REVIEW OF THE RELATIONSHIPS IN THE MONTMORILLONITE GROUP OF CLAY MINERALS[1]

by

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ABSTRACT

Since the publication of the paper on the minerals of the montmorillonite group by Ross and Hendricks (1945) some species have been added to the group, and minor changes in the acceptable species have become advisable. No radical changes are proposed, but a review of the members and their grouping will be presented. The acceptable dioctahedral members of the group appear to be montmorillonite, nontronite and volchonskoite. Beidellite should be discontinued. The acceptable trioctahedral members of the group appear to include saponite, hectorite, sauconite, stevensite and medmontite. Griffithite is probably a useful term for an iron-rich saponite. Representative chemical analyses and formulas have been assembled to illustrate relationships.

INTRODUCTION

The paper by Ross and Hendricks (1945) on the minerals of the montmorillonite group laid the foundation for our understanding of that group, and although refinements have been made and some new minerals added since that time, there have been no basic modifications. However, it seems opportune to review briefly the present status of the various members of the montmorillonite group.

Ross and Hendricks (1945) described montmorillonite, beidellite and volchonskoite as the dioctahedral members, and saponite and hectorite as the trioctahedral members. None of these names were new; all had been previously used. Ross (1946) later added sauconite, the zinc member, and discussed the relations of iron-rich griffithite. Faust and Murata (1953) added stevensite, a magnesian member, and Chukhrov and Anosov (1950) described medmontite, a copper member.

DISCUSSION OF RELATIONSHIPS

The various members of the montmorillonite group that have been postulated and those which seem acceptable in the light of present-day knowledge are listed below.

Dioctahedral members :
- montmorillonite (well defined)
- nontronite (well defined)
- volchonskoite (probably acceptable)
- beidellite (name discarded).

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Trioctahedral members:
- saponite (well defined)
- hectorite (well defined)
- sauconite (well defined)
- stevensite (well defined)
- medmontite (well defined)
- griffithite (an iron-rich saponite, but useful term).

TABLE 1.—CHEMICAL ANALYSES OF REPRESENTATIVE MEMBERS OF THE MONTMORILLONITE GROUP OF MINERALS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	50.37	40.72	45.70	42.99	39.64	55.86	57.30	35.95	43.88
Al_2O_3	17.11	4.96	4.85	6.26	9.05	0.13	none	6.57	13.25
Fe_2O_3	2.68	29.57	6.36	1.83	7.32	0.03	0.32	2.36	3.25
Cr_2O_3	—	—	15.02	—	—	—	—	—	—
FeO	0.20	0.71	—	2.57	7.83	—	none	—	—
ZnO	—	—	—	—	—	—	—	33.70	—
MgO	4.59	0.74	0.58	22.96	15.80	25.03	27.47	1.26	0.59
MnO	—	—	—	0.11	—	none	0.21	0.04	0.06
CaO	1.23	1.98	3.10	2.03	2.93	tr.	0.97	0.62	1.58
CuO	—	—	—	—	—	—	—	—	20.96
NiO	—	—	0.54	—	—	—	—	—	—
K_2O	0.09	—	—	tr.	none	0.10	0.03	0.10	0.87
Na_2O	0.56	—	—	1.04	0.71	2.68	0.03	0.44	0.44
Li_2O	—	—	—	—	—	1.05	—	—	—
TiO_2	—	0.02	—	—	—	none	—	0.07	0.72
F^-	—	—	—	—	—	5.96	none	—	—
H_2O^-	12.29	15.46	16.38	13.65	12.31	9.90	6.69	11.34	7.02
H_2O^+	10.93	6.66	7.37	6.85	4.90	2.24	7.17	7.24	7.52
Total	100.05	100.82	99.90	100.29	100.49	102.98 $-O=F$ 100.47	100.19	99.69	100.14

Locality and references :

(1) Montmorillonite from Lemon, Miss., Ross and Hendricks (1945, p. 34, analysis no. 20).

(2) Nontronite, Spokane, Wash., Ross and Hendricks (1945, p. 35, analysis no. 59).

(3) A slightly impure volchonskoite, Lyalevo, Bulgaria (Dimitrov, 1942).

(4) Saponite, Abmeek mine, Mich., Palache and Vassar (1925, p. 418).

(5) Saponite (iron rich) (described as griffithite) Griffith Pass, Calif., Larsen and Steiger (1928, p. 1–12).

(6) Hectorite, Hector, Calif., Ross and Hendricks (1945, p. 35, analysis no. 76).

(7) Stevensite, Springfield, N.J., Faust and Murata (1953, p. 974).

(8) Sauconite, New Discovery mine, Leadville, Colo., Ross (1946, p. 418).

(9) Medmontite, Dzhezkazgan, copper deposit, Steppes of Kazakhstan, Chukhrov and Anosov (1950, pp. 23–27).

Montmorillonite, the dominant member of the dioctahedral group, is well defined, has received much detailed study, and requires no additional discussion. Nontronite is well defined; it tends to range from an iron-bearing montmorillonite (ferrian montmorillonite) to a member in which Fe^{3+} is the dominant component occupying octahedral positions in the crystal lattice.

Volchonskoite, a chromium member of the group, was discussed by Ross and Hendricks (1945, p. 28) and a number of chemical analyses were presented. All the samples seem to contain impurities and no suitable formula for a member of the group can be calculated from the available analyses. One analysis, which seems to be the best available, is given in Table 1, column (3), but no corresponding formula is given in Table 2. However, these analyses obviously represent a material in which a chromium member of the montmorillonite group is the dominant component. Therefore, volchonskoite is an acceptable member of the group and a suitable analysis may be expected.

TABLE 2.—TYPICAL FORMULAS OF MINERALS OF THE MONTMORILLONITE GROUP

Dioctahedral Members

(1) Montmorillonite
$(\mathrm{Al_{1.43}Fe^{3+}_{0.16}Fe^{2+}_{0.01}Mg_{0.44}})\ (\mathrm{Si_{3.87}Al_{0.13}})\ \mathrm{O_{10}(OH)_2Mg/2_{0.09}Ca/2_{0.10}Na_{0.16}}$
(2) *Nontronite*
$(\mathrm{Fe^{3+}_{1.92}Fe^{2+}_{0.05}Al_{0.02}Mg_{0.01}})\ (\mathrm{Si_{3.52}Al_{0.48}})\ \mathrm{O_{10}(OH)_2Mg/2_{0.08}Ca/2_{0.18}}$
(3) Volchonskoite (see comments), best available analysis, no. 3 in Table 2.

Trioctahedral Members

(4) Saponite
$(\mathrm{Mg_{2.71}Fe^{2+}_{0.17}Fe^{3+}_{0.10}Al_{0.00}})\ (\mathrm{Si_{3.42}Al_{0.58}})\ \mathrm{O_{10}(OH)_2Ca/2_{0.17}Na_{0.16}}$
(5) Griffithite (iron-rich saponite)
$(\mathrm{Mg_{1.88}Fe^{2+}_{0.52}Fe^{3+}_{0.44}Al_{0.04}})\ (\mathrm{Si_{3.19}Al_{0.81}})\ \mathrm{O_{10}(OH)_2Ca/2_{0.25}Na_{0.11}}$
(6) Hectorite
$(\mathrm{Mg_{2.67}Li_{0.30}})\ (\mathrm{Si_{3.99}Al_{0.01}})\ \mathrm{O_{10}(F,\ OH)_2Na_{0.38}}$
(7) Stevensite
$(\mathrm{Mg_{2.88}Mn_{0.02}Fe^{3+}_{0.02}})\ (\mathrm{Si_4})\mathrm{O_{10}(OH)_2(Ca/2Mg/2)_{0.15}}$
(8) Sauconite
$(\mathrm{Zn_{2.40}Mg_{0.18}Al_{0.22}Fe^{3+}_{0.17}})\ (\mathrm{Si_{3.47}Al_{0.53}})\mathrm{O_{10}(OH)_2Ca/2_{0.13}Na_{0.09}}$
(9) Medmontite
$(\mathrm{Al_{0.89}Fe^{3+}_{0.20}Cu_{1.30}Mg_{0.07}})\ (\mathrm{Si_{3.61}Al_{0.39}})\mathrm{O_{10}(OH)_2Ca/2_{0.4}Na_{0.07}K_{0.09}}$

Ross and Hendricks (1945, pp. 26, 47) listed beidellite as a member of the group, but additional studies of the group, especially by Foster (1954) and Grim and Rowland (1942), have indicated that some of the analyses of high-alumina clays were made on impure materials. In suitable material the substitution of Al for Si in tetrahedral position is small, the usual amount of replacement not exceeding that represented by $Si_{3.80}\ Al_{0.20}$ (Foster, 1953, p. 153). This indicates that no naturally occurring member of the montmorillonite group has been observed in which Al proxies Si in tetrahedral positions in amounts justifying a distinct mineral name. Synthetic material having larger amounts of Al replacing Si has been reported by Roy and Sand (1956). Thus, aluminian montmorillonite is the best term for all natural aluminous members of the group so far observed.

The ions, Al^{3+}, Fe^{3+}, and Cr^{3+} can, no doubt, proxy one another in a wide range of proportions; intermediate members of the group have been described and others are to be expected. The term aluminian montmorillonite as a replacement for the name beidellite has already been mentioned. Some of the intermediate montmorillonite–nontronite series were described by Ross and Hendricks (1945, pp. 55–56) as corresponding to ferrian montmorillonite. A chromium-bearing member of the montmorillonite group has been examined but not analyzed in our laboratory. The index of refraction indicates a chromian montmorillonite with a few percent of Cr_2O_3.

The trioctahedral members are all well defined. Saponite, which may be taken as representative of the group, is widespread in occurrence but seems to be limited to small deposits. Hectorite is interesting as it represents a nearly alumina-free clay mineral and because of its high content of lithium and fluorine. Sauconite, a zinc member, is interesting because mineralogists long refused to credit their own definitive studies. How could there be a true zinc clay? However, Genth (1875), who possessed an almost uncanny mineralogical aptitude, recognized sauconite as a true mineral. Stevensite has been discussed by Faust and Murata (1953) and their statements need not be amplified here. Medmontite from the Steppes of Kazakhstan was described by Chukhrov and Ansov (1950) and is the only copper member that has been reported. However, the data presented seem to establish it as a valid member of the group.

Substitutions are characteristic of all members of the montmorillonite group, and certain new members are to be expected. Griffithite, a member with ferrous iron = 7.83 percent and ferric iron = 7.32 percent, was described by Larsen and Steiger (1928). Ross (1946) grouped it as an iron-rich saponite, a relationship confirmed by Faust (1955). It is unusual among the clay minerals as it contains an essential proportion of ferrous iron. Although it does not represent a distinct species, griffithite probably is a useful term.

Ross and Hendricks (1945, p. 35, analysis 101) cited an analysis of a very impure saponitic clay containing about 11 percent of NiO. This seemed to represent an impure nickeloan saponite, and indicated that a nickel member of the group may be expected. Dimitrov (1942) described a member of the group with $Al_2O_3 = 17.16$, $Fe_2O_3 = 11.00$, and $NiO = 3.58$ percent. This would make it a nickel-bearing ferrian montmorillonite. The chemistry and ionic radius are both suitable for the formation of a cobalt member of the group if the rather rigorous geologic prerequisites are fulfilled.

Chemical analyses of representative members of the montmorillonite group are given in Table 1. Formulas calculated from the analyses given in Table 1 are presented in Table 2. Those numbered (1) (Foster, 1951, p. 724), (2), (4), (5), (6) and (9) were calculated by Margaret D. Foster who has cooperated in the preparation of this paper. No. (7) was calculated by George T. Faust, and no. (8) by Ross (1946, p. 418).

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