CHEMICAL COMPOSITIONS OF BERTHIERINES—A REVIEW

INTRODUCTION

Berthierine is an iron aluminum 1:1-type layer silicate belonging to the serpentine group. Chemically it resembles the iron-rich chlorite, chamosite, in that silicon, aluminum, and ferrous iron are major components, and magnesium and ferric iron are present in smaller amounts. The name berthierine appears to have been used first by Beudant (1832) for specimens from Hayanges, Lorraine, previously studied by Berthier (1827) and was resuscitated by Orcel *et al.* (1949) to distinguish this serpentine-group mineral from a chemically similar chlorite. Its physical and chemical characteristics are not easily studied because of the heterogeneous nature of the specimens in which it occurs. The X-ray powder diffraction (XRD) data are often confusing. Berthierine with a 7-Å basal spacing and chamosite with a 14-Å basal spacing are distinguishable by the absence or presence respectively of a 14-Å reflection. How-

ever, the 14-Å reflection of iron-rich chlorite, chamosite, is weak or very weak, and therefore berthierine with a small admixture of clinochlore may easily be mistaken for chamosite. The *a* and *b* unit-cell parameters are similar for the two minerals, and many reflections have almost identical *d*-spacings. Greenalite, $Fe_3Si_2O_5(OH)_4$, is an iron-rich serpentine mineral which differs from berthierine in having little or no aluminum in its composition, and no confusion has arisen between greenalite and berthierine. A short survey of the minerals under consideration has been given by Bailey (1980).

XRD data of nearly pure specimens of berthierine when the name chamosite was still employed (Brindley, 1949, 1951; Brindley and Youell, 1953) showed that both orthorhombic and monoclinic polytypes exist, commonly together, in variable proportions. The data clearly indicated a serpentine-group layer structure. Youell (1955, 1958) recognized a variety

Table 1. Chemical compositions and structural formulae of berthierines.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	20.84	19.08	22.86	21.40	23.72	21.26	21.34	26.24	22.47	24.0	23.92	26.9	25.5	26.01
Al_2O_3	28.02	26.88	26.66	25.40	24.33	23.61	22.66	22.17	21.82	21.4	20.55	18.4	14.9	12.33
Fe_2O_3	5.38	4.29	3.85	0.25	3.75	5.08	0.46	6.62	0.22	4.3	5.50	—	—	5.32
FeO	32.29	34.52	32.20	37.40	29.64	34.62	35.79	32.54	37.24	36.4	35.00	36.8	35.6	37.07
MgO	2.02	1.55	0.97	2.04	7.13	2.92	1.91	1.58	2.57	3.2	2.54	8.15	5.6	6.13
MnO	—	—	—	0.05	—	—	0.04	0.035	—	—	—	—	1.0	0.04
H_2O	10.70	11.18	10.48	12.02	11.00	12.51	10.64	10.81	10.07	10.7	11.41	9.58	17.4	10.33
Σ	99.25	99.25	97.02	98.56	99.57	100.00	92.84	100.00	94.39	100.0	98.92	99.83	100.0	97.23
Si	1.146	1.097	1.274	1.224	1.276	1.207	1.287	1.427	1.325	1.335	1.357	1.457	1.535	1.517
Al(IV)	0.854	0.903	0.726	0.776	0.724	0.793	0.713	0.573	0.675	0.665	0.643	0.543	0.465	0.483
Al(VI)	0.961	0.919	1.025	0.936	0.818	0.787	0.897	0.848	0.841	0.737	0.730	0.631	0.592	0.365
Fe^{3+}	0.223	0.186	0.161	0.011	0.152	0.216	0.021	0.271	0.010	0.180	0.234	—	—	0.233
Fe^{2+}	1.485	1.661	1.501	1.790	1.334	1.644	1.805	1.480	1.836	1.693	1.660	1.667	1.792	1.808
Mg	0.165	0.133	0.081	0.174	0.572	0.247	0.172	0.128	0.226	0.265	0.215	0.658	0.503	0.533
Mn	—	—	—	0.002	—	—	0.002	0.002	—	—	—	—	0.051	0.002
□	0.166	0.101	0.232	0.087	0.124	0.106	0.103	0.271	0.087	0.125	0.161	0.044	0.062	0.059
O	5.036	5.000	5.050	5.000	5.024	5.000	5.000	5.038	5.018	5.004	5.000	5.268	5.000	5.000
OH	3.928	4.000	3.900	4.000	3.952	4.000	4.000	3.924	3.964	3.992	4.000	3.464	4.000	4.000
H_2O	—	0.147	—	0.296	—	0.371	0.142	—	—	—	0.160	—	1.496	0.012
M:Or[1]	M>Or	M>Or	M≧Or	Or≫M	M≫Or	M~Or	Or>M	Or	Or	Or>M	Or~M	—	Or	Or

Columns

1,2,3 Klekl (1979). Samples from Belgorod District, Kursk, USSR. TiO_2, respectively 0.51%, 1.44%, 1.19%, not included. No recorded impurities.

4 Brindley (1951). Sample from Wabana, Newfoundland. $CaCO_3$ 0.23%, $FeCO_3$ 0.32% deducted to remove CaO and CO_2.

5,6,11 Yershova *et al.* (1976). Samples from Voronezh anticline, Kursk, USSR. From samples 5 and 11, Na_2O, K_2O, H_2O- are omitted. For sample 6, total H_2O is reported.

7 Brindley (1951). Sample #874, Ayrshire. Additionally $CaCO_3$ 0.12%, $FeCO_3$ 0.89%, plagioclase 0.81%, muscovite 0.25% removed to eliminate CaO, CO_2, Na_2O, K_2O. Also TiO_2 3.63% not included.

8 Thurrell *et al.* (1970). Sample from Weald clay. After authors' corrections for 11.57% impurities.

9 Brindley and Youell (1953). Sample from Stanion Lane Pit, Corby.

10 Halbach (1970, p. 481). Sample from Pegnitz, Germany.

12 Floran and Papike (1975). Sample from Gunflint Iron Formation. All iron reported as FeO. CaO 0.05%, K_2O 0.12% omitted. H_2O taken as difference from 100%.

13 Deudon (1955). Sample from Sainte-Barbe. Corrected analysis given by Deudon; total impurities 65.1%.

14 Novak *et al.* (1959). Sample from Kank, Kutná Hora. CaO 0.48% omitted.

[1] M:Or signifies ratio of M (monoclinic) to Or (orthorhombic) form.

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of layer-stacking disorders which add to the difficulties of detailed crystal structure study. No further advance in the structural study of berthierine has been made since that time.

Subsequent studies involving berthierine, still often wrongly called chamosite or 7-Å-chamosite, have been mainly geological, but additional chemical analyses have been published. The impurities which are commonly present lead to some uncertainties; nevertheless it is useful to examine the available chemical data.

CHEMICAL ANALYSES AND STRUCTURAL FORMULAE

Analyses of fourteen berthierine specimens are presented in Table 1, arranged in order of decreasing Al_2O_3 content from 28 to 12 wt. %. The variations of SiO_2 (19–27%) and FeO (32–37%) are smaller, and Fe_2O_3 and MgO are present in relatively small proportions. The compositions are mainly those given in the original studies after possible corrections by the authors for impurities. Any additional corrections are mentioned in the notes appended to the table. Small TiO_2 contents have been assumed to arise from admixed anatase or rutile. Most authors differentiate between H_2O- and H_2O+, but in some analyses total H_2O appears to be given. Analyses in which all iron is reported as FeO have generally been omitted.

If, as the XRD data indicate, berthierine belongs to the serpentine mineral group, a formula of the type $(R^{2+}{}_a R^{3+}{}_b \square_c)$ $(Si_{2-x}Al_x)O_5(OH)_4$ can be assumed where R^{2+} and R^{3+} are cations occupying octahedral positions, $\square$ represents possible vacant octahedral positions, and $a + b + c = 3$. The least objectionable procedure in deriving formulae is to normalize the total valence of cations in tetrahedral and octahedral positions to $+14$. This procedure corresponds ideally to an oxygen + water content O_72H_2O or $O_5(OH)_4$ and does not utilize uncertain measurements of H_2O+. Also, it does not assume that all octahedral cation sites are filled. Cations such as Na, K, and Ca which cannot enter octahedral positions are commonly listed as small oxide percentages which can often be attributed to impurities. Approximate corrections can then be made to the total analysis. In other analyses, such oxides have been ignored when present in small amounts.

Table 1 lists the formulae so obtained. Tetrahedral positions not filled by Si are filled by Al cations. The remaining cations are placed in octahedral positions, and the deficit from a total of three is shown as $\square$. The calculation leads to compositions of the form $O_7(H_2O)_{2+n}$. Ideally n is zero and the anionic composition is $O_5(OH)_4$. When the water content is $(2 + n)$ the formulae are written $O_5(OH)_4 \cdot nH_2O$, and when the water content is $(2 - n)$ the formulae become $O_{5+n}(OH)_{4-2n}$. Table 1 shows that most of the analyses have anionic contents close to $O_5(OH)_4$.

DISCUSSION

In all of the formulae derived, the R^{3+} octahedral cations exceed the Al^{3+} tetrahedral cations and electrical neutrality of the layers is achieved by vacant octahedral sites. A similar charge-balancing mechanism in chlorites has been discussed by Foster (1962) and by McDowell and Elders (1980). The difference $R^{3+}(oct) - Al^{3+}(tet)$ is necessarily equal to $2\square$, or $b - x = 2c$. When $R^{3+}(oct)$ is plotted against $Al^{3+}(tet)$ (Figure 1), most of the data points lie on or near a line passing through the origin, except analyses 3 and 8 which give points rather far from this line. The linear relation corresponds to $b \sim 1.30x$. When this result is combined with the previous relation, $c \sim 0.15x$; a plot of c vs. x shows that most data points lie on or near this line, with analyses 3 and 8 giving points rather far from the line.

The possibility that the excess of $R^{3+}(oct)$ cations is related to oxidation of Fe^{2+} ions after formation of the mineral seems unlikely in view of the small content of Fe_2O_3 in the analyses.
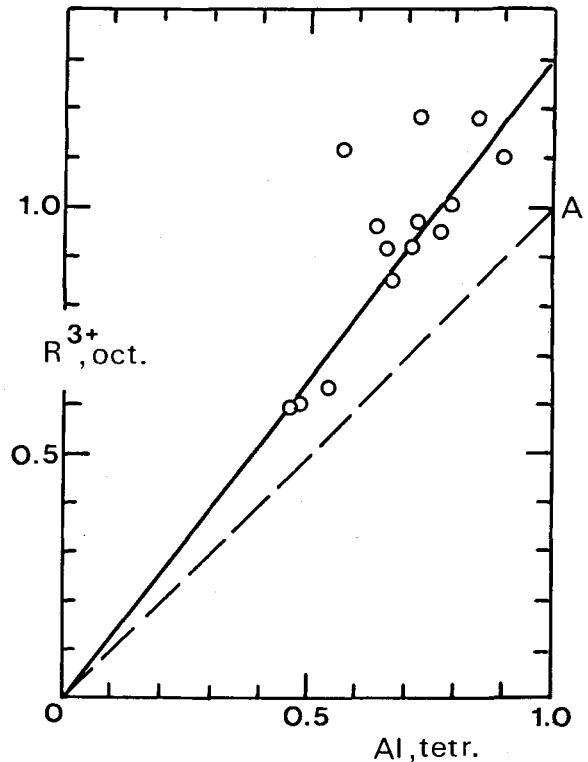

Figure 1. ΣR^{3+} (octahedral) vs. Al^{3+} (tetrahedral). Point A corresponds to composition of amesite when $R^{3+} = Al^{3+}$. Dashed line corresponds to $R^{3+}(oct) = Al^{3+}(tet)$. Circles = berthierines. Full line has slope = 1.30.

Foster (1962) discussed a similar situation in chlorites for which many more data and possibly more accurate data were available. She concluded that the greater number of R^{3+} ions was not dependent on Fe^{3+} ions; they could be any combination of Al^{3+} and Fe^{3+} ions. Therefore, some mechanism presumably exists which causes more R^{3+} ions to enter octahedral sites than are necessary to neutralize the negative tetrahedral sites. The excess of R^{3+} ions is balanced by vacant cation sites in the proportion $R^{3+}{}_2\square$; in other words, a situation develops analogous to a dioctahedral feature in a mainly trioctahedral layer structure. The result corresponds to a balancing of ionic charges locally in accordance with Pauling's rules.

A survey of XRD data for berthierines shows that too little information is available for any significant comparison to be made between unit-cell parameters and chemical compositions. However, it appears that the monoclinic form of berthierine is more common in samples with high Al_2O_3 content and that the orthorhombic, pseudo-hexagonal, form is more common in samples with low Al_2O_3, high SiO_2 contents. The ratio monoclinic : orthorhombic is indicated in the last line of Table 1.

Magnesium serpentines have compositions ranging from $Mg_3Si_2O_5(OH)_4$ for chrysotiles and lizardites to $(Mg_2Al)(SiAl)O_5(OH)_4$ for amesite with a partial range of intermediate compositions for aluminian lizardites (see Bailey, 1980, p. 22). These compositions are represented in Figure 1 by the dashed line extending from the origin to the point A which corresponds to amesite. The R^{3+} ions are principally Al^{3+}. Berthierines differ from lizardites in having dominantly

Fe^{2+} octahedral ions and an excess of R^{3+} ions, mainly Al^{3+}, with compensating vacant sites. Tetrahedral substitutions span the range $x = 0.45$ to $x = 0.90$. Berthierines may be described as ferroan aluminian analogues of lizardite.

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Department of Geosciences   G. W. BRINDLEY
The Pennsylvania State University
University Park, Pennsylvania 16802

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