THE INFLUENCE OF STRUCTURE ON BA AND K UPTAKE
BY A SYNTHETIC PHYLLOMANGANATE

E. PATERSON, R. SWAFFIELD AND L. CLARK

Division of Soils and Soil Microbiology, Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen AB9 2QJ, Scotland

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ABSTRACT: The uptake of Ba$^{2+}$ and K$^+$ by a synthetic Na-phyllomanganate has been studied by chemical analysis, X-ray diffractometry and X-ray photoelectron spectroscopy. The changes in basal spacing arising from cation exchange have been used to monitor the progress of the exchange reaction and confirm the selectivity measured by bulk chemical analysis. However, the selective uptake of Ba$^{2+}$ over Ca$^{2+}$ is much greater than that of K$^+$ over Na$^+$ and it is suggested that charge distribution in the interlayer is important. The results are discussed in the light of recent advances in our understanding of the phyllomanganate structure.

The interaction of counterions with the non-stoichiometric oxides of Mn is an important process in nature with widespread implications for both marine and terrestrial environments (Jenne, 1968). These interactions are very complex and can involve a range of mechanisms such as cation uptake on both constant- and variable-charge surfaces (for description see Davis & Kent, 1990), surface hydrolysis of sorbate ions producing hydroxy-cations (Murray et al., 1968) as well as absorption, whereby cation penetration into the manganese oxide phase occur, releasing Mn(II) into solution (Loganathan & Burau, 1973). When combined with the inherent structural complexity of the manganese oxide minerals, partly resulting from previous cation exchange reactions, the difficulties faced in providing a complete explanation of 'foreign' cation accumulations in manganese oxides may be appreciated and the requirement of synthetic model compounds justified. Unfortunately, in some cases, the model compounds have been so poorly characterized that they represent little advance on the naturally occurring forms.

Naturally occurring 'manganese oxides' may be considered as four distinct group of minerals (Giovanoli, 1985); the true oxides, such as ramsdellite and pyrolusite, the oxide/hydroxides, such as manganese, the phyllomanganese, such as birnessite and lithiophorite, and the tectomanganese, such as cryptomelane and hollandite. In the first two groups of minerals, the only essential cation in the structure is Mn whilst in the manganates other cations, as well as Mn, are essential structural constituents. A number of studies (see reviews by Chukhrov et al., 1980, Mackenzie, 1989 and Dixon et al., 1990) have shown that whereas manganates, both tecto- and phyllo-manganates, are common soil constituents, the pure oxides and oxide/hydroxides are less common. Thus, a model compound of the managanate group is the most useful to explain the behaviour of 'manganese oxides' in soils. Of the various model compounds that have been used for ion exchange studies, sodium manganese (II, III) manganate or synthetic buserite (Giovanoli et al., 1970) is the most appropriate, particularly in view of recent advances in the refinement of our understanding of its structure (Post & Veblen, 1990; Manceau et al., 1992). In addition, laboratory synthesis experiments have shown a synthetic K-phyllomanganate, prepared by cation exchange of Na-buserite, may be readily converted to cryptomelane (Chen et al., 1986) and that a similar procedure using Ba-phyllomanganate can produce psilomelane/hollandite intergrowths (Giovanoli & Balmer, 1983).

The aim of this study was to show how structural features of Na-buserite influence its cation-exchange properties and, hence, to suggest mechanisms by which selected cations may accumulate. Because of the occurrence of absorption reactions with cations of the First Transition Series, the study has been restricted to main

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group cations. X-ray diffraction (XRD) has been used to monitor the interlayer ion exchange selectivity of sodium manganate (II, III) manganate in mixed Na/K and Ca/Ba solutions. Bulk exchange selectivity has been measured by dissolution in acid oxalate solution followed by inductively coupled plasma (ICP) spectroscopy whilst surface exchange has been studied using X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Sodium manganese (II, III) manganate was synthesized by bubbling oxygen through a freshly precipitated suspension of Mn(OH)$_2$ for 6 h at high pH (Giovanoli et al., 1970). At the end of this period the black precipitate was washed with deionized water until the pH fell to around neutrality. In the latter stages of washing, 0.1 M NaCl solution, adjusted to pH 7, was used to inhibit peptization.

Homoionic forms of Na-, K-, Ca- and Ba-manganate were prepared by overnight equilibration at room temperature (20 ± 1°C) of 100 mg aliquots of Na-phyllomanganate, followed by washing three times with 50 ml aliquots of the appropriate 0.1 M chloride solution. The samples were then water-washed until the supernatants were chloride-free. After the final washing, the moist residues were stored at 5°C in a stoppered tube for further analysis. A similar procedure was carried out to equilibrate the manganate with mixed cation solutions of total molarity 0.1 M. For mixed solutions, washing was limited to 2 × 50 ml aliquots of water to minimize the likelihood of changes in composition.

Methods

X-ray diffraction was carried out on a Philips 1130/90 diffractometer using Fe-filtered Co-K$_\alpha$ radiation. The samples were prepared as oriented aggregates by sedimentation on a glass slide to enhance the basal reflections and examined moist.

Chemical analysis of the cation treated manganates was carried out by dissolution in acid ammonium oxalate (Schwertmann, 1973) and the concentration of Mn, Na, K, Ca and Ba determined using ICP spectroscopy.

X-ray photoelectron spectroscopy was carried out using a VG Escalab 2 instrument. The samples were prepared by pressing 50 mg of the manganate in a 10 mm stainless steel die in a hydraulic press using a force of 3 tonnes. The exciting radiation was Al-K$\alpha$ and, after an initial wide range scan (0–1000 eV), more detailed analyses over narrow regions were carried out using repeat scanning and signal averaging on the VGS 1000 data system.

RESULTS

The results from the bulk chemical analysis for the Na-phyllomanganate treated with mixed counter-ion solutions have been recalculated in the form of selectivity isotherms. The 'cross-over' point for the Na/K system i.e. the point at which 50% of the exchange sites are occupied by Na$^+$ and 50% by K$^+$, occurs at a K/(K + Na) mole fraction of 0.7 (K/Na = 2.33) showing that there is some preference for Na$^+$ when starting from the Na-saturated system (Fig. 1a). The plot of Na content vs. K content, with a gradient of −0.97 ± 0.02, clearly demonstrates the 1:1 stoichiometry of the reaction (Fig. 1b). The data for the reverse reaction i.e. K/Na treatment of K-phyllomanganate (Fig. 1c) give a cross-over point at a mole fraction of K/(K + Na) of 0.3 confirming the influence of the existing cation population on the exchange process. It is also clear that although the reaction retains its 1:1 stoichiometry, it is not fully reversible with ~20% of the K$^+$ retained even when pure NaCl solution is used for treatment (Fig. 1d).

The Ca/Ba exchange isotherms on Na-manganate, calculated from the bulk chemical analysis, show a marked change from the Na/K case with the cross-over point occurring at very much lower mole fractions of Ba$^{2+}$ in solution than for K (Fig. 2a). With a cross-over value of 0.03, the system demonstrates a very high selectivity for Ba$^{2+}$ over Ca$^{2+}$ although it is interesting to note that the rapid decrease in Ca content at Ba/(Ba + Ca) <0.1 is followed by a slow decline in Ca$^{2+}$ content and a slow increase in the content of Ba$^{2+}$. The plot of Ba content vs. Ca content demonstrates
the 1:1 stoichiometry of the reaction (Fig. 2b) and comparison with Fig. 1b shows that the molar ratio of monovalent to divalent cation uptake is around 2.0, consistent with the formal valencies of the counter-ions. The exchange isotherm for treatment of the Ba-saturated phyllomanganate with mixed Ba/(Ba + Ca) solutions show no cross-over point because most of the Ba is 'fixed', a result conformed by the stoichiometry plots (Fig. 2d).

As shown previously (Tejedor-Tejedor & Paterson, 1979) the moist Na- and K-phyllomanganates can be distinguished on the basis of their XRD characteristics with the Na-form giving a basal spacing of 1.0 nm and the K-form a spacing of 0.7 nm. The Ca- and Ba-forms can be similarly distinguished. X-ray diffraction of the products after treatment of the Na-form with mixed Na/K solutions shows that changes in the basal spacings occur at K/(K + Na) ratios as low as 0.2 with the appearance of a broad reflection at ~0.7 nm accompanying the much sharper main peak at 1.0 nm (Fig. 3a). As the K/(K + Na) ratio increases, the intensity of the 0.7 nm peak increases whilst that at 1.0 nm decreases until at a ratio of 0.8 the 0.7 nm peak, due to the K-form, is dominant. Because of possible differences in the intensities of the two peaks themselves, it is difficult to relate these changes quantitatively to the Na/K ratio of the mixed cation form of the phyllomanganate but it does appear that the cross-over point occurs at a lower value than that obtained from the bulk chemical composition. In addition, structural change is indicated over a much wider range of solution compositions.

In contrast to the Na/K example, there is a much closer relationship between the exchange isotherms calculated from the bulk chemical
analysis and the XRD results for the Ca/Ba phyllosilicate (Fig. 3b). The XRD trace for the Ca-saturated sample (not shown) is almost identical to that for the sample treated with a solution of mole fraction Ba/(Ba + Ca) = 0.005 but, after treatment with the 0.01 mole fraction solution, the 1.0 nm peak has broadened until at a mole fraction of 0.1 only the 0.7 nm peak of Ba-phyllosilicate can be seen. Thus, structural change appears to follow the cation selectivity isotherms fairly closely. Unlike the Na/K case, none of the samples exhibit both the 1.0 nm and 0.7 nm peaks, to the extent that, after treatment with Ba/(Ba + Ca) = 0.05, no clear peaks are seen on the XRD trace.

In contrast to the XRD results, which reflect changes in the interlayer regions of the phyllosilicate, XPS is a surface-specific spectroscopic technique and the analysis primarily reflects the surface composition on the exterior of the crystallites with smaller contributions from the interlayer regions. Although the exact depth of the analysis is difficult to define, it is known that there is an exponential decay of signal with depth (Hochella, 1988) and, by analogy with clay minerals, a total depth of analysis of 4-5 nm is a reasonable estimate, which would correspond to 4-6 interlayer regions.

For the Na/K system, the unresolved Mn 3p doublet at ca. 50 eV, the partially resolved K 3p doublet at ~295 eV and the Na KLL Auger peak at ~495 eV were located in the wide-scan X-ray photoelectron spectra of the Na- and K-manganates and narrow regions were set up for repeat scanning to obtain high quality spectra. The peak areas for the Mn, Na and K peaks in the various samples were then determined and used for comparison. Quantitative analysis is possible from XPS peak areas using the appropriate cross-sections for the electron transitions and correcting
for contaminant effects (Adams et al., 1977) but, in the present case, a more direct comparison of the various cation forms was considered more appropriate, not least because the Na peak was not an XPS peak per se but was due to an Auger transition. The results from this approach are
shown in Fig. 4a where the Na and K contents are given as a percentage of the saturation values. The cross-over point at a K/(K + Na) mole fraction of 0.7–0.8 occurs at a similar value to that observed from the bulk analysis suggesting that the selectivity on the outer surfaces is similar to that experienced in the interlayer positions.

Although the same basic procedure was used for the Ca/Ba system, an additional correction was required because of overlap of the Mn 3s peak and the Ba 4d doublet, used for peak area measurement. The selectivity plots (Fig. 4b) obtained after this procedure show much wider variation than is seen in the Na/K example, but this is partly due to the presence of salts in some samples as is evidenced by the presence of distinct Cl 2s and Cl 2p peaks in the spectrum. Despite this difficulty, the XPS results support those from the bulk analysis in that the Ca$^{2+}$ content only declines slowly above a Ba mole fraction of 0.1. Indeed, it would appear that the mean value might be higher than for the bulk analysis, suggesting surface enrichment of Ca$^{2+}$ but further work is required to substantiate this suggestion.

**DISCUSSION**

The most striking feature of the results presented is the very much higher selectivity for Ba$^{2+}$ over Ca$^{2+}$ compared to the uptake of K$^+$ over Na$^+$, yet both K$^+$ and Ba$^{2+}$ cause structural collapse and stabilize the 0.7 nm spacing (Tejedor-Tejedor & Paterson, 1979). This similarity in behaviour is largely driven by the reduction in hydration enthalpy of K$^+$ and Ba$^{2+}$ compared to Na$^+$ and Ca$^{2+}$. The basal spacing is effectively determined by the hydration of the interlayer cations and in the 1.0 nm phase the cations, Na$^+$ and Ca$^{2+}$, are surrounded by an octahedron of water molecules, whereas in the 0.7 nm phase only a single molecular layer of water is present (Tejedor-Tejedor & Paterson, 1979; Strobel et al., 1993). However, water can also play an important role in the transfer of charge between interlayer cations and charged structures (Farmer & Russell, 1972) and in order to explain the very high selectivity for Ba$^{2+}$, the structure of the interlayer region must be considered.

Giovanoli's rigorous studies (1970) of the structure of synthetic Na-buserite by conventional X-ray and electron diffraction techniques have been augmented recently by more sophisticated methods of structure refinement (Post & Veblen, 1990) and also by a wide range of spectroscopic probes from infrared spectroscopy (Potter & Rossman, 1979) to X-ray absorption fine structure (EXAFS) (Manceau et al., 1992). As a result, a clearer picture is beginning to emerge concerning the structure of the octahedral sheets and of the interlayer region (Manceau et al., 1992; Post & Veblen, 1990).

Although chalcophanite was originally taken as a model for the synthetic Na-phyllomanganate with Mn(II) ions replacing the Zn present in chalcophanite it seems likely that this model is not entirely satisfactory (Manceau et al., 1992). Instead, attention has been focused on the role played by interlayer cations particularly in relation to their influence on the periodicity of the structure along the c axis and their role in neutralizing the negative charge present on the manganate layers. Unlike clay minerals in which isomorphous substitution normally gives rise to a single negative charge at each substituent site, in...
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the phyllomanganates, whether the charge arises from structural vacancies or from substitution of Mn(II) for Mn(IV), each site will be a more concentrated source of charge. The EXAFS work, combined with selected area electron diffraction, suggests that when Na⁺ is the counterion, the interlayer cations have little impact on long-range ordering of successive phyllomanganate layers and require the operation of a delocalized charge transfer mechanism in the interlayer, where water molecules will play a crucial role—thus some selectivity for the more highly hydrated Na over K⁺ is observed. In contrast, the divalent cations Ca²⁺ and Ba²⁺ can interact directly with the source of negative charge on the manganate layers above and below the counter-ion site thus ordering the sequence of phyllomanganate layers, as observed by Manceau et al. (1992) and Post & Veblen (1990). In such a direct interaction, the larger Ba²⁺ ion will be favoured over the smaller Ca²⁺. This explanation is also consistent with the much greater irreversibility of Ba²⁺ uptake compared to that of the K⁺ ion.

The dominance of the interlayer regions in the ion exchange behaviour of the synthetic buserite is reflected in the changes observed on the XRD traces after exchange, and XPS indicates that similar selectivities are observed in the surface of the particles for monovalent cations although there may be less selectivity in the divalent case. High interlayer selectivity can explain the accumulation of Ba²⁺ by phyllomanganate to form hollandite, but the K⁺ required for the formation of cryptomelane must accumulate because of a relatively small ‘fixation’ but a much higher concentration than Ba²⁺ in the soil environment.

CONCLUSIONS

The results presented are consistent with the main features of the synthetic buserite structure by Manceau et al. (1992) and Post & Veblen (1990). They show clearly how structural features can play a crucial role in determining the cation-exchange selectivity in a synthetic phyllomanganate. The contrast between the selectivity for K⁺ and Ba²⁺ over Na⁺ and Ca²⁺, respectively, which both alter the basal spacings from 1.0 nm to 0.7 nm demonstrates the subtlety of this influence, with charge distribution in the parent manganate playing an important role. Future work will concentrate on the selective uptake of transition metal cations on this constant charge surface and in comparing main group and transition metal cation uptake on variable charge surfaces that may be present on other manganates.

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