Transformation of hexagonal birnessite upon reaction with thallium(I): Effects of birnessite crystallinity, pH, and thallium concentration.

Mismel Ruiz-Garcia §, Mario Villalobos §,*, Andreas Voegelin□, Teresa Pi-Puig‡, Nadia Martínez-Villegas†, and Jörg Göttlicher Δ

§ Molecular Environmental Geochemistry Laboratory, Laboratorio Nacional de Geoquímica y Mineralogía (LANGEM), Institute of Geology, Universidad Nacional Autónoma de México (UNAM), Mexico City, 04510, México.

□ Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, CH-8600 Dübendorf, Switzerland

‡XRD Laboratory, Institute of Geology, National Autonomous University of Mexico 04510, Mexico City, Mexico.

† Applied Geosciences Division, Instituto Potosino de Investigación en Ciencia y Tecnología (IPICyT) 78216, San Luis Potosí, México.

Δ Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation, KIT Campus North, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
**KEYWORDS:** manganese oxide, sorption, thalliomelane, tectomanganate, phyllomanganate, 2x2 tunneled Mn oxide, hollandite group, cryptomelane.

**Abstract art**

**ABSTRACT:** We examined the uptake of Tl(I) by two hexagonal birnessites and related phase transformations in laboratory experiments over twelve sequential additions of 0.01 molar Tl(I)/Mn at pH 4.0, 6.0 and 8.0. The Tl-reacted Mn oxides were characterized for their structure, Tl binding, and morphology using X-ray diffraction, X-ray photoelectron and X-ray absorption spectroscopies, and transmission electron microscopy. Very limited Tl oxidation was observed, in contrast to previous work where equal Tl(I)/Mn were added in a single step. Instead, both birnessites transformed into a 2x2 tunneled phase with dehydrated Tl(I) in its tunnels at pH 4, but only partially at pH 6, and at pH 8.0 they remained layered. The first four to nine sequential Tl(I)/Mn additions resulted in lower residual dissolved Tl⁺ concentrations than when the same amounts of Tl(I)/Mn were added in single steps. This study thus shows that the repeated reaction of hexagonal birnessites with smaller Tl(I)/Mn at ambient temperature triggers a complete phase conversion with Tl(I) as the sole reacting cation. The novel pathway found may be more
relevant for contaminated environments, and may help explain the formation of minerals like thalliomelane \([\text{TI}^{+}(\text{Mn}^{4+}_{4.75}\text{Cu}^{2+}_{0.5})\text{O}_{16}]\); it also points to the possibility that other reducing species may trigger similar Mn oxide transformation reactions.

1. Introduction.

Thallium is usually found in very low concentrations in the environment, mainly as the more stable and mobile\(^1\) Tl(I) species as compared to Tl(III). Regarding Tl retention in natural environments, its principal mineral associations are with sulfur\(^2–3\), aluminosilicates\(^4\) and manganese oxides\(^5–6\). Mine-metallurgical wastes are one of the main sources of Tl contamination of surface and groundwater\(^7\), and soils\(^8\). Tl is highly toxic to the biota, and its maximum permissible levels are generally among the lowest of the regulated inorganic pollutants\(^9\).

Natural manganese oxides originate from poorly crystalline (disordered) hexagonal birnessites, which have layered structures and are widely distributed minerals\(^10\) of biological origin. These birnessites have been broadly studied for their high reactivity towards cations, mainly as sorbents but also as oxidizing agents for redox-sensitive species\(^11–13\). Usually, in these studies, synthetic analogs of biogenic oxides have been used\(^5,6,10,14–17\).

One of the most utilized birnessites in laboratory studies is \(\delta\)-MnO\(_2\), a synthetic analog of vernadite\(^10\). The nano-sized particles of \(\delta\)-MnO\(_2\) are formed by two or three c-disordered layers of manganese octahedra\(^5\), evidenced by the (near-)absence of 001 and 002 reflections in their x-rays diffraction (XRD) patterns\(^18\). Another synthetic analog is acid birnessite\(^19\), with up to six disordered layers of manganese octahedra per crystal\(^18\). In these minerals the octahedral MnO\(_2\) layers are kept together by cations in the interlayer region that compensate for the negative charge\(^20\) arising from Mn vacant sites\(^10\). Another source of negative layer charge is when Mn(IV) ions are replaced by Mn(III) because the oxygen valences in the
Mn(III) octahedra are not fully satisfied; this is, for example the only source of layer charge in phases like triclinic birnessite (TBi), which contains no vacancies but considerable contents of Mn(III), arranged in orderly rows\(^{21}\). Therefore, it sorbs Tl(I) as outer-sphere complexes at the interlayers, and thus, it does not oxidize it\(^6\).

In contrast, the mechanism with hexagonal birnessites involves a combination of a sorption/oxidation process through inner-sphere complex formation above/below vacant sites\(^{16}\) that in a previous study showed to be independent of the amount of vacancies, the type of birnessite and the initial size of the particles, but highly dependent on pH\(^5\). To investigate this mechanism, single Tl(I) additions were made to equilibrate with the birnessites over a range in Tl(I)/Mn molar ratios from 0.01 to 0.45. The sorption/oxidation process begins with the binding of Tl(I) at the vacant sites of the octahedral layers and then its transfer of electrons to adjacent layer Mn(IV) species, to form Mn(II) and Tl(III) (equation 1).

\[
\text{MnO}_2(s) + 4H^+ + Tl^+ \rightarrow Mn^{2+} + Tl^{3+} + 2H_2O
\]  

(1)

The Tl(III) species remains bound to the vacancy as a triple-corner sharing (TCS) inner-sphere complex in tetrahedral\(^{16}\) or octahedral\(^6\) configuration [some Tl(III) may bind to the particle edges as a double edge-sharing (DES) complex\(^5\)]. Mn(II) can stay bound in the interlayer as well or be released (at least partly) to the solution depending on the pH\(^5\). According to this mechanism every Tl(I) sorption/oxidation, can produce a new vacancy and consequently the possibility of a new Tl(I) to be sorbed and oxidized, in a hypothetically endless cycle. However, Tl(I) oxidation eventually stops due to a more complex mechanism where a bound Mn(II) atom freshly formed may comproportionate with a layer Mn(IV) atom of the birnessite to form two Mn(III) atoms. This may limit the extent of this redox process because vacancies may no longer be available, although further Tl(I) added may still become sorbed to a large degree, to counterbalance the remaining -2 charge [= -4(vacancy)+2(two Tl(I)sorbed)], although most probably as outer-sphere complexes\(^6\).
According to the isotherms previously reported\textsuperscript{5}, as added Tl(I) increased above 0.02 Tl(I)/Mn, increasing fractions of the added Tl remained in solution after equilibration (5 days). Under these conditions, apparently an electrostatic barrier is created that repels most further Tl(I) cations from being sorbed, because when this aqueous Tl(I) was washed out, and fresh Tl(I) in the same proportion was added again, this new Tl(I) did get quantitatively sorbed/oxidized, suggesting a sorption mechanism highly dependent on the mode of Tl(I) additions. Nevertheless, more complex mechanisms may occur by this washing procedure, involving Mn(II) and Tl(I); for example, it was also found that at low pH values, stoichiometric concentrations of Mn(II) to the Tl sorbed/oxidized were released to the aqueous phase\textsuperscript{5}, suggesting that comproportionation processes may be limited or disproportionation favored under these conditions. Additionally, Wick et al. (2019)\textsuperscript{6} studied Tl(I) sorption on a variety of manganese oxides, and found that oxidative Tl uptake dominated sorbed Tl on $\delta$-MnO$_2$ up to Tl loadings of $\sim$0.02 Tl/Mn, that the fraction of non-oxidatively sorbed Tl increased with loading, and that only 40\% or less of the total sorbed Tl(I) was oxidized to Tl(III) at the highest Tl/Mn loadings of 0.127 and 0.182. In our previous work,\textsuperscript{5} the contribution of Tl(I) to the total Tl sorption may have been overlooked because of overabsorption problems with the collected spectra, since the Tl(III) EXAFS signal is highly predominant as compared to the Tl(I) signal\textsuperscript{6}.

When comparing Tl uptake by different Mn oxides, results obtained by recent studies\textsuperscript{1,2,6} demonstrated that layered structures showed higher sorption capacities than tunneled structures for Tl(I) and Tl(III). Also, although birnessite has shown high Tl(I) sorption/oxidation capacity\textsuperscript{5,6}, if Tl(I) is present in high concentrations (Tl(I)/Mn $>$0.12) while birnessite is being synthesized precipitation of avicennite (Tl$_2$O$_3$) inhibits birnessite formation\textsuperscript{22}.

In the present work, we expanded on the previous work\textsuperscript{5} by changing the mode of Tl(I) additions to lower, more environmentally relevant Tl(I)/Mn ratios equilibrated sequentially with the same reacting
birnessites at the same pH values. Our objectives were to confirm and determine the conditions for this increase in total sorbed Tl quantities on Mn(IV) birnessites when added in small sequential Tl(I)/Mn ratios, and to determine the mechanistic and structural reasons for this increase in Tl uptake. In this manner we sought to further the knowledge on both Tl environmental geochemistry and birnessite reduction pathways and transformations under environmental conditions.


2.1 Manganese oxides preparations.

Two different birnessites were synthesized and characterized for this and the previous work\textsuperscript{5}, which are the closest analogs to natural biogenic Mn oxides\textsuperscript{10,18}: $\delta$-MnO$_2$ and acid birnessite. $\delta$-MnO$_2$ was obtained by the redox reaction between Mn(II) and Mn(VII) \textsuperscript{9}. For this synthesis, a solution of MnCl$_2$ was slowly added over a strongly basic solution of KMnO$_4$ at room temperature. Acid birnessite was obtained by the reduction of a Mn(VII) (KMnO$_4$) solution with boiling HCl\textsuperscript{10}. The detailed synthesis reaction equations and procedures, including their washings to neutralize pH can be found in the literature\textsuperscript{10}. Both birnessites were equilibrated and washed several times with NaNO$_3$ solutions to have Na$^+$ as the predominant counterbalancing cation, and were confirmed to be poorly crystalline hexagonal birnessites by XRD, and their average Mn oxidation state to be 4\textsuperscript{5}. They are both quite stable solids in the pH range investigated (4-8)\textsuperscript{10}.

2.2 Batch experiments.

The detailed description is given in the Supporting Information (Section S1). Briefly, Tl(I) was equilibrated with the two birnessites at three different pH values (4, 6 and 8) by frequent manual adjustments using appropriate concentrations of NaOH and HCl, but unlike the previous work\textsuperscript{5}, Tl(I) was added in much smaller quantities relative to the solid (ca. 0.01 Tl/Mn), and sequentially, but waiting for
equilibration (5 days) after each fresh addition and before adding the next one. These values were achieved
by adding 50.96 µmoles Tl(I) to 0.5 g birnessite. Twelve additions were made in total for each birnessite
at each pH value, with an equilibration period each time of 5 days\(^5\) (with orbital shaking at 200 rpm). In
each step, the liquid phase was separated by ultracentrifugation at 11,000 g (Thermo Scientific SORVALL
ST 40) and by filtration through a nitrocellulose membrane (Millipore, pore size=0.05 µm). The leftover
solid paste in the tube was rinsed three times with ultrapure water and centrifuged and decanted after each
rinse. The solid paste was then freeze-dried (a procedure that has been tested to not change the mineralogy
of the original birnessites) and used for the next Tl(I) aliquot equilibration, repeating the above process
for every Tl(I) addition (60 days in total). All batch experiments were performed in triplicate. Tl(I)
concentrations were quantified in the filtrates by anodic striping voltamperometry (ASV) [detection limit
(D.L.) = 0.5 mg/L = 2.4 µmol/L], and the sorbed concentrations calculated by subtraction from the initial
concentration added.

2.3 Characterization techniques for solids.

The final mineral phases after twelve consecutive Tl(I) additions for both original minerals at three
different pH values (4, 6 and 8) and for δ-MnO\(_2\) at pH 4 after 5, 6, 7 and 8 Tl(I) additions were investigated
by XRD. For XRD experiments an EMPYREAN diffractometer equipped with a fine focus Cu tube, and
K\(_b\) filter, was used.

Specific surface area (SSA) and XAS measurements were performed on the samples after twelve Tl(I)
additions. X-Ray photoelectron spectroscopy (XPS) analyses were made on samples of δ-MnO\(_2\) at pH 4
after four, six, eight, and twelve additions of Tl(I). The results from XPS are shown in the SI. Final samples
after twelve Tl(I) additions were analyzed by Mn K-edge and Tl L\(_{III}\)-edge EXAFS spectroscopy at the
Karlsruhe Research Accelerator (KARA) at the Karlsruhe Institute of Technology (KIT, Germany). The
samples were pressed into 13-mm pellets and were analyzed at the SUL-X beamline. Spectra were
collected at room temperature in transmission mode, using a Si(111) double crystal monochromator for energy selection, and ionization chambers to record the incident and transmitted X-ray intensity. The reference spectra used for Mn were all Mn(IV)/Mn(III)-containing structures used from a previous work⁶:

For data extraction, normalization, contribution analysis by linear combination fits (LCF) and the characterization of the local coordination of Mn and Tl, the Demeter software package was used²³. Details about the reference spectra used for LCF, are provided in the SI section 8.1. In summary, the standards used for Mn K-edge XAS were: cryptomelane⁶, triclinic birnessite (TBi), δ-MnO₂, and “c-disordered” hexagonal birnessite (HBi) (the latter three were provided by courtesy of Sam Webb). For Tl L₃-edge XAS the standards were⁶: hydrated Tl(I) sorbed on TBi interlayers, dehydrated Tl(I) sorbed on cryptomelane inside the tunnel structure, and Tl(III) sorbed on δ-MnO₂ vacancies.

3. Results and discussion.

3.1 Batch sorption experiments.

The Tl(I) sorption behavior on the two birnessites at different pH values is shown in Figure 1 and compared with the results from the previous work at higher single Tl(I)/Mn additions.

**Figure 1.** Batch experiments of Tl sorption/oxidation (symbols) in (A) acid birnessite and (B) δ-MnO₂ at three different pH values (4, 6 and 8). Each birnessite sample was reacted twelve times in sequence.
with 0.01 Tl(I)/Mn. Lines are data from Cruz-Hernandez et al. (2019) where the birnessites were reacted with single Tl(I) additions. Insets show the same data for aqueous Tl(I) concentration up to 10 mg/L to clarify differences at the lowest dissolved Tl concentrations.

Two major macroscopic sorption differences may be observed when adding small sequential Tl(I)/Mn ratios as compared to adding larger ratios at a time, as was done in our previous work to the same two birnessites: (1) The net sorbed Tl concentrations are considerably higher and the sorption isotherms are steeper, i.e., show higher affinities, in the former case before Tl(I) is detected in aqueous solution in significant concentrations (the same ASV detection method was used in both studies). These depend on the particular birnessite and pH: for acid birnessite at pH 4, this maximum value is ca. 0.09 Tl/Mn, while at higher pH values it is between 0.11 and 0.13 Tl/Mn. For δ-MnO₂ these maxima are ca. at 0.05, 0.07, and 0.11 for pH values of 4, 6 and 8, respectively. These values contrast greatly with a common value of 0.02 Tl/Mn for both birnessites at all pH values, when added in larger single Tl/Mn ratios (see Fig. 1 insets for more clarity). (2) In the present study an increase in sorption affinity/capacity is suggested (and evident at pH 4) for acid birnessite as compared to δ-MnO₂, in contrast with the mode of single larger Tl(I)/Mn additions from the previous work, where no difference in the extent and mode of Tl sorption was observed between the two birnessites. As previously observed, sorption increased with pH, which could be explained by an increase in the net negative charge of the birnessites as pH increases.

Finally, the sorption isotherms in the small sequential Tl(I)/Mn additions mode appear to readily flatten out and are surpassed by the larger Tl(I)/Mn additions mode systems (see Fig. 1 insets for more clarity). This is especially evident in the case of δ-MnO₂ but is also suggested by the slope trends in the acid birnessite systems. This behavior is similar when comparing the present data with previous work and work summarized therein. Surprisingly, in the present work, negligible Mn²⁺ was released to the aqueous phase at pH 4 as compared to the previous work, where stoichiometric amounts of Mn²⁺ to the Tl(I) taken
up were released to solution. Also, no Mn$^{2+}$ was detected in solution at pH 6 (see SI – section 3, Figure S2), as was previously detected$^5$. The solid concentrations used were ca. 1,000 times higher than in the previous work$^5$, and in principle we cannot exclude some contributing effects arising from this increase, although Tl(I) concentrations added were scaled up accordingly and acid consumption was higher to achieve the same pH.

The behavior shown in Fig. 1 points to a significantly different Tl(I) sorption mechanism occurring and Mn oxide phases forming under each mode of Tl additions (including the net reaction time). These differences can only be explained by employing microscopic and molecular techniques, to understand the mechanisms involved in each case.

3.2 XRD of Tl(I)-reacted δ-MnO$_2$ at pH 4.

Possible transformations of δ-MnO$_2$ as it sorbed Tl(I) were monitored by XRD. δ-MnO$_2$ at pH 4 was initially selected since it is the sample to begin showing leftover Tl(I) in solution at lower Tl(I) additions as compared to all other conditions (cf. Fig. 1). The diffractograms of δ-MnO$_2$ at pH 4 from two to twelve additions of Tl(I) are shown in Figure 2.
The XRD patterns reveal that starting from the seventh to eighth additions of Tl(I) a new crystallographic phase begins to form. Although already some changes may be observed since the fifth...
Tl(I) addition in the region between 20 to 30 $2\theta$ in the form of a wide band, which increases in amplitude and widens as the number of additions increase. After seven additions, several small peaks appear, and at twelve additions the number and amplitude of the peaks increase considerably. The new phase formed was identified as a structural analog of the hollandite group of minerals \([\text{Ba}(\text{Mn}^{4+}\text{Mn}^{2+})\text{O}_{16}]\), which is a 2x2 tectomanganate formed by arrays of tunnels made from Mn(IV and III) octahedra, inside of which di- or mono-valent cations counterbalance the negative charge that occurs from the presence of Mn(III).

Some common analogs of hollandite are coronadite \([\text{Pb}(\text{Mn}^{4+}\text{Mn}^{2+})\text{O}_{16}]\), cryptomelane \([\text{K}(\text{Mn}^{4+}\text{Mn}^{3+})\text{O}_{16}]\), manjiroite \([\text{Na}(\text{Mn}^{4+}\text{Mn}^{3+})\text{O}_{16}]\)^24 and silver-hollandite \([\text{Ag}(\text{Mn}^{4+}\text{Mn}^{3+})\text{O}_{16}]\)^25. In these structures the position of the cation inside the tunnel is highly dependent on its ionic radius, where it is centered for large cations, such as Ba\(^{2+}\) and K\(^{+}\), or is shifted along the length of the tunnel for smaller cations such as Na\(^{+}\) and Pb\(^{2+}\). Three different Rietveld refinements were made: 1) using the structure of hollandite (replacing barium with thallium); 2) using the cryptomelane structure (replacing potassium with thallium); and 3) using both modified structures simultaneously. The best fit values (goodness of fit) were obtained for the third refinement using the hollandite and the cryptomelane structures at the same time (not shown). Within this mineral group, a relatively recent addition is thalliomelane \([\text{Tl}^{+}(\text{Mn}^{4+}\text{Cu}^{2+})\text{O}_{16}]\)^27, which contains Cu(II) in the place of Mn(III). The more intense lines in our tectomanganate structure XRD pattern closely match with the ones reported for thalliomelane\(^{27}\). The mineral formed in the present work when only Tl(I) is made to react with birnessite is a thalliomelane-like structure but where Mn(III), and probably a fraction of Tl(III), are the cations that produce the charge imbalance in the structure, and Tl(I) is most probably the balancing counterion, especially under saturation conditions (δ-MnO\(_2\) at pH 4 – cf. Fig. 1B).

3.3 XRD patterns for all samples after twelve Tl(I) additions.
The effect of pH and type of birnessite for the above transformation can be seen in the XRD patterns shown in Figure 3.

![XRD patterns](image)

**Figure 3.** XRD patterns of (A) acid birnessite and (B) δ-MnO₂ at zero and after twelve additions of 0.01Tl(I)/Mn at three different pH values (4, 6 and 8).

It is evident that protons play a key role in the transformation of both birnessites by Tl(I). For acid birnessite the basal plane layer-stacking bands at 7.33Å and 3.66Å decrease considerably at all pH values and disappear at pH 4. At pH 6 two small peaks emerge in the region between 4.92 and 3.08 Å. This layer stacking decrease at pH 4 arises from the phase change to a tunneled structure, but at pH 8, where no tectomanganate formed, it is not very clear and may be related to high concentrations of Mn(III) cations at the interlayers (from the comproportionation processes) that may destabilize the layer cohesion. For δ-MnO₂ even at pH 8 a broad band appears in the region 4.92 to 3.08 Å, and the thalliomelane-like phase was identified at pH 6, with an increase in crystallinity at pH 4. Additionally, we analyzed a blank sample of δ-MnO₂ at pH 4 to which an amount of Tl(I) was added equivalent to the sum of the twelve additions [0.12 Tl(I)/Mn] in one single addition leaving it to stir for 60 days in an orbital shaker at 200rpm (Figure 3B upper diffractogram). No phase transformation was observed by XRD, which helps reinforce the fact that the mechanism for conversion to the thalliomelane-like phase requires the small sequential Tl(I)/Mn equilibrations. These blanks were also performed at pH 6 and pH 8 (cf, Fig. S3). Although these
blanks were not subjected to the washing-centrifuging-decanting-freeze-drying cycle as the sequential
additions samples, since no Tl\(^+\) and nearly no Mn\(^{2+}\) were released during these washings (cf. Figs. S1 and
S2), we believe no experimental artifact was introduced during these cycles that would have induced the
phase transformation observed. There remains the question whether freeze-drying may have contributed
to this phase transformation; however, since high temperatures and pressures are usually the necessary
conditions to catalyze layered to tunneled structure transformations in manganese oxides\(^{18,21}\), and during
freeze drying the opposite conditions are applied, i.e., low temperatures and pressures, we do not think
this particular step was involved in the transformation observed. Also, no evidence was found that this
drying process promoted dehydration of Tl(I) and inner-sphere complex formation since at pH 8 (and
partly at pH 6), Tl(I) was bound as outer-sphere complexes at the interlayers of the reacting birnessites
(cf. section 3.4 on Tl EXAFS).

3.4 TEM images after twelve additions of 0.01 Tl(I)/Mn.

High-resolution TEM images of selected samples are shown in Figure 4. For samples at low and medium
pH a mixture of tectomanganate and phyllomanganate phases was observed (Figure S5 and S6). Figure
4A illustrates the highly crystalline thalliomelane-like mineral formed at low pH from \(\delta\)-MnO\(_2\), where the
well-defined lattice fringes of 0.313 nm correspond to the (310) planes detected by XRD (Figure 3B). 4B shows less clear crystallographic planes of the tectomanganate for acid birnessite at pH 6, and
at pH 8 (Figure 4C) it showed no change from the original layered structure. Other details and TEM
images are shown in the SI section 3.

3.5 Tl L\(_{III}\)-Edge EXAFS.

The Tl L\(_{III}\)-edge EXAFS spectra in k-space of three standards [0.021 T(III)/Mn in \(\delta\)-MnO\(_2\), T(I) in
cryptomelane and T(I) in TBi] and our six samples after twelve 0.01 Tl(I)/Mn additions are shown in
Figure 5A.
The k-space spectra of the birnessite samples after twelve Tl(I) additions (Figure 5A) as compared to the reference spectra confirms that most Tl in our samples is Tl(I). This is also supported by the XANES spectra shown in Figure S12, where the higher $E_0$ value for Tl(III) and the absence of the pre-edge shoulder in our samples suggest the predominance of Tl(I)$^6$. This agrees with the XPS Tl results where Tl(III) represents less than 10% of the total Tl present after twelve Tl(I) additions (cf. Fig. S7B and D).
Figure 5. Tl LIII-edge EXAFS spectra of (A) six samples after twelve 0.01 Tl(I)/Mn additions and three standards in k-space; (B) real and imaginary parts of experimental (full lines) and shell by shell fits (broken lines) of the corresponding FT of Tl-reacted δ-MnO₂ at pH 4.0, and (C) linear combination fits (LCF) results for all sample spectra shown in panel (A).

The k-space spectra of Tl(I)-reacted δ-MnO₂ at pH 4 and pH 6 and acid birnessite at pH 4 closely match the Tl(I)-reacted cryptomelane spectrum, where Tl(I) enters the tunnels in a dehydrated form replacing K⁺.6

The spectra of the remaining samples (acid birnessite at pH 6 and 8 and δ-MnO₂ at pH 8) closely resemble the spectrum of Tl(I) sorbed on TBi, where Tl(I) remains hydrated (as an outer-sphere complex)¹⁶. The results of the LCF of the normalized spectra are provided in Figure 5C. They confirm the
above qualitative observations, but they show that all samples contain variable proportions of dehydrated Tl(I) (in tunnels of cryptomelane-type Mn oxide) and hydrated Tl(I) (outer-sphere sorbed onto TBi), except those at pH 8 where only hydrated Tl(I) was observed. In contrast, at pH 4 most of both spectra are described by the Tl(I)-reacted cryptomelane. Tl(III) in δ-MnO₂ did not contribute to the LCF, confirming that after twelve Tl(I) additions, most of the total Tl sorbed was Tl(I), not Tl(III), in agreement with the XPS results (cf. Fig. S8D). This result is surprisingly low given the ratio of 1/8 Mn(III)/Mn₉Ot,initial in the cryptomelane/manjiroite-like phase, which in principle had been expected as a result of Tl(I) oxidation.

Tl L₃-edge EXAFS spectra of Tl-reacted TBi, acid birnessite at pH 6 and 8 and δ-MnO₂ at pH 8 (Figure 5A) show very low amplitudes, yielding poor quality data to determine the first coordination shell of Tl⁶,¹⁶. This is because Tl(I) in these conditions is expected as an outer-sphere complex at the interlayers of the birnessite structures, and the Tl-O bonds are weak and their distances are widely distributed¹⁶,²⁸. This is not the case for Tl-reacted δ-MnO₂ at pH 4 and pH 6 and acid birnessite at pH 4, which were modeled by shell-fitting. In agreement with a previous study of Tl(I) sorption onto cryptomelane, the parameters of the first Tl-O and Tl-Mn paths were calculated⁶. Tl-O distances modeled ranged from 2.63 to 2.79 Å, and Tl-Mn distances ranged from 3.60 to 3.68 Å (Table S3). Further information on these fits can be found in the supplementary information section S8.5. The fitted spectrum of δ-MnO₂ at pH 4 are shown in Figure 4B. Interatomic distances (R) and Debye Waller factors (σ²) were scaled according to fitted first shell distances based on crystallographic values, whereas numbers of near neighbor atoms (N) were fixed to crystallographic values for all shells; and amplitude was derived from fitting of the Tl₂O₃ spectrum.

3.6 Structural transformations from phyllomanganates to tectomanganates.
The formation of tunneled Mn oxide structures has been found to require birnessite-type layered structures as precursors. The importance of Mn(III) in triggering this conversion has been recognized early on; therefore, for birnessites with high average Mn oxidation states, Mn reduction is a required step to achieve this transformation, which has been mostly studied with Mn(II) as the reducing agent. Other important parameters that dictate the feasibility of the conversion process and the type of resulting tectomanganate are the temperature and pressure conditions, the relative Mn(II) concentration added, pH, and the type of major cation present to occupy the inside of the tunnels.

Application of hydrothermal-like conditions, i.e., high temperatures and pressures shorten the required times for the conversions to tectomanganates to hours, especially to todorokite (a 3x3 tunneled structure), which is the most common tunneled Mn oxide structure in nature. Neutral to alkaline conditions, higher temperatures and weakly binding cations on the birnessite precursor, such as Ca$^{2+}$ and Mg$^{2+}$ were found to favor the conversion to todorokite, and Na$^+$ to manjiroite (a 2x2 structure).

At ambient temperatures but longer reaction times, birnessites may transform to tunneled structures when made to react with Mn(II), but the products obtained vary widely and sensibly with the pH and the exposed Mn(II) concentration, or with their initial Mn(III) content. For example, Mn(III)-containing δ-MnO$_2$ was found to transform to cryptomelane (a 2x2 structure) at room temperature at low pH (3 and 4) after 10 years, but when a Mn(IV)-birnessite was made to react with a very high amount of Mn(II) [33 molar Mn(II)/Mn$_{tot}$] it transformed to the 2x2 manjiroite after two months. At lower Mn(II)/Mn$_{tot}$ (=0.137) a 4x4 tectomanganate formed beginning at 1 h and completely crystalizing after 25 days at circumneutral pH values. Na$^+$ and K$^+$ yield 3x3 todorokite and 2x2 cryptomelane, respectively at ambient temperatures. At intermediate Mn(II)/Mn$_{tot}$ additions (between 0.4 and 3 molar), the conversion was to Mn(III) oxyhydroxides and oxides, such as the tunneled manganite. Hexagonal birnessites are quite stable in water suspensions, but it has been reported in the past that a dialyzed suspension of an all
Mn(IV)-δ-MnO₂, originally synthesized under acidic conditions in NaCl, converted to manjiroite after less than nine months, whereas the same suspension equilibrated in 0.01 mol/L NaCl and kept either at pH 3.6 or at pH 8.1, remained structurally stable. And if a stronger reductant such as Fe(II) is added, the more complex structure of nsutite is obtained, containing a mixture of Mn(IV) oxide and a Mn(II) hydroxide. Also, very low pH values for the same Mn(II) reductant concentration may result in the formation of different structures such as nsutite and ramsdellite (an orthorhombic MnO₂), at pH 2.4.

Recently, it has been found that a crucial parameter for the size of the resulting tunneled manganate is the kinetics of the redox process, where the faster it is, the smaller the resulting tunnels. The authors found that under most natural conditions, the kinetics of redox cycling favor the formation of larger tunneled structures (such as 3x3 todorokite) in contrast to 2x2 tunnel structures, which require faster redox cycles.

The energy required to dehydrate the cation that occupies the centers of the tunnels also contributes to the net kinetics of the tunnel structure formation. Small cations, with large hydration shells, and thus large hydration energies, such as Na(I) (ΔGhydration=−365 kJ/mol) form 4x4 tunnels, while larger cations with lower hydration energies, such as K⁺ (ΔGhydration=−295 kJ/mol) and Tl(I) (ΔGhydration=−300 kJ/mol), form 2x2 tunnels. Previous studies show that Tl⁺ can exchange with K⁺ and enter into the cryptomelane tunnels. Under the high energy provided by hydrothermal conditions small tunnels (2x2) may be promoted through dehydration of Na⁺ to form the manjiroite mineral. However, the stronger the binding of the metal cation to the layered structure (as is the case for transition divalent metals), the lower the driving force to transform to a tunneled phase.
3.7. Tl sorption to hexagonal birnessite and sorbent transformation over repeated small Tl(I) additions. Environmental implications.

The suite of techniques utilized on Tl(I)-reacted poorly crystalline hexagonal birnessites in this work allows to set forth the plausible mechanisms that occur when Tl(I)/Mn is added in small sequential proportions and left to equilibrate for total longer times: Initial Tl(I) sorbed becomes oxidized to Tl(III), which remains bound above/below vacant sites, producing in turn reduced Mn, which ultimately becomes Mn(III) on the solids. However, this initial Mn(III) production, triggered by Tl(I) oxidation, continues on without further participation of this Tl(I) oxidation process, since EXAFS and XPS showed less than 10% of the total Tl(I) sorbed after the 12th addition was Tl(III). This amount corresponds at pH 4 to a Tl(III)/Mn of less than 0.1*0.085=0.0085 for δ-MnO₂, and of less than 0.1*0.13=0.013 for acid birnessite. These amounts are far lower than those required of oxidized Tl(I) to achieve the Mn(III) content in the final crytomelane-type [K, Na(Mn⁷⁺,Mn³⁺)O₁₆] (thalliomelane-like) structure, with a 1/8=0.125 Mn(III)/Mn₉ content, which would be produced by more than half of that of the Tl(III) produced, i.e., 0.0625 Tl/Mn, or by more than 5-7 times the Tl(III) that was actually detected.

One possible explanation for the larger amounts of Mn(III) that must form for the required tunneled structure is that water acts as the reducing agent, i.e., the nanoparticulate birnessite is able to oxidize water to produce O₂. No other reducing agent can be identified in the experimental systems to explain the Mn(III) contained in the tectomanganate formed. Tl(I) is a very stable species under oxic environments⁷,⁴³,⁴⁴ but is oxidized, at least partly, by MnO₂ nanoparticles. Therefore, it is inferred that the latter must have a higher oxidation potential than oxygen, and thus water must have a higher reduction potential than Tl(I) to reduce MnO₂, but may need an activation energy for the spontaneous process to occur, which probably is triggered by the initial Tl(I) oxidation to Tl(III). Water oxidation by Mn oxides is a topic of research and may be accomplished for example by applying high temperatures to Ca-bearing...
birnessites$^{32}$, or by intercalating Cu(II) ions in their structure$^{33}$. The conditions in those investigations may provide the activation energy required.

All additional Tl(I) sorbed would do it through a non-oxidative dehydration mechanism to occupy the inside of the tectomanganate tunnels. Three key parameters promote this transformation to the tunneled thalliomelane-like phase:

1. Small particle size and fewer layer vacancies. $\delta$-MnO$_2$, with a higher specific surface area (Table S1), lower vacancy contents (6% vs. 12%), and lower number of layers (2-3 vs. 6)$^{18}$ has a higher potential for transformation than acid birnessite. The interlayer region in acid birnessite is able to sorb more Tl(I) before it undergoes transformation from the layered to the tunneled structure.

2. The H$^+$ concentration promotes the phase transformation. Both birnessites showed their largest transformations at pH 4, and partially at pH 6, while no transformations at pH 8. This could be explained from the net stoichiometric redox reaction between MnO$_2$ and water: $2$ MnO$_2(s)$ + $2$ H$_2$O = $2$ Mn$^{2+}$ + O$_2(g)$ + $4$ OH$^-$, which is clearly favored at lower pH values. However, the fact that Mn$^{2+}$ was negligibly released into solution at pH 4, in contrast to what was previously found$^5$, and as would be expected from previous reduction work of birnessites with fulvic acids at low pH$^{45}$, suggests that the required Mn(III) for the conversion to the tectomanganate may have formed directly in the reduction reaction of the birnessites with water, and that it was stabilized, i.e., it did not disproportionate to Mn(IV) and Mn(II) at this low pH, precisely by the tunneled structure.

3. The initial small Tl(I) concentrations trigger the beginning of Mn(IV) reduction, and the additional Tl(I) promotes occupation of the tunneled structure through their dehydration, combined with equilibration times of several weeks. When sufficient Mn(III) has been produced to allow the folding of the original layers along Mn(III) edges, according to the mechanism previously proposed to form the tunnels$^{19}$, these will further sorb additional Tl(I) in a dehydrated form at their centers.
Tl(I) alone therefore shows the two net effects on birnessites that promote conversion to the tectomanganate: It triggers an initial Mn(IV) reduction ultimately to Mn(III) [through its oxidation to Tl(III)], which continues reducing without further Tl(I) participation; and a dehydration capacity to occupy the inside of the tunnels of the tectomanganate that is forming.

However, the mechanism depends strongly on the mode of Tl(I) additions, and only happens when these are made in small stepwise relative Tl(I)/Mn quantities. When added in larger Tl(I)/Mn additions at a time the oxidative Tl(I) uptake predominates and probably forms higher Mn(II/III) concentrations that prevent the birnessite transformation to the tectomanganate\(^5,6\). The accurate thalliomelane-like stepwise formation mechanism requires further research, specially to confirm the participation of water as the Mn(IV) reducing agent. In previous studies with Tl\(^+\), no tunneled manganate was produced probably because one or more of the above conditions were not met.

At pH values above 4, incomplete (pH 6) or no transformation (pH 8) to the tectomanganate occurs, and the partially reduced layered birnessite shows a higher Tl(I) sorption affinity and capacity with increasing pH, the mechanism of which also requires further investigation.

The mechanism found in this work is probably more relevant to real environmental scenarios, because aqueous Tl(I) is found in small concentrations, even in contaminated environments. This investigation points to a plausible and important natural transformation pathway of birnessites at ambient temperatures when entering in contact with aqueous Tl(I) and without addition of Mn(II), where the sole geochemical properties of the former cation provide both driving forces required for the conversion of a fully oxidized phyllomanganate to a partially reduced tectomanganate. This novel pathway may help explain the occurrence of minerals like thalliomelane \([\text{Tl(Mn}^{4+}_{7.5}\text{Cu}^{2+}_{0.5})\text{O}_{16}]\) since Cu(II) ions usually accompany trace metal-rich areas, and open new lines of research into the effects of other reducing agents in small concentrations towards conversion of birnessites to tunneled structures in the environment; and in this
manner provide ideas for designs of new remediation strategies for highly toxic pollutants found in extremely low concentrations.

ASSOCIATED CONTENT

Supporting Information:

Detailed description of the batch solution preparation, Tl(I) and Mn(II) concentrations in washing solutions, XRD patterns of blanks, Specific surface area results and discussion, TEM images of samples of $\delta$-MnO$_2$ at pH 4 after 4-7 additions of Tl(I) and $\delta$-MnO$_2$ and acid birnessite at pH 4, 6 and 8 after 12 additions of Tl(I), Tl and Mn XPS analysis of spectra, details on XAS data collection and extraction; complete set of XANES spectra and LCF fits; EXAFS spectra of references and selected samples and details of shell fits of spectra.

AUTHOR INFORMATION

Corresponding Author

* Laboratory of Molecular Environmental Geochemistry, Laboratorio Nacional de Geoquímica y Mineralogía (LANGE). Institute of Geology, Universidad Nacional Autónoma de México (UNAM), Mexico City, 04510, Mexico.

e-mail address: mariov@geologia.unam.mx (M. Villalobos).

Author Contributions

This manuscript was written by Mismel Ruiz-Garcia and Mario Villalobos, with input from the other authors. Mismel Ruiz-Garcia and Mario Villalobos designed the study and Mismel Ruiz-Garcia performed the laboratory experiments. Andreas Voegelin and Jörg Göttlicher collected XAS data and
commented on the manuscript; Andreas Voegelin additionally discussed the results extensively with the first two authors. Teresa Pi-Puig contributed with XRD determinations, pattern matching, refinements, and discussions of the results obtained. Nadia Martínez-Villegas contributed with the voltamperometric determinations. All authors have given approval to the final version of the manuscript.

**Funding Sources**

This work was supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT), and the projects: UNAM PAPIIT IG100215, and UC-MEXUS-CONACYT CN 15-44.

**Notes**

**Acknowledgments:**

M. R.-G. is thankful to the Consejo Nacional de Ciencia y Tecnología (CONACYT), Mexico City, for the PhD. grant provided. The authors are grateful for the support of CONACyT to the Laboratorio Nacional de Geoquímica y Mineralogía (LANGEM). M. R.-G. is thankful to Ulises Loredo Jasso for his help in performing the last experiment during the pandemic. A.V. and J.G. are thankful to Sam Webb for providing most of the Mn EXAFS reference spectra. The authors thank Silvan Wick for support with XAS sample preparation and analysis as well as Fernando Garrido for support with measurements and fruitful discussions. Finally, the authors are grateful for the comments of six anonymous reviewers, who helped improved considerably the manuscript.
References


Bożena Gołębiowska; Pieczka, A.; Zubko, M.; Voegelin, A.; Göttlicher, J.; Rzepa, G. Thalliometane, TlMn\(_4^+\)\(_{7.5}\)Cu\(_2^+\)\(_{0.5}\)O\(_{16}\), a New Member of Coronadite Group from Zalas, Southern Poland. *Am. Mineral.* **2021**, 1–32.


