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Structural mechanism of Co^{2+} oxidation by the phyllomanganate buserite

ALAIN MANCEAU,[1,*] VICTOR A. DRITS,[2] EWEN SILVESTER,[1,†]
CÉLINE BARTOLI,[1] AND BRUNO LANSON[1]

[1]Environmental Geochemistry Group, LGIT-IRIGM, University of Grenoble and CNRS, 38041 Grenoble Cedex 9, France
[2]Geological Institute of the Russian Academy of Sciences, 7 Pyzhevsky street, 109017 Moscow, Russia

ABSTRACT

The geochemistry of Co at the Earth's surface is closely associated with that of manganese oxides. This geochemical association results from the oxidation of highly soluble Co^{2+} to weakly soluble Co^{3+} species, coupled with the reduction of Mn^{4+} or Mn^{3+} ions, initially present in the manganese oxide sorbent, to soluble Mn^{2+}. The structural mechanism of this Co immobilization-manganese oxide dissolution reaction was investigated at the buserite surface. Co-sorbed samples were prepared at different surface coverages by equilibrating a Na-exchanged buserite suspension in the presence of aqueous Co^{2+} at pH 4. The structure of Co-sorbed birnessite obtained by drying buserite samples was determined by X-ray diffraction (XRD) and powder and polarized EXAFS spectroscopy. For each sample we determined the proportion of interlayer cations and layer vacancy sites, the $Co^{2+}/(Co^{2+} + Co^{3+})$ ratio, the nature of Co sorption crystallographic sites, and the proportion of interlayer vs. layer Co. From this in-depth structural characterization two distinct oxidation mechanisms were identified that occur concurrently with the transformation of low pH monoclinic buserite to hexagonal H-rich birnessite (Drits et al. 1997; Silvester et al. 1997). The first mechanism is associated with the fast disproportionation of layer Mn^{3+} according to $2Mn^{3+}_{layer} \rightarrow Mn^{4+}_{layer} + \square_{layer} + Mn^{2+}_{solution}$, where $\square$ denotes a vacant site. Divalent Co sorbs above or below a vacant site ($\square_1$) and is then oxidized by the nearest Mn^{3+}_{layer}. The resulting Co^{3+} species fills the $\square_1$ position while the reduced Mn migrates to the interlayer or into solution creating a new vacant site ($\square_2$). This reaction can be written: $Co^{2+}_{solution} + \square_1 + Mn^{3+}_{layer} \rightarrow Co^{2+}_{interlayer} + \square_1 + Mn^{3+}_{layer} \rightarrow Co^{3+}_{interlayer} + \square_1 + Mn^{2+}_{layer} \rightarrow Co^{3+}_{layer} + \square_2 + Mn^{2+}_{sol/inter}$. This mechanism may replicate along a Mn^{3+}-rich row, and, because the density of vacancies remains constant, it can result in relatively high Co concentrations, as well as domains rich in Co^{3+}_{layer}-Mn^{4+}_{layer}. During the low-pH buserite transformation, about one-half of the layer Mn^{3+} that does not disproportionate migrates from the layer to the interlayer space creating new vacancies, with the displaced Mn^{3+} residing above or below these vacancies. The second oxidation mechanism involves the replacement of $Mn^{3+}_{interlayer}$ by $Co^{3+}_{interlayer}$; the latter may eventually migrate into layer vacancies depending on the chemical composition of octahedra surrounding the vacancy. The criterion for the migration of Co^{3+} into layer vacancies is the need to avoid Mn^{3+}_{layer}-Co^{3+}_{layer}-Mn^{3+}_{layer} sequences. The suite of chemical reactions for this second mechanism can be schematically written: $Co^{2+}_{solution} + Mn^{3+}_{interlayer} + \square \rightarrow Mn^{2+}_{solution} + Co^{3+}_{interlayer} + \square \rightarrow Mn^{2+}_{solution} + Co^{3+}_{layer}$, the last step being conditional. In contrast to the first mechanism, this second mechanism decreases the density of vacant sites. At high surface coverage, Co-sorbed birnessite contains a substantial amount of unoxidized $Co^{2+}_{interlayer}$ species despite some non-reduced Mn^{3+} in the sorbent. This result can be explained by the sorption of $Co^{2+}_{solution}$ onto vacant sites located in Co^{3+}_{layer}- and Mn^{4+}_{layer}-rich domains devoid of Mn^{3+}. The number and size of these domains increase with the extent of oxidation and the total Co concentration in the solution, and this accounts for the decreasing capacity of buserite to oxidize Co. The weight of structural evidence indicates that Co is oxidized by Mn^{3+} rather than Mn^{4+}. Thermodynamic considerations indicate that under the solution pH conditions employed in this study Mn^{3+} is the more likely electron sink for the oxidation of Co^{2+}. This study also shows that the high affinity of Co for man-

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[*] Alain.Manceau@obs.ujf-grenoble.fr
[†] Present address: CSIRO, Division of Minerals, Box 312, Clayton South Victoria, Australia, 3169.

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ganese oxides is not only due to its oxidation to weakly soluble Co^{3+} species, but also because of the reducted layer strains from the substitution of Co^{3+} for Mn^{3+}.

Results obtained for these model compounds were compared with those for natural Co-containing asbolane and lithiophorite (Manceau et al. 1987). This comparison indicates that the different structural mechanisms explored in the laboratory can satisfactorily account for the observations made on natural samples. Specifically, the present study proves that Co substitutes for Mn in natural phyllomanganates and allows us to eliminate the possibility of precipitation of discrete CoOOH particles.