

Evidently therefore a complete non-stoichiometric series exists between the disordered hydrated oxides hydrohausmannite— $\alpha$ - $\text{MnO}(\text{OH})$  affording an interesting comparison with the anhydrous series  $\text{Mn}_3\text{O}_4$ — $\gamma$ - $\text{Mn}_2\text{O}_3$  which is analogous to the better known  $\text{Fe}_3\text{O}_4$ — $\gamma$ - $\text{Fe}_2\text{O}_3$  (Verwey and deBoer, 1936). The transition  $\text{R}_3\text{O}_4$  to  $\gamma\text{R}_2\text{O}_3$  is believed due to the oxidation of the metal ions  $\text{R}^2$  to  $\text{R}^3$  with concomitant vacant sites, the structure throughout being essentially that of spinel. For  $\gamma\text{R}_2\text{O}_3$  one ninth of the metal atoms are randomly missing with no special distinction between tetrahedral or octahedral sites. However recent work on  $\text{In}_2\text{S}_3$ , the high temperature form of which has the  $\gamma\text{R}_2\text{O}_3$  structure indicated that vacancies were more frequent in the octahedral sites (Hahn and Klingler, 1949) as in hydrohetaerolite which we have seen corresponds to the  $\text{R}_3\text{O}_4$  side of the series. One may therefore expect many intricate orderings within systems of this type, but a less speculative approach is hampered by the lack of specimens suitable for single crystal methods of structure analysis.

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## SECONDARY ALTERATION OF CHROMITE

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Readers of Roswell Miller's (1953) paper on the Webster-Addie Ultramafic Ring and the secondary alteration of its chromite, may be interested in similar alteration phenomena found in serpentinites of the Belledonne Massif near Grenoble, S. E. France, and described by the present author in a Ph.D. thesis for the University of Leyden (Holland). As the results are contained in a publication of rather difficult access, they are here summarized as far as the study of chromites is concerned.

Scattered grains of chromite occur in the serpentinitized ultrabasic core of a funnel-shaped basic intrusion in the hercynian basement of the Western Alps (Belledonne Range). The grains are coated with a highly ferromagnetic, black, opaque material which is also seen to penetrate along fissures in the grains. A colorless chlorite usually surrounds the

mantles and sometimes fills in fissures that have been left open after the formation of the black mesh structure in the original chromite. Optically the chlorite was found to be extremely rich in the amesite molecule.

Fractional panning and subsequent treatment with Clerici solution and the permanent magnet provided concentrations of the ore fraction sufficient for *x*-ray powder determination. Diffraction line doublets of the spinellide pattern for  $\delta$ -angles larger than 25–30° indicated the presence of two distinctly sized spinel lattices. Their unit cell dimensions were calculated from the outstanding (440) diffraction lines. One of these shows a very restricted range from 8.395 to 8.397 Å and evidently represents practically pure magnetite. The other *a* ranges from 8.16 to 8.269 Å and is believed to indicate various isomorphous mixtures of the Fe''-Mg-Al-chromite series. The part played by the magnetite molecule is of no consequence in this structure as the ferromagnetism of the chromite, especially where not coated with magnetite, is extremely weak.

A quantitative chemical analysis of the ore fraction of a serpentinite was carried out by the Petrochemical Laboratory of the University of Leyden and gave weight percentages of the following oxides:

SiO<sub>2</sub> 5.68; Al<sub>2</sub>O<sub>3</sub> 15.77; Cr<sub>2</sub>O<sub>3</sub> 10.12; Fe<sub>2</sub>O<sub>3</sub> 44.26; FeO 15.34; MgO 9.28; CaO 0.00; TiO<sub>2</sub> 0.00; Total 100.45

Equiv. Weights	At	Be	Al <sub>2</sub> O <sub>3</sub>	Mt	Fe <sub>2</sub> O <sub>3</sub>
Si 95	95				
Al 310	190	43	77		
Cr 133		133			
Fe''' 554				330	224
Fe'' 213		48		165	
Mg 230	190	40			
Total 1535	475	264	77	495	224
		341		719	
Molecular norm in per cent	31		22		47
Modal comp. in vol. per cent	±25		±25		±50

At = amesite; Be = beresofite; Mt = magnetite.

In the accompanying table the equivalent weights have been calculated according to Niggli's method (multiplication of the weight percentages of the oxides by 1000 and division of the respective molecular

weights into the figures so obtained). All available silica has been used in the formation of amesite (At). All chrome and remaining magnesia have gone into a non-ferric chromite whose proportions of ferrous iron and alumina were determined by plotting the line  $a = 8.269 \text{ \AA}$  on Simpson's four constituent diagram of the non-ferric chromites and finding its intersection with the line representing the given Mg:Cr ratio. A chrome-rich beresofite (Be) was thus found, but the excess alumina is probably contained in the structure making it roughly a 1:1 chromespinel. The remaining magnetite must have a similar quantity of excess  $\gamma\text{-Fe}_2\text{O}_3$  as no trace of either hematite or corundum have been detected in the x-ray powder diagrams. Kordes (1935) claims that equal quantities of excess  $\text{R}_2\text{O}_3$  can be admitted to the spinel-structure without appreciably affecting its unit cell dimension.

The overall excess of the  $\text{R}_2\text{O}_3$  molecule seems to indicate a high degree of oxidation during the formation of the magnetite mantles which are found coating the chromite grains in the *Triassic* but not in the *Carboniferous* basal conglomerate. These considerations exclude the possibility of a deuteric origin of the solutions causing the magnetite, and probably also the serpentine to develop. The alteration of the chromite is definitely post-basic-rock-consolidation and must have occurred at comparatively shallow depth.

Altered chromite in a serpentinite containing bastite after diallage is pale brown translucent and its smaller unit cell dimension ( $a = 8.228 \text{ \AA}$ ) suggests a higher Al:Cr ratio, of primary origin because the volume percentage of magnetite coating is roughly equal to that found on the chromite with  $a = 8.269 \text{ \AA}$ .

Unaltered chromite in a highly silicified ultrabasic boulder from the Carboniferous basal conglomerate shows no signs of corrosion and its brown color and very small unit cell dimension ( $a = 8.16 \text{ \AA}$ ) indicate an even higher Al:Cr ratio of doubtlessly primary nature.

Therefore, if the formation of magnetite and amesite has at all resulted in a composition change of the chromite, the latter must have been relatively enriched in chrome by the abstraction of alumina, whilst the removal of both magnesia by the amesite and ferrous iron by the magnetite could explain the excess  $\text{R}_2\text{O}_3$  as well as the possible increase in unit cell dimension of the remaining chromite.

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