NOTES AND NEWS

OXIDATION OF MONTMORILLONITE DURING LABORATORY GRINDING

W. D. KELLER, *University of Missouri, Columbia, Missouri.*

Oxidation of iron in montmorillonite may occur sufficiently during laboratory grinding of the clay to be observable by simple tests. This reaction appears to be important in implications beyond the simple laboratory experiment.

The Cheto (Chambers), Arizona, bentonite is well known because of its extensive use in industry. When freshly mined, it is a grayish white clay containing scattered fine, dark gray spots. Although it is a relatively pure Ca-montmorillonite

$$(Al_{1.61}Fe_{.13}Mg_{.40})(Al_{.07}Si_{3.93})O_{10}(OH)_2\left(Na_{.02}\frac{Ca}{2}{}_{.37}\right),\text{ Kerr, } \textit{et al.}\text{ 1950,}$$

it does not stain blue when benzidine solution is applied to the lumps. The fact that it does not react with benzidine is not unique, because Page (1941) pointed out long ago the unreliability of the benzidine reaction for identification of montmorillonite. He showed that benzidine is oxidized to a blue compound by an ion which transfers a single electron, that the blue stain is really an indicator of an oxidant, and that available ferric ions, which are likely to occur in nature, are notably efficient oxidants of benzidine to the characteristic blue semiquinone.

Failure of the fresh Cheto lump clay to stain with benzidine indicates, therefore, the absence of available ferric ions. If the clay is pulverized by grinding in air for a few minutes with a laboratory mortar and pestle, it takes on a faint buff color which can be observed by comparing the lump and pulverized clays. This pulverized clay now stains a brilliant blue when wetted with benzidine solution. This reaction indicates the presence of available oxidizing ions, and the very light tan color suggests that iron in the clay has been changed to iron oxide which presumably is now effective in oxidizing benzidine to a blue substance. Several results and implications arise from the oxidation.

1. Another geologic example is given of the unreliability of the benzidine test for montmorillonite.
2. An oxidized outcrop of montmorillonite may stain with benzidine although the fresh clay may not.
3. By grinding montmorillonite and exposing more surface, tan-colored iron oxide is visibly formed.
4. It seems likely that the ferric-ferrous iron ratio would differ between lumps and pulverized material. How much this would affect analytical results is not known, but because analytical chemists ordinarily

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.

REFERENCES

KERR, P. F., HAMILTON, P. K., AND PILL, R. J., A.P.I. Project 49, *Rpt. No.* **7,** *Am. Pet. Inst.*, New York, p. 53 (1950).

PAGE, J. B., *Soil Sci.*, **51,** 133 (1941).

WILLIAMS, F. J., ELSLEY, B. C., WEINTRITT, D. J., *Abstracts, Second Conf. Clays and Clay Minerals, Natl. Res. Council*, p. 16 (1953).

HYDROHAUSMANNITE AND HYDROHETAEROLITE

A. D. WADSLEY*

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

---

* Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.