

Supporting information of Dehydration Mechanism of Na and K birnessites: A Comprehensive Multitechnique Study

E. André,^{1,*} D. Cornu,^{1,*} L. Pérez Ramirez,^{2,3} P. Durand,⁴ J.-J. Gallet,^{2,3} F. Bournel,^{2,3} F. Rochet,^{2,3} C. Ruby,¹ C. Carteret,¹ R. Coustel^{1,*}

1 - Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France

2 - Sorbonne Université, CNRS (UMR 7614), Laboratoire de Chimie Physique Matière et Rayonnement, 75252 Paris Cedex 05, France

3 - Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France

4 - Université de Lorraine, CNRS, CRM2, F-54000 Nancy, France

Vibrational spectroscopies and DFT

DRIFT spectra were collected with a Thermo Nicolet 8700 spectrometer, equipped with a KBr beamsplitter, an MCT detector and using an environmental cell with a Harrick Praying Mantis, with a 4 cm⁻¹ resolution. Measurements were performed on pure Na-bir and K-bir powders in ambient condition (air at RT) as well as under vacuum (down to 10⁻⁵ mbar) at temperature up to 200°C. Each spectrum is the average of 40 scans. Measurements were also performed at RT under a humid atmosphere (1 bar). Humid atmosphere with controlled RH was generated using an in-house dynamic system mixing a dry and a wet N₂ flow controlled using a mass flow meter. Using such a setup, an RH up to 100% can be generated with an uncertainty of 0.3–0.5%.

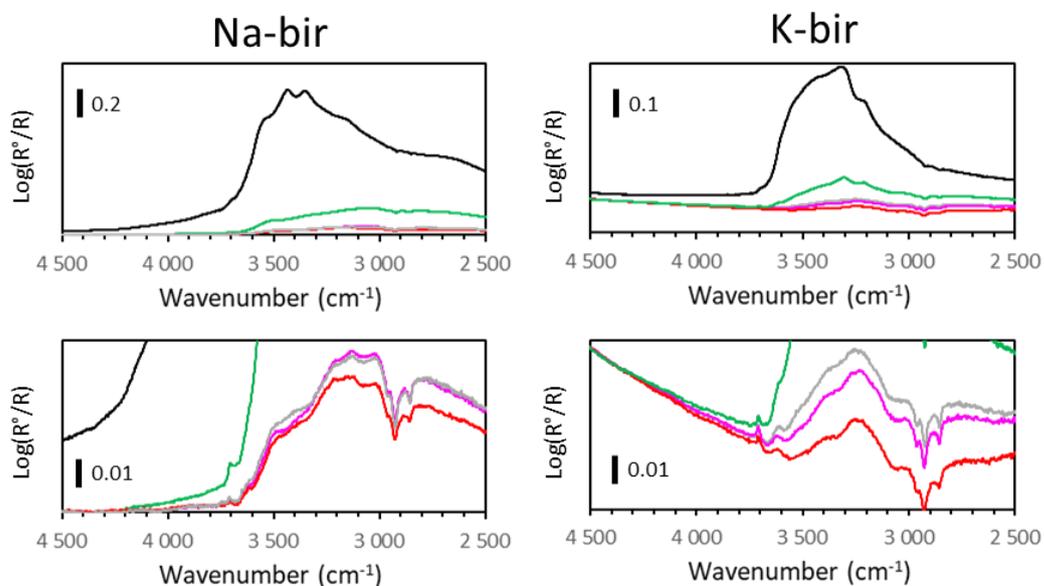


Figure S1: DRIFT spectra of Na-bir (left) and K-bir (right) under air (black) and 10⁻⁵ mbar (grey) at RT (spectra recorded during vacuuming are shown (green)). Pink and red: spectra recorded under 10⁻⁵ mbar at 100°C and 200°C, respectively. Signal in the 2800–3000 cm⁻¹ range mainly arises from improperly compensated carbonaceous compounds.

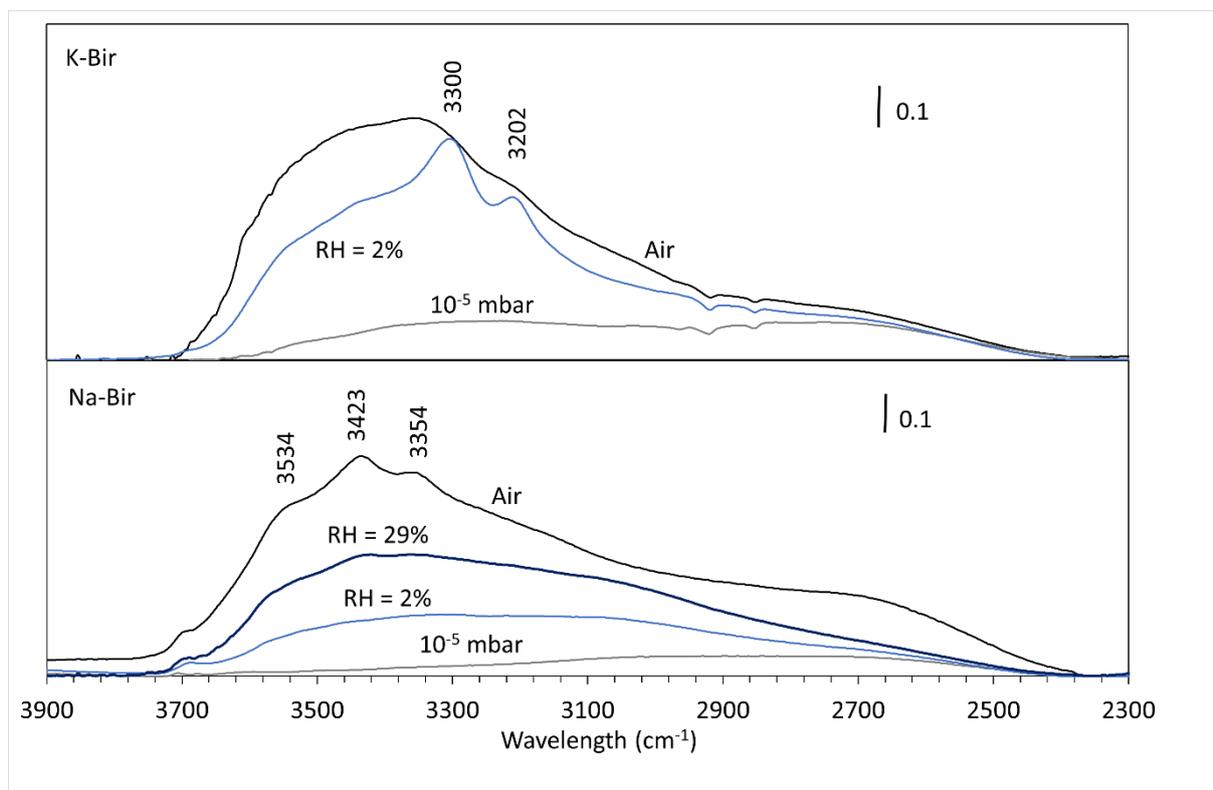


Figure S2: DRIFT spectra of Na-bir (bottom) and K-bir (top) under air (black), 10^{-5} mbar (red), 2% (light blue), and 29% (dark blue) RH in N_2 at RT.

Raman spectroscopy

Raman spectra were recorded on a Renishaw inVia Qontor microspectrometer equipped with a confocal microscope and an Olympus X50 objective (N.A = 0.55). A 532 nm exciting radiation was used with a laser power below 0.05 mW for all samples to prevent their degradation. The spot area was a few μm^2 . Several locations were probed on each sample. The spectral resolution was about 4 cm^{-1} and the precision on the wavenumber was lower than 1 cm^{-1} .

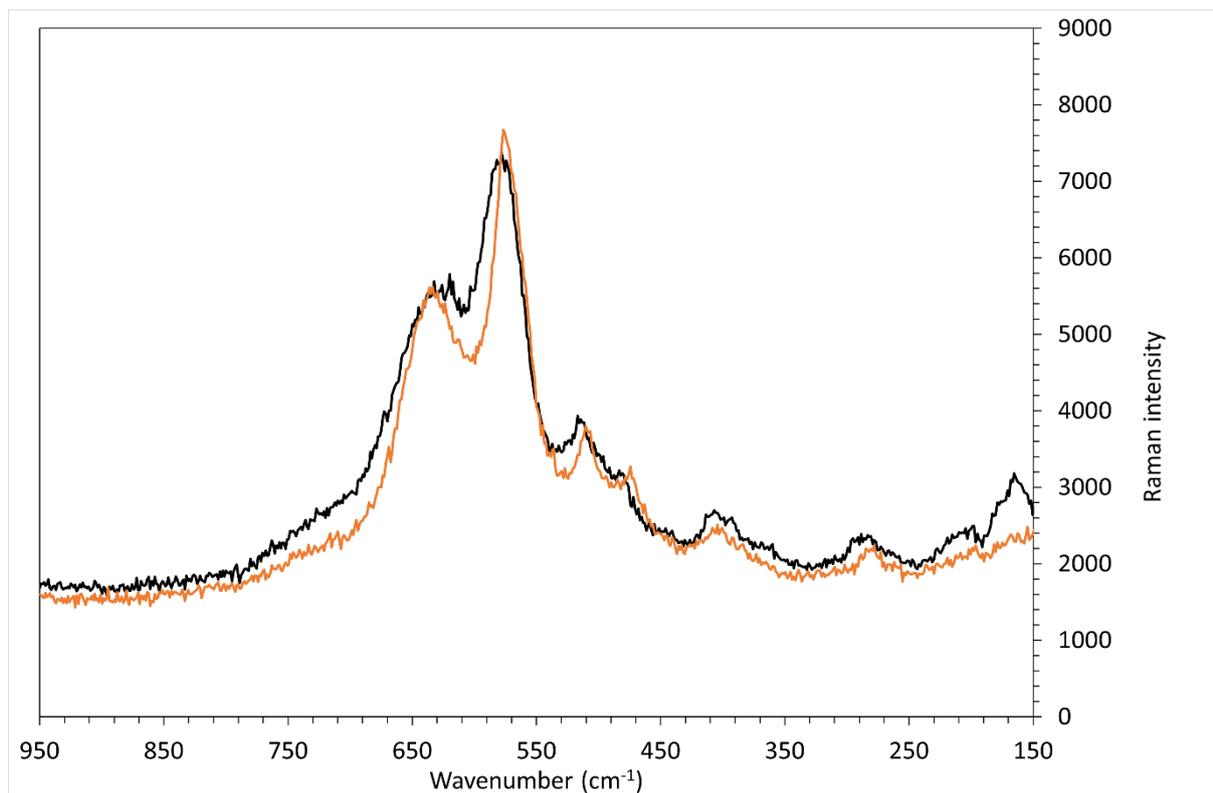


Figure S3: Raman spectra of Na-bir (black) and K-bir (orange) under air at RT.

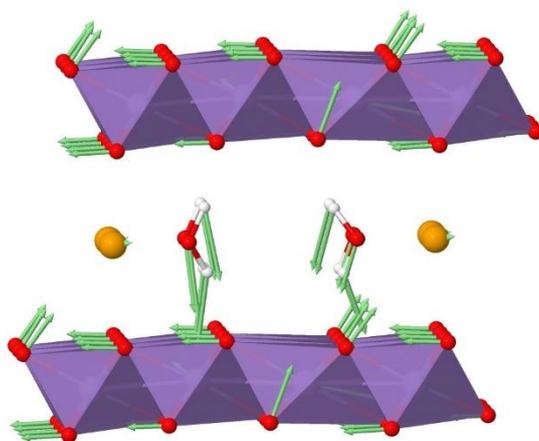


Figure S4: Scheme indicating the calculated direction of the displacement of the atoms during the vibration at 292 cm^{-1} in Na-bir.

NAP-XPS

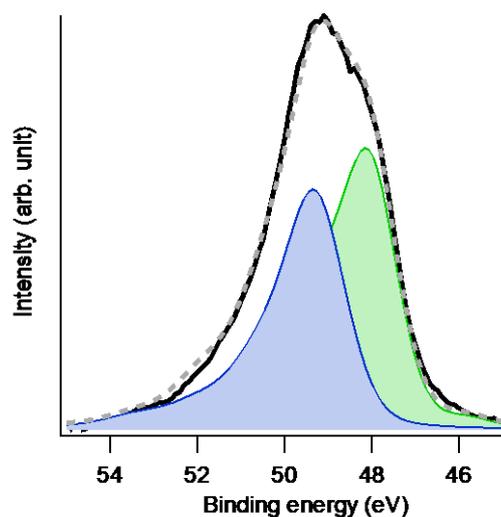


Figure S5: Mn 3p XPS spectra of Na-bir ($h\nu = 420$ eV) at $RH = 0.0$ (black; 293 K, UHV). The spectrum obtained from deconvolution (grey dash line) and its components (Mn(III): green, Mn(IV): blue) are shown. Deconvolution procedure was given in ref¹.

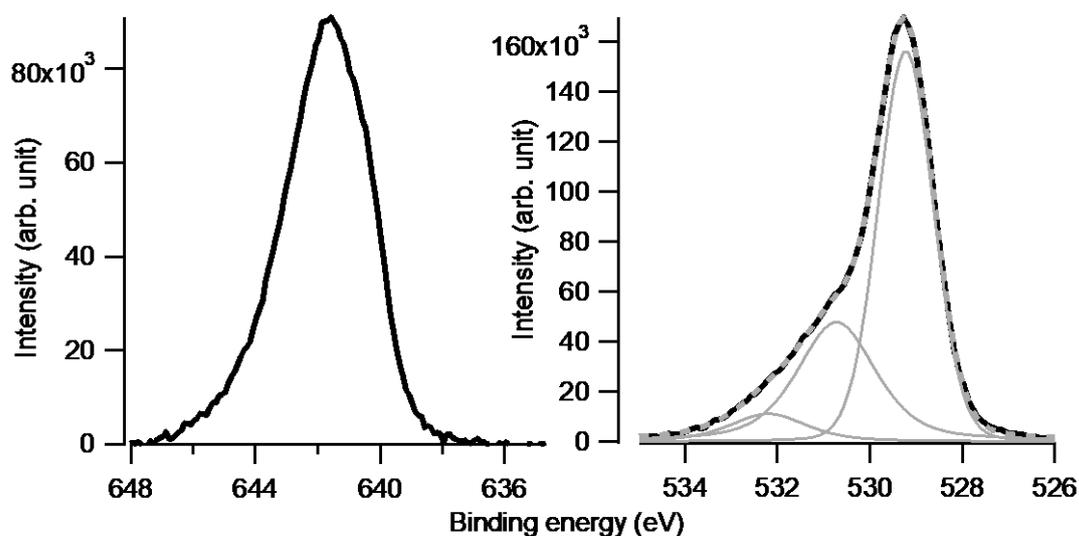


Figure S6: Mn $2p_{3/2}$ (left) and O 1s (right) XPS spectra of Na-bir ($h\nu = 1100$ eV) at $RH = 0.0$ (black; 293 K, UHV).

The O 1s spectrum of Na-bir obtained under UHV is presented in Figure S6. Curve fitting was carried out with sums of Gaussian functions. The most intense component of the O 1s spectrum at 529.2 eV is attributed to the O^{2-} ions of the lattice. Components at higher binding energies (530.7 and 532.2 eV) are assigned to partial hydroxylation of the oxide layers.¹

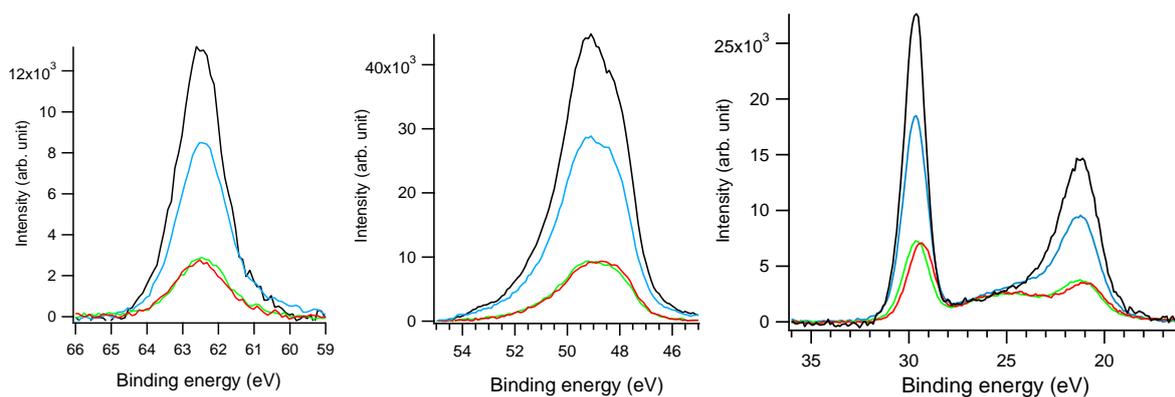


Figure S7: Na 2s (left), Mn 3p (middle) and Na 2p & O 2s (right) XPS spectra of Na-bir ($h\nu = 420$ eV). $RH = 0.0$ (black; 293 K, UHV), $RH = 0.4\%$ (blue; 293 K, 0.1 mbar water), $RH = 9\%$ (green; 293 K, 2 mbar water), $RH = 31\%$ (red; 274 K, 2 mbar water).

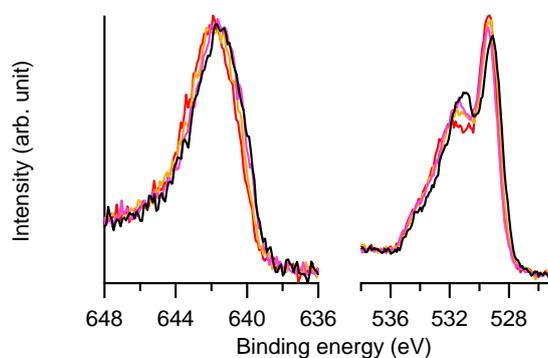


Figure S8: Mn $2p_{3/2}$ (left) and O 1s (right) XPS spectra of Na-bir ($h\nu = 1100$ eV) at $RH = 9\%$ (293 K, 2 mbar water). Four spectra (red, yellow, pink and black) were recorded successively on the same spot under irradiation.

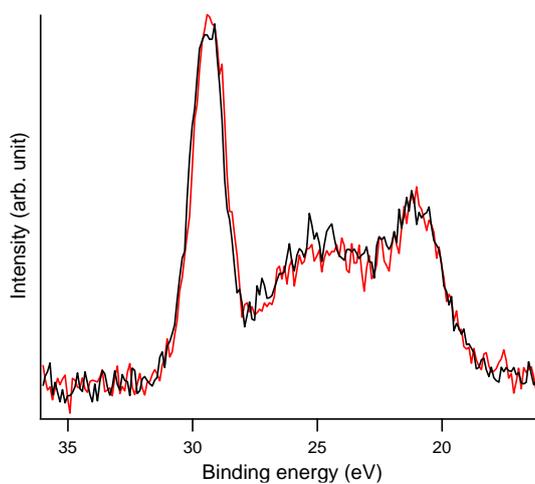


Figure S9: Na 2p and O 2s (1st scan: red, 9th scan: black) NAP-XPS spectra of Na-bir ($h\nu = 420$ eV) at $RH = 31\%$ (274 K, 2 mbar water). Spectra were recorded successively on the same spot under irradiation.

Prolonged irradiation ($h\nu = 1100$ eV) of hydrated Na-bir leads to Mn reduction (Mn 2p feature shifts to lower binding energy) and material hydroxylation (decrease and increase of O^{2-} and OH components, respectively, of the O 1s spectrum, see Figure S8). This material alteration should be attributed to water radiolysis effects as previously evidenced on different hydrated clays.²⁻⁴ To avoid material alteration, irradiation time was limited: each NAP-XPS spectrum was acquired on different spot. For a given spectrum, different recorded scans were compared to exclude any birnessite evolution under the X-ray beam (see, for example, Figure S9). Therefore, the modification of the Na 2p spectrum at $RH = 31\%$ with respect to what is observed at lower RH , cannot be attributed to radiolysis effects (see Figure 7).

References

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