

Intercalation of synthetic buserite by dodecylammonium chloride

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Abstract

The basal spacing of Na-buserite increases from 10Å to 25.6Å on treatment with dodecylammonium chloride. Both X-ray diffraction and high resolution electron microscopy have been used to characterize the product obtained. The intercalation reaction may be useful in the characterization of naturally-occurring manganese oxides.

Introduction

Buserite is a naturally-occurring hydrous oxide of manganese which has been identified as a constituent of deep-sea manganese nodules (Giovanoli and Bürki, 1975) and which may be the precursor of birnessite in soils and sediments. Although the relationship between buserite and other manganese oxides such as todorokite is still the subject of some controversy (Burns and Burns, 1977), diagnostic criteria for the identification of buserite by X-ray and electron diffraction have been proposed by Giovanoli *et al.* (1970). The most important of these is the presence of a 10Å reflection, representing the d_{002} spacing of the layer structure proposed for buserite. However, recent work has shown that either a 10Å or a 7Å spacing can be obtained for synthetic buserite depending on the saturating cation and the relative humidity at which the sample is examined (Tejedor-Tejedor and Paterson, 1979). Consequently, since naturally-occurring hydrous oxides of manganese are likely to contain a mixture of saturating cations, the interpretation of the somewhat diffuse diffraction patterns yielded by these poorly-crystallized materials is likely to be difficult.

In view of this, a study of the influence of saturating cations on the X-ray diffraction characteristics of synthetic buserite has been extended to include a quaternary ammonium salt, dodecylammonium chloride which is known to intercalate normally non-expanding minerals such as mica (Mackintosh *et al.*, 1971). In addition the high length to width ratio of the molecule should make the interpretation of changes in the basal spacing of the complex easier.

Experimental

Na-buserite was synthesized using the method described by Giovanoli *et al.* (1970). 250 ml of 5.2 M sodium hydroxide solution was added rapidly to 200 ml of 0.5 M manganese (II) sulphate solution in a 1000 ml measuring cylinder. Oxygen was immediately passed through the suspension of manganese (II) hydroxide at a flow rate of 2 l min⁻¹ using a fritted glass tube to produce a stream of small bubbles and thus ensure oxidizing conditions at the outset. After 5 hours the black precipitate was allowed to settle and the supernatant liquid poured off. The precipitate was then washed free of sulphate with distilled water and stored in aqueous suspension. A sample of the product was characterized in the same way as that used previously (Tejedor-Tejedor and Paterson, 1979). The Na-buserite was then immersed in 0.1 M solution of dodecylammonium chloride at room temperature for 16 hours, the suspension centrifuged, and the residue washed twice with the saturating solution. After the final wash, the supernatant liquid was poured off and the residue dispersed in sufficient deionized water to give a suspension concentration of 10 mg cm⁻³. No attempt was made to remove the excess organic salt because, in similar studies on clay minerals (Walker, 1967), the basal spacings of this type of complex have been shown to be particularly sensitive to such removal.

Both X-ray diffraction and electronoptical techniques were employed to examine the complex. For X-ray examination, 1.5 cm³ of suspension was placed on a glass slide, the bulk of the liquid allowed to evaporate, and the sample transferred quickly to a

Philips 2 kW X-ray diffractometer and examined, while still moist, using Fe-filtered $\text{CoK}\alpha$ radiation. It was allowed to dry on the diffractometer and re-examined. The sample was then removed from the slide and mixed with Spurr's resin, which was allowed to set before cutting ultra-thin sections of the buserite on an LKB ultratome. The thin sections were mounted on copper grids and examined on a Siemens 102 transmission electron microscope. The calibration of the electron microscope was checked using a sample of mica which has a well-defined, stable lattice spacing and by comparing the measured spacings with those obtained for the same sample in the diffraction mode.

Results and discussion

Na-buserite, which has a 10\AA basal spacing when moist yields a 7\AA reflection on dehydration to Nabirnessite (Giovanoli and Bürki, 1975). However, on saturation with dodecylammonium chloride, considerable lattice expansion occurs and a sharp diffraction peak at 25.6\AA with a rational series of orders was observed (Fig. 1) for both moist and dry samples, indicating that the complex has a well defined structure and periodicity along the c axis. The spacing was reproducible and variation of experimental conditions, such as the temperature of saturation did not cause any change. Extensive washing of the product did, however, tend to broaden the peaks suggesting that, as with vermiculite (Walker, 1967), excess salt stabilizes the complex.

The interaction between alkylammonium ions and phyllosilicates has been extensively studied and Walker (1967) has shown that both single-layer and double-layer complexes can occur, the ammonium groups being in contact with each surface and the alkyl chains extending into the interlayer space. In the double-layer complex these alkyl chains do not interpenetrate, but in the single-layer complex complete interpenetration occurs. Limited overlap of the alkyl chains, leading to a partial collapse of the double-layer complex, can also occur but this is frequently accompanied by a variability in the basal spacings of successive preparations. If the model developed for the vermiculite-dodecylammonium complex (Walker, 1967) is applied to buserite, then the single-layer complex would have a basal spacing of 17.9\AA and the double-layer complex 32.9\AA .

There are three possible reasons for the discrepancy between the observed value of 25.6\AA and the calculated values for the single- and double-layer complexes. The first is that the model chosen is incor-

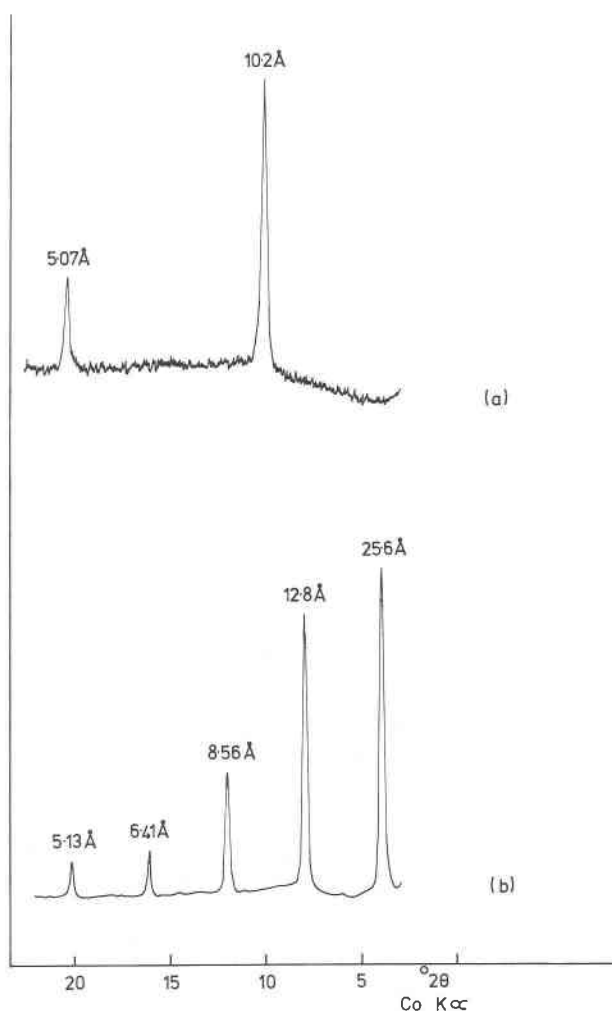


Fig. 1. X-ray diffraction pattern for an oriented aggregate of (a) moist Na-buserite and (b) moist dodecylammonium-buserite.

rect: in particular that the assumptions that (a) the alkyl chains are straight and (b) they form an angle of 55° to the surface are erroneous. As regards (b), the angle is essentially determined by the molecular geometry of the amine and even if the angle is assumed to be 90° , the single-layer spacing would only increase to 21.9\AA whereas the reduction of the double-layer spacing to 25.6\AA would entail a decrease in the angle between the alkyl chains and the basal planes to about 35° . The first assumption, however, is justified only by analogy with the clay minerals. A second possible explanation is that the double-layer complex has partially collapsed, allowing some interpenetration of alkyl chains from opposite walls of the interlayer. When this process occurs in clay minerals, considerable variation is observed in the basal spacings of the intercalated material, whereas for dodecyl-

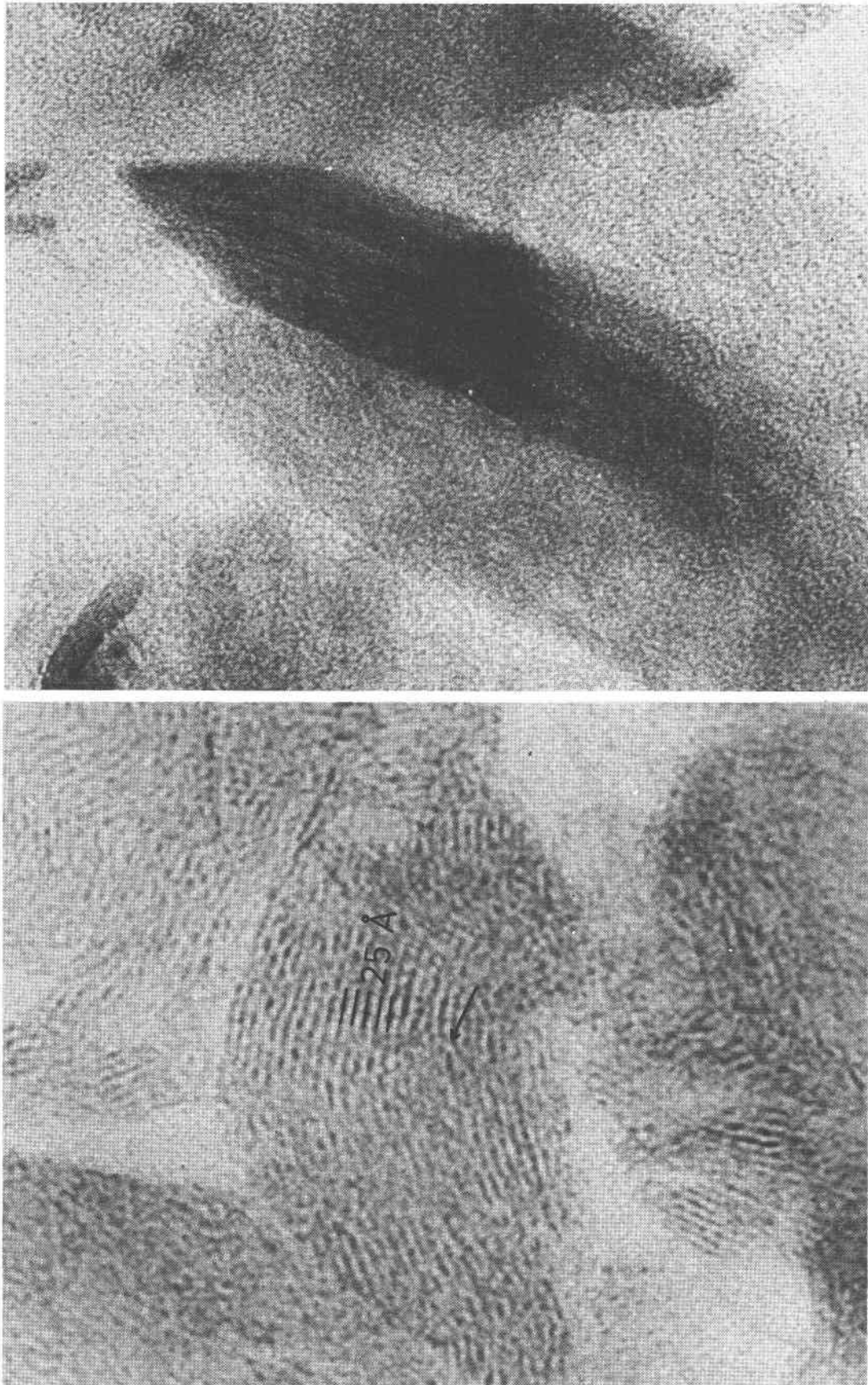


Fig. 2. Electron micrograph of a thin section of (a) dodecylammonium-buserite showing 25 Å spacing and dislocation (arrowed) and (b) Ca-buserite showing 7 Å spacing.

ammonium-buserite the value of 25.6Å remains constant despite variations in the saturating conditions. Finally, the coincidence of the experimental value of 25.6Å and the mean of the calculated values for a single-layer and double-layer complex could indicate the occurrence of a regularly interstratified single-layer/double-layer sequence. This would give rise to a repeat distance of 50.8Å along the *c* axis and a d_{002} spacing of 25.4Å, indicating that the observed spacings represent the 00*l* series where *l* is an even number.

However, examination of an ultra-thin section of dodecylammonium-buserite shows, by direct lattice imaging, a repeat distance of 25Å along the *c* axis (Fig. 2a), in agreement with the X-ray diffraction results. In order to eliminate the possibility that the expanded phase observed by direct lattice imaging represents the buserite intercalated with Spurr's resin, a sample of Ca-buserite, which has a basal spacing of 7.1Å in the dehydrated state (Tejedor-Tejedor and Paterson, 1979), was examined and the micrograph clearly showed only the presence of layer spacings of 7Å (Fig. 2b). In dodecylammonium-buserite there is no indication whatever of any interstratification of 32.9Å and 17.9Å repeat units, suggesting that the discrepancy discussed above must be due either to limited interpenetration of alkyl chains or to bending of the chains in the interlayer of buserite; this question can only be resolved by further studies. The micrograph also reveals dislocations in the structure where two layers apparently coalesce into one. This observation may explain the irreversibility of dehydration in a number of different ion-forms of buserite (Tejedor-Tejedor and Paterson, 1979).

Conclusions

Quaternary ammonium salts such as dodecylammonium chloride can enter the interlayer space of

synthetic buserite causing an expansion of the basal spacing from 10Å to *ca* 25Å. Although it is not yet possible to describe in any detail the structure of the organic complex formed, the technique of intercalation may prove to be valuable in the X-ray identification of the manganese oxide minerals and, in particular, the elucidation of the so-called "todorokite controversy"—*viz.* whether todorokite has a structure similar to that of hollandite or has a layer structure similar to buserite. In view of this a full range of alkylammonium derivatives are currently being prepared and studied in more detail.

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