

pulverize clay samples prior to dissolving them, it is likely that error is introduced into the analysis by the sample preparation.

5. The appearance of a light tan color on the pulverized clay suggests (a) that ferrous iron in the octahedral layer of the clay crystal was exposed to the air and oxidized to ferric oxide, or (b) that ferric iron originally in symmetrical octahedral coordination with oxygen and hydroxyl within the octahedral layer suffered disruption of bonds on one side (asymmetrical) as it was exposed by grinding, and ferric oxide was formed.

In either case drastic changes in the crystal chemistry of the clay have occurred as more surface was exposed. These changes are probably of the same order of violence as occurs in some mineral inversions or replacements.

6. It seems probable that oxidized clay on an eroded outcrop may differ in physical and chemical properties from that occurring in the fresh interior. This is borne out by the observations of Williams, Elsley, and Weintritt (1953) who found in Wyoming bentonite, "The highest grade clay has a yellow color while the other type, a blue clay, is customarily found to be of lower grade. . . . The primary cause of variation in properties is due to the Na/Ca ratio in the exchange positions regardless of whether the iron in the clay is in the ferrous or ferric state."

7. Because the oxidized surface of the pulverized Cheto clay differs from the interior, it illustrates the principle that a reaction between an external medium and the surface of a reference mineral whose bulk composition is  $A_nB_m$  occurs actually with a surface whose composition is not  $A_nB_m$ . One wonders how significant this relationship (or difference) is in weathering, ore deposition, metamorphism, and other mineral reactions.

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#### HYDROHAUSMANNITE AND HYDROHETAEROLITE

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Frondel (1953) recently described two new manganese oxide minerals one of which, hydrohausmannite  $(Mn^{2+}, Mn^{3+})_{3-8}(O,OH)_4$ , although closely resembling hausmannite  $Mn_3O_4$ , is differentiated by the presence of sev-

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eral per cent of water and some details in the *x*-ray powder pattern. From the cell dimensions, the structures of  $Mn_3O_4$  and  $ZnMn_2O_4$  (hetaerolite) are evidently similar, and a further close analogy may well exist between Frondel's new mineral and hydrohetaerolite which also contains "structural water" (Frondel and Heinrich 1942). The writer recently determined the crystal structure of hydrohetaerolite, and a brief discussion of the possible relations of the two minerals may be appropriate.

TABLE 1. X-RAY DATA FOR MANGANESE MINERALS WITH DEFORMED SPINEL STRUCTURE

	Hausmannite	Hetaerolite	Hydrohausmannite	Hydrohetaerolite
Cell dimen- sions in Å $\left\{ \begin{array}{l} a \\ c \end{array} \right.$	5.75 9.42	5.74 9.15	5.79 9.49	5.75 9.05
Space group	$I4_1/am\bar{d}$	$I4_1/am\bar{d}$	—	$I4_1/am\bar{d}$
Unit cell con- tents	$Mn_4^2Mn_8^3O_{16}$	$Zn_4Mn_8^3O_{16}$	Uncertain probably ( $Mn^2$ , $Mn^3$ ) $_{12-\delta}$ (O, OH) $_{16}$	$Zn_4Mn^{3+}_{6\ 2/3}O_{12}(OH)_4$
Reference	Aminoff (1919)	Frondel & Heinrich (1942)	Frondel (1953)	Wadsley (1954)

Hydrohetaerolite has the same structure as hausmannite, except that one sixth of the trivalent manganese occupying the octahedral sites are randomly absent, and the balance of charge is supplied by hydrogen bonds (Wadsley, 1954). The powder diffraction data for hydrohausmannite, indexed as body centred tetragonal with  $a=5.79$ ,  $c=9.49$  contains the strong line (002) at  $4.65 \text{ \AA}$  which distinguishes it from hausmannite. This reflection, however, is incompatible with the fourfold screw axis of the space group  $I4_1/am\bar{d}$  in which (00 $l$ ) can be present only if  $l=4n$ . Although closely related chemically to hydrohetaerolite, the new mineral therefore possesses important crystallographic differences, an explanation of which may be sought in the following way.

It is well known that manganous hydroxide is rapidly oxidized, and Frondel (1953) found evidence of hydrohausmannite in several specimens of pyrochroite which had been exposed to the air. Pyrochroite has a layer structure, of which brucite (or cadmium iodide) is the typical member (Aminoff 1919). It consists of two-dimensional sheets of  $Mn^2(OH)_6$  octahedra stacked so as to give hexagonal close packing of the anions in the adjacent layers which are held together by weak secondary forces. If we assume hydrohausmannite to be closely related to the tetragonal Mn spinels, and the cell dimensions leave little doubt about this,

it is clear that its formation from pyrochroite is a matter of considerable ease despite the apparent dissimilarity in atomic arrangement of the two structural types.

It is convenient for our purposes to picture the tetragonal spinel as a layer compound. Each of the planes represented by the form  $\{101\}$  contains a brucite-type layer with every fourth octahedron regularly missing to form a hexagonal grouping. In one orientation the layers lie parallel in cubic close packing so as to form two kinds of interstitial sites, one tetrahedral, one octahedral. In the case of hausmannite, the tetrahedra coordinated to  $Mn^{2+}$  are located on each side of a layer and sharing the oxygens bounding a vacant octahedral site, the octahedra formed by  $Mn^{3+}$  are situated between triads of octahedra in adjacent layers and irrespective of position all sites are occupied. This is illustrated in Fig. 1. In hydrohetaerolite the vacancies are distributed at random over all the  $Mn^{3+}$  sites with certain reservations which are discussed elsewhere (Wadswley 1954).

The transformation of the brucite type lattice to that of niccolite ( $NiAs$ ) may occur for the nonstoichiometric tellurides of Ni, Co, V, Ti and selenides of V and Ti (Ehrlich 1949, for a recent review) simply by

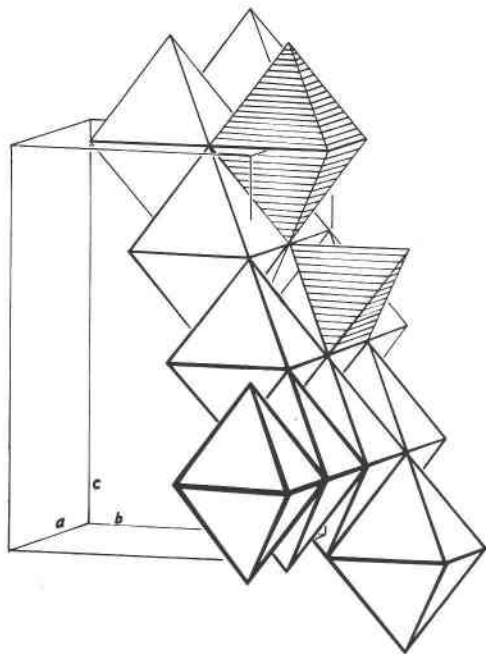


FIG. 1. The tetragonal spinel structure drawn (in part) as a layer of octahedra lying in the direction of the plane (011). The "interstitial" polyhedra are hatched, and for the sake of clarity only one of each type on only one side of the layer is drawn.

the interpolation of additional metal ions to the octahedral sites between the sheets with little change of symmetry or even of unit cell dimensions. In order to form a spinel however, the brucite structure must undergo three major changes:

- (a) The packing of the layers changes from hexagonal to cubic. The two unit cells, therefore, are not readily related by a simple matrix expression.
- (b) Every fourth metal atom leaves the sheet to take an interstitial position,  $Mn^2$  tetrahedral,  $Mn^3$  octahedral and possibly also tetrahedral. The analysis quoted by Frondel (1953) indicates that the oxidation has proceeded beyond that of hydrohetaerolite.
- (c) Oxidation occurs by the formation of ions of higher valency at the expense of hydrogen ions which presumably leave the structure as water molecules.

The oxidation of pyrochroite proceeds therefore by the migration of ions to their interlayer positions in the direction normal to (0001). It may be assumed that the tetrahedral positions are occupied first since no valence change is involved in the movement of  $Mn^2$  ions. When the population of each octahedral interstitial site is equal to that of each site in the residual layer sheets (as in the case of hydrohetaerolite), the symmetry could correspond to  $4_1$  (or  $4_3$ ) and the layer structure is thereby completely destroyed. If incomplete, however, the atoms in the layers and in the interlayer sites are not present in equivalent amounts, and hence related by the fourfold screw axis in position but not in scattering power. Reflections (00*l*) for the unit cell with  $l=4n+2$  could then occur, and as a consequence the symmetry although strongly pseudotetragonal would be lower. It is not possible without single crystal data to do other than speculate upon the space group, or lacking additional chemical analyses to determine the proportions of ions in the positions in the unit cell which correspond in the orientation given by Frondel to the spinel structure.

In a study of the formation of MgO crystallites by the dehydration of crystalline brucite, Garrido (1951) found that rapid heating induced supplementary spectra which he attributed to some periodicity of vacant lattice sites. It is possible therefore that the octahedral manganese atoms are completely equivalent only when the formation of hydrohausmannite is exceedingly slow, and also when the composition is analogous to that of hydrohetaerolite, i.e.  $Mn^2Mn^{3}_{1/3}O_3(OH)$ . Chemical studies of the oxidation of  $Mn(OH)_2$  indicated that synthetic hydrohausmannite is progressively oxidized to  $\alpha$ - $MnO(OH)$  which is unrelated to manganite (Feitknecht and Marti, 1945) or to groutite. The *x*-ray powder pattern of  $\alpha$ - $MnO(OH)$  indexed as tetragonal with  $a=8.3$ ,  $c=9.3 \text{ \AA}^*$  is again dominated by a line at or near  $4.6 \text{ \AA}$ .

\* This is for the double face-centred cell. The body centred elements are  $a=5.9$ ,  $c=9.3 \text{ \AA}$ .

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