

Unit cell data of serpentine group minerals

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ABSTRACT. Least-squares analyses of powder X-ray diffraction data have been undertaken for minerals and synthetics of composition $(\text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni})_{3-x}\text{Si}_2\text{O}_5(\text{OH})_4$. New polytypes of nepouite and greenalite have been established, and eleven new or altered unit cells have been calculated. Baumite is an unnecessary varietal name for a manganian ferroan lizardite-1T; tosalite is an unnecessary varietal name for a manganian greenalite; clinochrysotile is an unnecessary polytype name for chrysotile-2M₂₁; orthochrysotile is an unnecessary polytype name for chrysotile-2O_{r21}; ortho-antigorite and ortho-hexagonal serpentine are unnecessary names for lizardite-6T₁; and septechlorite should not be used. The powder data of the serpentine group are in general, poor.

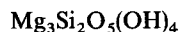
THE kaolinite-serpentine group has a layered crystal structure with a 7 Å thickness, which consists of a tetrahedral sheet joined to an octahedral sheet. The distortions to the sheets in order to fit them together have been discussed by Radoslovich (1963). Originally some species were included within the chlorite group, but later cronstedtite (Hendricks, 1939), amesite (Gruner, 1944) and berthierine (Brindley, 1950) were proven to be members of the kaolinite-serpentine group. Some species are dioctahedral with two trivalent cations (e.g. Al), whereas other species are trioctahedral with three divalent cations (e.g. Mg, Mn, Fe, Co, Ni). Although the over-all composition of the kaolinite-serpentine group is similar to that of the chlorite group, the chlorite formula contains twice the number of atoms as the kaolinite-serpentine group formula, because chlorite has a 14 Å thick layered crystal structure with two tetrahedral and one octahedral sheets plus an interlayer hydroxyl sheet.

In the octahedral sites, complete solid solution appears possible between the divalent cations Mg, Mn, Fe, Co, and Ni with a formula of $(\text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni})_{3-x}\text{Si}_2\text{O}_5(\text{OH})_4$. Some of the octahedral sites may be vacant as represented by the value x , after partial oxidation of Fe or Mn, or to counterbalance some hydroxyl vacancies. Some Al may be accepted in both octahedral and tetrahedral sites by the substitution of $(\text{Al})^{\text{VI}}(\text{Al})^{\text{IV}} \rightleftharpoons (\text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni})^{\text{VI}}(\text{Si})^{\text{IV}}$, however, in this solid-solution

range there appears to be a distinct miscibility gap (Bailey, pers. comm.), which is approximately represented by the trioctahedral chlorites (Bayliss, 1975). At the end of this solid solution range, the formula $[(\text{Mg}, \text{Mn}, \text{Fe}, \text{Ni}, \text{Zn})_{2-x}\text{Al}](\text{SiAl})\text{O}_5(\text{OH})_4$ is represented by the species amesite, kellyite, berthierine, brindleyite (formerly nimesite), and fraipontite. There are many different polytypes described within these species.

The literature contains many sets of powder X-ray diffraction data of serpentine group minerals with the formula $(\text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni})_{3-x}\text{Si}_2\text{O}_5(\text{OH})_4$. Inconsistencies were found in these data during a review of the Mineral Powder Diffraction File by Bayliss *et al.* (1980). This paper records the new unit cell values calculated, and also comments on nomenclature.

Methods. All powder data sets have been refined with the least-squares program of Appleman *et al.* (1972). By using indices obtained from one mineral species, it has been possible to index other mineral species of the same polytype with better agreement. All powder data have been indexed on a C-type Bravais lattice. A flat-layer polytype cannot be uniquely defined unless $k \neq 3n$ reflections are present that identify a regular and unique defined layer sequence and that have intensities agreeing with calculated values. Reflections 020 and 040 do not qualify, since they may represent edges of two-dimensional bands from random stacking. Therefore some powder data are not adequate to specify polytypes, but may only be used to place the powder data in groups A to D of Bailey (1969). When the crystal structure belongs to the trigonal or hexagonal system, the Powder Diffraction File convention of indexing on an orthohexagonal cell with $b = \sqrt{3}a$ has been used.



The unit cell of baumite recorded in Table I has been calculated from the powder data and indices of Frondel and Ito (1975). The powder data and unit cell are similar to those of lizardite 1T. Since

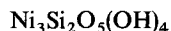
the chemical formula of baumite ($Mg_{1.4}Mn_{0.6}Fe_{0.4}^{2+}Zn_{0.3}Al_{0.2}Fe_{0.1}^{3+}(Si_{1.8}Al_{0.2})O_5(OH)_4$) is also similar to lizardite $Mg_3Si_2O_5(OH)_4$, baumite is a manganoan ferroan variety of lizardite-1T and hence the name baumite is superfluous.

Wicks and Whittaker (1975) have demonstrated that clinochrysotile and orthochrysotile are polytypes and have used chrysotile- $2M_{c1}$ and chrysotile- $2Or_{c1}$ instead. Therefore the names clinochrysotile and orthochrysotile are superfluous. The powder data from synthetic material by Dalmon and Martin (1968) were indexed originally on a one-layer orthorhombic cell and wrongly called antigorite. Since the powder data would not refine on this cell, they have been successfully reindexed as chrysotile- $2M_{c1}$ with its revised unit cell recorded in Table I and its new indices recorded in PDF 21-1262.

A six-layer polytype, which was described incorrectly by Brindley and von Knorring (1954) as ortho-antigorite, was found to be a serpentine with a 6-layer orthohexagonal cell (PDF 9-444) by Zussman and Brindley (1957). A slightly different name, six-layer orthohexagonal serpentine, is used by Olsen (1961). Wicks and Whittaker (1975) suggest that all flat-layer magnesium serpentines should be regarded as polytypes of lizardite. This superior nomenclature of lizardite- $6T_1$ has been used by Hall *et al.* (1976). Therefore the names ortho-antigorite and orthohexagonal serpentine are superfluous.

Aluminian lizardite. The 6-layer ortho-serpentine of Gillery (1959), the 6(2)-layer aluminous serpentine with a pseudo two-layer unit and the 6(3)-layer aluminous serpentine with a pseudo three-layer unit of Bailey and Tyler (1960), and the hexagonal Al-serpentine with a 9-layer structure of Jahanbagloo and Zoltai (1968) have compositions closer

to amesite, $(Mg_2Al)(SiAl)O_5(OH)_4$, than to lizardite $Mg_3Si_2O_5(OH)_4$. Wicks (1979) indicates a solid solution series between lizardite and amesite, so that Wicks and Whittaker (1975) have used amesite-9T for the hexagonal Al-serpentine with a 9-layer structure of Jahanbagloo and Zoltai (1968). Bailey (pers. comm.) states there is no evidence that amesite deviates from tetrahedral Si:Al = 1:1 by more than 10%, and seriously questions that Al-rich serpentines with higher Si:Al ratios and quite different crystal structures can legitimately be called amesite, so that it is better to use aluminian lizardite.



Garnierite has been redefined by Brindley and Pham Thi Hang (1973) as a general term for hydrous nickel silicates.

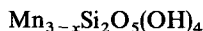
The powder data of nepouite indexed on a two-layer monoclinic cell quoted by Mikheev (1957) have been reindexed upon a one-layer orthorhombic-shaped cell, and its revised unit cell is recorded in Table I. Similar powder data from synthetic material have been indexed by Martin *et al.* (1967) on a one-layer orthorhombic-shaped cell, although it has been wrongly called 'antigorite du nickel'. Maksimović (1973) has compared his unindexed powder data to those of Montoya and Baur (1963) and also to those of lizardite. From this comparison, he has concluded that nepouite-lizardite is an isomorphous series. These powder data were indexed on a one-layer orthorhombic-shaped cell and their unit cells are recorded in Table I. A comparison of the powder data of Maksimović (1973) with the theoretical polytype data of Bailey (1969) shows that it belongs to group C and is probably the 1T polytype.

TABLE I. Unit cell data calculated from X-ray powder data in literature

Mineral species name	Dominant octahedral cation	Unit cell parameters				Reference	Name in reference	PDF number
		a	b	c	β			
Lizardite-1T	Mg	5.34	9.23	7.19	—	Fron del and Ito (1975)	Baumite	29-704
Chrysotile- $2M_{c1}$	Mg	5.30	9.19	14.64	93° 10'	Dalmon and Martin (1968)	Antigorite	21-1262
Nepouite	Ni	5.27	9.14	7.24	—	Mikheev (1957)	Nepouite	15-580
Nepouite	Ni	5.28	9.15	7.28	—	Maksimović (1973)	Nepouite	—
Nepouite	Ni	5.30	9.17	7.28	—	Montoya and Baur (1963)	Nepouite	—
Nepouite	Ni	5.31	9.20	14.50	—	Ulrych (1971)	Nepouite	25-524
Pecoraite	Ni	5.26	9.16	14.7	92°	Faust <i>et al.</i> (1969)	Pecoraite	22-754
Greenalite	Fe	5.54	9.55	7.44	104° 20'	Gruner (1936)	Greenalite	2-1012
Greenalite	Fe	5.58	9.63	7.38	104° 20'	Yoshimura (1970)	Tosalite	23-301
Caryopilite	Mn	5.660	9.810	7.530	104° 30'	Yoshimura <i>et al.</i> (1958)	Bementite	19-789
Caryopilite	Mn	5.68	9.76	7.52	104° 30'	Welin (1968)	Ektropite	25-545
—	Co	5.40	9.35	7.15	—	Dalmon and Martin (1968)	Antigorite	21-872

The nepouite powder data of Ulrych (1971) have been indexed upon a two-layer orthorhombic cell and the unit cell is recorded in Table I. A comparison of these powder data with the theoretical polytype data of Bailey (1969) shows that it belongs to group B, which includes $2Or$, $2M_2$, and $6H$. Therefore a second polytype of the mineral species nepouite has been described.

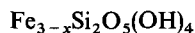
The nickel analogue of chrysotile- $2M_{c1}$ (\equiv clino-chrysotile), which has been called pecoraite, has been described by Faust *et al.* (1969). These powder data are similar to those of Montoya and Baur (1963); however, they index marginally better on a two-layer monoclinic cell than a one-layer orthorhombic-shaped cell as is expected when a larger cell with more parameters is used. The evidence so far to differentiate this mineral species of pecoraite from nepouite is therefore its cylindrical morphology only. However, new unpublished data (Milton, pers. comm.) belong to group A polytypes of Bailey (1969), which include $2M_1$. The calculated monoclinic unit cell is recorded in Table I. The synthetic garnierite of Noll *et al.* (1958a) also has cylindrical morphology.



Caryopilite is the preferred mineral species name for a manganese 1:1 layer type mineral (Bailey, 1980). The name bementite has been wrongly used by Yoshimura *et al.* (1958), because this mineral name has priority for a Mn-rich mineral that belongs to the friedelite group and is not a layer silicate (Kato, 1963). The powder data of Yoshimura *et al.* (1958) have been completely indexed and a revised unit cell is recorded in Table I. The polytype belongs to group A of Bailey (1969). Similar powder data from the mineral originally called ektropite (= karyopilite?) have been given by Welin (1968). These data have been indexed and a unit cell is recorded in Table I.

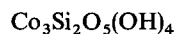
The electron probe data of Peacor and Essene (1980) show the octahedral to tetrahedral cation ratio of 8:6 for some specimens called caryopilite. Although some specimens may be friedelite-group members, their paper does not provide any crystallographic evidence to prove that all caryopilite specimens belong to the friedelite group. Since caryopilite powder data belong to group A polytypes, they differ from the powder data of most other serpentine minerals, which belong to group B and C polytypes. The powder data of caryopilite from Yoshimura *et al.* (1958) index better than all other serpentine powder data recorded in Table I. The caryopilite chemical formula of Kato (1963) indicates that the three octahedral sites are not filled so that the octahedral to tetrahedral cation

ratio is lower than 9:6. Even if caryopilite is not found in the type locality of Långban, Sweden, the mineral species name caryopilite should continue to be used for $Mn_{3-x}Si_2O_5(OH)_4$ in the serpentine group, because this is the presently widely accepted meaning.



The earlier powder data of greenalite by Gruner (1936) have been indexed on a one-layer monoclinic cell similar to that for caryopilite. The unit cell is recorded in Table I and the polytype fits Group A of Bailey (1969). These data are suspect because of a non-indexable reflection and several reflections of $k \neq 3n$ where the observed intensities are significantly different from the calculated intensities. From the chemical analysis of tosalite determined by Yoshimura (1970), the chemical formula has been calculated as $(Fe_{1.71}^{2+}Mn_{0.49}Mg_{0.18}Al_{0.27}Fe_{0.18}^{3+})(Si_{1.89}Al_{0.11})O_5(OH)_4$. Therefore tosalite is a manganoan greenalite, and hence the name tosalite is superfluous. The powder data have been indexed on a one layer monoclinic cell, and the unit cell is recorded in Table I.

Steadman and Youell (1958) and PDF 11-265 give powder data for greenalite based upon a one-layer orthorhombic-shaped cell that appears to fit Group C polytypes of Bailey (1969). Therefore a second polytype of the mineral species greenalite has been described.



Dalmon and Martin (1968) have published powder data from synthetic $Co_3Si_2O_5(OH)_4$ based upon a one-layer orthorhombic-shaped cell. Since the data are indexed poorly, they have been re-indexed to calculate a revised unit cell, which is recorded in Table I. The polytype belongs to group C of Bailey (1969) and is probably the $1T$ polytype.

A synthetic 'Kobalt chrysotil' with a tubular morphology has been prepared by Noll *et al.* (1958b).

Group Name

The suggested name of septechlorite for the serpentine mineral group has not been approved by the AIPEA committee (Bailey, 1980), and therefore the name septechlorite should not be used.

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