudomorphic after plagioclase from the Liberty mine. Air dried and untreated.

The basal spacing of air-dried material is 15.0 Å. Treatment with ethylene glycol expands the basal spacing to 17 Å. Li-saturated material has a basal spacing of 12.4 Å, and, after heating it at 200° C. for 16 hours, the basal spacing is found to be collapsed to 9.9 Å. This heated Li-saturated montmorillonite does not expand upon treatment with glycerol but does re-expand to 17 Å upon further treatment with ethylene glycol.

Using glycerol as an expanding agent, Greene-Kelly (1953) observed that Li-saturated montmorillonite collapses irreversibly when heated to 200°–300° C., whereas beidellite similarly treated does not. According to these criteria the material described here would be classified as montmorillonite. Chemical analyses show the material to be intermediate in composition between beidellite and montmorillonite, but closer to montmorillonite (MacEwan, 1961, p. 155–158). Upon glycolation of the heated Li-saturated material, no rational or irrational series of reflections was found which would have indicated either a regular or irregular

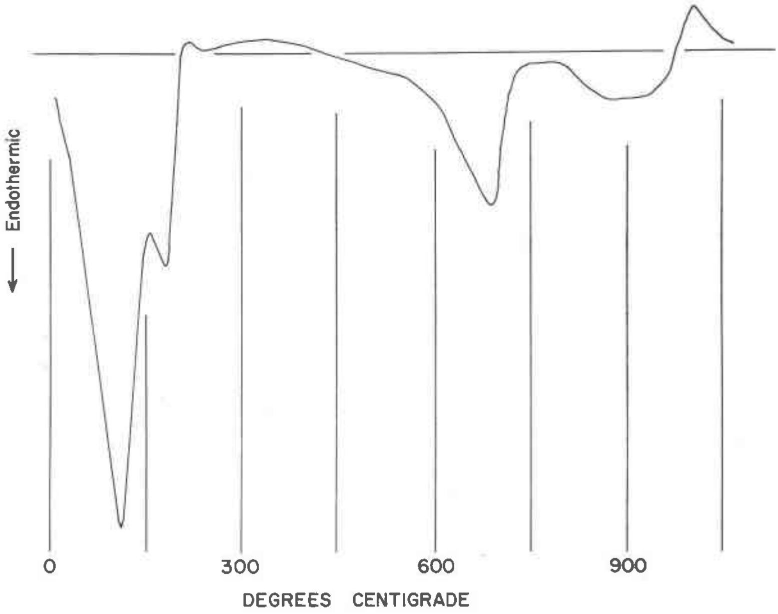

FIG. 2. DTA pattern of montmorillonite pseudomorphic after plagioclase from the Liberty Mine. Air dried and untreated. Heating rate equals 12½° C. per minute.

TABLE 3. EXCHANGEABLE CATIONS IN MONTMORILLONITE.

Cation	Milliequivalents per 100 grams	
	Sample 1	Sample 2
Mg Predicted Measured[1]	28 28±3	18 21±3
Ca Predicted Measured[1]	82 84±3	86 86±3
Na Predicted Measured[2]	1.9 1.6±1	2.6 1.9±1
K Predicted (All K in muscovite) Possible (All K in montmorillonite) Measured[2]	0 11.8 0.6±0.4	0 15.2 0.6±0.4

[1] Analyst: Paul Elmore.

[2] Analyst: Jack J. Rowe.

interstratification of beidellite and montmorillonite end members.

DTA charts show a characteristic endothermic doublet with maxima centered at 110° and 182° C. Another endothermic reaction starts at about 600° C. and reaches a maximum at 670° C. The low temperature doublet peak is generally correlated with saturation with a divalent exchangeable cation. An endothermic maximum near 700° C. is considered to be characteristic of montmorillonite as contrasted with an endothermic maximum at 550° C. for beidellite, (Greene-Kelly, 1957).

ACKNOWLEDGMENTS

The author wishes to thank the Nevada Mines Division of the Kennecott Copper Corporation for extending permission to enter the Liberty mine and collect material for further laboratory study.

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THE AMERICAN MINERALOGIST, VOL. 50, MAY–JUNE, 1965

COMPOSITION OF PALERMOITE[1]

CLIFFORD FRONDEL AND JUN ITO,

Department of Geological Sciences, Harvard University, Cambridge, Massachusetts, and Mineralogical Institute, Univerity of Tokyo, Tokyo, Japan.

An account of this new species from the Palermo pegmatite at North Groton, New Hampshire, has been given by Mrose (1953). Neither the

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[1] Mineralogical Contribution No. 417, Harvard University.