

with a decreased intensity. Some lines have even disappeared. The last diagram shows the fewer, broader and weaker lines, characteristic of a very poorly crystallized kaolinite (Chile, W9.).

From the same three samples electron micrographs have been made to investigate the particle size and the degree of crystal perfection. The results appear in good agreement with the  $x$ -ray examinations. Since in all samples the clay particles are about the same size, it seems likely that the broadening and the decreasing intensities of the lines, as shown in Fig. 3, are not only caused by decreasing particle size but in addition by crystal imperfections (cf. Fig. 4).

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#### MINERALOGICAL CHANGES IN WEATHERED SEDIMENTARY IRONSTONES

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The sedimentary ironstones of Liassic and Oolitic ages vary in the state of oxidation of their iron content from ferrous in the green ores to ferric in the red-brown ores which have undergone weathering at deposition or on exposure. Taylor (1) has surveyed the principal physical, chemical and mineralogical changes which accompany weathering. Loss of

lime, magnesia, alumina and carbonate takes place during the oxidation of iron. Previous workers have attributed the formation of kaolinite, sericite or hydrous mica, goethite and "clay" to the alteration of the chamosite which occurs in the parent ore. Recent research (2) on the properties of chamosite has enabled a fresh approach to be made to the study of weathered ironstones.

A stable oxidized chamosite has been identified as a common constituent of weathered ironstones. Its composition is  $(\text{Fe}^{3+}, \text{Al}, \text{Mg})_{2.9} (\text{Si}, \text{Al})_2 \text{O}_{6.9} (\text{OH})_{2.1}$  for half the orthohexagonal unit cell, corresponding to  $(\text{Fe}^{2+}, \text{Al}, \text{Mg})_{2.9} (\text{Si}, \text{Al})_2 \text{O}_{5.0} (\text{OH})_{4.0}$  for the parent mineral. Laboratory oxidation of the latter under hydrating conditions gave a closely similar product to the natural oxidized form, whereas dehydrating conditions (2) had given a composition with only  $\text{O}_{7.3} (\text{OH})_{1.0}$  per half unit cell. Its appearance resembles goethite, and much material formerly classed as goethite or limonite must now be regarded as oxidized chamosite. The colour of weathered ores is of little value as a guide to the mineral content, as both goethite and oxidized chamosite may appear in rocks coloured yellow, brown or red. The inference by Taylor (1) that "a silicate of ferric iron" might be present in weathered ironstones has proved an accurate prediction.

The first stage of alteration of siderite-chamosite ores is the breakdown of the siderite to a fine state of subdivision, followed by conversion to goethite. The second stage, which may to some extent overlap the first, is the conversion of chamosite to the ferric form; in some specimens chamosite and oxidized chamosite occur in equal amounts. The final stage is the breakdown of the oxidized chamosite to goethite and a residue which is usually amorphous and consists of the silicate sheets,  $\text{Si}(\text{Al})\text{-O}_x$ , leached of all octahedral ions. The Al replacing Si in these sheets is more resistant than octahedral Al, and the residue has an Al/Si ratio less than for kaolin and chamosite, for which it is about unity.

There is no evidence that kaolinite, sericite or "clay" is produced from chamosite during alteration. The kaolinite which has been inferred from chemical analytical data is often the chamosite residue. Bannister's conclusion, in Taylor (1), that kaolinite is invariably present in weathered ironstones is not confirmed. The oxidized chamosite has similar (00 $l$ ) spacings to kaolinite, and these reflections might be attributed to kaolinite in  $x$ -ray analysis of a mixture. Where a kaolin mineral occurs, the amount detected by  $x$ -ray diffraction is in general very much less than that deduced from chemical data. True kaolinite is rare, and in the Northampton Sand Ironstone is confined to the chamosite-kaolinite beds; the kaolin mineral which usually occurs gives a "fireclay" diffraction pattern.

Sericite, or hydrous mica, appears to be formed, not from chamosite,

but from small amounts of primary mica present in the parent ore, and detectable by  $x$ -ray analysis of the residue from acid extraction, even when it cannot be detected optically. The mica becomes hydrated during weathering and is concentrated by removal of soluble parts of the ore.

The occurrence of oxidized chamosite in weathered ironstones throws some light on the formation of "Box-stones," which consist of alternating layers of red and brown material concentrically arranged and sometimes enclosing unweathered ore. Although the mechanism of their production is not fully understood, it involves the transport of ferric iron as a solution or a colloid. The formation of box-stones is not solely a function of the iron content of the ore. The stability of oxidized chamosite except in extreme conditions of weathering means that the iron content, even if ferric, is not capable of solution and redeposition until a late stage. Siderite, however, produces finely divided goethite very early in the weathering process, and this apparently facilitates mobility of the ferric iron. Ores with only a low iron content, but entirely as siderite (siderite mudstones) produce box-stones, while ores containing much larger amounts of iron as chamosite (chamosite-kaolinite beds) tend to produce uniform brown weathering instead of box-stones. The state of the iron, carbonate or silicate, appears to be the controlling factor in box-stone formation. In general, the red layers of box-stones are richer in goethite, and the brown layers are richer in quartz, mica and kaolin. Unoxidized siderite is often present even in well-developed box-stones.

In some cases, doubt has arisen as to whether goethite is present in oolites in the ore as a primary constituent or as an alteration product. If accompanied by a white residue, formerly identified as "clay," the goethite is probably an alteration product of chamosite. If not so accompanied, it may be either primary, or secondary after siderite.

Considerable attention has been directed to the problem of beneficiation of sedimentary ironstones. The occurrence of chamosite in unweathered ores is an obstacle to beneficiation processes based on physical methods, since the iron is chemically combined with slag-forming silica and alumina. The identification of oxidized chamosite in weathered ores means that a similar difficulty arises in this case, although previous work had indicated that the iron and the slag-forming constituents were not chemically combined.

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