# Structure of Aerugite ($Ni_{8.5}As_3O_{16}$) and Interrelated Arsenate and Germanate Structural Series

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## Abstract

Aerugite ($Ni_{8.5}As_3O_{16}$), $M_r = 979.8$, trigonal, $R\bar{3}m$, $r = 9.8105\,(7)$ Å, $\alpha = 35.312\,(1)°$, $[a = 5.9511\,(5)$, $c = 27.5676\,(20)$ Å, hexagonal cell], $V = 281.9$ Å$^3$, $Z = 1$, $D_x = 5.772$ g cm$^{-3}$, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 231.25$ cm$^{-1}$, $F(000) = 465$, room temperature, final $R = 0.023$ for 925 unique reflections. The space group of $(Ni,Mg)_{10}Ge_3O_{16}$ is revised to $R\bar{3}m$ (final $R = 0.013$). Aerugite is isomorphous with $Mg_{8.5}As_3O_{16}$ and has a close-packed layer structure ($[001]_{hex}$ stacking direction), with tetrahedral $As^{5+}$ and octahedral $As^{5+}$ and $Ni^{2+}$ cations. Charge balance of the structure is achieved by partial occupancy (5/6) of the Ni(1) position in layers of mixed As(1)$O_6$ and Ni(1)$O_6$ octahedra. Partial occupancy is associated with local positional disorder about Ni(1) sites but there is no indication of vacancy ordering. The aerugite structure is closely related to the $(Ni,Mg)_{10}Ge_3O_{16}$ structure, and cation charge per single close-packed layer is conserved between them. The aerugite structure may be analyzed in terms of a regular intergrowth of olivine-type and rock-salt-type layers parallel to $(011)_{rh}$. This suggests the possibility of new structural series of the type $M_{3n+5.5}As_{2n+1}O_{8(n+1)}$ ($M$ = Ni, Co, Mg), analogous to that reported earlier for germanate compounds, with aerugite and xanthiosite ($Ni_3As_2O_8$) corresponding to the end members $n = 1$ and $n = \infty$, respectively, for the Ni series.

## Introduction

Recent studies (Barbier, 1987*a,b*; Fleet & Barbier, 1988) have determined the structure of the compound $(Ni_xMg_{1-x})_{10}Ge_3O_{16}$, with $x \approx 0.4$–$0.5$, and have shown that it belongs to a new structural family $M_{4n+6}Ge_{2n+1}O_{8(n+1)}$ built from the regular intergrowth of $n$ olivine layers with a single rock-salt-like layer parallel to $(011)_{rh}$. The O atoms in $(Ni,Mg)_{10}Ge_3O_{16}$ form a cubic close-packed array, and its structure may also be viewed as an intergrowth of alternate $\{111\}$ triple layers of spinel-like structure with a single layer of rock-salt-like structure stacked in the direction of

$[001]_{hex}$. Fleet & Barbier (1988) reported the space group of $(Ni,Mg)_{10}Ge_3O_{16}$ to be $R\bar{3}$. Further consideration (this study) showed that both cobalt and magnesium arsenate [$Co_8As_3O_{16}$, Krishnamachari & Calvo (1970*a*); $Mg_{8.5}As_3O_{16}$, Bless & Kostiner (1973)] have analogous crystal structures to $(Ni,Mg)_{10}Ge_3O_{16}$, but with space group $R\bar{3}m$. We realized at this time that $R\bar{3}m$ was a possible space group for $(Ni,Mg)_{10}Ge_3O_{16}$, and that the reported structure closely corresponded to $R\bar{3}m$ symmetry. Subsequently, R. E. Marsh and Y. Le Page (personal communications, 1988) both drew our attention to this problem, Le Page noting that $R\bar{3}m$ symmetry was favoured by the program *MISSYM* (Le Page, 1987). We therefore report the revised structure in the higher space group.

From the work of Taylor & Heyding (1958) and Krishnamachari & Calvo (1970*a*), the mineral aerugite (Davis, Hey & Kingsbury, 1965) is isomorphous with the cobalt and magnesium arsenates, and the similar crystal chemistries of $Mg^{2+}$ and $Ni^{2+}$ in oxide compounds suggest that aerugite has the formula $Ni_{8.5}As_3O_{16}$. This is confirmed in the present study of the structure of synthetic aerugite. Finally, the arsenate and germanate structures are compared leading to the recognition of new structural series for the divalent metal arsenates.

## Experimental

$Ni_{8.5}As_3O_{16}$

Aerugite from South Terras mine, Cornwall (Davis *et al.*, 1965) was too fine-grained for single-crystal X-ray study. Synthetic aerugite crystals were grown from a commercial amorphous nickel arsenate compound (with an Ni:As atomic ratio of 4:5 as determined by neutron activation analysis) heated in air in a platinum dish at about 1470 K for 1 h. Initial melting and evaporation of arsenic oxide resulted in a mixture of a yellow microcrystalline phase and larger dark-green crystals of aerugite which were tabular with $\{001\}_{hex}$ dominant. The yellow phase has been identified by powder X-ray diffraction as a tetragonal form

of $Ni_3As_2O_8$, i.e., a polymorph of the mineral xanthio-site. It is probably isostructural with $Mg_3As_2O_8$ (Krishnamachari & Calvo, 1973) and with the te-tragonal form of $Co_3As_2O_8$ (Gopal, Rutherford & Robertson, 1980). The X-ray powder pattern of synthetic aerugite closely corresponds to that of natural aerugite (Davis et al., 1965) and the unit-cell param-eters ($a = 5.952$, $c = 27.561$ Å, $c/a = 4.631$, obtained with a Guinier–Hägg camera and Cu $K\alpha_1$ X-radiation) were similar to those of $Mg_{8.5}As_3O_{16}$. Single crystals were removed from the dish by soaking in distilled water for 24 h at room temperature. The crystal used for data collection was tabular, bound by $\{001\}_{hex}$ and rhombohedral faces, with approximate dimensions $0.13 \times 0.13 \times 0.15$ mm and a calculated volume of $0.25 \times 10^{-2}$ mm$^3$. X-ray precession photographs con-firmed that the Laue class was $\bar{3}m$. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ X-radiation. 20 reflections in $2\theta$ range $51.8$–$62.8°$ for cell parameters. Reflection data collected by $\theta$–$2\theta$ scan; scan angle ($2\theta$) $= 2.4°$, with dispersion correction. 4709 $hkl$, $\bar{h}kl$ reflections (hexagonal indices) allowed by space group $R\bar{3}m$ out to $2\theta = 90°$ measured; $-11 \le h \le 11$, $-11 \le k \le 11$, $0 \le l \le 54$. Standard reflections 220, $\bar{2}40$, $0\bar{2}8$; $R_{int} = 0.01$, no significant variation in intensity. Background, Lorentz, polarization and absorption corrections applied; trans-mission factors (by Gaussian integration with a $12 \times 12 \times 12$ grid) varied from $0.052$ for $\bar{1}11$ to $0.161$ for $2\bar{1}\bar{1}7$. 925 unique reflections. 297 reflections considered unobserved on the basis of $I < 3\sigma(I)$ $\{\sigma(I) = [I_m + 0.002^2(I_m - B)^2 + 0.005^2(I - I_m)^2]^{1/2}; I_m,$ measured intensity and $B$, background$\}$ and procedure below.

Structure refinement proceeded in space group $R\bar{3}m$ (Bless & Kostiner, 1973) using atomic positions equivalent to those in the structure of $(Ni,Mg)_{10}Ge_3O_{16}$ (Table 1) with $M(1)$ vacant, $M(2) \equiv Ni(1)$ with $5/6$ occupancy, and $M(3) \equiv Ni(2)$. $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2$; weak reflections $[|F_o| < (|F_o|_{max}/20)]$ were given a low weight ($\sigma = 1000$). Refinement using all reflections out to $2\theta = 90°$ and 35 variable parameters converged to $R = 0.023$, $wR = 0.026$, $S = 0.233$, $(\Delta/\sigma)_{max} = 5 \times 10^{-8}$, $\rho = -4.1$ e Å$^{-3}$ [near $As(2)$] to $5.7$ e Å$^{-3}$ [near $O(2)$]. The isotropic extinction param-eter for type I extinction ($g$; Coppens & Hamilton, 1970) is $1.20$ (2) $\times 10^{-4}$. Scattering factors for neutral atomic species and $f'$, $f''$ taken, respectively, from Tables 2.2B and 2.3.1 of International Tables for X-ray Crystallography (1974). Computations carried out with DATAP77 and LINEX77 (State University of New York at Buffalo).

**$(Ni,Mg)_{10}Ge_3O_{16}$**

The structure of $(Ni,Mg)_{10}Ge_3O_{16}$ was refined in space group $R\bar{3}m$, with the following new values (cf.

Table 1. *Positional and equivalent isotropic thermal parameters* (Å$^2$) *for aerugite* ($Ni_{8.5}As_3O_{16}$) *and* $(Ni,Mg)_{10}Ge_3O_{16}$ *in* $R\bar{3}m$ (*rhombohedral setting*)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

| | Equi-point | x | y | z | $B_{eq}$ |
|---|---|---|---|---|---|
| Aerugite ($Ni_{8.5}As_3O_{16}$) | | | | | |
| Ni(1) | 3(e) | 0.0 | 0.5 | 0.5 | 0.456 (9) |
| Ni(2) | 6(h) | 0.75281 (9) | 0.25478 (5) | y | 0.316 (6) |
| As(1) | 1(a) | 0.0 | 0.0 | 0.0 | 0.236 (9) |
| As(2) | 2(c) | 0.19203 (2) | x | x | 0.210 (8) |
| O(1) | 2(c) | 0.12956 (14) | x | x | 0.362 (44) |
| O(2) | 2(c) | 0.37881 (18) | x | x | 0.682 (51) |
| O(3) | 6(h) | 0.67168 (46) | 0.10604 (25) | y | 0.546 (30) |
| O(4) | 6(h) | 0.10195 (48) | 0.63450 (25) | y | 0.509 (24) |
| | | | | | |
| $(Ni,Mg)_{10}Ge_3O_{16}$ | | | | | |
| M(1) | 1(b) | 0.5 | 0.5 | 0.5 | 0.312 (13) |
| M(2) | 3(e) | 0.0 | 0.5 | 0.5 | 0.257 (5) |
| M(3) | 6(h) | 0.75735 (6) | 0.24897 (3) | y | 0.293 (4) |
| Ge(1) | 1(a) | 0.0 | 0.0 | 0.0 | 0.208 (5) |
| Ge(2) | 2(c) | 0.18915 (1) | x | x | 0.222 (3) |
| O(1) | 2(c) | 0.12717 (6) | x | x | 0.416 (23) |
| O(2) | 2(c) | 0.37637 (6) | x | x | 0.382 (23) |
| O(3) | 6(h) | 0.65943 (20) | 0.11284 (10) | y | 0.397 (12) |
| O(4) | 6(h) | 0.12209 (19) | 0.62598 (10) | y | 0.389 (10) |

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *in aerugite* ($Ni_{8.5}As_3O_{16}$)

| | | | | |
|---|---|---|---|---|
| Ni(1)–O(2) | 2.127 (3) | | Ni(1)–O(3$^i$) | 2.129 (2) |
| Ni(2)–O(4$^i$) | 2.035 (2) | | Ni(2)–O(2) | 2.066 (3) |
| Ni(2)–O(1) | 2.079 (2) | | Ni(2)–O(3$^{ii}$) | 2.105 (2) |
| As(1)–O(3) | 1.835 (2) | | As(2)–O(1) | 1.722 (4) |
| As(2)–O(4$^{iii}$) | 1.678 (2) | | | |

| | | | | |
|---|---|---|---|---|
| O(2)–Ni(1)–O(2$^{iii}$) | 180.0 | | O(2)–Ni(1)–O(3$^i$) | 90.72 (8) |
| O(2)–Ni(1)–O(3$^{ii}$) | 89.28 (8) | | O(3$^i$)–Ni(1)–O(3$^{iv}$) | 104.51 (12) |
| O(3)–Ni(1)–O(3$^{ii}$) | 180.0 | | O(3)–Ni(1)–O(3$^i$) | 75.49 (12) |
| O(4$^i$)–Ni(2)–O(4$^{iv}$) | 102.29 (14) | | O(4$^i$)–Ni(2)–O(2) | 87.17 (9) |
| O(4$^i$)–Ni(2)–O(1) | 92.92 (7) | | O(4$^i$)–Ni(2)–O(3$^{ii}$) | 166.61 (9) |
| O(4$^i$)–Ni(2)–O(3$^v$) | 90.95 (10) | | O(2)–Ni(2)–O(1) | 179.87 (14) |
| O(2)–Ni(2)–O(3$^{ii}$) | 91.59 (11) | | O(1)–Ni(2)–O(3$^{ii}$) | 88.31 (9) |
| O(3$^{ii}$)–Ni(2)–O(3$^v$) | 75.76 (13) | | O(3)–As(1)–O(3$^i$) | 89.54 (11) |
| O(3)–As(1)–O(3$^{iii}$) | 180.0 | | O(3)–As(1)–O(3$^{ii}$) | 90.46 (11) |
| O(1)–As(2)–O(4$^{iii}$) | 106.86 (10) | | O(4$^{iii}$)–As(2)–O(4$^{ii}$) | 111.95 (9) |

Symmetry code: (i) $z, x, y$; (ii) $-y, -x, -z$; (iii) $-x, -y, -z$; (iv) $y, z, x$; (v) $-y, -z, -x$.

Fleet & Barbier, 1988): 940 unique reflections, 300 considered unobserved; 40 variable parameters con-verged to $R = 0.013$, $wR = 0.008$, $S = 0.058$, $(\Delta/\sigma)_{max} = 3 \times 10^{-6}$, $\rho = -0.36$ to $0.24$ e Å$^{-3}$; $g = 0.174$ (1) $\times 10^{-4}$. Statistical tests and the satisfactory refinement both confirm the space group $R\bar{3}m$.

**Discussion**

Positional parameters are given in Table 1, and selected interatomic distances and bond angles for aerugite are given in Table 2.* A drawing of the aerugite structure projected on $(011)_{rh}$ is shown in Fig. 1; a similar projection of the $(Ni,Mg)_{10}Ge_3O_{16}$ structure is shown in

Fig. 1 of Fleet & Barbier (1988) and in Fig. 3(a) of Barbier (1987b).

## Aerugite (Ni$_{8.5}$As$_3$O$_{16}$)

The O atoms in aerugite form a cubic close-packed array stacked in the direction of [001]$_{hex}$ ([111]$_{rh}$) and the As and Ni atoms combine with them to form layers of polyhedra parallel to (001)$_{hex}$. Three-layer structural units [comprised of two layers of Ni(2)O$_6$ octahedra enclosing a layer of As(2)O$_4$ tetrahedra] are interspersed by a single layer of rock-salt-like structure [comprised of mixed As(1)O$_6$ and Ni(1)O$_6$ octahedra; R in Fig. 1]. Aerugite (Ni$_{8.5}$As$_3$O$_{16}$) is clearly isomorphous with Mg$_{8.5}$As$_3$O$_{16}$ (Bless & Kostiner, 1973). Arsenic is in the 5+ oxidation state as confirmed by the average octahedral and tetrahedral As—O bond lengths (1·835 and 1·695 Å, respectively; Table 2) which are in very good agreement with values predicted from the ionic radii (Shannon, 1976). The partial occupancy of the Ni positions required to charge balance the arsenate
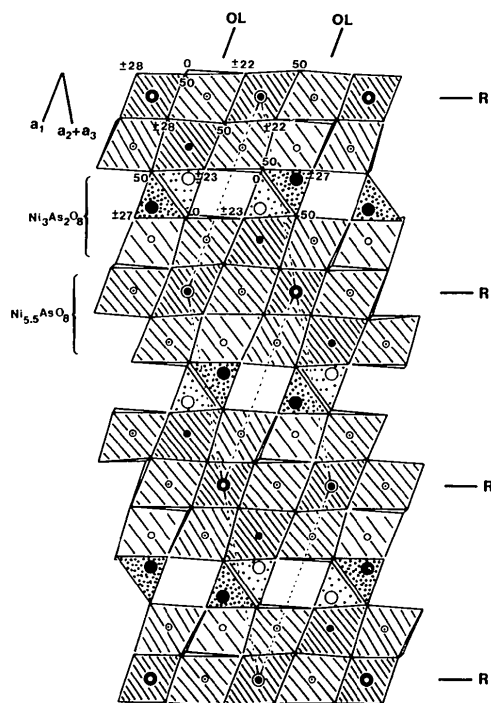


Fig. 1. The structure of aerugite (Ni$_{8.5}$As$_3$O$_{16}$), projected on (011)$_{rh}$. Large and small circles represent As and Ni atoms, respectively. O atoms occupy the corners of the polyhedra. Open, filled and dotted circles are at heights 0, 50, and ±25, respectively. Atom heights are expressed in 1/100th of the repeat distance in the projection direction (5·95 Å). The rock-salt layers (R) parallel to (111)$_{rh}$ are cation deficient: their Ni sites [Ni(1)] have a partial occupancy of 5/6. Other octahedral layers parallel to (111)$_{rh}$ accommodate Ni(2) atoms. The (011)$_{rh}$ layers denoted 'OL' are cation-deficient olivine-type layers also found in other arsenate structures (cf. Figs. 2 and 3). The aerugite structure is closely related to the (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ structure [cf. Fig. 1 of Fleet & Barbier (1988) and Fig. 3a of Barbier (1987b)].

Table 3. *Mean bond distances (Å) in nickel, magnesium and cobalt arsenates*

| | Ni$_{8.5}$As$_3$O$_{16}$ | | Mg$_{8.5}$As$_3$O$_{16}$[a] | Co$_8$As$_3$O$_{16}$[b] | |
|---|---|---|---|---|---|
| Ni(1)—O | 2·09[c] | 2·128 | Mg(1)—O | 2·158 | Co(1)—O | 2·14 |
| Ni(2)—O | | 2·071 | Mg(2)—O | 2·088 | Co(2)—O | 2·13 |
| As(1)—O | 1·86[c] | 1·835 | | 1·857 | | 1·84 |
| As(2)—O | 1·74[c] | 1·689 | | 1·684 | | 1·68 |

References: (a) Bless & Kostiner (1973); (b) Krishnamachari & Calvo (1970a); (c) ideal values, Shannon (1976).

group within the cubic close-packed oxygen array is limited to Ni(1). Krishnamachari & Calvo (1970a) suggest the analogous cobalt arsenate to be Co$_8$As$_3$O$_{16}$, charge-balanced by a small proportion of As$^{3+}$ and with Co$^{2+}$ distributed equally over both divalent metal positions. In view of the isomorphic nature of aerugite (Ni$_{8.5}$As$_3$O$_{16}$) and Mg$_{8.5}$As$_3$O$_{16}$ further study of the cobalt arsenate seems desirable.

Comparison of the bond lengths for (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ (Fleet & Barbier, 1988) and aerugite (Tables 2 and 3) shows that the partial occupancy of the Ni(1) site results in an increase in mean Ni(1)—O bond length: M(2)—O = 2·095 vs Ni(1)—O = 2·128 Å; M(3)—O = 2·078 vs Ni(2)—O = 2·071 Å. A similar effect has been reported for Mg$_{8.5}$As$_3$O$_{16}$ (Bless & Kostiner, 1973).

## Relation to (Ni,Mg)$_{10}$Ge$_3$O$_{16}$

Comparison of the (011)$_{rh}$ projections of aerugite and (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ shows both structures to have similar rhombohedral unit cells based on cubic close-packing of O atoms with identical layer stackings in the [111]$_{rh}$ = [001]$_{hex}$ direction. The only difference arises from the presence (in the aerugite structure) of both empty and partially occupied octahedral metal sites; these are naturally imposed by the different valence states of As$^{5+}$ and Ge$^{4+}$, leading to a metal/arsenic ratio of 8·5/3 in the arsenate and a metal/germanium ratio of 10/3 in the germanate. As a consequence, the aerugite structure contains (001)$_{hex}$ layers built up of AsO$_4$ tetrahedra only, which, owing to the short As(2)—O tetrahedral bonds, result in a compression of the structure along the [001]$_{hex}$ direction: c = 27·5676 Å and c/a = 4·632 for Ni$_{8.5}$As$_3$O$_{16}$ whereas c = 28·6135 Å and c/a = 4·862 for (Ni,Mg)$_{10}$Ge$_3$O$_{16}$. The presence of octahedral vacancies in these tetrahedral [As(2)O$_4$] layers precludes description of the aerugite structure in terms of {111} spinel slabs similar to those identified in the (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ structure (Barbier, 1987a,b). However, it is interesting to note that a similar vacancy configuration exists in the structure of spinel-related orthovanadates such as Ni$_3$V$_2$O$_8$ and Mg$_3$V$_2$O$_8$ (Krishnamachari & Calvo, 1971).

As a result of the partial occupancy of the Ni(1) site in aerugite, the layers of mixed As(1)O$_6$ and Ni(1)O$_6$ octahedra (R in Fig. 1) correspond to cation-deficient

rock-salt layers with $Ni_{2.5}AsO_4$ composition. The random distribution of $Ni^{2+}$ cations within these layers is consistent with the overall rhombohedral symmetry of the aerugite structure, and no indication of vacancy ordering (leading to a lower symmetry cell) has been observed in either powder or single-crystal X-ray diffraction experiments.

As already noted by Bless & Kostiner (1973), the cation distribution in the aerugite structure results in the formation of neutrally charged double close-packed layers with compositions $Ni_{5.5}AsO_8$ and $Ni_3As_2O_8$ (Fig. 1). Similar neutral layers in the $(Ni,Mg)_{10}Ge_3O_{16}$ structure have the stoichiometries $(Ni,Mg)_6GeO_8$ and $(Ni,Mg)_4Ge_2O_8$, respectively. It would seem that the same charge-balance scheme could be expected for the cobalt arsenate analogue, even though its structure (as determined by Krishnamachari & Calvo, 1970a) seems to be somewhat different. We also point out that the cation charge per *single* close-packed layer is the same in the aerugite and $(Ni,Mg)_{10}Ge_3O_{16}$ structures. For example, with reference to the aerugite structure (Fig. 1), the close-packed layers with tetrahedral As(2) cations have $(2 \times 5 + 1 \times 0) = 10+$ units of charge per formula unit, which compares with $(2 \times 4 + 1 \times 2) = 10+$ in $(Ni,Mg)_{10}Ge_3O_{16}$; and the close-packed layers with octahedral As(1) and Ni(1) cations (R in Fig. 1) have $(1 \times 5 + 3 \times 5/6 \times 2) = 10+$ units of charge per formula unit which compares with $(1 \times 4 + 3 \times 2) = 10+$ in $(Ni,Mg)_{10}Ge_3O_{16}$. Thus, conservation of layer charge may be a significant factor in the stability of these compounds.

### Arsenate and germanate structural series

The crystal structures of two cobalt arsenates, $Co_{6.95}As_{3.62}O_{16}$ (Krishnamachari & Calvo, 1974) and $Co_3As_2O_8$ [the analogue of xanthiosite, $Ni_3As_2O_8$; Krishnamachari & Calvo (1970b)], are depicted in equivalent projections (Figs. 2 and 3).

Like aerugite, both structures are based on approximate close-packings of O atoms. The $Co_{9.65}As_{3.62}O_{16}$ structure corresponds to a two-layer hexagonal stacking of close-packed (001) layers, and apart from the partial occupancies of some sites, it is isostructural with olivine. The $Co_3As_2O_8$ structure is also built-up of similar olivine-type layers, albeit with a mixed hexagonal–cubic four-layer stacking in the [010] direction. Moreover, in order to achieve a Co/As ratio of 3/2, one quarter of the octahedral sites are vacant in such a way that all layers are identical with the $Co_3As_2O_8$ composition. [Similar layers exist in the structures of sarcopside-type orthophosphates such as $Ni_3P_2O_8$ (Calvo & Faggiani, 1975)]. It is also noteworthy that this vacancy ordering in $Co_3As_2O_8$ avoids the face-sharing of tetrahedral and octahedral sites along the cubic close-packed oxygen layer (cf. Fig. 3).

Olivine-type layers are also present in the aerugite structure, parallel to $(011)_{rh}$ and denoted 'OL' in Fig. 1. As a result of the partial occupancy of the Ni(1) site within the rock-salt layers (R), the olivine-type layers in
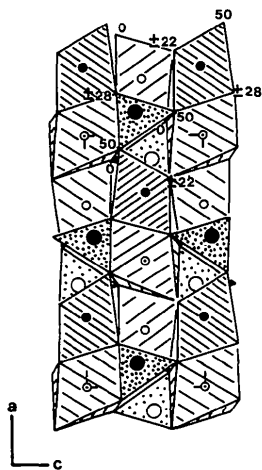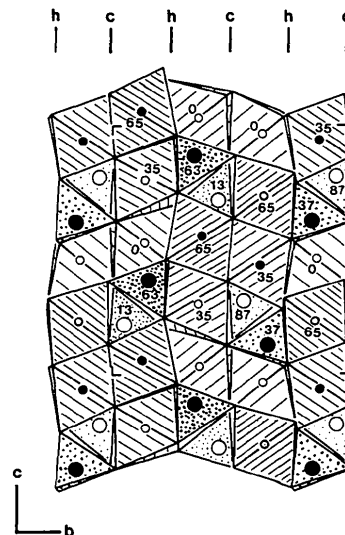


Fig. 2. The structure of $Co_{6.95}As_{3.62}O_{16}$ projected on (010). Large and small circles represent As and Co atoms, respectively. O atoms occupy the corners of the polyhedra. Open, filled and dotted circles are at heights 0, 50, and $\pm 25$, respectively. Atom heights are expressed in units of $b/100$. The structure corresponds to an hexagonal stacking of (001) close-packed layers and is of the olivine type. Note, however, that some Co sites (at heights $\pm 25$) and the As sites are partially occupied.



Fig. 3. The structure of the xanthiosite analogue $Co_3As_2O_8$, projected on (100). Large and small circles represent As and Co atoms, respectively. O atoms occupy the corners of the polyhedra. For clarity only the cation heights have been indicated. The structure consists of a mixed hexagonal–cubic (h,c) stacking of similar (010) close-packed layers. All layers are of the olivine type with $\frac{1}{4}$ of the Co sites empty (thus avoiding face-sharing between octahedra and tetrahedra on the 'c' oxygen layers). Note that the Co atoms at height 0 are displaced from the centres of their octahedra.

aerugite are nickel-deficient with a stoichiometry of $Ni_{3.67}As_2O_8$. Charge balance occurs by alternation with cation-deficient $Ni_{4.83}AsO_8$ octahedral layers. An analogous description of the $(Ni,Mg)_{10}Ge_3O_{16}$ structure in terms of $(Ni,Mg)_4Ge_2O_8$ olivine layers and $(Ni,Mg)_6GeO_8$ rock-salt layers (Barbier, 1987a) led to the recognition of a new structural family of germanate compounds, $M_{4n+6}Ge_{2n+1}O_{8(n+1)}$ $(M = Ni + Mg)$, of which the members $n = 1$ $(M_{10}Ge_3O_{16})$, $n = 2$ $(M_{14}Ge_5O_{24})$ and $n = \infty$ $(M_2GeO_4$ olivine) have been identified as stable phases (Barbier, 1987b). The structural relationship between aerugite ($Ni_{8.5}As_3O_{16}$ and its Co analogue), xanthiosite ($Ni_3As_2O_8$ and its Co analogue), and the olivine-like phase $Co_{6.95}As_{3.62}O_{16}$ and its possible but as yet unreported Ni analogue, suggest that the nickel and cobalt arsenates (and perhaps the magnesium arsenates) may form a structural series similar to the germanate series, with aerugite and xanthiosite corresponding to the end members $n = 1$ and $n = \infty$, respectively. Indeed, work presently in progress indicates the existence of yet another new nickel arsenate phase with a composition intermediate between those of aerugite and xanthiosite and with unit-cell parameters corresponding to a six-layer close-packed structure, possibly similar to that of the $n = 2$ member of the germanate series, $M_{14}Ge_5O_{24}$ (cf. Barbier, 1987b).

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# A Structural Analysis of Barium Magnesium Hollandites

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## Abstract

The composition range, lattice parameters and ordering of the Ba ions in the monoclinic hollandite system $Ba_x(Mg_xTi_{8-x})O_{16}$ have been investigated using X-ray powder diffraction data. Rietveld refinement of high-resolution neutron powder diffraction data has also been carried out on the end members $Ba_{1.14}(Mg_{1.14}Ti_{6.86})O_{16}$ and $Ba_{1.33}(Mg_{1.33}Ti_{6.67})O_{16}$. The increasing monoclinic distortion in these compounds with increasing Ba concentration arises from a change in the shape of the b-axis tunnels. No significant deformation of the tunnel walls occurs and the cell volume remains constant. The distortion is stabilized in the $x = 1.33$ hollandite by the Mg ions preferentially occupying one particular type of O octahedra. Off-centring of the octahedral cations within the O octahedra appears to reduce the extent of three-dimensional ordering in Ba hollandites. This probably arises because the electrostatic shielding between adjacent tunnels is increased when large dipole moments are set up by off-centre cations in the tunnel walls. Reasonable agreement is obtained between the observed and calculated positons of the X-ray superlattice lines in $Ba_x(Mg_xTi_{8-x})O_{16}$ for $x \le 1.23$. In the vicinity of $x = 1.33$ the observed $2\theta$ positions differ significantly from the values calculated