

WESTERVELDITE, (Fe,Ni,Co)As, A NEW MINERAL FROM LA GALLEGA, SPAIN

I. S. OEN, *Geologisch Instituut der Universiteit van Amsterdam, Amsterdam*, E. A. J. BURKE, *Instituut voor Aardwetenschappen der Vrije Universiteit, Amsterdam*, C. KIEFT, *Netherlands Organisation for the Advancement of Pure Research (ZWO), Amsterdam*, and A. B. WESTERHOF, *Geologisch Instituut der Universiteit van Amsterdam, Amsterdam*.

ABSTRACT

A Co-bearing nickel-rich iron monoarsenide corresponding in composition and structure to a Ni-rich member of the orthorhombic FeAs-(Fe,Ni)As solid solution series of synthetic alloys occurs in chromite-niccolite ores from La Gallega, Spain. The name westerveldite is proposed for minerals in this solid solution series. The average composition of Co-bearing nickeloan westerveldite from La Gallega as determined by microprobe analyses is $(\text{Fe}_{0.635}, \text{Ni}_{0.400}, \text{Co}_{0.015})_{1.050} \text{As}_{1.000}$. The orthorhombic unit-cell has $a = 3.46\text{\AA}$, $b = 5.97\text{\AA}$, $c = 5.33\text{\AA}$, all $\pm 0.01\text{\AA}$. The mineral shows strong reflection pleochroism in brownish and brownish grey colours, strong anisotropism between crossed nicols, a higher polishing hardness and apparently somewhat lower reflectance than maucherite. Westerveldite occurs in chromite-niccolite ores, where adjacent to later serpentine veinlets the niccolite is replaced by intergrowths of maucherite and westerveldite.

INTRODUCTION

During a mineralogical investigation of chromite-niccolite ores from La Gallega, Spain, a then unknown mineral was found intergrown with maucherite. Electron microprobe and X-ray analyses showed that the mineral has a composition and structure close to that of the Ni-rich end-member in the orthorhombic FeAs-(Fe,Ni)As series of synthetic alloys. Minerals corresponding to this series have not been previously reported and the presently described one is therefore a new mineral, for which the name westerveldite has been proposed by the authors and has been approved unanimously by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The name is for Dr. Jan Westerveld (1905-1962), Professor of Economic Geology and Mineralogy in the University of Amsterdam from 1945 to 1962. Two chips of rock containing the type specimen of westerveldite are deposited with the Geological Institute of the University of Amsterdam and with the Institute of Earth Sciences of the Free University at Amsterdam, respectively.

The first author is responsible for the text of the paper, the micro-

scopic work and, together with the fourth author, for the collection of material; X-ray work and microprobe analyses were done by the second and third author, respectively. Microprobe work was made possible by courtesy of Prof. W. Uytendogaardt, Free University at Amsterdam, and the WACOM, a working group for analytical geochemistry subsidized by the Netherlands Organisation for the Advancement of Pure Research (ZWO).

OCCURRENCE AND PARAGENESIS

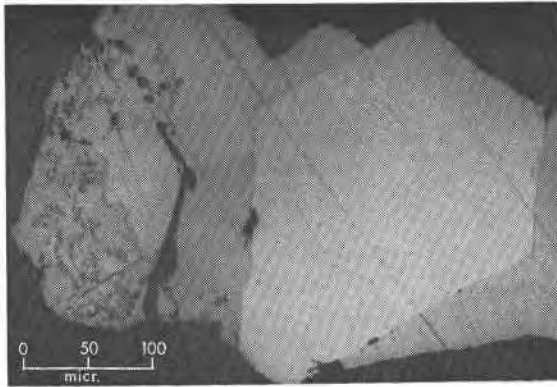
The mineral westerveldite was found in one out of a dozen of samples of chromite-niccolite ores collected from the dumps at the abandoned mine of La Gallega, about 3 km east of the village of Ojén, North of Marbella in the province of Málaga, Spain.

The chromite-niccolite ores from La Gallega are fine-grained rocks consisting of about 80 vol. percent chromite, 10 vol. percent niccolite with accessory nickeliferous loellingite, (Fe,Co)-rich gersdorffite and (para?) rammelsbergite, and 10 vol. percent other minerals, mainly cordierite, plagioclase, serpentine, mica, and chlorite. These rocks occur associated with and locally grade into massive cordierite rocks. Chromite-niccolite ores and associated cordierite rocks occur in schlieren and as veins and veinlets in serpentinised ultrabasic rocks. The nickeliferous loellingite and (Fe,Co)-rich gersdorffite in the ores are characterized by unusual compositions described by the authors in a separate paper (Oen, Burke, Kieft, and Westerhof, 1971).

Niccolite forms an intergranular and intrafractural network of veinlets in polygonally textured chromite aggregates, with grain sizes generally not exceeding 0.3 mm. The chromite-niccolite textures are often transected by millimeter-thick, apparently later veinlets and crack fillings of serpentine. The niccolite near these veinlets often appears partially replaced by gersdorffite, but one sample contains late serpentine veinlets adjacent to which the niccolite appears partly to completely replaced by intergrowths of maucherite and the new mineral westerveldite (Figs. 1 and 2). Nickeliferous loellingite, (Fe, Co)-rich gersdorffite and (para?) rammelsbergite, which originally occur with the niccolite, are found with unmodified forms adjacent to or enclosed in the maucherite-westerveldite intergrowths.

The maucherite-westerveldite intergrowths consist mainly of maucherite; westerveldite occurs as irregularly shaped blebs and stringers with dimensions between 0.001 and 0.025 mm as disseminated inclusions in the maucherite (Figs. 1 and 2); occasionally westerveldite is observed in contact with maucherite and niccolite. Maucherite grains contain one or two groups of westerveldite inclusions, each group

(a)



(b)

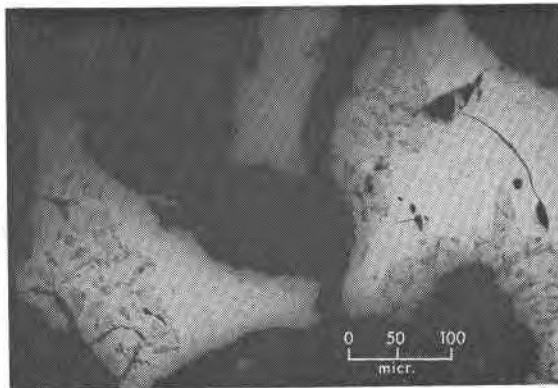


FIG. 1 (a). A lozenge-shaped section of nickeliferous loellingite surrounded by niccolite; at the left niccolite is traversed by a serpentine veinlet (black) and partially replaced by maucherite-westerveldite intergrowths. The fine-grained westerveldite (darker vermicular areas) clusters in and along cracks in the maucherite; note also shrinkage crack marking maucherite-niccolite boundary. Surrounding black areas are of chromite.

(b). A serpentine veinlet (black) crosses the niccolite areas from the middle upper to the lower part of the figure; the niccolite (light grey) to the right of this veinlet is partially replaced by maucherite-westerveldite, to the left of the veinlet the niccolite (same dark grey tint as maucherite) shows no sign of replacement. Westerveldite (dark grey) clusters around cracks, which show a tendency to a radial arrangement in the maucherite. Along chromite (black)-niccolite boundaries below the center of figure are grains of nickeliferous loellingite (same tint as maucherite but devoid of westerveldite).

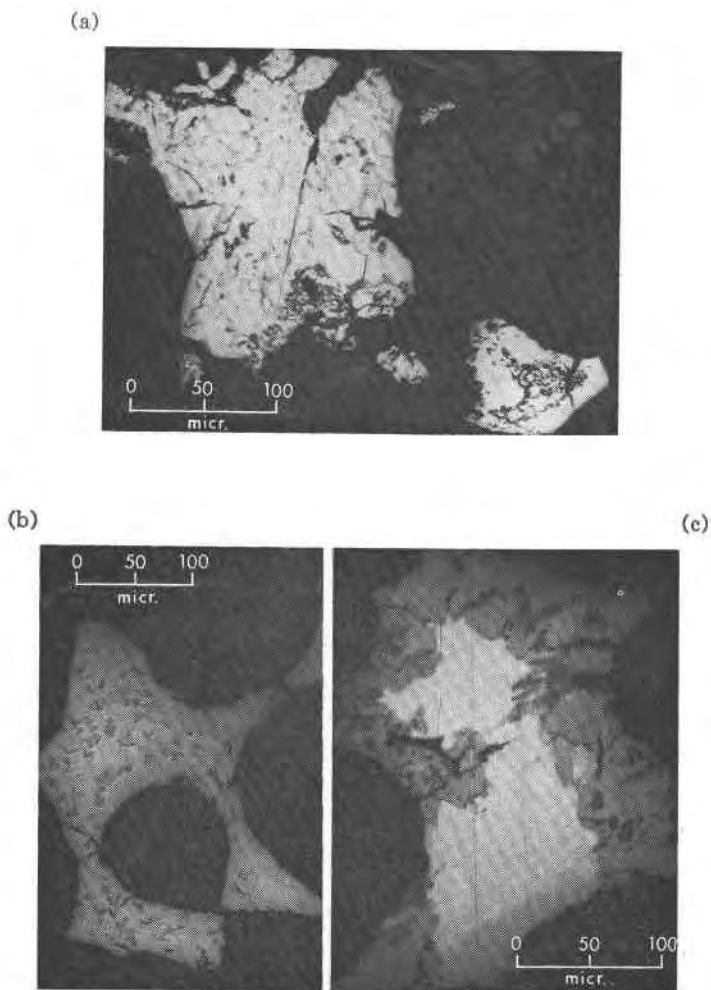


FIG. 2. (a). Maucherite-westerveldite intergrowths resulting from replacement of niccolite. Serpentine (black) fills larger cracks in and forms vermicular intergrowths with the maucherite. Westerveldite (darker grey) clusters in and around openings in the maucherite. Surrounding black areas are of chromite and serpentine.

(b). Maucherite-westerveldite intergrowths. Along chromite (black) boundary at the right is still some niccolite.

(c). Maucherite-westerveldite intergrowth replacing niccolite (light grey). The picture taken with crossed nicols shows the uniform optical orientation of the strongly anisotropic westerveldite (appearing dark, close to extinction position) in the maucherite (dark grey). Chromite black.

characterized by a uniform optical orientation, indicating that the maucherite and westerveldite are crystallographically intergrown (Fig. 2c). The maucherite-westerveldite intergrowths show systems of radiating and irregular, often vermicular, very fine cracks, not unlike shrinkage openings, which are limited to these intergrowths and absent in adjoining parts of niccolite; the westerveldite, generally forming 25–35 vol. percent of the intergrowths, shows a strong tendency to cluster around and to fill up these cracks. Some of the broader radiating cracks are filled with serpentine.

CHEMISTRY

Microprobe analyses were performed with a Cambridge Instrument Co. Geoscan operated at an acceleration potential of 20 kV and 25 kV. Pure metal standards were used. Results were corrected according to a computer program adapted from Springer (1967) with some modifications.

Preliminary analyses of westerveldite after correction gave totals of determined Ni, Co, Fe, and As of less than 100 percent. Sulphur is present in quantities of less than 0.05 weight percent; a qualitative goniometerscan indicates the absence of detectable amounts of other elements. The deficit in the results of analysis is ascribed to the scattering effect of the numerous fine cracks causing an excessively low pulse-output. In further analysis care was taken to select somewhat larger grains and results with totals very near to 100 percent were then obtained. In Table 1 analyses of westerveldite are given together with analyses of the associated maucherite and niccolite. The range of analytical values obtained for westerveldite from La Gallega can be expressed by the formula: $(\text{Fe}_{0.60-0.74}, \text{Ni}_{0.30-0.44}, \text{Co}_{0.01-0.02})_{1.00-1.06} \text{As}_{1.00}$, indicating a Co-bearing Ni-rich Fe-monoarsenide with variable Fe/Ni ratio. The average of 11 analyses on material in sample 14b is given by the formula: $(\text{Fe}_{0.635}, \text{Ni}_{0.400}, \text{Co}_{0.015})_{1.05} \text{As}_{1.00}$.

In the system Ni-Fe-As there are two stable monoarsenides: orthorhombic FeAs (Heyding and Calvert, 1957), which has not been reported before as a mineral, and hexagonal $\text{Ni}_{1\pm x}\text{As}$, corresponding to niccolite. Buseck (1963) showed that at 800° C there is extensive but incomplete solid solution between FeAs and $\text{Ni}_{1\pm x}\text{As}$; the Ni-rich limit of (Fe,Ni)As solid solution at 800° C is at 48 ± 1 wt percent or about 47 mol. percent NiAs; the Fe-rich limit of (Ni,Fe)As solid solution lies at about 48 wt percent FeAs (Fig. 3). The name westerveldite is proposed for the orthorhombic FeAs-(Fe,Ni)As solid solution series; westerveldite from La Gallega is a Co-bearing nickeloan westerveldite with a composition close to the Ni-rich end-member in this series.

TABLE 1. MICROPROBE ANALYSES (WT %) OF NICKELOAN WESTERVELDITE, MAUCHERITE, AND NICCOLITE FROM LA GALLEGA

	1	2	3	4	5	6	7
Fe	29.1	27.1	26.6	26.1	1.7	1.0	0.8
Ni	15.4	16.0	17.4	17.2	49.5	50.5	42.7
Co	0.7	0.7	0.6 ⁵	0.6 ⁵	0.5	0.5	0.6
As	55.7	57.0 ⁵	55.5 ⁵	55.8 ⁵	48.1 ⁵	48.2	56.0
	98.9	100.8 ⁵	100.2	99.8	99.8 ⁵	100.2	100.1

Nickeloan Westerveldite:

1. (Fe_{0.700}Ni_{0.305}Co_{0.015})_{1.020}As_{1.00}; sample 14a
2. (Fe_{0.635}Ni_{0.360}Co_{0.015})_{1.010}As_{1.00}; sample 14a
3. (Fe_{0.640}Ni_{0.400}Co_{0.015})_{1.055}As_{1.00}; sample 14b, average of 8 points measured at 25 KV
4. (Fe_{0.630}Ni_{0.390}Co_{0.015})_{1.035}As_{1.00}; sample 14b, average of 3 points measured at 20 KV

Maucherite:

5. (Ni_{10.49}Fe_{0.59}Co_{0.11})_{10.99}As_{8.00}; sample 14a
6. (Ni_{10.68}Fe_{0.22}Co_{0.10})_{11.00}As_{8.00}; sample 14a

Niccolite:

7. (Ni_{0.97}Fe_{0.02}Co_{0.01})_{1.00}As_{1.00}; sample 14a

X-RAY CRYSTALLOGRAPHY

Table 2, column 3, lists X-ray diffraction lines obtained from a powder drilled out of a grain, about 100 by 200 microns in section, consisting of maucherite-westerveldite intergrowths with some niccolite. Elimination of the diffraction lines of maucherite and niccolite leaves 10 diffraction lines, marked ws in Table 2, which can be ascribed to the nickeloan westerveldite and from which unit-cell dimensions were calculated by the least squares method, using *hkl*-indices in the crystal setting usually adapted for synthetic orthorhombic FeAs (Strunz 1970, p. 122; the X-ray Powder Data File of the A.S.T.M., card 12-799, gives a different crystal setting); the orthorhombic unit-cell of nickeloan westerveldite has: $a = 3.457 \pm 0.01\text{\AA}$, $b = 5.971 \pm 0.01\text{\AA}$, $c = 5.332 \pm 0.01\text{\AA}$, $a:b:c = 0.579:1:0.893$. Table 2, column 2, gives the X-ray diffraction pattern of nickeloan westerveldite as calculated from the cell dimensions.

Allowing for the effects of composition in shifting positions and intensities of the diffraction lines, the X-ray powder diagrams of synthetic FeAs and nickeloan westerveldite appear sufficiently similar

(Table 2) to assume that both compounds belong to the same space group, *i.e.*, D_{2h}^{16} - $Pm\bar{c}n$ (XPDF card 12-799) or group 62 of the International Tables for X-ray Crystallography, 1952.

From the unit-cell dimensions, the average formula given before, and assuming four formula units in the unit-cell (Strunz, 1970), a

Table 2. X-ray diffraction data for synthetic FeAs, nickeloan westerveldite, maucherite, and niccolite.

Synthetic FeAs XPDF 12-799 orthorhombic $a = 3.3724 \text{ \AA}$ $b = 6.0242 \text{ \AA}$ $c = 5.4361 \text{ \AA}$			Nickeloan westerveldite orthorhombic $a = 3.45(7) \text{ \AA}$ $b = 5.97(1) \text{ \AA}$ $c = 5.53(2) \text{ \AA}$			Maucherite- nickeloan westerveldite- niccolite mixture; La Gallega ^a)			Maucherite XPDF 8-85			Niccolite XPDF 9-1		
<i>I</i>	<i>hkl</i> ^{b)}	<i>d</i> Å(obs.)	<i>hkl</i>	<i>d</i> Å(calc.)	<i>I</i>	<i>d</i> Å(obs.)	<i>I</i>	<i>hkl</i>	<i>d</i> Å(obs.)	<i>I</i>	<i>hkl</i>	<i>d</i> Å(obs.)		
6	110	2.942	110	2.991	1 3.12 1 3.06 1 2.992 ws 8 2.700 9 2.655 8 2.604 ws		1 120 3.04 9 008 2.69			1 100 3.14				
55	021	2.635	111	2.609						10 101 2.66				
100	111	2.588	021	2.605										
6	012	2.478	012	2.434										
18	102	2.116	102	2.111	6 2.367 1 2.308 1 2.113 ws 2 2.083 ws 9 2.023		2 222 2.37 1 027 2.307*							
35	121	2.076	121	2.080			10 226 2.01							
35	022	2.019	112	1.990	4 1.988 ws									
60	112	1.996	022	1.988			2 029 1.977			9 102 1.961				
10	031	1.844	031	1.864	8 1.961 2 1.900 1 1.864 ws 8 1.804		3 230 1.899			8 110 1.811				
12	013	1.735	200	1.728	10B 1.718 1 1.703 ws 2 1.624 1 1.595 ws 1 1.528 ws		2 0.0.12 1.814 10 040 1.713							
30	130	1.723	130	1.723			3 2.2.10 1.621							
18	200	1.686	013	1.703										
6	032	1.616	032	1.595										
6	023	1.553	113	1.528	2 1.492 2 1.481		2 0.2.13 1.503			2 201 1.497 2 103 1.475				
10	113	1.543	023	1.527										
8	132	1.457	132	1.448										
8	041	1.452	221	1.440	5B 1.450		5 048 1.449							
12	221	1.421	041	1.437										
6	123	1.410	123	1.397										
6	004	1.3590	004	1.333	1 1.366 5 1.329 1B 1.302		1 0.0.16 1.361 ‡ 249 1.299			3 202 1.328				
4	014	1.3255	222	1.304										
6	222	1.2942	014	1.301										
6	104	1.2605	231	1.267	1 1.263 1 1.245					1 004 1.256				
6	231	1.2564	104	1.244										
1	114	1.2337	114	1.217	6 1.214		1 0.4.12 1.247 6 { 440 1.212							
8	213	1.2093	213	1.213										
1	051	1.1763	232	1.172										
4	232	1.1663	051	1.165										
4	124	1.1629	124	1.148										
4	223	1.1423	223	1.144	3B 1.149 2 1.133					2 211 1.152 1 203 1.142				
6	034	1.1253	034	1.107			4 2.4.13 1.133							
1	151	1.1107	311	1.107										
14	143	1.0954	151	1.104	3 1.108		5 448 1.108							
6	311	1.0829	143	1.085										
4	015	1.0699	204	1.055	2 1.086 3 1.070		5 { 2.2.18 1.083 0.0.20 1.068			4 212 1.071				
6	204	1.0582	015	1.050	1 1.049 ws 2 1.043 2 1.035		3 266 1.039			2 300 1.043 3 114 1.033				

a) X-ray powder diagram obtained with a Straumanis-type 114.83 mm diameter Debye-Scherrer camera, Philips FW 1008 X-ray generator; Ni-filtered Cu-K α radiation, $\lambda = 1.54178 \text{ \AA}$, 40 kV and 16mA; exposure time 17 hours; film wrapped in Al-foil to reduce darkening by fluorescence; film shrinkage corrections applied; intensities visually estimated; the powder was taken in a ball of rubber solution.

ws - Diffraction line of westerveldite not coinciding with lines of maucherite or niccolite.

B - Broad or diffuse line.

* - Diffraction line of maucherite according to Yund (1961).

b) In XPDF card 12-799, *hkl*-indices are given for a crystal setting with reversed *a*- and *c*-axes.

density of 8.13 g/cc was calculated for the nickeloan westerveldite (synthetic FeAs 7.861 g/cc, XPDF card 12-799).

From the data in Table 2 unit-cell dimensions were also calculated for the associated niccolite, $a = 3.61 \pm 0.01\text{\AA}$, $c = 5.05 \pm 0.01\text{\AA}$, and maucherite, $a = 6.86 \pm 0.01\text{\AA}$, $c = 21.84 \pm 0.05\text{\AA}$.

OPTICAL PROPERTIES

Optical properties of the fine-grained nickeloan westerveldite could only be qualitatively assessed. The mineral is brownish white to gray against maucherite in air; in oil the brownish color is more distinct. Reflection pleochroism is distinct in air and in oil; in one position the mineral is only slightly more brownish than maucherite; 90° from this position the brownish color is distinct. Anisotropy effects under crossed nicols are distinct in air and strong in oil with orange-brown and bluish polarization colors. The mineral appears somewhat darker and seems to have lower reflectance than maucherite and niccolite. The polishing hardness is higher than those of maucherite and niccolite. According to Buseck (1963) synthetic alloys of Ni-rich FeAs and Fe-rich NiAs have almost identical appearance in reflected light.

FORMATION AND STABILITY OF MAUCHERITE-WESTERVELDITE INTERGROWTHS

Phase relations in the system Ni-Fe-As (Buseck, 1963; Maes and De Strycker, 1967) suggest that maucherite and westerveldite will in general not coexist as a stable mineral pair (Fig. 3).

Niccolite, nickeliferous loellingite, and (Fe, Co)-rich gersdoffite in the ores of La Gallega were allegedly formed at unusually high temperatures between 800° and 400° C (Oen, Burke, Kieft, and Westerhof, 1971), but presumably the crystallization of niccolite was completed, cooling had proceeded, and arsenic partial pressures had dropped, before the introduction of later serpentizing solutions caused local reheating of the rocks in very narrow zones adjacent to late serpentine veinlets. The arsenic partial pressures were then presumably below those required to stabilize niccolite at the temperatures of reheating and as a result niccolite decomposed into maucherite and arsenic vapor or fluid. Hawley and Hewitt (1948a, 1948b) and Hewitt (1948) have observed the partial breakdown of niccolite into maucherite and arsenic vapor on heating NiAs in sealed tubes at temperatures around 450° C. The reaction, which involves a decrease in volume of the solid phase and the formation of shrinkage openings (Oen and Sørensen, 1964) may be depicted by the following equation (niccolite analysis

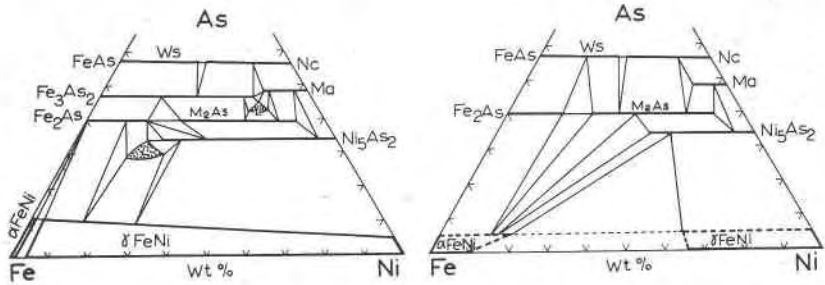
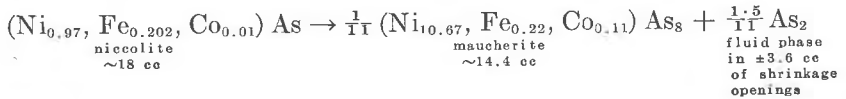
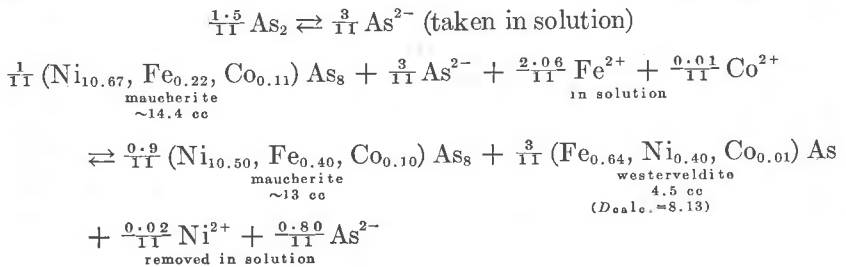


FIG. 3. The Fe-Ni-rich part of the condensed system Fe-Ni-As at 800° C (left) and at room temperature (right) according to Maes and De Strycker (1967). L — liquid; Ws — westerveldite; Nc — niccolite NiAs; Ma — maucherite Ni₁₁As₈; M₂As corresponds in composition to the mineral oregonite. Westerveldite and maucherite do not in general form a stably coexisting mineral pair.

7, Table 1; approximate molar volumes derived from densities given in Dana and Ford, 1932):



Maucherite analysis 6, Table 1, is consistent with that expected from this equation. Fe-richer maucherite (analysis 5, Table 1) and nickeloan westerveldite might then have been formed by reaction of Fe-bearing serpentinizing solutions with maucherite and the arsenic phase contained in the shrinkage openings; this would explain the clustering of the westerveldite around openings in maucherite:



The quantitative aspects of the above equations are only very approximative; the amount of westerveldite formed and the amounts of elements introduced or removed depend on the activities of As, Fe, and Ni, or the concentrations of these elements that can be taken into solution under the given physicochemical conditions; all these factors are not exactly known. The equations were made to fit the

estimated volumetric proportions of minerals in the maucherite-westerveldite intergrowths and they indicate in a general way the trend of reactions envisaged. Heating of niccolite by metasomatizing solutions caused the decomposition of niccolite along the binary Ni-As join in the system Ni-Fe-As into a heterogeneous phase assemblage of maucherite and arsenic vapor or fluid contained in shrinkage cracks; the latter arsenic phase was much faster in its reaction with Fe-bearing metasomatizing solutions than the solid phases and the formation of nickeloan westerveldite by reaction of arsenic, maucherite, and metasomatizing solutions could be considered as having taken place in a partial system isolated in shrinkage openings and significantly close to the Fe-As join in the system Ni-Fe-As. In the ternary Ni-Fe-As system westerveldite cannot exist stably besides maucherite and its persistence is presumably due to the notoriously slow equilibration rates of arsenides.

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