

# CRYSTALLOCHEMICAL CLASSIFICATIONS OF PHYLLOSILICATES BASED ON THE UNIFIED SYSTEM OF PROJECTION OF CHEMICAL COMPOSITION: III. THE SERPENTINE-KAOLIN GROUP

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*(Received 15 February 1989; revised 20 July 1989)*

**ABSTRACT:** A unified system of projection of chemical composition, prepared initially for micas and chlorites, has been applied to minerals of the serpentine-kaolinite group. It has been shown that the chemical composition in the projection field is controlled by the formula, the unit of which is:  $(R_u^{2+}R_y^{3+}\square_z)(Si_{(2-x)}Al_x)O_5(OH)_4$ , where  $u + y + z = 3$ ,  $z = y - x$ . Using projection fields for different chemical systems it has been shown that among the most important end-members are kaolinite minerals, true serpentines, berthierine, brindleyite, amesite, cronstedtite, greenalite, nepouite and their analogues having different substitutions in the octahedral sheets.

## CRYSTALLOCHEMICAL CLASSIFICATION

As shown for micas (Part I) and chlorites (Part II), the chemical composition and its relation to structure may be represented using the vector concept. If significant chemical composition, as given by the crystallochemical formula, is assigned to a definite point located at the intersections of isolines, this concept becomes also a useful basis for crystallochemical classification of minerals characterized by the 7 Å repeat unit, *i.e.* the serpentine-kaolin group.

As for micas and chlorites, the projection field contains isolines:

- |R<sup>2+</sup> – sum of divalent cations, Mg, Fe<sup>2+</sup>, Ni and Mn per three octahedral positions;
- |R<sup>3+</sup> – sum of trivalent cations, Al, Fe<sup>3+</sup> and Cr per three octahedral positions;
- |\square – number of vacant sites per three octahedral positions;
- |Si<sub>(4-x)</sub> – number of Si per two tetrahedral positions, where  $x$  is the number of trivalent cations substituting for Si.

The nodes at the intersections of the following isolines:

$$\begin{array}{llll} |R^{2+} = 3, & |R^{3+} = 0, & |\square = 0, & |Si = 2 \\ |R^{2+} = 2, & |R^{3+} = 1, & |\square = 0, & |Si = 1 \\ |R^{2+} = 0, & |R^{3+} = 2, & |\square = 1, & |Si = 2 \end{array}$$

are chosen as three corners delimiting the projection field for the serpentine-kaolin minerals (Fig. 1).

A layer of serpentine and kaolin contains one tetrahedral and one octahedral sheet as compared to two of each in a layer of chlorite, so the crystallochemical formula unit is:  $(R_u^{2+}R_y^{3+}\square_z)(Si_{(2-x)}Al_x)O_5(OH)_4$ , where  $u + y + z = 3$ ,  $z = y - x$ . A composition projecting in any point of the field is controlled by this formula.

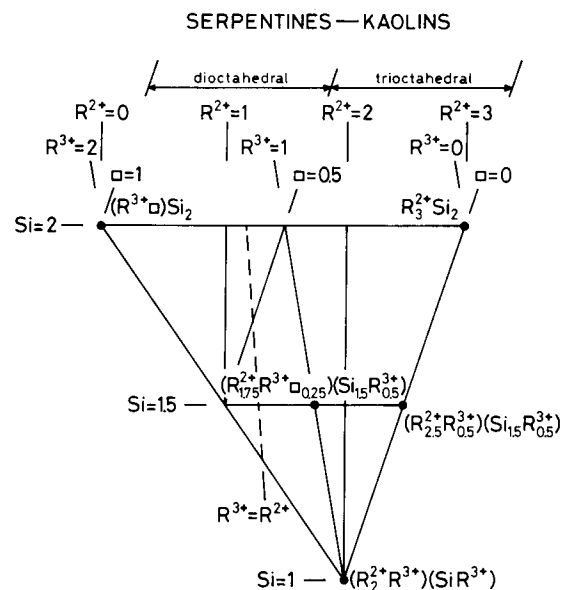


FIG. 1. Projection field for the condensed chemical composition of 1:1 phyllosilicates. Composition isolines:  $R^{2+}$ -Mg,  $Fe^{2+}$ , Ni, Mn, Zn;  $R^{3+}$ -Al,  $Fe^{3+}$ , Cr;  $\square$ -vacancies.

The projection field is divided along the isoline  $|\square| = 0.5$  into two parts. They correspond to the trioctahedral subgroup, the serpentines, and the dioctahedral subgroup, the kaolins.

Further differentiation must be carried out within certain chemical systems. Kaolins are aluminium silicates but serpentines are magnesium or iron (rarely nickel or manganese) silicates, aluminosilicates or ferrosilicates. The chemical composition of the most frequent serpentines and kaolins may be enclosed in the polyhedron (Fig. 2) belonging to the Al-Mg- $Fe^{2+}$ - $\square$  system of the composition of the octahedral sheet. The bottom, the right wall (Fig. 3), and the top (Fig. 4) of this polyhedron are good two-dimensional approximations of this system and are convenient to represent end-member compositions of such minerals, like lizardite and other Mg-serpentines, berthierine, amesite, greenalite and kaolins. For cronstedtite, another polyhedron must be constructed, the top of which is presented in Fig. 5.

*Kaolins* are characterized by a simple and uniform chemical composition such as that represented in the left-hand corner of the triangle in Figs. 1-6. In contrast to most other phyllosilicates, they are free of isomorphous substitutions. Some authors claim to find substitutions in octahedral or tetrahedral sites, related to big cations in the interlayer space, but fully documented substitution in kaolin polymorphs has been described only in Cr-halloysite by Maksimović & White (1973). Structural layers with  $Fe^{3+}$  in octahedra that might build theoretical  $Fe^*$ -kaolinite (left-hand corner in Fig. 5) exist only in chapmanite and bismutoferrite, due to the stabilizing effect of the interlayer Sb and/or Bi (Zhoukhlistov & Zvyagin, 1977).

End-member *serpentines* with such cations as Ni, Zn and Mn usually constitute solid-solution series with those serpentines presented in Fig. 2, e.g. nepouite is the Ni analogue of lizardite, and zinalsite and kellyite are the Zn and Mn analogues of amesite. Other Ni-, Zn-

\* In this work such a prefix indicates the predominant octahedral cation. It should not be confused with exchangeable interlayer cation not considered here.

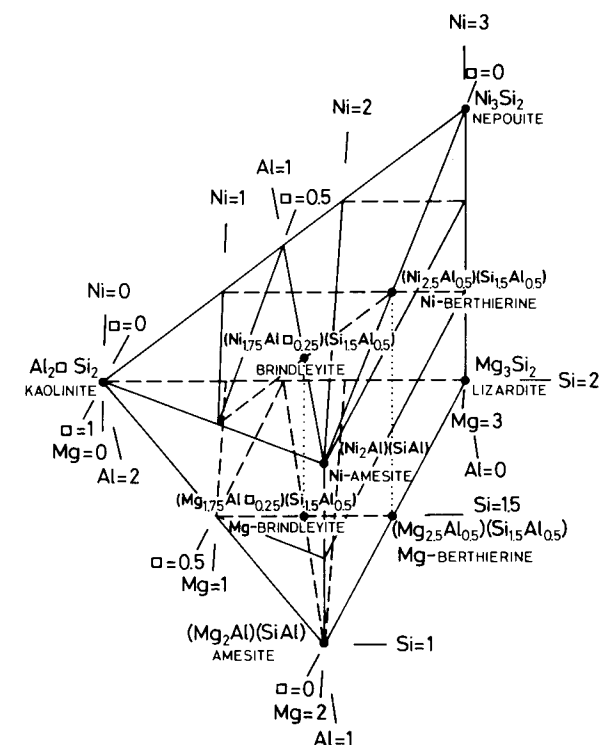
Mg-Ni-Al- $\square$ -SERPENTINES-KAOLINITES

FIG. 2. Composition polyhedron for 1:1 phyllosilicates with Mg,  $Fe^{2+}$ , Al and  $\square$  in octahedra.

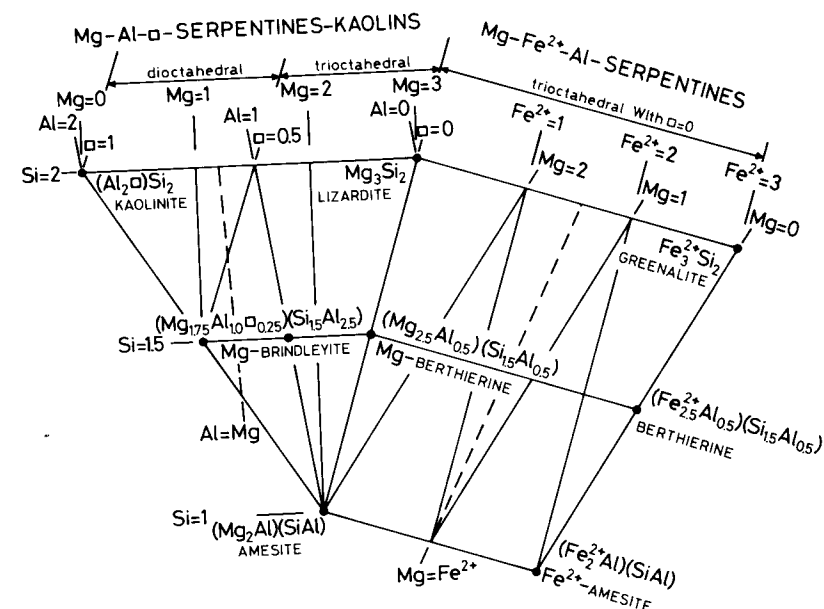
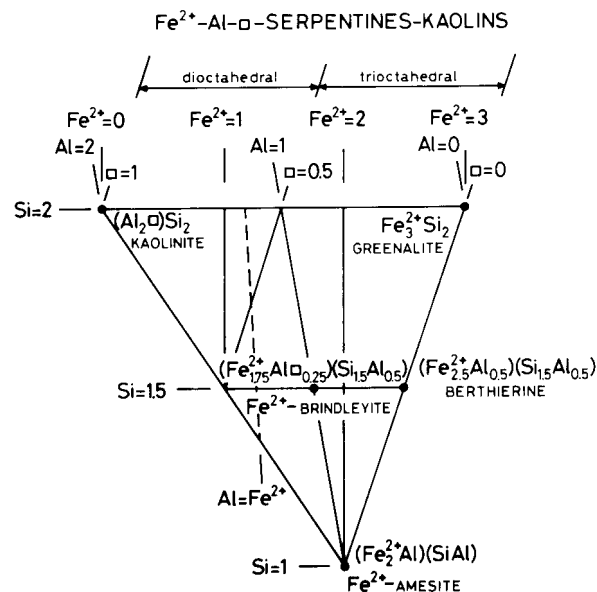
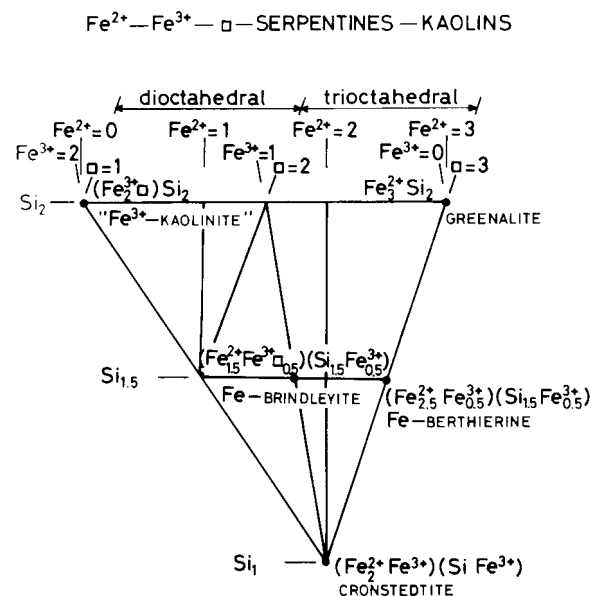
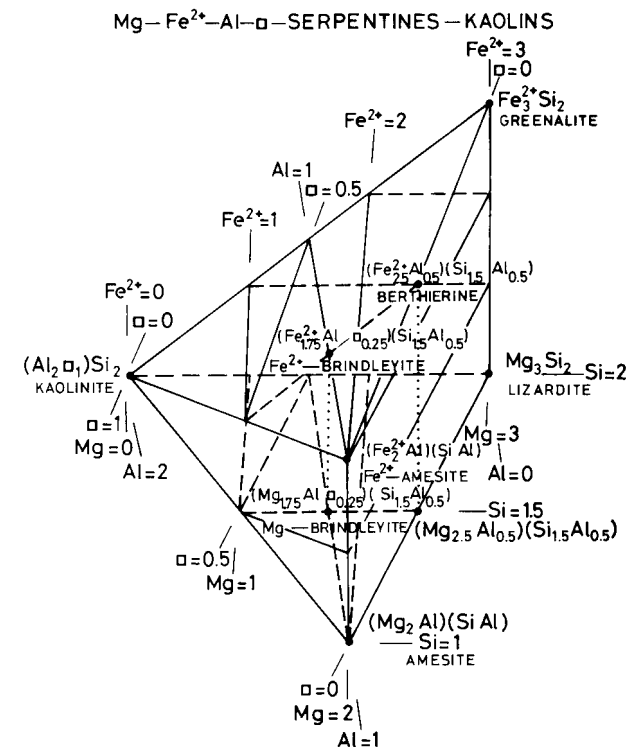


FIG. 3. Projection field for phyllosilicates with Mg, Al and  $\square$ , (a bottom) and with Mg,  $Fe^{2+}$  and Al (a side wall of Fig. 2).

FIG. 4. Projection field for 1:1 phyllosilicates with  $\text{Fe}^{2+}$ , Al and  $\square$  in octahedra.FIG. 5. Projection field for 1:1 phyllosilicates with  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\square$  in octahedra.

and/or Mn-serpentines are brindleyite, baumite, and caryopilite, respectively; tosalite is regarded as manganoan greenalite (Bayliss, 1981). From among the three specified elements the most important seems to be Ni. A polyhedron is then constructed for the system Mg-Ni-Al- $\square$ , representing the composition of the octahedral sheet (Fig. 6). Apart from the known end-members of the trioctahedral minerals such as lizardite, amesite, nepouite and brindleyite, the Ni analogue of amesite is placed under the name Ni-amesite, as nimesite has

FIG. 6. Composition polyhedron for 1:1 phyllosilicates with Mg, Ni, Al, and  $\square$  in octahedra.

been rejected by the Nomenclature Committee of the IMA (Maksimovič & Bish, 1978) on the basis that it is too similar to nimite (Ni-chlorite).

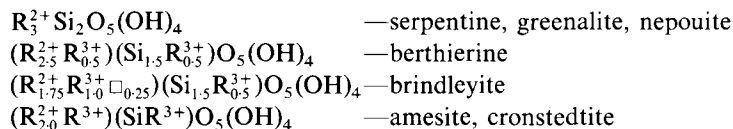
*Brindleyite*, a nickeloan aluminous serpentine mineral  $(\text{Ni}_{1.75}\text{Al}_{1.0}\square_{0.25})(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_5(\text{OH})_4$  (Maksimovič & Bish, 1978) is not an analogue of berthierine as postulated by these authors. It occupies a distinct position in the projection field (Fig. 3); it is then a definite species having its own crystallochemical characteristics different from berthierine. The difference is in the octahedral vacancies, and twice the content of octahedral Al as compared to berthierine, apart from the Ni content. It is justified to leave the name brindleyite for the nickeloan brindleyite, as it has been approved by the IMA Commission on New Minerals and Mineral Names. Therefore its Mg-variety will be distinguished by a prefix, Mg-brindleyite, similarly to Mg-berthierine which was originally iron bearing.

*Odinite*, a newly reported clay mineral (Bailey, 1988) has 'the structure based on 1:1 serpentine-like layer that is intermediate between dioctahedral and trioctahedral'. In odinite, octahedral-cations range from 2.3–2.54 per three sites for ten samples. Evidently the unstable chemical composition makes it impossible to project the



crystallochemical formula for the purest sample in one point of the projection field, as the formula does not fulfil the condition  $z = y - x$  (compare  $\square_{0.6}$  and  $z = 1.36 - 0.21 = 1.15$ ). However, points which are obtained from projection using orthogonal and oblique coordinates indicate that the structure of odinite is dioctahedral.

The classification presented for the serpentines includes several important compositional joins. Among the most important, participating in solid-solutions are:



The listed names of distinctly different mineral species should be considered as the pre-eminent representatives of the trioctahedral subgroup of 1:1 minerals.

It is very significant that all the *sensu stricto* serpentines are located at/or close to isoline  $|\square| = 0$  intersecting  $|Mg| = 3$  (Figs. 1–6). This indicates the tendency to fill all the octahedra in the structures with the comparable big cations. The net result is a bigger unit mesh of the octahedral than the tetrahedral sheet. This reflects in an unusual morphology from the normal planar type prevailing in lizardite, via alternating waves of antigorite, to cylindrical rolls of chrysotile.

#### ACKNOWLEDGMENTS

Sincere thanks are due to Dr. Mackenzie and Prof. Bailey for critical reading and corrections in all three parts of the manuscript, and to Prof. Dr. J. M. Serratos of the Institute of Material Science in Madrid for providing assistance for drawing reproducible figures. This work was fulfilled within project CPBP 03.04.

#### REFERENCES

- BAILEY S.W. (1988) Odinite, a new dioctahedral-trioctahedral  $Fe^{3+}$ -rich 1:1 clay mineral. *Clay Miner.* **23**, 237–247.
- BAYLISS P. (1981) Unit cell data of serpentine group minerals. *Mineral. Mag.* **44**, 153–156.
- MAKSIMOVİČ A.P. & WHITE J.L. (1973) Infrared study of chromium-bearing halloysites. *Proc. Int. Clay Conf. Madrid*, 61–73.
- MAKSIMOVİČ Z. & BISH D. (1978) Brindleyite, a nickel-rich aluminous serpentine mineral analogous to berthierine. *Am. Miner.* **63**, 484–489.
- ZHOUKHLISTOV A.P. & ZVYAGIN B.B. (1977) Crystal structure determination of chapmanite and bismutoferrite by high-voltage electron diffraction. *Kristallografiya* **22**, 731–738 (in Russian).