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A New Mg-Al-Ni Asbolane[1]

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Asbolanes are major concentrator minerals of economically important elements such as Mn, Ni, and Co [1]. The crystallochemical nature of these finely divided minerals has been established by electron microdiffraction and energy-dispersive analysis of the particle composition directly in the electron microscope [4]. It has proved particularly helpful to combine these methods with infrared spectroscopy, thermogravimetric analysis, and X-ray photoelectron spectroscopy, which have provided information on the contents of molecular water and OH groups, the coordination of Mn, Co, and Ni, the valencies of these, and their local distribution.

Asbolanes are minerals whose structures are formed by the orderly or disorderly intercalation along the *c* axis of layers differing in composition, which may also differ in structure and which are not codimensional in the (001) planes. The minerals are described in terms of two sublattices inserted one in the other, which differ in the basal unit-cell parameters. A very important feature that distinguishes asbolanes from all other minerals is that the two-dimensional continuous layers of one type as a rule coexist with defective (insular) layers of the other type. The asbolane structures may be composed either only of octahedral layers (e.g., Co-Ni asbolane and Ni asbolane) or of octahedral and tetrahedral layers alternating along the *c* axis (Co asbolane).

The layers in the asbolane structure are usually populated on a trioctahedral law. On the other hand, Ni asbolane from the Lipov deposit in the Middle Urals and from the Batasha deposit in Kazakhstan show differing modes of population in the differing types of layer. There are Mn^{4+} and Ni octahedral layers with ordered intercalation in this mineral along the *c* axis. The first of these layers is populated on a trioctahedral pattern, while the second is populated in the main on a dioctahedral one. The Mn^{4+} layers are two-dimensionally continuous, while the Ni layers are defective (insular). Between the layers of different types in the asbolane, there are always electrostatic and hydrogen bonds: the positive charge on the two-dimensionally continuous Mn^{4+} layers is balanced by the negative charge on the defective layers; the oxygen atoms in the Mn^{4+} layers form O-H...O hydrogen bonds with hydroxyl groups in the defective layers. We have found a new variety of this mineral, Mg-Al-Ni asbolane, in buried Fe-Mn crusts at a guyot in the Pacific Ocean. Here we examine this asbolane variety in detail.

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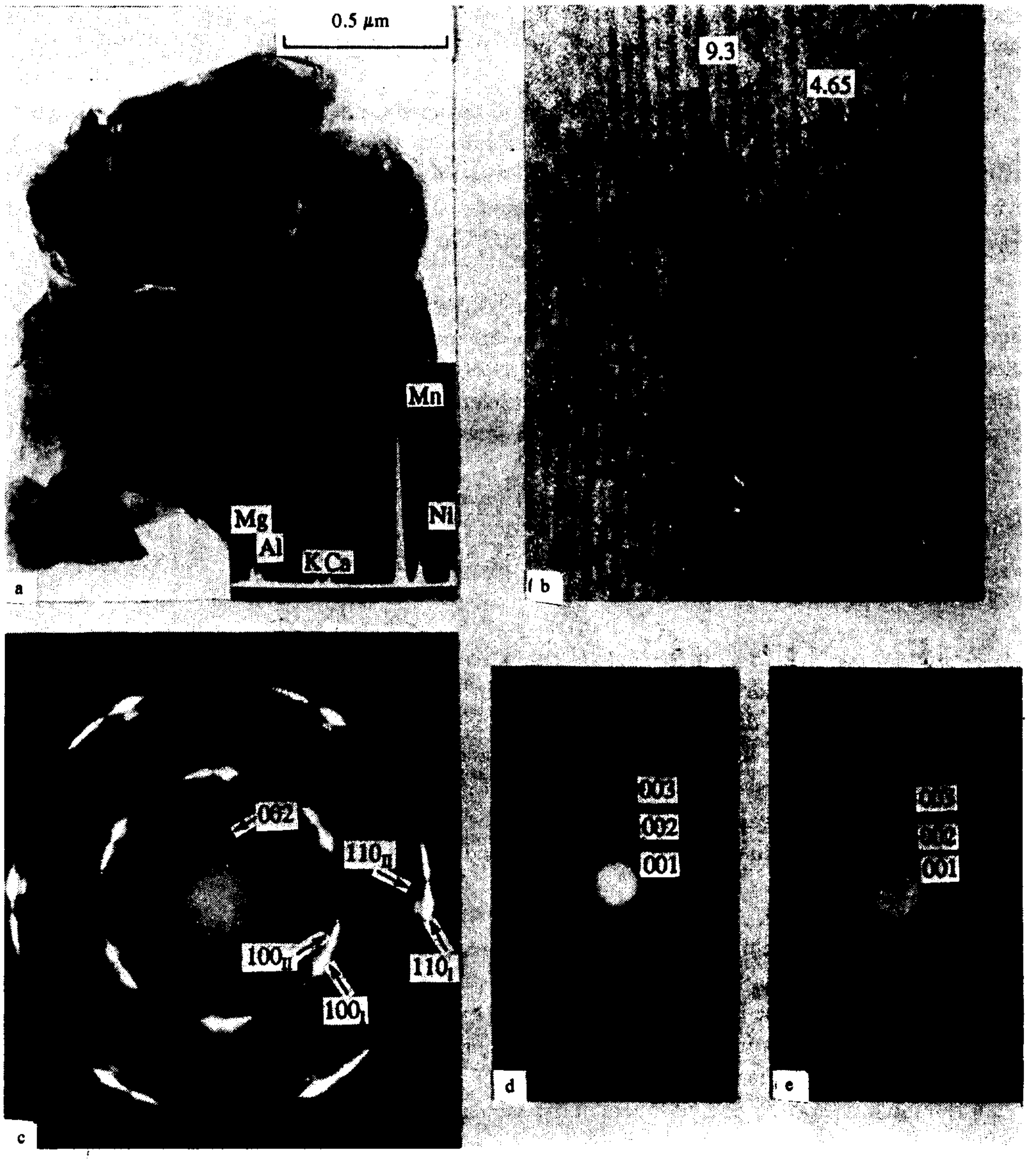
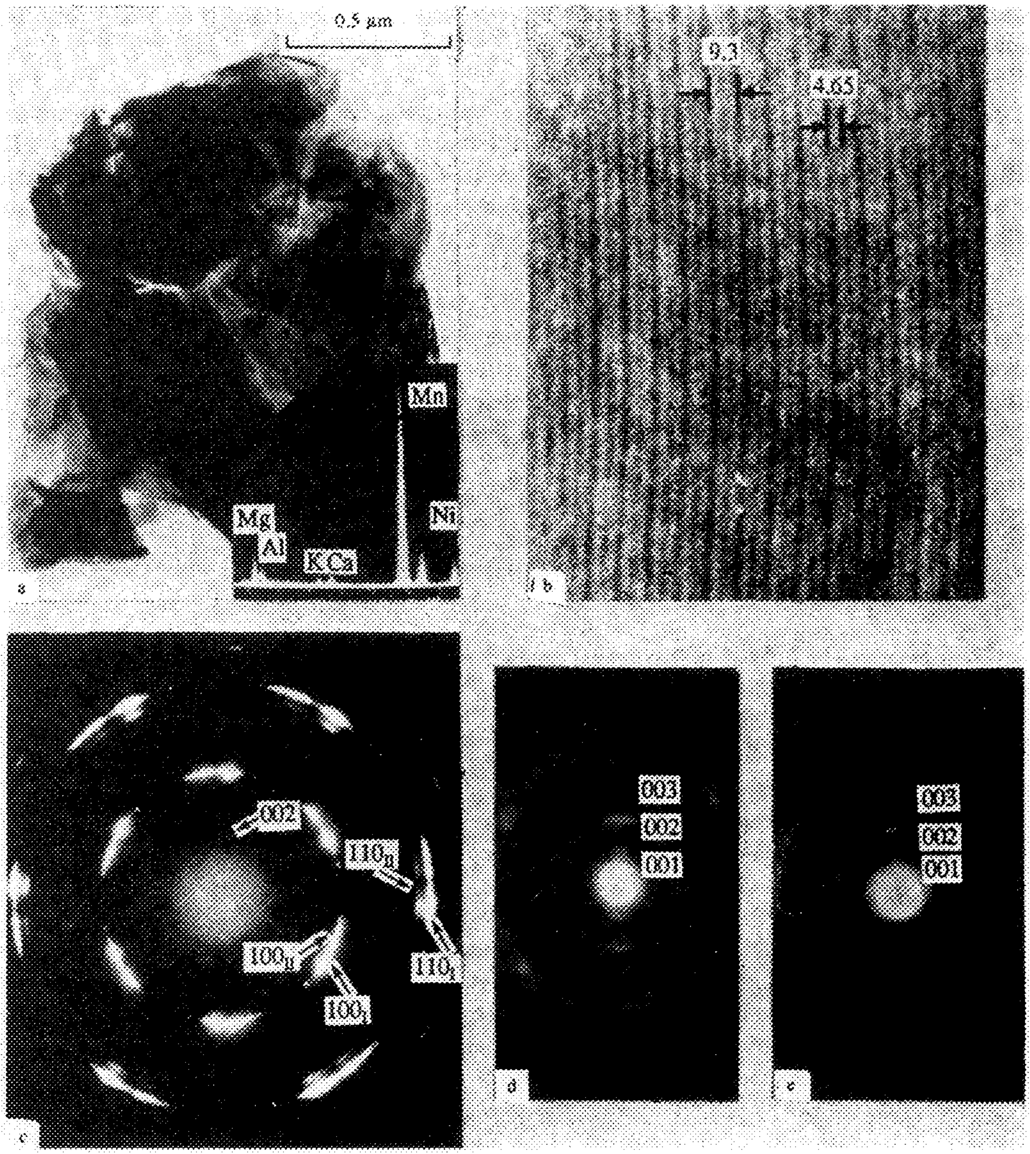


Fig. 1. a) Transmission electron micrograph of platy particles of Mg-Al-Ni asbolane and energy-dispersive spectrum recorded from one of them; b) high-resolution image of the layered lattice in this mineral; c, d, and e) electron-diffraction patterns containing *hk*0 and 00*l* reflections (c) and 00*l* ones (d and e).

The asbolane was examined with a JEOL JEM-100C analytical electron microscope fitted with a goniometer providing tilts of ±60° and a Kevex-5100 energy-dispersive spectrometer. High-resolution pictures were recorded with a Philips CM-30 electron microscope.

The Mg-Al-Ni asbolane was observed in specimens of Fe-Mn crusts from the Wodejebato guyot in the Northwest Pacific on a voyage by the *Joides Resolution* drilling ship: Fe-Mn crusts were also brought on board on drilling the crests of the guyots [5].



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Electron microdiffraction patterns were recorded with the electron beam perpendicular to the basal planes of the particles, which revealed two systems of hexagonally disposed reflection networks (Fig. 1c).

The intensities of the reflections forming the hexagonal net closer to the center were less by a substantial factor than those of reflections forming the net further from the center. The diffraction patterns from the bent edges of the platy particles (Figs. 1c to 1e) record a single series of basal reflections having $d_{00l} = 9.3/l$ Å. The asbolane particles (inset in Fig. 1a) contain Mn, Mg, Al, and Ni, and also small amounts of K and Ca.

We conclude from the combination of a single integer series of basal reflections from the bent edges and the two hexagonal nets of *hk*0 reflections that the structure of this Mg-Al-Ni asbolane consists of layers of two types with an ordered alternation on the law ABAB..., with the layers differing one from another in the basal a_0 parameters of the unit cells. Such a structure can be described in terms of two hexagonal sublattices inserted one in the other [4].

The electron-diffraction patterns (Fig. 1c) gave the hexagonal-cell parameters of the two sublattices: $a_0 = 2.83$ Å, $c_0 = 9.30$ Å (sublattice I) and $a_0 = 3.03$ Å, $c_0 = 9.30$ Å (sublattice II); the c_0 parameter corresponds to the sum of the thicknesses of the Mn^{4+} and Mg-Al-Ni layers constituting the structure.

Parameter $a_0 = 2.83$ Å of hexagonal sublattice I indicates that it corresponds, as in other asbolanes [4], to octahedral layers filled with Mn^{4+}; the larger parameter $a_0 = 3.303$ Å of sublattice II agrees with the view that the corresponding octahedral layers contain Mg, Ni, and evidently Al, which are larger than Mn^{4+}. Octahedral coordination of those elements in the layers for this asbolane agrees also with the ratio of the intensities of the basal reflections I_{100} and I_{110}, which characterize each of these two sublattices and are $I_{100}/I_{110} = 0.5$, since approximately such relations between those reflections correspond to the octahedral layers in Co-Ni and Co asbolanes [4].

The minimum possible parameters for the two sublattices indicate that the corresponding octahedral layers are populated by Mn^{4+} and Mg-Al-Ni cations on a trioctahedral law; the *hk*0 reflections from sublattice II are much weaker than the corresponding ones from I, so the volumes of the diffracting regions in the Mg-Al-Ni component are much smaller, and the total volume of them is small by comparison with that of the Mn^{4+} component. This means that the Mg-Al-Ni layers resemble the Co-Ni and Ni layers in the asbolanes previously studied [4] in being defective (insular). We confirmed [2] the insularity of the Ni layers in Ni asbolane from the Lipov deposit in the Middle Urals directly by means of high-resolution electron microscopy. We used the basal 00*l* reflections from kinks and flexures in the platy particles in suspension preparations in order to obtain high-resolution images of the layer structure. We used this method also here to identify the defectiveness (insularity) of the Mg-Al-Ni layers. The high-resolution picture clearly showed intercalation of parallel dark bands differing in blackening (Fig. 1b). The distances between the darker bands (and also between the less dark ones) are about 9.3 Å, which corresponds to the distance along the normal between two two-dimensional continuous Mn^{4+} layers (or between defective Mg-Al-Ni layers). The distances between adjacent dark bands are about 4.75 Å, which corresponds to the distance between those layers of different types. The darker bands correspond to two-dimensionally continuous Mn^{4+} octahedral layers, and the less dark ones to defective Mg-Al-Ni ones. The defectiveness of the latter is seen not only in the general reduction in blackening relative to the lines representing the Mn^{4+} layers but also by the discontinuities (discreteness).

Table 1

Composition of Mg-Al-Ni asbolane calculated from analysis of 12 particles*

Oxide	Content, %	Spread, ±%	Detection limit, %	Formula coefficient
MgO	9.96	1.67	0.97	0.28
Al_2O_3	4.12	1.23	0.62	0.09
K_2O	0.69	0.56	0.23	0.02
Ca_2O	2.06	0.68	0.21	0.04
MnO	76.83	2.38	0.47	1.00
NiO	6.34	0.39	0.40	0.10

*Analysis under conditions of normalization to 100 percent.

These data directly confirm previous conclusions on the origin of the defects [4] in one of the sublattices. We calculated the structural formula from quantitative analysis performed with the energy-dispersive spectrometer directly in the electron microscope by Mokhov's method [3]; Table 1 gives results averaged over 12 particles. We calculated the formula on the assumption that there is an analogy with Co-Ni and Ni asbolanes [4] in that the Mg-Al-Ni layers have a negative charge of -0.4 and the two-dimensionally continuous Mn^{4+} layers have correspondingly a change of +0.4. The formula is then

$$[Mn_1^{4+}O_{1.6}(OH)_{0.4}]^{+0.4} \times [(Mg_{0.28}Al_{0.09}Ni_{0.1})Ca_{0.04}K_{0.02}(OH)_{1.53}]^{-04} nH_2O.$$

The hydroxyl water nH_2O has been written by analogy with the other asbolanes. Its molecules coordinate Ca and K cations between the insular Mg-Al-Ni layers. The formula of this asbolane has element contents in the two types of layer that make it virtually identical with the formulas of Co-Ni and Ni asbolanes [4]. Figure 2 gives a scheme for the structure of the Mg-Al-Ni asbolanes.

We confirmed the uniform intercalation of Mn^{4+} and Mg-Al-Ni layers along the *c* axis from the intensities of the 00*l* reflections. We calculated the Φ_t^2 structural factors for the Fig. 2 model, which were compared with the experimental intensities of the corresponding reflections subject to the condition that $I(00l) = K \cdot \Phi^2(00l)$.

The calculated $\Phi_t^2(00l)$ for the 001, 002, and 003 reflections are respectively 14, 60, and 5; they correspond quite well to the values of $\Phi^2_{ext}(00l)$ estimated from several electron-diffraction patterns as 17, 60, and 7.

The formation of the mixed-layer Mg-Al-Ni asbolane can be represented as follows. This mineral in buried crusts is in close association with asbolane-buserite. The cation compositions

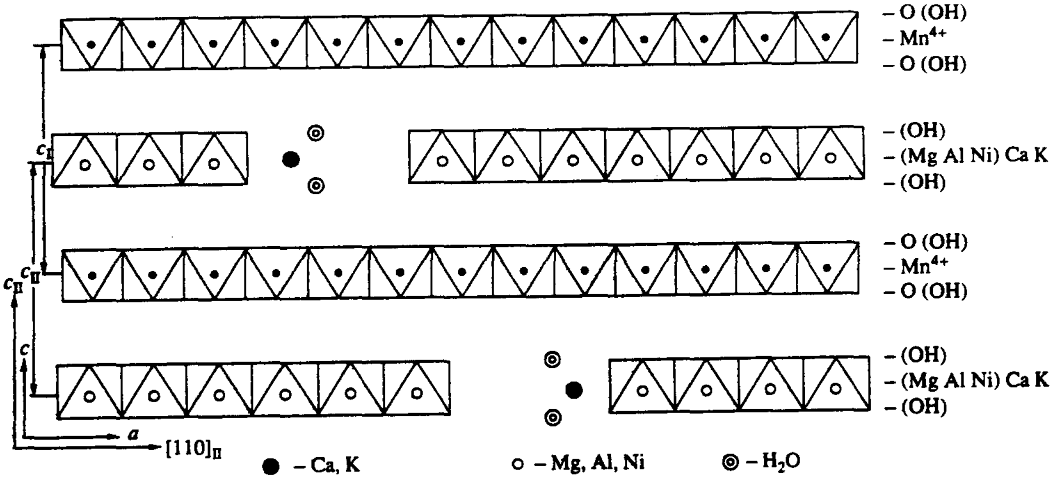

Fig. 2. Scheme for the structure of Mg-Al-Ni asbolane in projection on the (010) plane.

of these mixed-layer minerals are indicated as virtually identical by energy-dispersive X-ray analysis. It has been found that asbolanes from New Caledonia and the Middle Urals were formed directly by solid-state replacement of asbolane-buserite [4]. The formation of our asbolane may be explained similarly. The basis of the structure in asbolane-buserite and asbolane is constituted by octahedral Mn^{4+} layers [4], between which in asbolane-buserite lie with a disordered intercalation along the *c* axis not only exchangeable Mg, Al, and Ni cations and H_2O molecules but also hydroxyl insular Mg-Al-Ni$(OH)_x$ layers (Fig. 2). To transform asbolane-buserite to asbolane it is necessary for the Mg, Al, and Ni cations in the corresponding interlayer gaps to produce insular hydroxyl Mg-Al-Ni$(OH)_x$ layers simply by rearrangement and replacement of H_2O by OH. That solid-state process occurs quite readily in the Wodejabato buried crusts in the Pacific when the sediment ages.

An experimental confirmation of this is that electron-diffraction patterns from various platy particles in the specimens enable one to trace an almost continuous transition from asbolane-buserite to asbolane.

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