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SUPERGENE COBALT MINERALS FROM NEW CALEDONIA

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ABSTRACT

A study of cobalt mineralization present in weathered ultramafic rocks from New Caledonia revealed the following minerals: heterogenite (*2H* and *3R* polytypes), asbolan (with cobalt and nickel), lithiophorite, intermediate phases between asbolan and lithiophorite, cryptomelane, ramsdellite and todorokite; only lithiophorite and cryptomelane had previously been characterized in New Caledonia. Cryptomelane, ramsdellite and todorokite contain only traces of cobalt. The other minerals, the main cobalt bearers, occur not only as cryptocrystalline aggregates but also as crystals or fibers up to several hundred μm long. They form concretions, but more often occur as pseudomorphs after silicates and plant roots, which are habits not previously documented for these minerals. Microprobe analyses show that (1) the heterogenite is much more nickeliferous (up to 7.5% NiO) and the lithiophorite, more cobaltiferous (up to 11.5% Co_2O_3), than those found elsewhere; (2) the asbolan shows more variable compositions than those described elsewhere, ranging from purely cobaltiferous to purely nickeliferous end-members; and (3) new phases exist with compositions between those of asbolan and lithiophorite. Thermal, chemical and crystallographic data suggest structural models that differ from those in the literature, and allow for the existence of continuous series, between cobaltiferous and nickeliferous end-members of asbolan and between asbolan and lithiophorite.

Keywords: cobalt, asbolan, heterogenite, lithiophorite, weathering, ultramafic rocks, New Caledonia.

SOMMAIRE

L'étude des minéralisations à cobalt présentes dans les latérites de roches ultrabasiques en Nouvelle-Calédonie a mis en évidence les minéraux suivants: hétérogénite (polytypes *2H* et *3R*), asbolane (à cobalt et nickel), lithiophorite, phases intermédiaires entre asbolane et lithiophorite, cryptomélane, ramsdellite et todorokite; seuls lithiophorite et cryptomélane avaient déjà été signalés en Nouvelle-Calédonie. Cryptomélane, ramsdellite et todorokite ne renferment que des traces en cobalt. Les autres minéraux, principaux porteurs de la minéralisation, se présentent non seulement à l'état cryptocristallin, mais aussi en cristaux ou fibres atteignant quelques centaines de μm; ils forment des concrétions, mais le plus souvent remplacent les silicates et les racines, formes d'expression nouvelles pour ces minéraux. Les analyses à la microsonde montrent que (1) les hétérogénites sont nettement plus nickelifères (jusqu'à 7.5% NiO) et la lithiophorite, plus cobaltifère (jusqu'à 11.5% Co_2O_3) que celles étudiées ailleurs; (2) les asbolanes présentent des compositions plus variées que celles décrites ailleurs, allant de termes purement cobaltifères à des termes purement nickelifères; (3) de nouvelles phases existent, de compositions intermédiaires entre les asbolanes et la lithiophorite. Les données thermiques, chimiques et cristallographiques suggèrent des modèles structuraux différents de ceux proposés dans la littérature et autorisant l'existence de séries continues, d'une part au sein des asbolanes, d'autre part entre asbolanes et lithiophorite.

Mots-clés: cobalt, asbolane, hétérogénite, lithiophorite, latérite, roches ultrabasiques, Nouvelle-Calédonie.

INTRODUCTION

Ultrabasic rocks constitute more than a third of the surface of New Caledonia. They are essentially composed of harzburgites and dunites, serpentinized to various degrees (Troly *et al.* 1979). These rocks are deeply weathered and covered by a thick mantle composed of two horizons. In the lower horizon, in which the structure is preserved (saprolite), the silicates are hydrolyzed; the earthy residual upper horizon is essentially composed of iron hydroxide (Trescases 1975, Troly *et al.* 1979). These weathering profiles host supergene cobalt mineralization of economic interest; no detailed studies have previously been made of such mineralization.

This paper reports the mineralogical results of the first comprehensive study of the cobalt mineralization in New Caledonia. The cobalt minerals are identified, and details of their chemical composition, structure and physical properties are given. The metallogenic results are described in detail elsewhere (Llorca 1990).

REVIEW OF PREVIOUS STUDIES ON NEW CALEDONIAN ORES

Glasser (1903) proposed that the cobalt in New Caledonia is present in noncrystalline or poorly crystalline manganese oxides called "asbolans"; these black products were used as the only guide to mineralization. However, to date, the exact nature of these products and their precise location within the

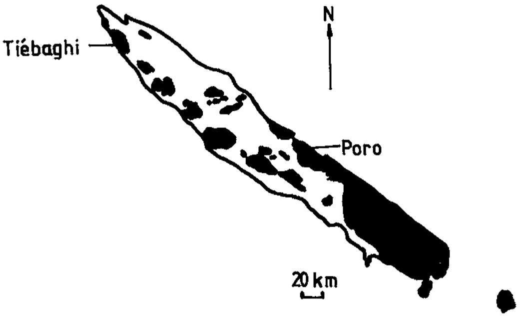


FIG. 1. Occurrences of ultrabasic rocks in New Caledonia and location of the two main areas that were sampled for this study.

weathering profiles remained obscure. Some authors (Queneau 1971, Perseil 1972, Trescases 1975) attempted to determine the nature of these phases; Perseil identified lithiophorite and cryptomelane.

GEOLOGICAL OCCURRENCE AND SAMPLING

Cobalt mineralization in New Caledonia results from the supergene concentration of the cobalt, which occurs as traces in silicates and oxides of the fresh ultrabasic rocks. The present studies were focussed principally on the Poro and Tiébaghi blocks (Fig. 1), which are considered to be representative of the ultrabasic rock types, climates and types of cobalt mineralization known throughout the island. Geological and geochemical studies of various representative profiles located principally on these blocks (Llorca 1986a, 1990) showed that cobalt content gradually increases from the fresh rock (150 ppm) to a transition horizon between saprolite and the ferruginous horizon, where it is concentrated owing to downward leaching from the ferruginous horizon. In areas such as the Poro block, where the depth of weathering is highly variable because the parent rock is variously serpentinized, accumulation is stronger in depressions (Llorca 1986a, 1990). Cobalt values in the transition horizon, usually 0.55%, attain 1.30% in those depressions. Cobalt mineralization occurs as bluish black-grey products that can exist as spots, coatings or concretions along joints and cracks, particularly in the saprolite, or as root fossils and impregnations in the overlying earthy material. Cobalt concentration is not, however, proportional to the quantity of visible "black products" (Llorca 1986a, 1990).

From the profiles examined, 40 samples having a minimum cobalt content of 0.5%, and representing the various macroscopic forms, horizons, geological and morphological settings observed (Fig. 2), were selected for mineralogical studies. For all mineralogical techniques using powders, the black products (except for a few samples with 4 to 10% Co) were concentrated by washing off the limonite and sieving; the 100–250 μm fraction was collected. Further concentration could in some cases be obtained by a 15-minute treatment in 12N HCl. In order to preserve the structure of the soft samples for microscopic study as polished blocks, these samples were collected by hammering 20-cm long 5-cm diameter PVC tubes into the mine faces. The samples were then impregnated under vacuum and under pressure (70 bars).

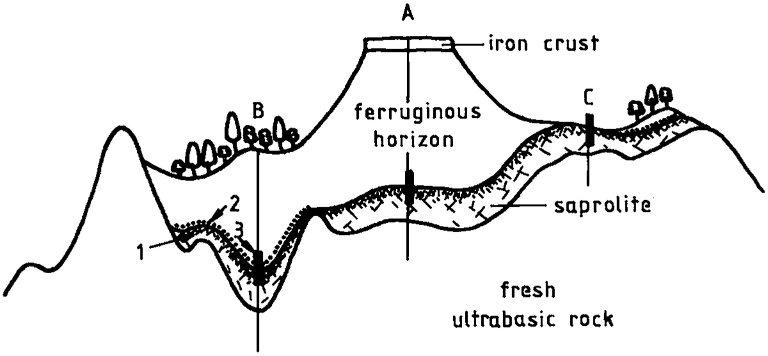


FIG. 2. Generalized diagram showing the cobalt mineralization and sample locations in the various types of profiles observed. 1: Co mineralization as spots, coatings or concretions along the joints and cracks. 2: Co mineralization as root fossils and impregnations. 3: Sampling interval A: Complete profile, Tiébaghi (samples C,F,G, in particular). B: Profile with strong Co accumulation, truncated and pedoturbed, Poro (samples A,B,E,H,I,J,K, in particular). C: Surficial cobalt mineralization, truncated profile, Tiébaghi (samples D,L, in particular).

MINERALS IDENTIFIED

Nature and nomenclature

In her paper on the presence of lithiophorite and cryptomelane in a sample from New Caledonia, Perseil (1972) concluded that the "asbolans" are mixtures of cobaltiferous varieties of these two minerals. More recently, Chukhrov *et al.* (1980a,b, 1982) studied "asbolans" from the Urals; they did not find any cobaltiferous varieties of previously known manganese oxides, but instead a new mineral consisting of Mn layers alternating with Co and/or Ni layers. These authors referred to this new mineral as asbolan *sensu stricto.* It is in this restricted sense that the term *asbolan* is used in this paper.

Mineralogical study of the 40 selected samples showed that the "black products" of the New Caledonian profiles are made up, in various proportions, of several minerals with different cobalt contents. However, each of these minerals occurs under particular Eh–pH and chemical conditions that limit their occurrence to a particular horizon or area (Llorca 1990).

Three of these minerals, cryptomelane, ramsdellite and todorokite, are rare (found in three samples) and contain only traces of cobalt (0.7). The others, more widespread and in which cobalt is a major constituent, can be considered as responsible for the cobalt mineralization and have been examined in detail. These minerals are heterogenite (found in 8 samples, and dominant in 4 of them), asbolan (17 samples, 12 of which contain no other cobaltiferous phase), lithiophorite (10 samples, 6 of which contain no other cobaltiferous phase), and members of a series between asbolan and lithiophorite (20 samples, dominant in 10). Only lithiophorite and cryptomelane had previously been noted in New Caledonia (Perseil 1972). This is the first report of heterogenite forming as the result of supergene concentration of cobalt from trace quantities in ultrabasic rocks. Before this study, heterogenite had been found only in the oxidation zone of cobaltiferous sulfide deposits (mainly in Shaba, Zaire: Deliens 1974). This is the first evidence of a series existing between asbolan and lithiophorite, the members of which are referred to as "asbolan–lithiophorite intermediates".

Textures

Microscopic examination of polished blocks of the "black products" revealed a variety of habits (Fig. 3). It showed not only cryptocrystalline aggregates (optically isotropic), but also larger crystals with observable optical properties. Cryptocrystalline aggregates, as well as microcrystalline aggregates (with crystallites showing anisotropy), were observed for all the minerals except ramsdellite. Asbolan, lithiophorite, "asbolan–lithiophorite intermediates" and heterogenite also were observed as flexible acicular crystals, up to 50 μm long, occurring either as individuals (independent or tangled) or joined side by side (parallel or divergent), forming tufts (Fig. 3.7), spherulites, or monocrystalline areas about 100 to 500 μm across (Figs. 3.3, 3.2). Heterogenite, lithiophorite and ramsdellite also form prismatic crystals about 20 μm long (Figs. 3.1, 3.8).

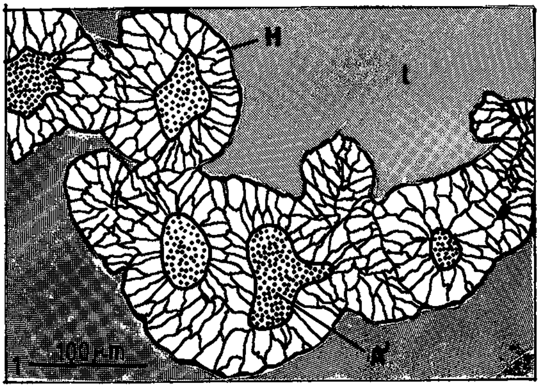
These crystalline forms can produce concretions. More commonly, however, they occur as pseudomorphs after the primary silicates or after plant roots, habits which were previously unknown for these minerals. The pseudomorphs after the silicates (serpentine, olivine, and talc derived from the pyroxene in the early stages of weathering) occur along joints, giving a macroscopic appearance of black spots or coatings.

Cobalt minerals commonly replace veinlets of serpentine. In the least common occurrence, bands of squat crystals of heterogenite crudely replace the serpentine veinlets (Fig. 3.1). Images of these crystals obtained with a scanning electron microscope (Fig. 4) show barrel-shaped crystals terminated on the (0001) face, a previously unreported habit for heterogenite. Between these crystals, rose-petal-shaped crystals show well-developed growth striae. Crystals of both shapes have the same chemical composition and commonly show orthogonal associations, probably twins, which had not been noted before. In the second, more common type of replacement of the serpentine, single crystals are formed, accurately reproducing the serpentine veinlets (Fig. 3.2); Ni-rich asbolan and Ni-rich "asbolan–lithiophorite intermediates" commonly occur in this habit.

Synchronous pseudomorphs after talc crystals were commonly observed for the prominent minerals (asbolan, Ni-rich in particular, "asbolan–lithiophorite intermediates", heterogenite, lithiophorite; Fig. 3.3). Crystallinity of the newly formed phases is invariably good, as there is oriented growth of the fibers from and perpendicular to the cleavage planes and faces of the dissolving talc crystals.

Cavities between the serpentine veinlets, previously occupied by olivine cores, are in some cases filled with a disordered cryptocrystalline cobaltiferous material. These pseudomorphs, composed essentially of heterogenite or Ni-rich asbolan, are asynchronous or subsynchronous with the dissolution of olivine (Figs. 3.1, 3.2). They are less commonly observed than the pseudomorphs after talc or serpentine.

Fossilized roots are common. Microscopic and macroscopic examinations show that the root is first molded by an optically isotropic cryptocrystalline mass, which can even enter the pores and fill the inner wall while the plant is alive. The tissues them-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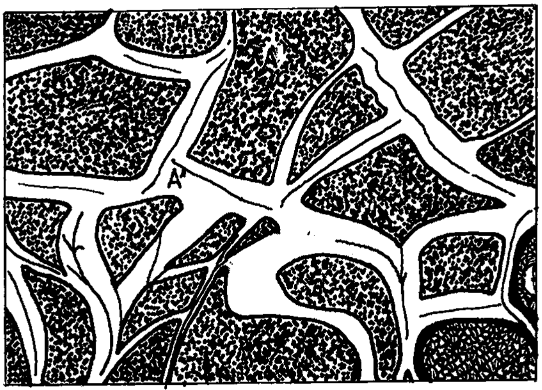
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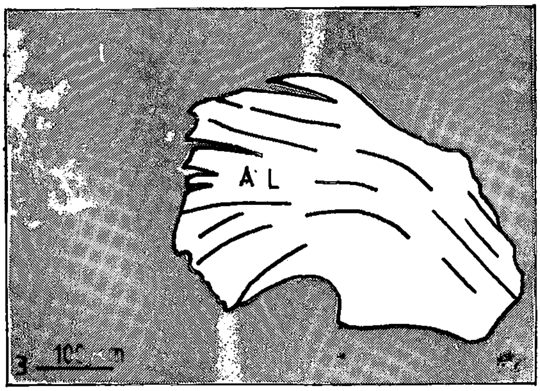
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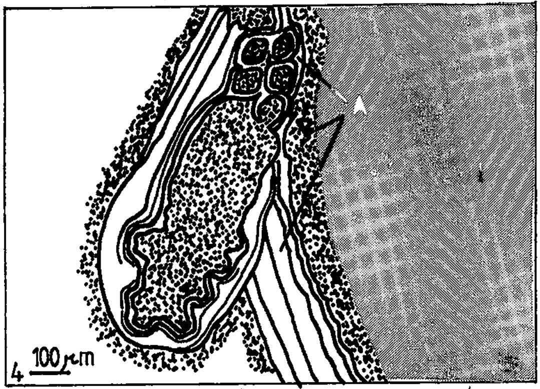
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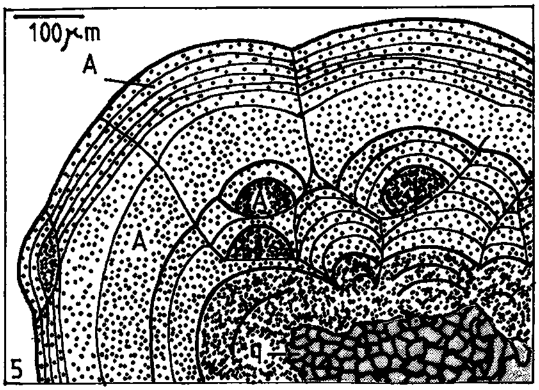
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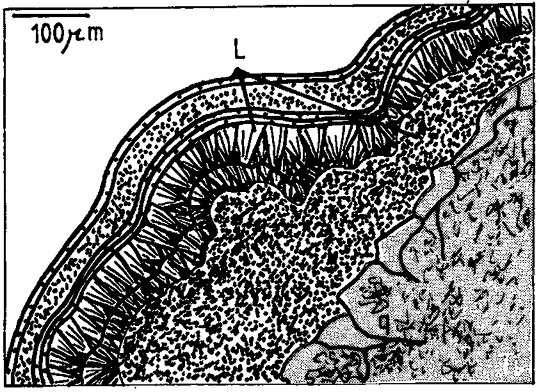
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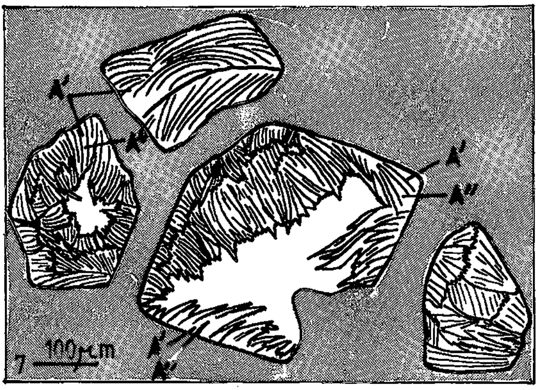
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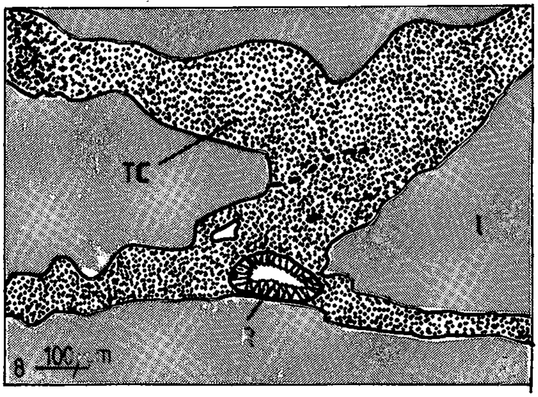
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selves are then more or less completely replaced, sometimes at the level of individual cells (Fig. 3.4), by an optically anisotropic material of the same nature, usually "asbolan–lithiophorite intermediates", but also Co-rich asbolan or lithiophorite.

Around the roots in particular, where the porosity is high, cobalt minerals can impregnate the earthy mass. Microscopic examination of such impregnations showed an isotropic and cryptocrystalline material with irregular or diffuse contours. The same minerals are found here as in fossilized roots.

Various forms of concretions (colloform or fibrous) were observed (Figs. 3.5, 3.6). These concretions consist of alternating layers of smaller or larger crystallites, possibly reflecting seasonal variations. Co-rich asbolan, lithiophorite and "asbolan–lithiophorite intermediates" were found as concretions that had developed on the walls of open fractures. Some lithiophorite concretions also were observed as cement in surface colluvium.

Cobaltiferous fibers, consisting particularly of asbolan, and showing a tendency to spherulitic arrangement, were found to have grown in cavities left by the dissolution of rock-forming silicates (talc or olivine?) (Fig. 3.7). In this case, the pseudomorphs are subsynchronous with the dissolution, and only the outer shape of the mineral is preserved.

In addition, cryptocrystalline or microcrystalline aggregates or fibers can fill small open fissures. In particular, microkarsts filled with a corroded cryptocrystalline material typically composed of cryptomelane–todorokite mixtures (cobalt-poor phases) were observed; in the small cavities caused by corrosion, squat crystals have developed, which consist exclusively of ramsdellite (cobalt-poor phase) (Fig. 3.8).

Optical properties

Heterogenite, asbolan and lithiophorite show a reflectance of about 20%, a white color with a pleochroism in the whites and greys, and a strong anisotropy, in agreement with previous observations made elsewhere. However, the anisotropy appears with some color tints, which had not previously been observed in lithiophorite or asbolan. The tints are pale (lightly tinted white with pale yellow or beige) in the least cobaltiferous asbolan and lithiophorite, and more pronounced (straw-yellow to ochre) in the cobalt-rich varieties. They are brown in the heterogenite. The "asbolan–lithiophorite intermediates" show the same optical properties as observed for the asbolan and lithiophorite. Between uncrossed polarizers, the tints are straw-yellow and blue in all minerals. Occasionally, the todorokite–cryptomelane mixtures also give a strong anisotropy colored with ochre, whereas ramsdellite shows a strong anisotropy with beige and brown. These optical similarities may have led to the misidentification of some of these minerals in the past.

Thermal data

Thermal data collected from the heterogenite-rich samples are comparable with those obtained by Deliens (1974) for heterogenite from Shaba; an endothermic peak at about 340°C (Fig. 5) may be followed by a less marked one at about 930°C. The asbolan shows endothermic reactions at 130–190°C, 420–460°C and 570–625°C (Fig. 5), similar to those reported by Chukhrov *et al.* (1980) for the asbolan from the Urals. The Co-rich asbolan, however, shows an additional endothermic reaction at about 270°C (Fig. 5), not reported by Chukhrov *et al.* The lithiophorite and the "asbolan–lithiophorite intermediates" both show two endothermic reactions, one at 440–450°C and a smaller one at 625–650°C, analogous to those of asbolan (Fig. 5).

Chemical data

Microprobe analyses of the heterogenite reveal even higher nickel contents (4.5 to 7.5% NiO) than in heterogenite-*2H* from Shaba (1.9% NiO) (Table 1; Llorca 1986b). However, there is a notable absence of copper, which attains several percent in heterogenite-3*R* from Shaba (Deliens 1974).

The lithiophorite contains very little lithium compared with the type mineral from Postmasburg (Table 1) and in this respect is similar to most examples found elsewhere in the world. However, it is much richer in cobalt than lithiophorite from other localities, which generally contain none or very little (Table 1, Fig. 6a).

Asbolan has a more variable composition than that from the Urals (Table 1, Fig. 6b). Three varieties of

FIG. 3. Principal habits shown by the cobaltiferous minerals from New Caledonia. 1. Heterogenite and asbolan occurring as crude pseudomorphs after serpentine veinlets and olivine (sample A). 2. Perfect pseudomorphic replacement of serpentine veinlets (sample G). 3. Pseudomorphic replacement of a talc crystal (sample I). 4. Pseudomorphic replacement of a root (represented here: part of the outer wall) (sample J). 5. Colloform concretions (sample B). 6. Fibrous concretions (sample D). 7. Automorphous fibers, here showing spherulitic tendency (sample C). 8. Cryptocrystalline mass filling a dissolution cavity (from sample K). Symbols: H, heterogenite; A, Co-rich asbolan; A',A", Ni-rich asbolans; AL, "asbolan–lithiophorite intermediate"; L, lithiophorite; TC, todorokite–cryptomelane mixture; R, ramsdellite; l, "limonite"; q, quartz.

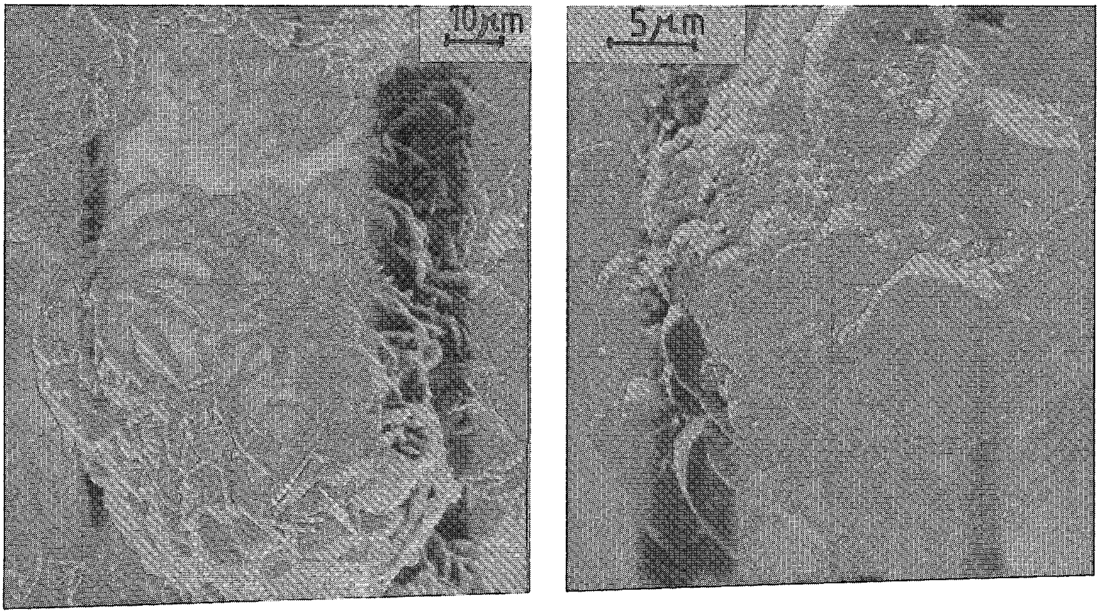

FIG. 4. Scanning electron micrographs of heterogenite showing barrel and rose-petal shapes, with common 90° associations (sample A).

asbolan were described in the Urals, referred to as "Co–Ni asbolan", "Ni-asbolan" and "Co-asbolan" (Chukhrov *et al.* 1980a,b, 1982). Samples from New Caledonia contain asbolan varieties similar in composition to those from the Urals, as well as varieties showing intermediate compositions, which were referred to as "Co > Ni asbolan" and "Ni > Co asbolan" (Llorca 1988). However, none of the above terms was submitted to the IMA Commission on New Minerals and Mineral Names, as the use of prefixed chemical symbols is not accepted by the Commission. For these reasons and to avoid unnecessary confusion, the expressions "Ni-rich asbolan" and "Co-rich asbolan" are preferred in this paper, covering respectively the Ni-dominant and Co-dominant varieties.

About half of the cobaltiferous grains analyzed using the electron microprobe show a composition between those of heterogenite, lithiophorite and the various types of asbolan, but mostly between lithiophorite and asbolan (Table 1, Fig. 6c). Two cases can be distinguished:

1. Grains that look like imperfect single crystals under the microscope. They occur in association with other cobaltiferous grains of various compositions. Slight compositional variations can be observed within them under the microprobe. A scanning electron microscope coupled with energy dispersion (EDAX) reveals a mosaic of domains with various compositions but identical orientation. Grains with a composition intermediate between that of heterogenite and the other minerals are made of these subtle mixtures.
2. Euhedral crystals or grains that look like perfect single crystals under the microscope. They occur in association with other cobaltiferous grains of identical composition. No compositional variations were observed within them under the microprobe. Transmission electron microscopy coupled with energy dispersion (EDAX) of two finely crushed and dispersed samples confirmed their chemical homogeneity. These pure phases, with compositions between those of lithiophorite and the asbolan varieties, have been termed "asbolan–lithiophorite intermediates".

Crystallographic data

In most cases, X-ray diffractometry of concentrates prepared from samples containing lithiophorite, asbolan or "asbolan–lithiophorite intermediates" gave only the main diffraction lines at about 4.75 Å (002) and 9.50 Å (001) that are common to these minerals; mixtures gave broader and multiple lines. Concentrates from samples containing heterogenite usually showed only one line, at 4.45 Å. However, more complete patterns were obtained for the various minerals from the purest samples (Table 2).

A heterogenite-rich sample gave a pattern comparable to that from crystalline heterogenite

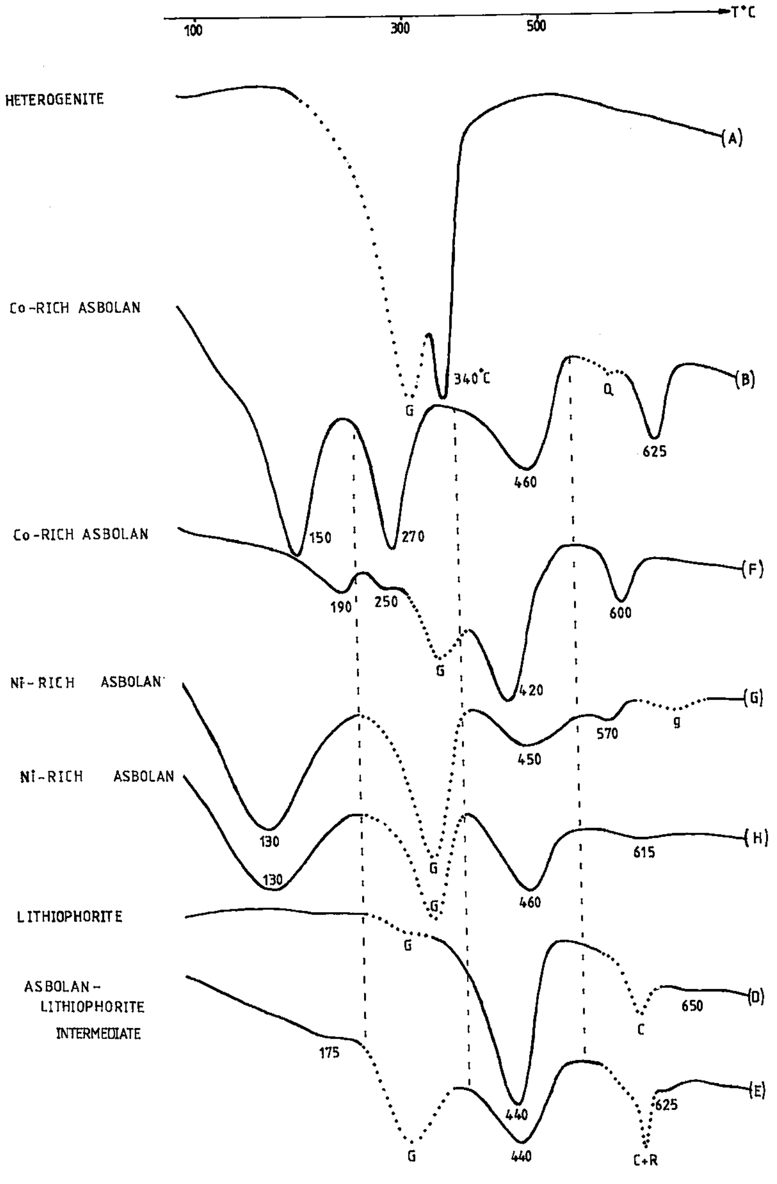

FIG. 5. Results of differential thermal analyses of the cobaltiferous minerals from New Caledonia (from samples A,B,D,E,F,G,H). G, goethite; Q, quartz; g, garnierite; C, cryptomelane; R, ramsdellite.

from Shaba (Deliens 1974), which is interpreted as a mixture of both the 2*H* and 3*R* polytypes (Table 2). The (002) and (003) reflections of the respective polytypes are superimposed, giving an intense line at about 4.45 Å. The identification of the heterogenite-2*H* polytype makes New Caledonia only the second known locality for this polytype. Two samples of Co-rich asbolan gave X-ray-diffraction patterns and electron-microdiffraction patterns from which numerous lines and spots could be indexed (Table 2). Some of these reflections were not reported by Chukhrov *et al.* (1980a,b) for the asbolan from the Urals, as the samples from New Caledonia are purer and better crystallized. A lithiophiorite-rich sample gave a very complete X-ray-diffraction pattern (Table 2), similar to those in the literature

TABLE 1. CHEMICAL COMPOSITION OF COBALT-BEARING MINERALS FROM NEW CALEDONIA, SHABA, THE URALS AND POSTMASBURG

	1	2	3	4	5	6	7	7'	8	8'	9
Li_2O	-		0.3*	8.2	-	-					0.01*
MgO	-		-		1.2	-			0.2		0.2
Al_2O_3	-		25.9	22.8	0.6	0.1			0.8		11.7
SiO_2	0.3	0.3	4.0		0.6	0.6			80.0		5.0
CaO	-		-		1.0	-	1.6	1.9	0.3	1.8	0.5
MnO_2	0.2		46.0	47.0	48.3	66.7	46.9	56.6	10.0	55.1	45.4
MnO	-	0.4	-	8.0	-	-			-		-
Fe_2O_3	0.7	0.01	0.2		0.9	0.9	15.3+	-	0.4		1.3
Co_2O_3	76.7	84.6	7.9		23.4	1.0					13.9
CoO	-		-		-	-	6.9	8.3	0.1	0.4	-
NiO	4.7	1.9	1.5		10.7	17.9	11.4	13.8	3.9	21.6	2.7
CuO	-	0.1	-		-	-					-
BaO	-		-		-	-			0.3		-
H_2O	17.4+	12.7	14.2+	14.	13.3+	12.8+	17.9(-)	19.4	3.8(-)	21.1	19.3+
TOTAL (wt.%)	100	100	100	100	100	100	100	100	99.8	100	100

Compositions were derived from electron-microprobe data unless stated otherwise. 1. Heterogenite from New Caledonia (sample A). 2. Heterogenite-2H from Shaba (Deliens 1974). 3. Lithiophorite from New Caledonia (sample D). 4. Lithiophorite from Postmasburg (from the structural formula given by Pauling & Kamb 1982). 5. An example of Co-rich asbolan from New Caledonia (sample B). 6. An example of Ni-rich asbolan from New Caledonia (sample C). 7. "Co-Ni asbolan" from the Urals, analyzed by wet-chemical means (Chukhrov et al. 1980a), in column 7' recalculated for the pure phase. 8. "Ni-asbolan" from the Urals, analyzed by wet-chemical means (Chukhrov et al. 1980b), in column 8' recalculated for the pure phase. 9. An example of "asbolan-lithiophorite intermediate" (sample E). *: obtained by atomic absorption on the whole sample, then recalculated. +: obtained by difference from 100%. -: obtained from weight losses incurred during thermal analysis.

[that of type-locality lithiophorite from Postmasburg for example: Wadsley (1950) quoted in Mitchell & Meintzer 1967)].

Crystallochemical data

Cobalt, nickel and manganese X-ray-absorption spectra (EXAFS and K-thresholds) were collected from samples rich in heterogenite (sample A), Co-rich asbolan (sample B), lithiophorite (samples D and L) and "asbolan-lithiophorite intermediate" (sample I). It is the first time that this very high resolution technique of investigation has been used on such minerals. Details of these analyses and their interpretation are given in Manceau *et al.* (1987). In short, the results show that cobalt is invariably in the trivalent state. It is never simply adsorbed on the layers but always integrated into the structure, surrounded by ions with an atomic mass comparable to its own. It occupies octahedral sites, comparable in size with those of manganese and clearly smaller than those of nickel. It is probably low-spin, the ionic radius of Co^{3+} low spin being 0.53 Å, and thus very similar to Mn^{4+} (0.54 Å) and clearly different from Ni^{2+} (0.69 Å). In the lithiophorite-rich samples, nickel is surrounded by light atoms, and the high structural order around Co contrasts with the structural disorder observed around Mn.

DISCUSSION

Review of previous concepts of crystal structure

Two polytypes of heterogenite were defined: the 3*R* polytype, CoOOH, is rhombohedral, with single layers stacked along the *Z* axis with a 13.157 Å periodicity (Hey 1962); the 2*H* polytype is hexagonal, has a 8.805 Å periodicity along *Z*, and contains up to 2% NiO, resulting in an idealized formula (Co,Ni)OOH (Deliens & Goethals 1973).

The asbolan from the Urals was described (Chukhrov *et al.* 1980a,b, 1982) as hexagonal, with layers of octahedra $Mn^{4+}O_{2-x}(OH)_x$ regularly alternating with discontinuous layers of $(Co,Ni,Ca)^{2+}{}_y(OH)_{2y+x}$ or $(Ni,Ca)^{2+}{}_y(OH)_{2y+x}$ or $Co^{3+}{}_y Ca^{2+}{}_z O_{(3y/2)+z+(x/2)}$, depending on the variety, stacked along the *Z* axis (x, y and $z < 1$). According to the authors, these three varieties have well-differentiated structures. In the Co–Ni variety, Co^{2+} and Ni^{2+} ions would indiscriminately occupy the same octahedral sites; two superimposed sublattices are observed, with the same *Z* axis, identical *c* parameters (9.34 Å) and slightly different *a* parameters (2.83 and 3.04 Å), which would be due, respectively, to Mn layers and Co–Ni layers. In the Ni variety, there are also two sublattices, one of which has an *a* parameter almost double the other; this led the authors to consider a dioctahedral Ni layer (one empty site out of three). In the Co variety, cobalt would be trivalent and in tetrahedral coordination.

Lithiophorite is hexagonal (Pauling & Kamb 1982) and would consist of $Al_{14}Li_6(OH)_{42}$ and $Mn^{2+}{}_3 Mn^{4+}{}_{18}O_{42}$ layers regularly alternating along the *Z* axis, six layers being necessary for the unit cell having an *a* of 13.37 Å and a *c* of 28.20 Å. The presence of Mn^{2+} cations in this formula is due to a decrease in the number of positive charges of the Mn layer in order to compensate for the introduction of lithium in the normally vacant sites of the hydrargillite layer. Hydrogen bonds permit the transfer of the charges.

New concepts derived from the New Caledonian data

Crystallochemical data recorded for the heterogenite confirm that cobalt is in the trivalent state and occupies octahedral sites, and thus support the structural hypotheses of Hey (1962) and Deliens & Goethals (1973). According to Deliens (1974), the endothermic reactions recorded for the heterogenite at 340°C and 930°C are due, respectively, to dehydroxylation (transformation of CoOOH into Co_3O_4 spinel) and reduction of the spinel to Co monoxide. In the New Caledonian samples, however, the second reaction is without doubt due to the presence of talc, which is invariably associated with the heterogenite.

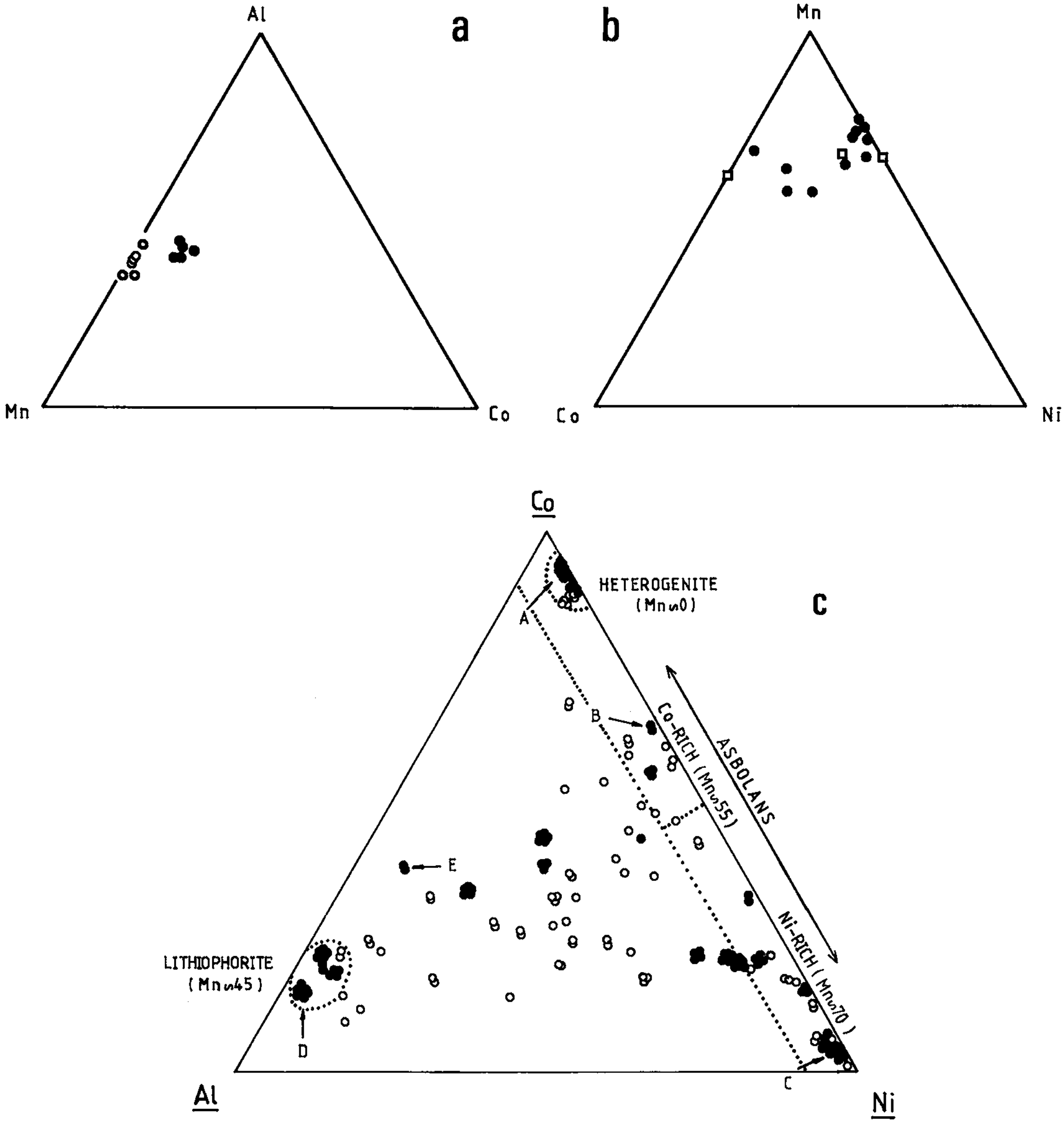

FIG. 6. (a) Cationic composition in terms of Mn–Al–Co of five samples of lithiophorite from New Caledonia, analyzed several times by electron microprobe (filled circles). Comparison with the lithiophorite from Lecht (Wilson *et al.* 1970), Mikhalkovo (Int. Mineral. Association 1982), Charlottesville (Mitchell & Meintzer 1967), Ottré (Fransolet 1979), Postmasburg (in Pauling & Kamb 1982) and Groote Eylandt (Ostwald 1984) (open circles). (b) Cationic composition in terms of Mn-Co-Ni of ten samples of asbolan from New Caledonia, analyzed several times by electron microprobe (filled circles). Comparison with asbolan from the Urals (Chukhrov *et al.* 1980 a,b, 1982) (open squares). (c) Cationic composition of 158 areas analyzed by electron microprobe in 36 cobaltiferous samples from New Caledonia (Mn is indicated in brackets). A,B,C,D,E analyses given in Table 1. Symbols: • pure phase, o possible mixture.

Crystallographic data show that both 2*H* and 3*R* polytypes of heterogenite are present in New Caledonia. An examination with the microprobe suggests that heterogenite-3*R* can, like the 2*H* polytype, contain some nickel. This systematic presence and high values of nickel and the absence of copper in the heterogenite from New Caledonia, compared with that from Shaba, obviously reflect the ultrabasic

TABLE 2. DIFFRACTION LINES OF THE COBALT-BEARING MINERALS FROM NEW CALEDONIA, SHABA, THE URALS AND POSTMASBURG

Caledonian heterogenite (A)				Caledonian asbolan										Caledonian lithiophorite (D)			'Asbolan – lithiophorite intermediate' (E)	
2H+3R		2H	3R	Co-rich (B)			Co-rich (F)			Ni-rich (C)		sublattice I (Mn+Co)	sublattice II (Ni)					
d	I	hkl	hkl	d	I	$\underset{\longrightarrow}{d^*}$	d	I	$d^{\underline{*}}$	d	I	hkl	hkl	d	I	hkl	d	I
				9,60	s		9,55	s		9,5	m	001	001	9,50	60	001	9,55	m
				4,83	s		4,78	vs		4,77	s	002	002	4,73	100	002	4,77	s
						4,75							100					
4,45	100	002	003															
				3,23	w		3,18	w				003	003	3,16	5	003	~3,15	w
						2,71(s)							110					
2,47	20	110																
~2,45	<20		$\bar{1}01$	2,446	mw	2,38	2,44		2,38			100		2,46	2	$\bar{2}01$	~2,45	
2,39	10	101		2,38	w		2,38	w				101		2,35	10	$\bar{2}02$		
2,32	50		102															
2,20	2	004																
2,17	25	102					2,17	w				102		2,17*	3	$\bar{2}03$		
1,88	5	103					1,93	w				103		1,88	10	$\bar{2}04$		
1,81	25		105	1,81	w								203					
						1,79							120					
						1,78							210					
1,654	20	104					1,7					104						
														1,55*	1	$\bar{1}15$		
				1,54	m	1,58							300	1,54*	2	204,006		
1,433	10	110	110	1,42	m	1,36	1,42	m	1,36			110		1,44*	5	$\bar{3}11$,020		
														1,43*	2	$\bar{2}06$		
1,369	5		108											1,37	3			
1,364	20	112	113															
						1,30							310					
						1,30							130					
									1,19			200						
						1,04							410					
						1,03							140					
									0,88			210						
									0,79			300						
									0,68			220						

Heterogenites from Shaba								Asbolan from the Urals												Lithiophorite from Postmasburg			
2H+3R		2H(*)			3R			Co-Ni			sublattice I (Mn)		sublattice II (Co+Ni)		Ni	sublattice I (Mn)		sublattice II (Ni)					
d	I	d_c	I	hkl	d_c	I	hkl	d	I	$\underset{\longrightarrow}{d^*}$	d_c	hkl	d_c	hkl	$\underset{\rightleftarrows}{d^*}$	d_c	hkl	d_c	hkl	d	I	d_c	hkl
4,85								9,60	w	9,33	9,34	001	9,34	001	9,18	9,18	001	9,18	001	9,45	m	9,39	001
4,40	100	4.403	vvs	002	4.377	vvs	003	4,82	s	4,67	4,67	002	4,67	002	4,59	4,59	002	4,59	002	4,70	s	4,70	002
															4,50			4,51	100				
																		4.105	101				
																		3,22	102				
										3,09	3,11	003	3,11	003	3,06	3,04	003	3,04	003	3,12	mw	3,13	003
										2,63			2,63	100	2,60			2,61	110				
2,47	20	2.476	ms	100				2,445	mw	2,45	2,445	100	2,534	101	2,45	2,45	100					2,52	$\bar{2}01$
																						2,51	110
2,43	7				2.425	m	$\bar{1}01$															2,49	200
																						2,48	$\bar{1}11$
2,38	5	2.384	mw	101						2,37	2.365	101	2.29	102	2,36	2.37	101			2,39	mw	2,39	$\bar{2}02$
																						2,37	111
2,32	30				2.310	vs	102															2,35	004
2,20	7	2.201	vvw	004	2.188	vw	006															2,30	$\bar{1}12$,201
2,16	40	2.159	s	102						2,17	2.166	102			2,17	2.16	102	2,19	210			2,15	$\bar{2}03$
																		2,02	202			2,13	112
1,980	8				1.972	vw	$\bar{1}04$															2,05	$\bar{1}13$,202
1,886	15	1.893	vw	103						1,93	1.923	103	2.01	103	1,89	1.91	103			1,88	m	1,89	$\bar{2}04$
1,805	23				1.798	s	105											1,82	203			1,88	005,113
1,644	30	1.645	s	104				1,7	vw	1,7	1.69	104	1.74	104	1,67	1.68	104					1,80	$\bar{1}14$
																						1,79	203
																						1,65	$\bar{2}05$
																						1,64	114
1,501	12				1.493	mw	$\bar{1}07$			1,51			1,518	110	1,49			1,50	300	1,51	w	1,58	$\bar{1}15$
1,467	5																					1,57	204,006
1,429	23	1.430	mw	110	1.424	ms	110	1,419	››	1,41	1.412	110			1,41	1.415	110			1,46	vw	1,46	$\bar{3}11$,020
1,374	6				1.366	vw	108			1,22	1,222	200			1,22	1.225	200			1,45	vw	1,45	$\bar{2}06$
1,359	25	1.360	mw	112	1.354	m	113															1,44	$\bar{3}12$,115,
																				1,40	vw		310,021

d, distances (in Å) obtained by X-ray diffractometry, with Fe K_α, or CuK_α + back monochromator; d*, by electron microdiffraction; $d^{\underline{*}}$, with 001 azimuth; dc, calculated distances; $\longrightarrow$, a-axis of the two sublattices are superimposed; $\rightleftarrows$, different from each other by 30°; I, intensity; s, strong; vs, very strong; vvs, very very strong; m, medium; mv, medium weak; w, weak; vw, very weak; vvw, very very weak; hkl, crystallographic indices. (*), obtained by removing the 3R-polytype lines (reported by Hey, 1962) from the mixture.

nature of the parent rock in New Caledonia. Because of the nickel content, it is not possible to leave this element out of the structural diagram, as did Deliens & Goethals (1973). It is unlikely that nickel replaces cobalt randomly, because of the difference in their ionic radii. It is more likely that the nickel forms separate domains, such as those in the asbolan (Fig. 7).

Asbolan from New Caledonia shows a whole range of compositions between the Co and Ni varieties, which seems to indicate a continuous series. Crystallochemical data indicate that cobalt is in the trivalent state and occupies octahedral sites that are different from those occupied by Ni^{2+}. These data are inconsistent with the models suggested by Chukhrov *et al.* (1980a, 1982) for the Co and Co–Ni varieties from the Urals, and indicate the presence of separate domains for Co and Ni within the discontinuous layer of the asbolan. As previously observed for the asbolan from the Urals, our crystallographic data show two hexagonal sublattices with the *Z* axis in common. One of these sublattices can be attributed to the Mn layers and Co domains, and the other to dioctahedral Ni domains, such as those suggested by Chukhrov *et al.* (1980b) for the Ni variety from the Urals.

According to Chukhrov *et al.* (1980), endothermic reactions at 130–190°C, 420–460°C and 570–625°C reflect 1) the loss of molecular water present between the layers and between the domains of the discontinous layer, 2) the loss of the hydroxyl groups of this layer (Co–Ni or Ni), 3) the loss of the hydroxyl groups of the fault-free Mn-layer. With the New Caledonian samples, however, an additional endothermic reaction at 270°C was observed for the most cobaltiferous specimens. This reaction can be attributed to the hydroxyl groups attached to the cobalt, and the one at 420–460°C to the hydroxyl groups attached to the nickel only (Llorca 1988). Weight losses measured for these two reactions relate to the decomposition of heterogenite-type CoOOH domains into Co_3O_4 and the decomposition of $[Ni(OH)_3]^-$ dioctahedral domains into NiO, respectively (Llorca 1988).

All data recorded for the asbolan from New Caledonia are consistent. They indicate a continu-

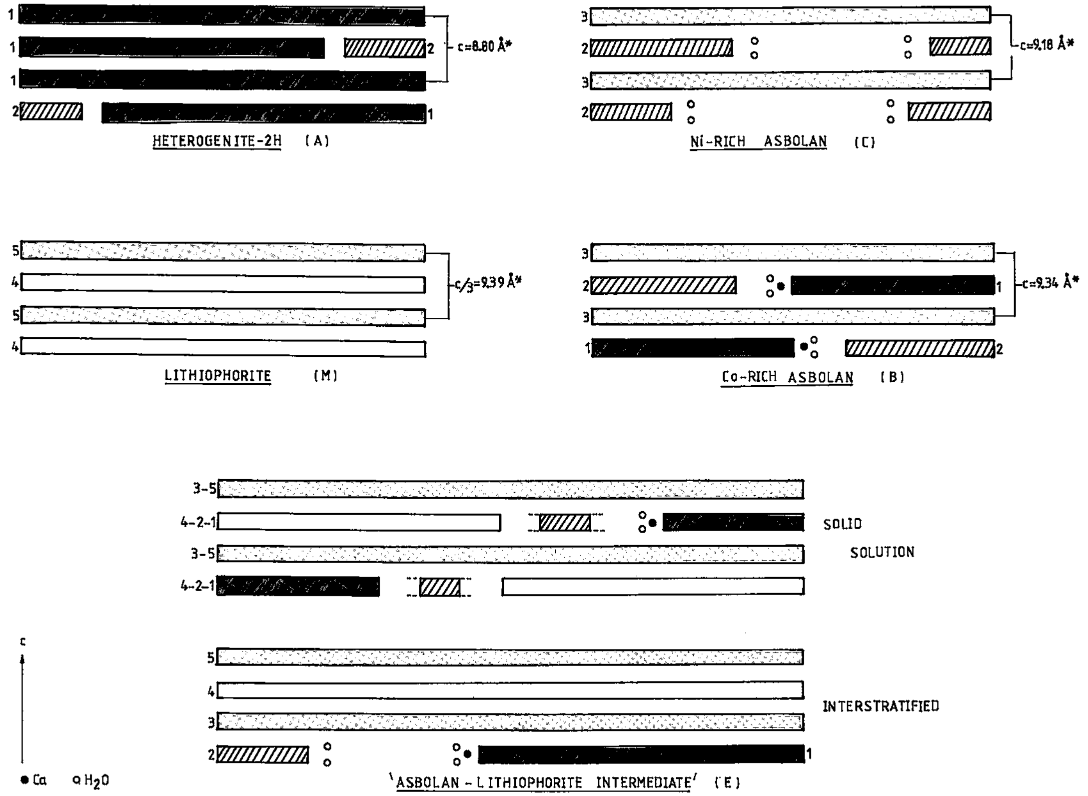

FIG. 7. Structural models suggested for the cobalt-bearing minerals from New Caledonia. The various layers consist of a single layer of octahedra. Cobalt is trivalent, nickel divalent, manganese tetravalent, aluminum trivalent. 1. CoOOH; all sites are occupied. 2. $[Ni(OH)_3]^-$; 2 sites out of 3 are occupied. 3. $[MnO_{2-x}(OH)_x]^{x+}$, with x = Ni cations/Mn cations; all sites are occupied. 4. $[Al_{0.7}Ni_{0.04}Li_{0.02}(OH)_2]^{0.2+}$; one site out of 5 is empty. 5. $[Mn_{0.08}Co_{0.02}O_2]^{0.2-}$; all sites are occupied. The projection is perpendicular to [001]. A,B,C,E samples; M average; *calculated.

ous series between Co and Ni end-members, with a structure comparable to that suggested by Chukhrov *et al.* (1980b) for the Ni-variety from the Urals, with the addition, for the cobaltiferous varieties, of heterogenite-type CoOOH domains next to the $[Ni(OH)_3]^-$ domains (Fig. 7). Because the Ni domains have to be small (Chukhrov *et al.* 1980b), samples of asbolan close to the Ni end-member can contain more water. They are also less stable, as shown by their easy dissolution in HCl, and can even be leached with water (Llorca 1986a).

Chemical data show that the lithiophorite from New Caledonia is enriched in cobalt. It has a high Al content, which precludes the possibility both of inclusions of heterogenite or asbolan (both Al-free), as well as diadochic or topotactic replacement of Al by Co. Crystallochemical data show that cobalt is not adsorbed on the layers but integrated into the structure. It is surrounded by ions with an atomic mass comparable to its own, that is to say it is integrated in the Mn layer. It occupies octahedral sites comparable in size with those of manganese. Cobalt sites, however, show a higher structural order than those of manganese, suggesting that Mn and Co are not distributed at random in the Mn layer. Small amounts of nickel also are present; crystallochemical studies show that nickel is surrounded by light atoms, which means it is distributed in the hydrargillite layer.

In the lithiophorite from New Caledonia (Fig. 7), the nickel present in the hydrargillite layer would, together with the excess Al^{3+} cations, replace some of the missing lithium. The presence of Li^+, Ni^{2+} and excess Al^{3+} cations in some of the normally empty sites of this layer creates an excess of positive charges. The cobalt is located in the MnO_2 layer, where its presence creates a lack of positive charges in the right proportion to compensate for the charge of the other layer (Llorca 1987). Hydrogen bonds would allow the transfer of charges. It is thus not necessary here to suggest the presence of Mn^{2+} ions in the MnO_2 layer to compensate the charge of the other layer, as suggested for the Postmasburg-type lithiophorite by Pauling & Kamb (1982).

A whole range of new phases with compositions between those of lithiophorite and the members of the asbolan series were found, termed "asbolan-lithiophorite intermediates". There is a marked similarity among the structures of heterogenite, asbolan and lithiophorite (Fig. 7): they all consist of single layers of octahedra stacked along the *Z* axis, with comparable periodicities. In both asbolan and lithiophorite, every second layer is a Mn layer, which is separated from the next Mn layer by 9.34 and 9.39 Å, respectively. It thus is not surprising that asbolan and lithiophorite form a continuous series (solid solutions or interstratifications) (Fig. 7).

Heterogenite, asbolan, lithiophorite and "asbolan-lithiophorite intermediates" form a homogeneous group with similar structures and crystal chemistry: only four cations are present in these phases, Co^{3+}, Mn^{4+}, Ni^{2+}, Al^{3+}, all forming layers of octahedra, CoOOH, MnO_2, $[Ni(OH)_3]^-$ and $Al(OH)_3$, in different combinations to form the various species. This structural mimicry influences the physical properties of these minerals, making their identification difficult, particularly for asbolan, lithiophorite and the "intermediates". Only chemical analysis (microprobe) can lead to unambiguous identification of these minerals and discrimination among their varieties.

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