Bulletin du BRGM (deuxième série)
Section II, n° 3, 1978, pp.225à230,4 fig., 2 tabl.

Nickel minerals from Barberton, South Africa : VIII. The spinels cochromite and nichromite, and their significance to the origin of the Bon Accord nickel deposit

Minéraux de nickel de Barberton Afrique du Sud : VIII. Les spinelles cochromite et nichromite et leur importance concernant l'origine du gisement de Bon Accord

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Mots clés : Nouveau, Spinelle (Cochromite, Nichromite), Co, Cr, Ni, Serpentine, Genèse, Effet-de-choc, Météorite, Transwaal (Bon Accord, Barberton), Trévorite.

Abstract

Two new spinels, a cobalt-chromium spinel called cochromite, and a nickel-chromium spinel called nichromite, are described. These minerals are intermediate members in a replacement reaction in which an original chromite with approximate inferred composition

$$Fe^{2+}_{6,5}Mg_{1,5}Cr_{11}Al_5O_{32}$$

is altered to trevorite. The reduced nature of the original spinel is seen as further evidence of the meteoritic origin of the Bon Accord nickel deposit.

Résumé

Deux nouveaux spinelles l'un cobalt-chrome appelé "cochromite", l'autre nickel-chrome appelé "nichromite" sont décrits. Ces minéraux sont des phases intermédiaires dans une réaction de remplacement dans laquelle une chromite originale ayant une composition probable

$Fe^{2+}_{6,5}Mg_{1,5}Cr_{11}Al_5O_{32}$ est changée en trévorite.

Le caractère réduit du spinelle original confirme la nature météoritique du gisement de Bon Accord.

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List of illustrations

1. Introduction

The nickel occurrence at Bon Accord, Barberton, South Africa, has a unique mineralogy. The nickel minerals trevorite [WAAL S.A. DE, 1972], liebenbergite [WAAL S.A. DE and CALK L.C., 1973], bonaccordite [WAAL S.A. DE et *al.*, 1974], bunsenite, and millerite formed a high-temperature metamorphic assemblage and were later, during a serpentinization process [WAAL S.A. DE, in press], replaced by nepouite, pecoraite, willemseite [WAAL S.A. DE, 1970a], nimite [WAAL S.A. DE, 1970b], gaspeite, heazlewoodite, and breithauptite. These mineral assemblages grade into the high-magnesium, talcose serpentinites of the Jamestown Igneous Suite, through intermediate members of the trevorite-magnetite [WAAL S.A. DE, 1969], willemseite-talc, nepouite-(pecoraite-) serpentine, and nimite-clinochlore mineral series [WAAL S.A. DE, in press]. Surface oxidation of the nickel-rich minerals yielded reevesite [WAAL S.A. DE and VILJOEN E.A. 1971], violarite, goethite, and quartz [WAAL S.A. DE, in press].

Recently, two new spinels were encountered in the liebenbergite-trevorite-bunsenite-bonaccordite assemblage. These minerals are remnants of a spinel that predates the metamorphic assemblage, and, as such, constitute the only relics of the pre-metamorphic (original ?) mineral assemblage. Since spinels of this composition are not known from the two most common types of nickel deposit, laterites and magmatic sulphides, the Bon Accord deposit most probably represents neither of the two types.

This paper contains a description of the two new spinels, cochromite and nichromite, and a discussion of the significance of these minerals to the origin of the Bon Accord deposit.

2. Cochromite

The cochromite occurs typically within larger silicate masses that are interstitial to the nodular; trevorite-rich segregations [WAAL S.A. DE, in press] in the trevorite-liebenbergite-bunsenite assemblage. It is, invariably, partly replaced by trevorite that forms distinct rims around the individual spinel remnants. This relation indicates that the cochromite is unstable in the high-temperature, metamorphic assemblage (DE WALL, in preparation), and is, therefore, a physical remnant of an earlier mineral assemblage (fig. 1 and 2).

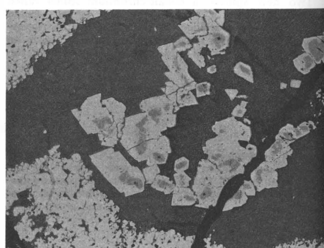

Fig. 1. — Photomicrograph of remants of original spinel (medium grey) mantled by trevorite with euhedral outlines (light grey), set in a seggregation of silicate (dark grey), which is surrounded by finegrained trevorite — silicate material. (Enlargement 70X, dray objective).

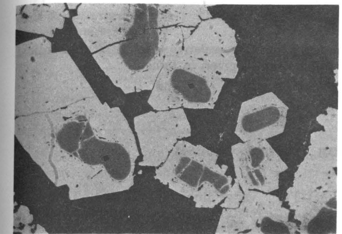

Fig. 2. — Close-up view of the spinel remnants (medium to dark grey) in trevorite (light grey) with euhedral outlines. Diamond-shaped indents of microhardness test show hairline cracks. (Enlargement 225X, oil immersion objective).

The physical properties of cochromite are listed in table 1 and the chemical data from three grains that were analysed with an electron microprobe are given in table 2.

The small grain size of the cochromite remnants, and the fact that they are invariably rimmed by trevorite, made physical separation of the mineral impossible. For this reason, no density determination could be made. The cell edge quoted is that of cobaltian chromite (tabl. 2), the only grain that was large enough to give an X-ray diffraction pattern with measurable lines. However, it is expected that this value will be close to that of the cochromite-proper. Because hairline cracks radiating from the indent could not be avoided, the micro-hardness quoted may be fractionally too low.

TABL. 1. — Physical properties of cochromite

Colour	: Dark, probably black, with a metallic lustre
Fracture	: Conchoidal
Streak	: Greenish-grey
Optical character	: Isotropic in reflected light (air and oil immersion)
Structure	: Cubic, Fd3m (assumed)
Cell edge	: 8,292 ± 0,002 Å (cobaltian chromite, Table 2)
Calculated density	: about 4,99 g/cm^3
Reflectivity	: Dry objective, 50X ; SiC as standard 14,3(4) % at 480 nm, 13,7(2) % at 546 nm, 14,0(3) % at 589 nm, 13,9(4) % at 656 nm,
Micro-hardness	: 1 218 (100) kg/mm^2 with 50 gm load
Grain size	: Average diameter of inscribed circle of 33 grains = 21 μm, median diameter of inscribed circle of same population = 13μm. (not distinguished here between cochromite and nichromite).

TABL. 2. — The chemical composition of cochromite, nichromite and a cobaltian chromite.

Chemical Analyses

	Cobaltian Chromite	Cochromite			Nichromite
NiO	6,57	7,11	5,49	7,67	15,86
CoO	12,65	16,9	16,70	17,45	12,49
ZnO	* n.d.	0,59	0,45	0,59	* n.d.
MgO	2,15	0,76	0,82	0,95	0,40
MnO	0,58	0,82	0,78	0,84	0,21
(FeO)	13,63	11,00	11,91	11,18	17,32
FeO *calc.	12,91	9,78	10,98	7,45	6,45
Fe_2O_3 *calc.	0,80	1,35	1,03	4,14	12,06
TiO_2	1,24	1,34	1,08	1,26	1,13
SiO_2	0,12	0,13	0,14	0,11	0,20
Al_2O_3	11,89	12,56	9,77	9,11	7,46
Cr_2O_3	51,72	49,49	53,39	50,38	45,56
Σ oxides	100,63	100,83	100,63	99,95	101,83

Mineral formula calculated to 32 oxygen ions using FeO *calc. and Fe_2O_3 *calc.

Ni	1,467	1,597	1,243	1,772	3,647
Co	2,817	3,798	3,796	4,009	2,873
Zn	0	0,118	0,102	0,120	0
Mg	0,883	0,319	0,340	0,412	0,172
Mn	0,133	0,202	0,187	0,206	0,052
Fe^{2+} *calc.	3,000	2,286	2,604	1,789	1,548
Fe^{3+} *calc.	0,167	0,286	0,221	0,895	2,598
Al	3,883	4,134	3,268	3,079	2,512
Cr	11,350	10,941	11,966	11,406	10,305
Ti	0,267	0,286	0,238	0,275	0,240
Si	0,033	0,034	0,034	0,034	0,052
ΣM^{2+}	8,300	8,320	8,272	8,308	8,292
$\Sigma M^{3+} + M^{4+}$	15,700	15,681	15,727	15,689	15,707
Σ Cations	24,000	24,001	23,999	23,997	23,999

Explanation

* n.d. : not detected
* calc. : Calculated on the charge-balance principle

Standard used for analyses :

Element	Concentration %	Standard
Ni	7,79	Synthetic (NiFe)S
Co	67,40	Synthetic CoS
Zn	67,09	Synthetic ZnS
Mg	9,16	Chromite
Al	7,78	Chromite
Mn	3,69	Ilmenite
Ti	27,40	Ilmenite
Fe	21,86	Chromite
Cr	41,74	Chromite
Si	19,38	Pyrope

3. Nichromite

Nichromite is similar in general appearance and mode of occurrence to cochromite. However, it contains nickel as the major cation among the two-valent species. Its chemical composition is given in table 2.

4. The origin of the Bon Accord deposit

In an earlier paper [WAAL, S.A. DE, in press] a detailed description of the Bon Accord deposit, and a discussion of possible modes of origin were given. It was argued that the deposit is neither a metamorphosed laterite nor a reworked massive sulphide body, mainly because of its high Ni tenor (a maximum of about 38 per cent NiO). A possible hydrothermal deplacement origin as proposed by earlier workers [ANHAUESSER C.R., 1963], was also discounted because of the massive nature and the absence of granitic material in the ore. Finally, two possible modes of origin were considered: that the deposit represents either an oxidized lump of awaruite, or that it is the oxidized remnant of a nickel-iron meteorite that fell in Archean times. Of these two possibilities the meteorite hypothesis was favoured because:

1) The high Ni to Fe ratio of awaruite (generally 1,8 to 3) against the relatively low value for the deposit (about 1).

2) The resemblance of the material in the core of the deposit to nickel-iron meteorites in general.

3) The Co to Ni ratio of the core material in the deposit tallies with that of meteorites (though the extent of this correspondence may be debatable).

4) The known abundance of meteorites 3 giga-years ago, as evidenced by the history of the Moon [SMITH J.V., 1974].

Inspection of the chemical variation of the cobaltian magnetite, through cochromite, nichromite, and, finally, trevorite shows a very definite line of evolution. A plot of (Ni + Co) in the unit cell (i.e., per 32 oxygen ions) against the other metal ions in the unit cell, as in figure 3, yields the following information. (Subscript u.c. indicates that reference is made to the cations in the unit cell, r is the correlation coefficient).

1) Fe^{2+}_{uc} varies linearly with $(Ni+Co)_{uc}$. In fact, this relation can be expressed by the equation

$$Fe^{2+}_{uc} = 6,517 - 0,794\,(Ni+Co)_{uc} \quad (r = -0,99) \quad \text{(i)}$$

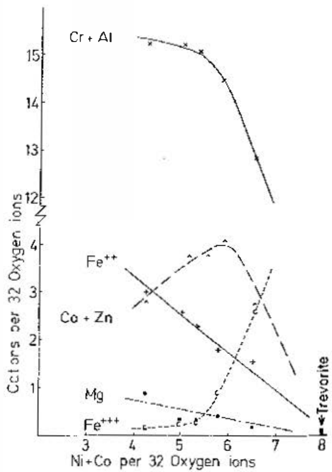

Fig. 3. — Variation in $(Cr+Al)_{uv}$, Fe^{2+}_{uv}, $(Co+Zn)_{uv}$, Mg_{uv}, and Fe^{3+}_{uv} relative to $(Ni+Co)_{uv}$. Note that Fe^{3+}_{uv} is the negative image of $(Cr+Al)_{uv}$. Trevorite is included in the calculation of the lines of best-fit for Fe^{2+}_{uv} and Mg_{uv}.

2) The variation of Mg_{uc} against $(Ni+Cu)_{uc}$ can be interpreted, in a similar fashion, as a straight line.

$$Mg_{uc} = 1,504 - 0,196\,(Ni+Co)_{uc} \quad (r = -0,87) \quad \text{(ii)}$$

3) Both Co_{uc} and Zn_{uc} shows smooth curves, with maxima at $(Ni+Co)_{uc} \approx 5$ to 6. In figure 3, $(Co+Zn)_{uc}$ is plotted.

4) $(Cr+Al)_{uc}$ follows a smooth curve with a major flexure at about $(Ni+Co) \approx 5$ to 6. Cr_{uc} and Al_{uc}, not shown individually in figure 3, both show some scatter, with a general ratio of Al to Cr of about 0,3.

5) Fe^{3+}_{uc} follows a trend exactly opposite to that of $(Cr+Al)_{uc}$. It defines a smooth curve that has an exponential form for which

$$\log Fe^{3+}_{uc} = 0,579\,(Ni+Co)_{uc} - 2,448 \quad (r = 0,98) \quad \text{(iii)}$$

This relation is also depicted in figure 4.

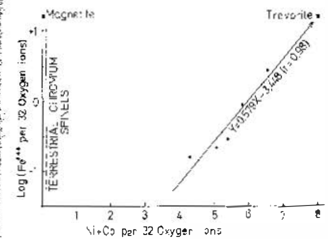

Fig. 4. — The logarithm of Fe^{3+}_{uv} plots as a straight line ($r = 0,98$) against $(Ni+Co)_{uv}$. The arrowhead on the line of best-fit of the data points (trevorite included in calculations) indicates the direction of change from an original spinel, through cobaltian chromite, cochromite, and nichromite, to trevorite. The reduced nature of this original spinel, relative to the common, terrestrial chromium spinel, is clearly illustrated.

6) Among the remaining minor elements (not shown in figure 3), Mn_{uc} shows a pattern cohering to that of $(Zn+Co)_{uc}$. The Ti_{uc} variation has no obvious trend pattern, but the value for Si_{uc} seems to increase with increasing $(Ni+Co)_{uc}$.

It is clear from the data given (tabl. 2) that the cobaltian chromite, the cochromites, and nichromite are all intermediates in a replacement sequence in which an unknown spinel is finally converted to trevorite. The composition of this unknown spinel can be estimated on the assumption that it had $(Ni+Co)_{uc} \approx 0$, as is generally the case for meteoritic chromites, and for terrestial chromites associated with mafic and ultramafic rocks. (See IRVINE T.N., 1967; BLISS N.W. and MAC LEAN W.H., 1975; WAAL S.A. DE, 1975; DICKEY J.S., 1975, and many others).

By substituting the value $(Ni+Co)_{uc} \approx 0$ in equations (i), (ii), and (iii), and by extrapolation of the curves in figure 3 to this value, one arrives at the composition of a highly-reduced chromite with a composition approximating

$$Fe^{2+}_{6,5}\, Mg_{1,5}\, (Cr_{11}\, Al_5)\, O_{32} \quad (Fe^{3+} = 0,0004)$$

Such reduced chromites, which have a high chromium content ($Cr_{uc} \approx 11$), combined with a $Mg/Mg+Fe^{2+}$ of less than 0,20, are known only from meteoritic materials (see BUNCH and KEIL, 1971; BUNCH et al., 1967; BUNCH and OLSEN, 1975). It would thus appear that the present data substantiate the meteorite hypothesis proposed earlier (DE WAAL, in press) to explain this unique nickel deposit at Bon Accord.

Acknowledgements

Acknowledgement is made to the National Institute for Metallurgy (NIM) for permission to publish this paper. Thanks are also due to Dr. S.A. HIEMSTRA, Director of NIM's Mineralogy Division, for his critical reading of the manuscript, and to E.A. VILJOEN and E. VAN DER WALT, for the microprobe analyses.

Discussions :

D.L. BISCH : Do you ever find Co-Cr spinels or liebenbergite in meteorites and if not, how do you explain the occurrence of these minerals in your deposit ?

S.A. DE WAAL : I am not aware of these minerals in known meteorites, but, as pointed out in my presentation, the Bon Accord deposit probably represents an oxidized and thermally metamorphosed nickel iron meteorite. The nickel and cobalt chromium spinels appear to be intermediate members in a replacement series in which a reduced iron magnesium spinel in the original meteorite is altered to trevorite.

Z. MAKSIMOVIC : I would like to draw your attention to the occurrence of very peculiar nodules found in the Blanguette karstic bauxite deposite in Var by J. DIETRICH *et al.* These nodules occur in the lower portion of the deposit near the footwall limestone, and are composed of nickeline, erythrite and spolaterite.

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