

*American Mineralogist*  
Vol. 57, pp. 284-287 (1972)

## A LOW-TEMPERATURE CRUSHING TECHNIQUE APPLIED TO MANGANESE NODULES

BRUCE A. BROWN,<sup>1</sup> *Department of Geology & Mineralogy,  
University of Oxford*

### ABSTRACT

Crushing ferromanganese oxides from deep-sea nodules at 77°K in a pool of liquid nitrogen resulted in improved X-ray powder photographs. This technique may reduce orientation effects in mounting, will inhibit oxidation during crushing and in subsequent storage, and may have application to other water-bearing minerals.

### INTRODUCTION

10 Å manganite ( $4\text{MnO}_2 \cdot 2\text{Mn}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) and hydrous  $\delta\text{-MnO}_2$  are authigenic oxides in deep-sea ferromanganese nodules (Buser, 1959). The former exhibits a basal structure similar to that of lithiophorite (Wadsley, 1952). Water layers are sandwiched between layers, each consisting of Mn and other cations in octahedral coordination with O and OH. Partial oxidation of initially adsorbed  $\text{Mn}^{2+}$  may result in a continuous range of oxidation grades between those of 10 Å manganite and  $\delta\text{-MnO}_2$ . Oxidation during formation of  $\delta\text{-MnO}_2$  will result in at least partial loss of water.

If the initial oxidation grade of a nodule is low, post-depositional oxidation and dehydration will, in the writer's opinion, lead to shrinkage, development of internal stresses, and to eventual brecciation. Angular fragments of nodules are frequently recovered from the sea floor (Mero, 1965).

In previous investigations the poor quality of powder photographs has been attributed mainly to the fine grain size of the oxides (Bricker, 1965; Mero, 1965). However, both loss of water and structural disorders resulting from inclusion of cations of differing size (especially larger ions such as  $\text{Ca}^{2+}$ ) will contribute to the poor quality of powder photographs.

Examination of several hundred powder photographs suggested that X-ray results might be strongly influenced by preferred orientation of platelets in mounts. In addition, damage to the structure of the oxides, especially dislocation on the basal planes, may take place during crushing. Consequently, a low temperature crushing method was de-

<sup>1</sup> Present address: P. O. Box N/4205, Nassau, Bahamas.

vised in order to obtain a random fracture across the basal structures and to retain water in the mineral.

#### METHOD

Specimens were crushed in a pool of liquid nitrogen (B.P. 77°K) in a deep-sided mortar. A pestle with a 15 cm wooden handle was found satisfactory for this operation.

Immediately after crushing, specimens were packed into a 0.3 mm diameter glass capillary and exposed to  $Fe_{K\alpha}$  radiation with a Mn filter for a period of 24 hours. A 114.6 mm diameter Debye-Scherrer powder camera and a Phillips model 1010 X-ray apparatus were used.

#### RESULTS

With ordinary crushing in air or under acetone the ferromanganese oxides smeared on the agate and lightened appreciably in color. This color change is probably caused by the intimate association of hydrous ferric oxides, mainly  $Fe(OH)_3$  of colloidal size, with the manganese oxide. On crushing with liquid nitrogen there was neither adherence to the agate nor lightening in the color of the powder.

Figure 1 shows the improvement in powder patterns for two of six nodules investigated, all of which showed similar results. The outer films are from the two nodules crushed under acetone, and the adjacent inner films are from the same oxide materials crushed at low temperature. The two patterns on the right are from a Scripps Institute of Oceanography nodule coded 2P-52 (Albatross 13, Lat. 09°57'N, Long. 137°47'W, depth 4930 m) and those on the left are from a second Pacific Ocean nodule coded 2P-36 (Lat. 16°35'S, Long. 146°24'W, depth 1900 m).

With ordinary preparation both nodules showed strong, broad lines at 2.44 Å (attributed to superposition of 004, 210, 012, 400, and other diffractions) and at 1.42 Å (020,007, and others). A line near 10 Å was barely visible and is not of sufficient intensity to show in Figure 1. Following crushing at low temperature, very strong basal diffractions are evident. The innermost, at 9.86 Å are attributed to 001 and 100 lines (which in this monoclinic (pseudoorthorhombic) oxide do not exactly coincide). Similarly, the next line at 4.86 Å is equally broad and consists of 200 as well as the basal 002 diffractions. Other lines visible in Figure 1 are 3.18 Å (003), 3.03 Å (103,301), and 2.44 Å, which may be seen on all four films. No evidence of a 7.04 Å line was found in any of these specimens. This line was found in only 5 of 35 deep-sea nodules and is attributed to a 101 plane rather than to a 7.27 Å vicinity basal structure, as found in birnessite (Jones and

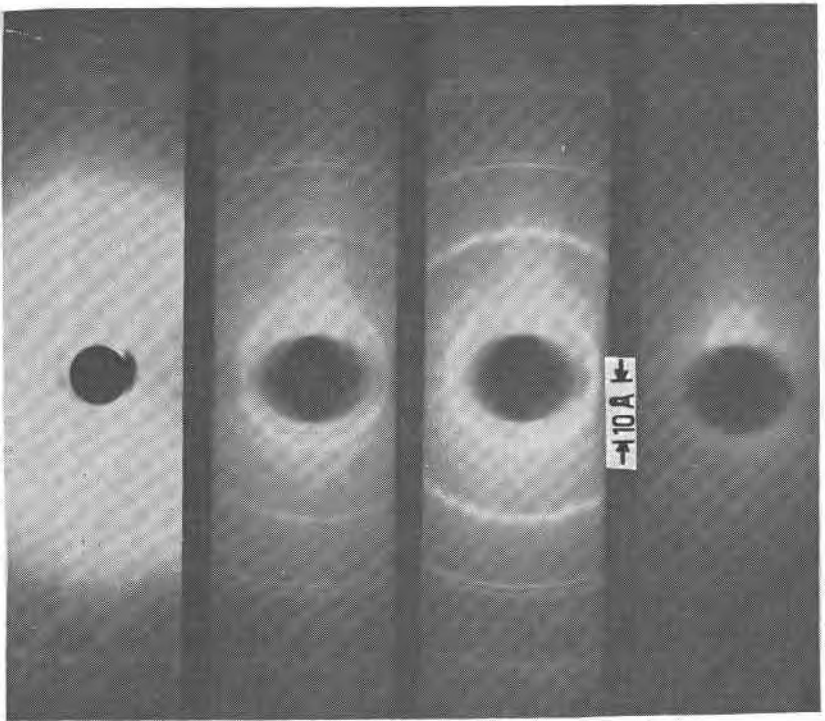


Fig. 1. X-ray powder patterns of two deep-sea nodules. Outer: oxides crushed under acetone. Inner: crushed under liquid nitrogen. Same exposure time for all patterns.

Milne, 1956). The latter could result from a partial collapse of 10 Å manganite.

#### CONCLUSIONS

The difference in quality of X-ray powder photographs obtained on identical specimens crushed under acetone and under liquid nitrogen is clear evidence of crystallographic damage incurred during crushing. This may be attributed to both dehydration and dislocations in the basal structure. Since scattering of X-rays, especially evident in the far left film, is much reduced in the low temperature crushings, ferromanganese oxides from nodules appear to be much better crystallized than has previously been suspected. Hydrrous ferric oxides, however, still exhibited no powder patterns. Positively charged colloidal ferric oxides are therefore most likely adsorbed from seawater on the electronegative nodule surface (Healy *et al.*, 1966).

Low temperature crushing should also be an effective method of

preventing specimen oxidation. In addition, some of the liquid nitrogen can be poured off with the powder. On boiling, released nitrogen gas will purge the storage container of oxygen before it is sealed.

## ACKNOWLEDGMENTS

A British Petroleum Fellowship in the Department of Geology and Mineralogy, University of Oxford, is gratefully acknowledged. Specimens were obtained from Scripps by Professor Roger G. Burns, who is also thanked for his suggestions and helpful criticisms of the manuscript.

## REFERENCES

- BRICKER, O. P. (1965) Some stability relations in the system  $Mn-O_2-H_2O$  at  $25^\circ C$  and one atmosphere total pressure. *Amer. Mineral.* 50, 1296-1354.
- BUSER, W. (1959) The nature of the iron and manganese compounds in manganese nodules. In M. Sears, ed., *Int. Oceanogr. Congr.*, Preprint, AAAS Publ., Washington, D. C., 962-963.
- HEALY, T. W., A. P. HERRING, AND D. W. FUERSTENAU (1966) The effect of crystal structure on the surface properties of a series of manganese dioxides. *J. Colloid Interface Sci.* 21, 435-444.
- JONES, L. H., AND A. A. MILNE (1956) Birnessite, a new manganese mineral from Aberdeenshire, Scotland. *Mineral. Mag.* 31, 283-288.
- MERO, J. L. (1965) *The Mineral Resources of the Sea*. Elsevier Oceanography Series Number 1. Elsevier, Amsterdam, 312 p.
- WADSLEY, A. D. (1952) The structure of lithiophorite,  $(Al, Li)MnO_2(OH)_2$ . *Acta Crystallogr.* 5, 676-680.

*American Mineralogist*  
Vol. 57, pp. 287-291 (1972)

THE STAINING MECHANISM OF POTASSIUM FELDSPAR  
AND THE ORIGIN OF HIERATITE<sup>1</sup>

CHARLES B. SCLAR, *Department of Geological Sciences,*  
*Lehigh University, Bethlehem, Pa. 18015*

AND

JOSEPH J. FAHEY, *U. S. Geological Survey,*  
*Washington, D. C. 20242*

## ABSTRACT

K-feldspar must be exposed to HF vapor or immersed in HF in order to stain it yellow with sodium cobaltinitrite. The white product from the reaction of HF vapor with K-feldspar and leucite is hieratite (cubic  $K_2SiF_6$ ) and aluminum

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.