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Communications

A New Iron Oxyhydroxide Phase: The Molybdate-Substituted Analogue of Akaganéite

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The iron oxyhydroxide phase akaganéite (β -FeOOH) has a structure in which four double chains of $\text{FeO}_3(\text{OH})_3$ octahedra form a 0.5 nm \times 0.5 nm tunnel running along [010]. The tunnel is partly occupied by chloride anions, which substitute for hydroxide and are believed to play an important role in stabilizing the structure. In fact, the presence of a halide ion is often said to be essential for the formation and stabilization of the akaganéite structure.¹⁻³ The akaganéite structure can be represented by the formula $(\text{FeO}(\text{OH})_{1-x}\text{Cl}_x)$.¹

The acid hydrolysis of condensed iron(III) hydroxide gels has been extensively studied as a means of preparing uniform colloidal hematite particles,^{1,4} and in chloride media, this reaction is known to follow a pathway involving initial precipitation of the poorly crystalline

phase ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), phase transformation to akaganéite, and finally dissolution and reprecipitation as hematite. In investigating the effect of additives on this reaction, we have found that the presence of only a small amount of molybdate anion (added as Na_2MoO_4) stabilizes the intermediate akaganéite phase and completely inhibits the transformation to hematite. Furthermore, molybdate is incorporated into the akaganéite structure, forming an akaganéite analogue that is considerably more stable than the chloride form.

Having observed that molybdate can be incorporated into the akaganéite structure, the question arises as to whether the molybdenum is substituting for iron(III) within the lattice, or occupying the tunnel sites in place of the chloride ion. To test whether the molybdate ion was indeed occupying the tunnel sites, we carried out the acid hydrolysis reaction using Fe(III) nitrate in place of the chloride salt. (The material was synthesized as follows: In a 50-mL screw-cap flask, 25 mL of 2.0 mol L^{-1} iron(III) nitrate solution was added to 30 mL of a 4.0 mol L^{-1} solution in NaOH and 0.6 mol L^{-1} in Na_2MoO_4 and the resulting suspension mixed thoroughly by vigorous shaking of the flask. The pH was adjusted to 2.0 with a little HNO_3 , and the suspension was aged at 98 °C for 7 days in a laboratory oven. The solid product was collected by repeated centrifugation/resuspension cycles in water and ethanol and then dried in air at 60 °C. Molybdenum and iron contents of the sample were determined by I.C.P.O.E.S. analysis and found to be Mo: 17.7 wt %, Fe: 41.2 wt %.) We found that the molybdate anion promoted the formation of a stable akaganéite phase even in the absence of a halide ion, suggesting that molybdate is able to template the β -FeOOH structure in the same way as the halides are said to do.

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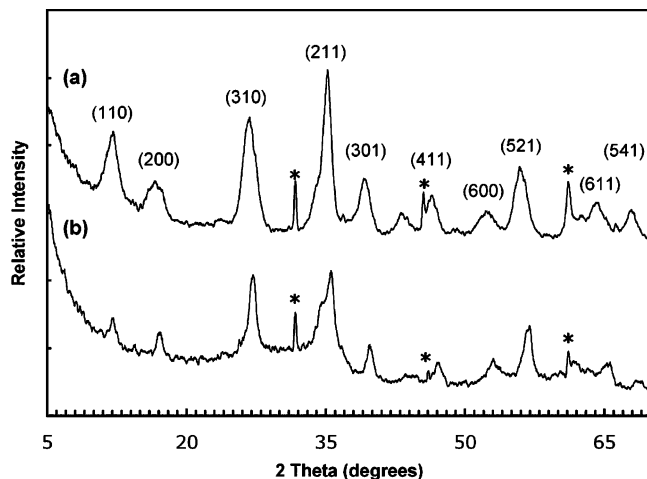


Figure 1. Powder XRD patterns of (a) akaganéite synthesized according to the method given in ref 6 and (b) molybdate-akaganéite synthesized from Fe(III) nitrate solution in the presence of 25 mol % Mo. Asterisks denote peaks due to the internal standard (NaCl). X-ray diffraction was carried out at 298 K using Cu K α radiation (40 kV, 30 mA) on a Siemens D500 diffractometer. The samples, containing added NaCl (~10 wt %) as an internal standard, were step scanned from 3° to 70° 2 θ , at 0.02° increments, using a counting time of 5 s per increment.

The sample prepared from iron(III) nitrate solution, with an added molybdate concentration of 25 mol % with respect to Fe(III), gave an XRD pattern comprising 10 broad reflections as shown in Figure 1. The pattern for a sample of akaganéite prepared from iron(III) chloride solution as described by Cornell and Schwertmann⁵ is also shown for comparison. The XRD pattern of the molybdate-substituted material indicates that the hollandite-like structure of akaganéite is retained, but most reflections have been shifted relative to the chloride form. Intensities are also modified; for example, the relative intensities of the (211) and (310) peaks are of similar magnitude in the molybdate-substituted sample. Unit cell refinement from the powder pattern of the chloride akaganéite sample provides results that are in good agreement with the monoclinic (*I*2/m) cell dimensions obtained by Post and Buchwald,⁶ with $a = 1.0568(6)$ nm, $b = 1.0135(6)$ nm, $c = 0.3028(4)$ nm, and $\beta = 89.88(3)^\circ$. The spectrum of the molybdate-substituted akaganéite, however, was found to fit well to a tetragonal symmetry with $a = 1.0382(8)$ nm and $c = 0.3021(3)$ nm.

If the molybdate anion is occupying tunnel sites within the akaganéite structure, then the contraction of the unit cell associated with molybdate incorporation is surprising given that the molybdate anion is considerably larger than chloride. Anions that have previously been found to exchange with chloride in the tunnel sites of akaganéite include fluoride, bromide,² and nitrate,⁷ while both iodide and perchlorate ions appear to be too large to be accommodated.⁸ Predicted ionic volumes⁹ for the relevant ions are listed in Table 1, and it can be seen that the molybdate anion is indeed larger than

Table 1. Ion Volumes of Halides, Group IVB Oxyanions and Others, from Ref 9

anion	volume (nm ³)	anion	volume (nm ³)
F ⁻	0.025	MoO ₄ ²⁻	0.088
Cl ⁻	0.047	WO ₄ ²⁻	0.088
Br ⁻	0.056	NO ₃ ⁻	0.064
I ⁻	0.072	ClO ₄ ⁻	0.082
CrO ₄ ²⁻	0.097		

iodide or perchlorate. Nonetheless, a similar unit cell contraction ($a = 1.046$ nm and $c = 0.302$ nm) has been reported for a naturally occurring akaganéite mineral incorporating tungstate at a level of 17.7 wt %.¹⁰ Our attempts to prepare tungstate and chromate analogues of akaganéite, by applying the same synthetic method as for molybdate, have been unsuccessful. Condensed iron(III) hydroxide gels containing 25 mol % tungstate or chromate showed evidence of only partial transformation to hematite after 7 days at 98 °C, and the samples appeared to contain predominantly 2-line ferrihydrite. This shows that chromate and tungstate, and/or their polyanions, in common with molybdate, adsorb strongly to the ferrihydrite phase and inhibit transformation to hematite, but they do not share the tendency to form an akaganéite analogue. It should be noted that, at the concentrations we have studied, the heptamolybdate Mo₇O₂₄⁶⁻ is expected to be in equilibrium with MoO₄²⁻ and/or its protonated forms at pH 2 or below.¹¹

The decrease in unit cell dimensions, coupled with the large size of the molybdate ion relative to the akaganéite tunnels, would seem to suggest that the anion incorporation might involve formation of Mo–O–Fe bonds within the akaganéite structure (i.e., between Mo and the FeO₆ octahedra making up the sides of the akaganéite tunnels, rather than a simple anion inclusion of the kind proposed for chloride). This kind of structural incorporation has been postulated for the sulfate ion in schwertmannite, but in that case, the basic akaganéite structure is distorted to the extent that the powder XRD pattern of schwertmannite is very different from that of akaganéite,¹² and the characteristic low-angle (110) and (210) reflections normally seen in the akaganéite XRD pattern are absent. This was also the case in the XRD spectrum of the reported nitrate analogue,^{6,10} indicating that this compound may also have the distorted hollandite structure that has been proposed for schwertmannite.

The Raman spectrum of akaganéite has four peaks at about 314, 400, 550, and 720 cm⁻¹,¹³ the strongest being those at 314 and 400 cm⁻¹, due to Fe–O vibration modes of the two distinct octahedral Fe sites in the akaganéite structure.^{6,13} In contrast, the laser Raman spectrum of the molybdate-substituted akaganéite displayed peaks that were greatly broadened in comparison to the chloride form, and in place of the strong bands at 400 and 314 cm⁻¹, we observed two broader bands

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at 380 and 190 cm^{-1} . In addition, the spectrum contained two peaks at 930 and 860 cm^{-1} that were not observed in the spectrum of the chloride form akaganéite, and we attribute these to vibrations of the incorporated molybdate species. Unfortunately the Raman spectra do not allow us to draw a definitive conclusion on whether the incorporated species is a molybdate or heptamolybdate anion,¹⁴ but the frequencies of the observed bands are certainly consistent with a molybdate anion bound to an oxide through 2 or 3 bridging Mo–O–Fe bonds. The band at 930 cm^{-1} can be attributed to the symmetric stretching mode, ν_1 , of the Mo–O bonds in the molybdate tetrahedron, as reported by Boucherit et al.¹⁵ for an Fe–Mo oxide corrosion product. The band at 860 cm^{-1} may be due to several modes, including the Fe–O–Mo vibrations,¹⁴ and provides further evidence that the MoO_4^{2-} species is covalently bound to the iron oxide lattice.

The XRD patterns of akaganéite samples containing only surface-adsorbed molybdate anion were readily distinguished from that of the molybdate-substituted akaganéite shown in Figure 1. Samples of chloride-form akaganéite exposed to 1.0 mol L^{-1} sodium molybdate solutions for 5 h at both room temperature and 98 °C were found to adsorb 13 and 19 mol % molybdenum, respectively, but their XRD patterns remained identical to the original (chloride) akaganéite. The Raman spectra of these samples displayed the two characteristic akaganéite bands at 400 and 314 cm^{-1} , but also contained the 930 and 190 cm^{-1} bands seen in the molybdate–akaganéite phase. Thus, the broad band at 190 cm^{-1} may also be attributed to Fe–O–Mo bridging modes. These results suggest that the molybdate ion does not exchange with chloride in preformed akaganéite, although it is readily incorporated into the structure when

coprecipitated with the oxyhydroxide phase—an observation providing further support for the idea that the incorporated MoO_4 is covalently bonded within the iron oxyhydroxide lattice.

The molybdate-form akaganéite, prepared from iron(III) nitrate solution in the presence of 25 mol % molybdenum, was found to contain Mo: 17.7 wt % and Fe: 41.2 wt %, which is in reasonable agreement with values expected for the formula $(\text{FeO})_4(\text{OH})_4(\text{HMoO}_4)$ (expect Mo: 18.58 wt %, Fe: 43.26 wt %). The XRD pattern of this sample (Figure 1b) appears to have broad, low-intensity reflections underlying the peaks of the akaganéite-like phase, suggesting that the sample probably contains some 2-line ferrihydrite, so a more accurate determination of the elemental composition of the akaganéite phase is problematic, and our proposed formula must be regarded as an estimation at this stage.

In conclusion, we have shown that the molybdate anion can stabilize the β -FeOOH structure in the absence of a halide ion. This leads us to believe that the molybdate anion may be occupying the tunnel sites usually occupied by chloride anions. The evidence from XRD and Raman spectroscopy indicates that the molybdate species is covalently bound to the iron oxyhydroxide lattice through bridging Mo–O–Fe bonds, but the exact structural nature of molybdate incorporation has not yet been determined. Our ongoing research into the structure of this material may provide a better understanding of the structure of the related schwertmannite phase and offers the possibility of discovering new mixed iron oxide hydroxides with the potential to display interesting properties and applications.

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