

INTRODUCTION

Layered manganese (Mn) oxides are the major naturally-occurring Mn-oxides in soils and sediments. They have extraordinary ability to sorb metal cations and oxidize redox-active species, playing an important role in metal(loid) and nutrient cycling. Layered Mn oxides usually occur as nanoparticles, such as vernadite, in the environment. The oxides are enriched with Mn vacant sites and accordingly are negatively charged (Figure 1). Thus, a large quantity of cations can be sorbed on vacant sites for charge compensation.

Surface sorption has been shown to be able to affect nanoparticle bulk structure, such as H₂O adsorption on ZnS nanoparticle surfaces (Zhang et al., *Nature*, 2003). Extensive previous studies have investigated metal sorption on layered Mn oxide nanoparticles by focusing on the metal side. It remains largely unknown whether sorbed cations can also alter the crystal structure of MnO₂ nanoparticles.

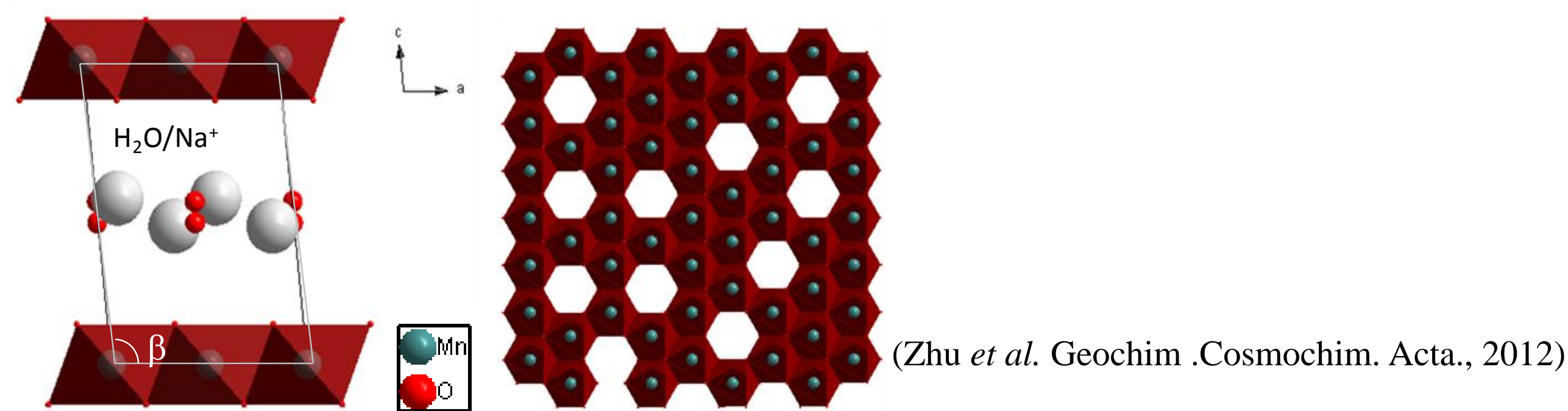


Figure 1. δ-MnO₂ crystal structure obtained by pair distribution function analysis.

Pair distribution function (PDF) analysis is an excellent tool to study nanoparticle structure. In this study, we used PDF analysis to determine possible structural changes of δ-MnO₂ induced by sorption of H⁺, Zn²⁺, and Ni²⁺. The results indicate that H⁺ (by controlling pH) and Zn²⁺ sorption caused contraction of δ-MnO₂ structure whereas Ni²⁺ showed negligible impacts. The effects were ascribed to the charge compensation that reduced internal electrostatic repulsion. In addition, differential PDF analysis on the Zn²⁺ and Ni²⁺ sorbed δ-MnO₂ revealed that Zn²⁺ and Ni²⁺ sorption occurred on vacant sites, consistent with previous EXAFS studies.

MATERIALS AND METHODS

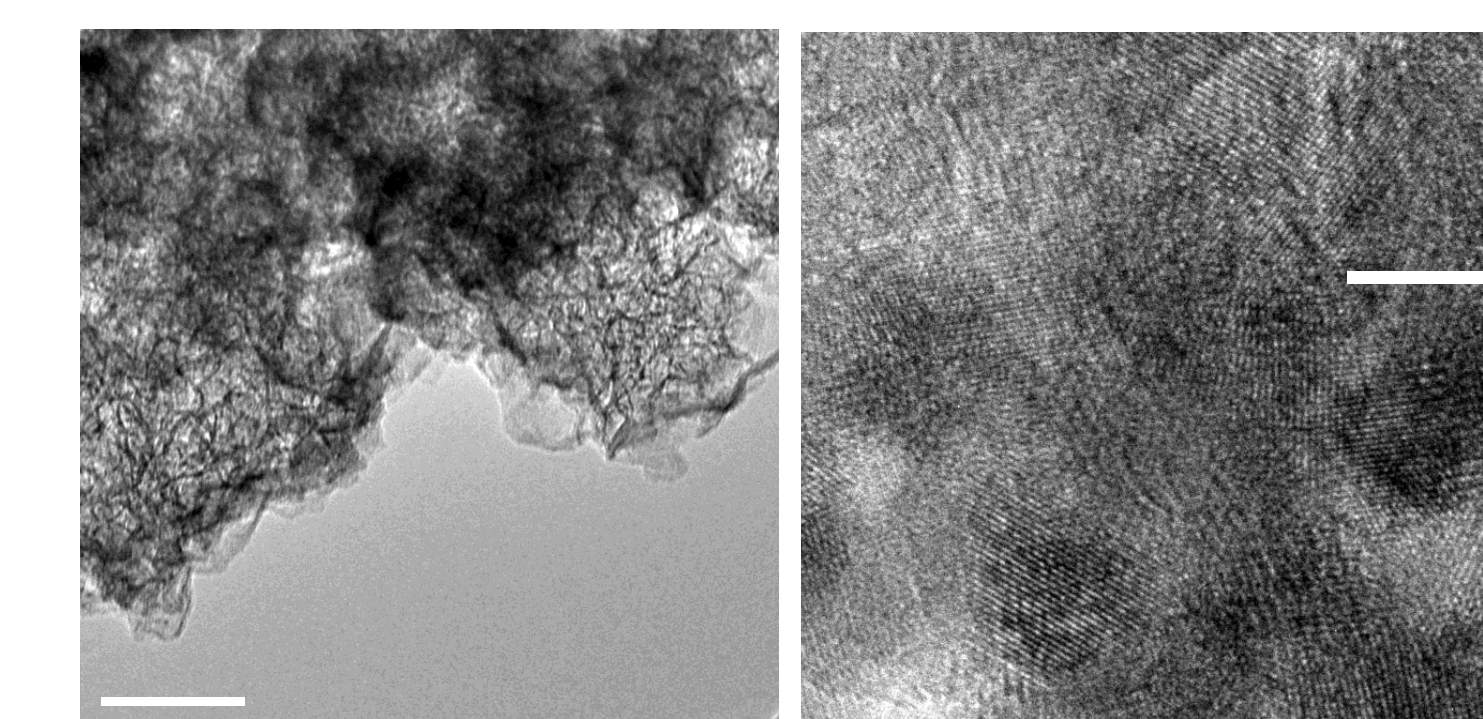


Figure 2. High-resolution TEM images of δ-MnO₂ particles.

δ-MnO₂ was synthesized via reduction of KMnO₄ by Mn(NO₃)₂ in solutions.

- pH effects** (pH = 1, 3, 4, 5 and 7) : NaOH or HNO₃ was used to adjust pH of five δ-MnO₂ suspensions to target pH values. pHs were maintained for 24 hours.
- Zn/Ni sorption**: Sorption experiments were conducted at pH 4. Various loadings of metal were added to δ-MnO₂ suspension. The reaction last for 24 hours. Background electrolyte used was 0.01 M NaNO₃. The reacted δ-MnO₂ was collected by vacuum filtration and then air-dried.

Total X-ray scattering analysis: Data were collected from 11-ID-B at the Advanced Photon Source, Argonne National laboratory, IL. After background removal and appropriate correction, the data were converted to pair distribution functions (PDFs) using the software PDFgetX. The PDF modeling was performed using PDFgui.

RESULTS

1. pH effects on δ-MnO₂ structure

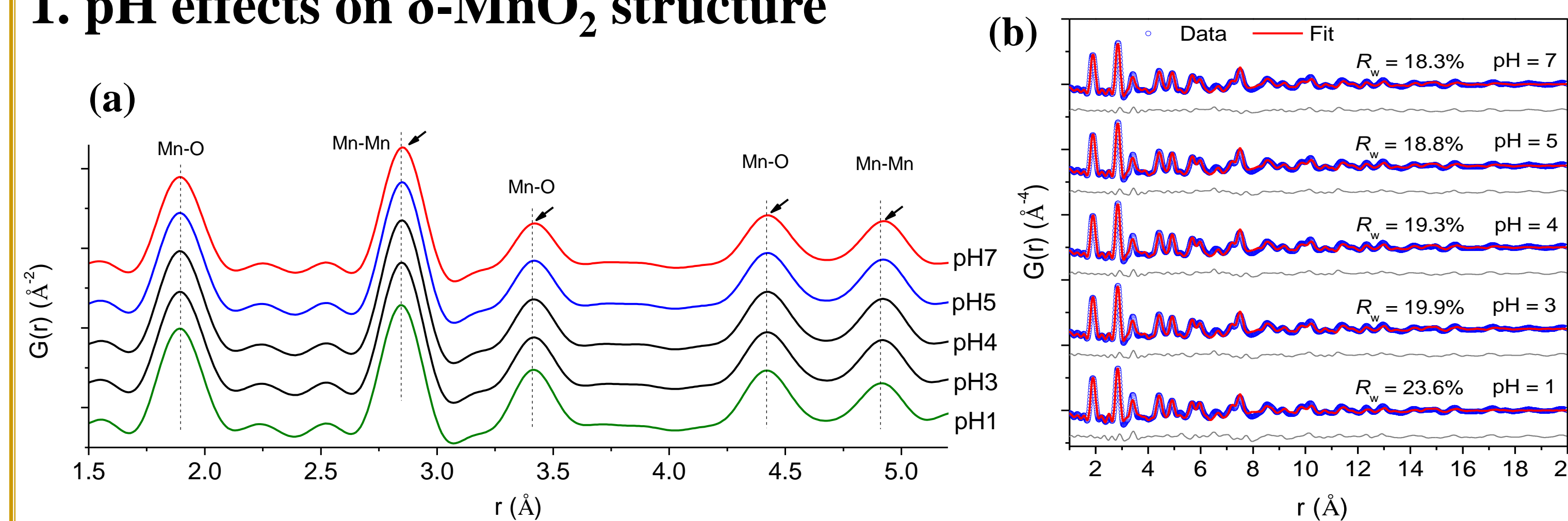


Figure 3. (a) PDFs within 10 Å for a closer inspection. The arrows indicate right shifts of the peaks, suggesting structural expansion. (b) Comparison of PDF experimental data and modeling. The modeling was performed over 1-20 Å and the results are summarized below.

Table 1. Unit cell and atom-independent parameters of δ-MnO₂ obtained from PDF modeling using spherical shape.

Unit Cell	pH 1	pH 3	pH 4	pH 5	pH 7
<i>a</i> (Å)	4.948	4.953	4.952	4.953	4.957
<i>b</i> (Å)	2.815	2.815	2.815	2.816	2.818
<i>ab</i>	1.758	1.759	1.759	1.759	1.759
<i>c</i> (Å)	7.130	7.134	7.139	7.137	7.162
<i>β</i>	98.882	98.102	97.868	97.902	97.829
<i>Scale</i>	1.419	1.419	1.4566	1.440	1.416
<i>diameter</i> (Å)	23.6	25.6	25.51	25.88	25.69
<i>R_w</i> (%)	23.6%	19.9%	19.3%	18.8%	18.3%

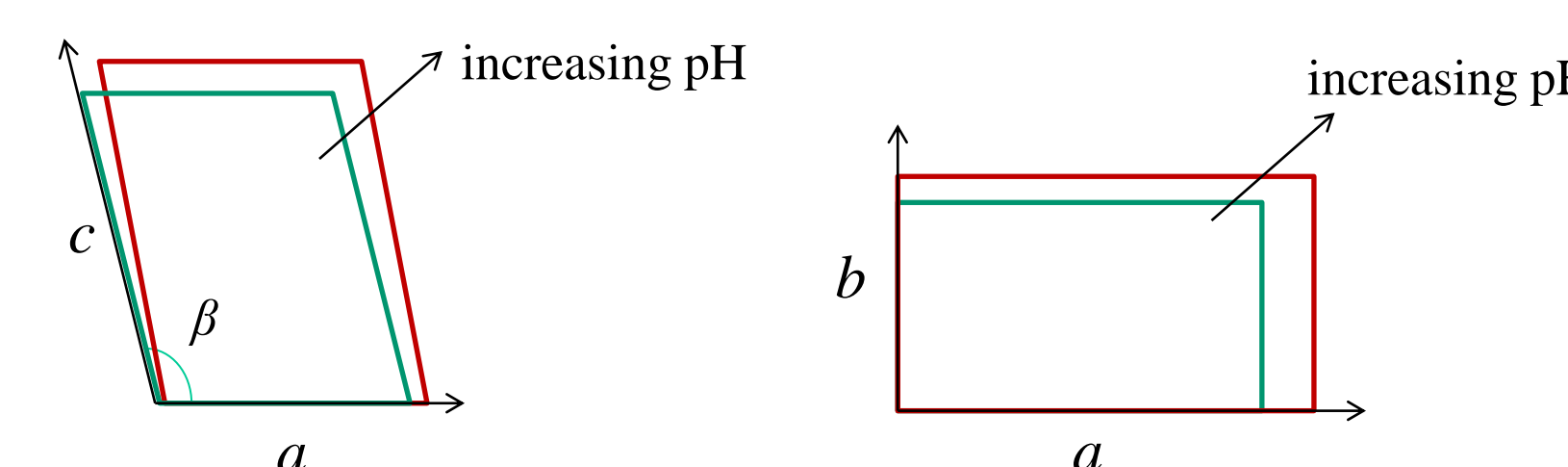


Figure 4. The obtained δ-MnO₂ unit cell dimension (*a*, *b* and *c*) increased as pH increased whereas the stacking angle (*β*) decreased. These indicate that increasing (decreasing) pH caused structural expansion (contraction) of δ-MnO₂.

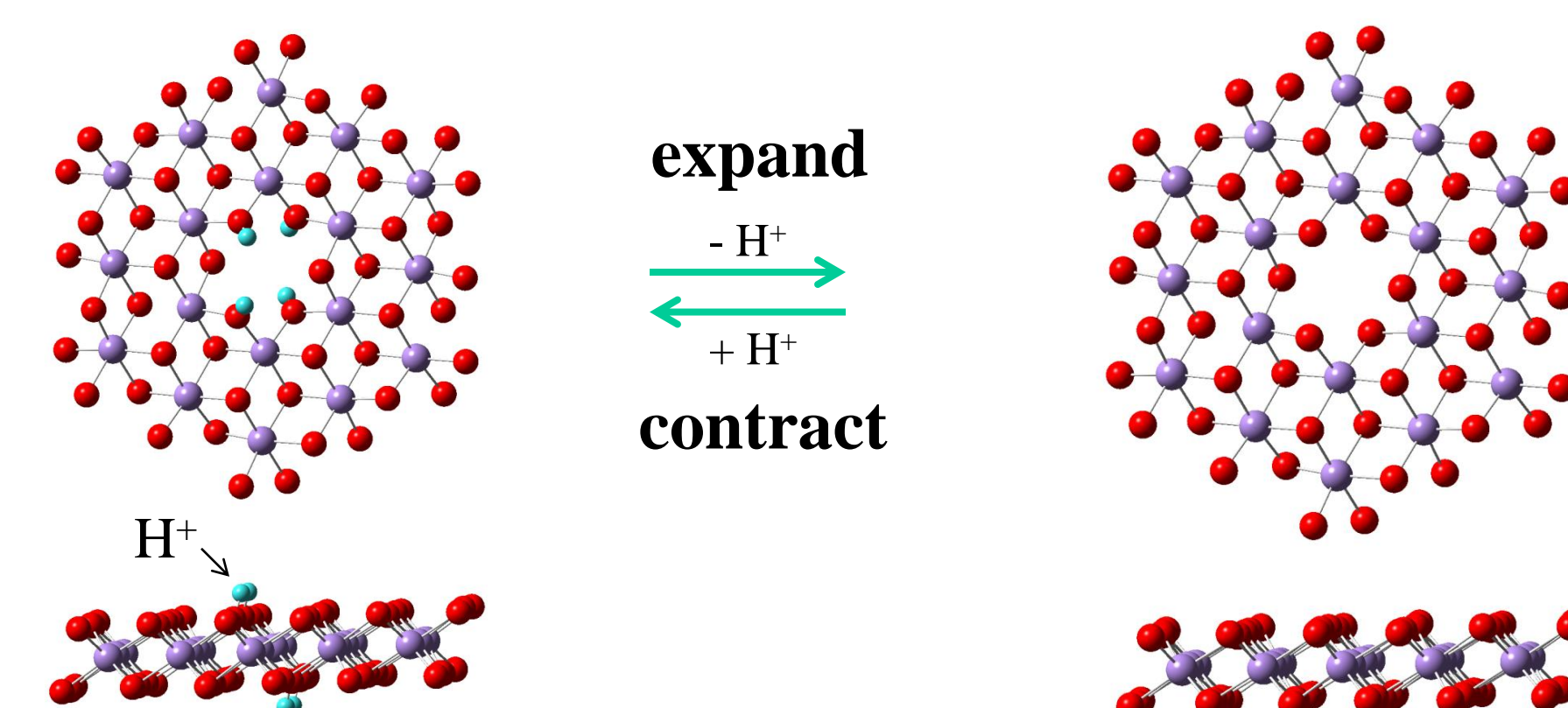


Figure 5. Protonation and deprotonation of O atoms of Mn vacant sites. Protonation decreased the negative charge of Mn layers and internal electrostatic repulsion, and accordingly inter-atomic distances (i.e., structural contraction).

ACKNOWLEDGEMENTS

We would like to thank beamline scientists Dr. Karena Chapman and Dr. Peter Chupas on beamline 11-ID-B at the Advanced Light Source, Argonne National Laboratory (APS).

2. Metal-sorption effects on δ-MnO₂ structure

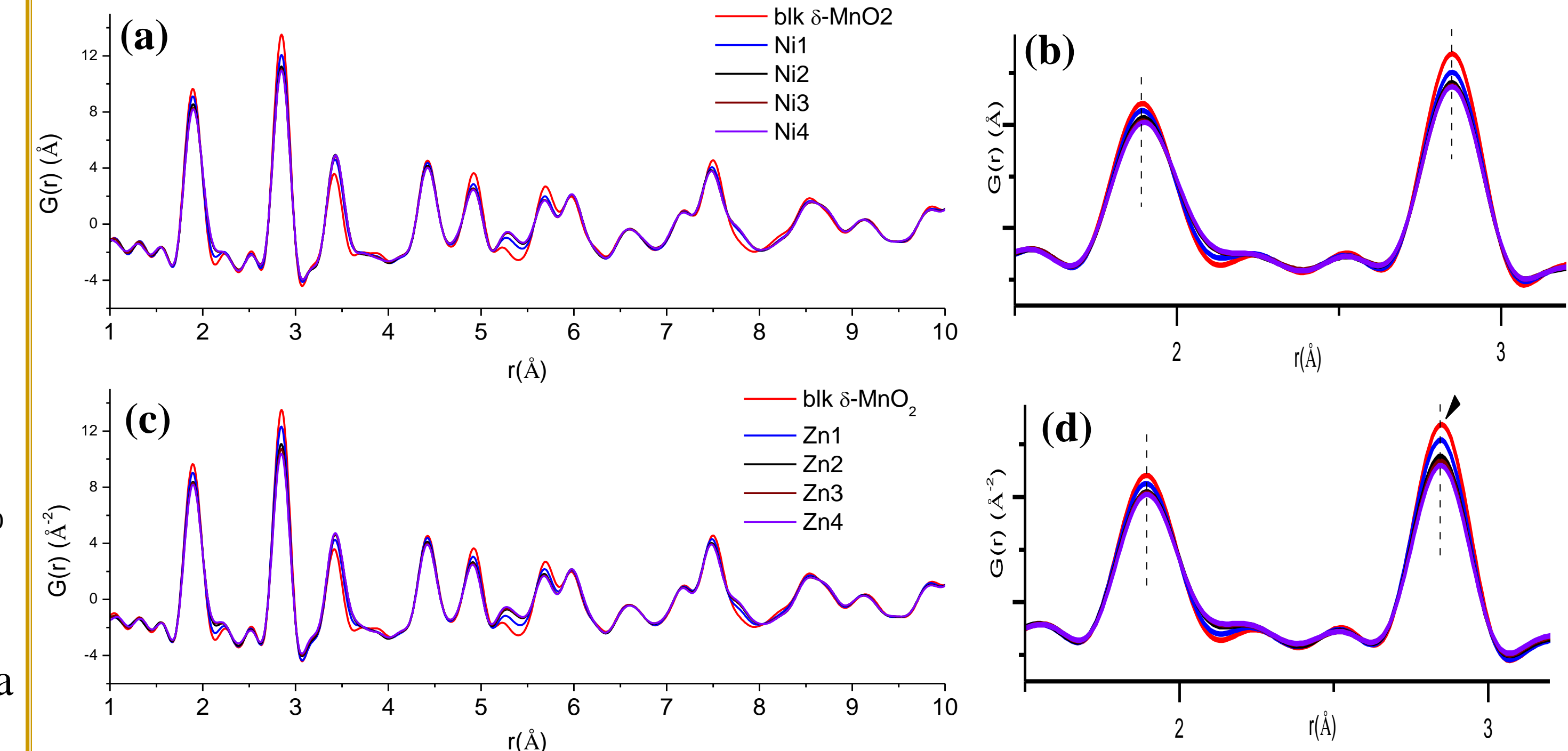


Figure 6. PDFs of Ni²⁺ (a and b) and Zn²⁺ (c and d) sorbed δ-MnO₂. In the order of Zn/Ni1, Zn/Ni2, Zn/Ni3 and Zn/Ni4, the sorption loadings increased. Zn²⁺ sorption decreased the nearest Mn-Mn distance whereas the impact from Ni²⁺ sorption is less evident. The induced change is ascribed to decreased internal electrostatic repulsion.

3. Differential PDF for metal sorption geometry

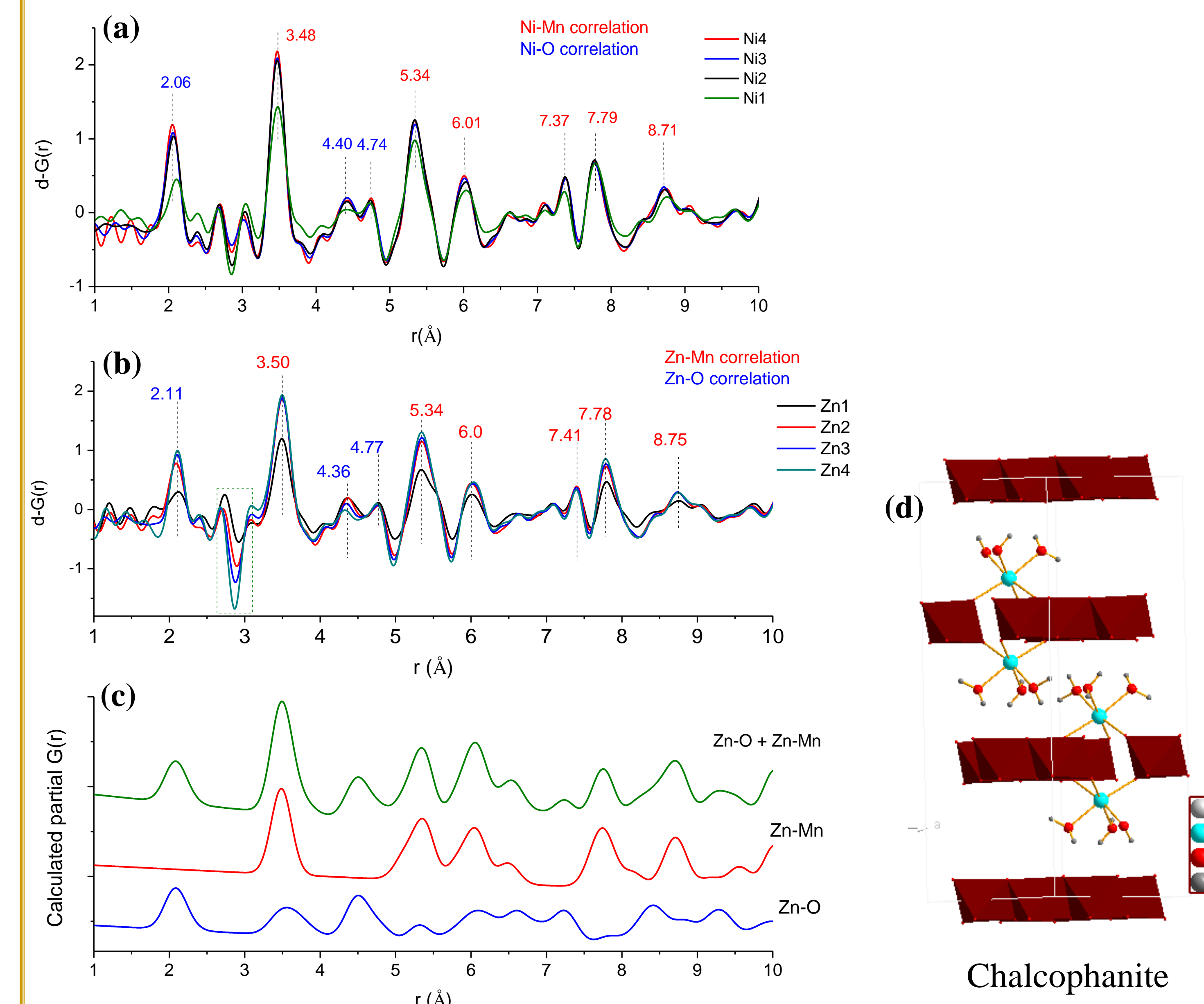


Figure 7. Differential PDF of Ni²⁺ (a) and Zn²⁺ (b) sorbed δ-MnO₂ with respect to pristine δ-MnO₂. (c) Calculated partial atomic correlations involving Zn atoms from chalcophanite, ZnMn₃O₇·3H₂O. (d) Chalcophanite crystal structure. The good alignment of d-G(*r*) to chalcophanite partial G(*r*) indicates Zn²⁺ and Ni²⁺ sorption occurred on the vacant sites of δ-MnO₂.

CONCLUSIONS AND IMPLICATIONS

pH and heavy metal sorption are able to alter the δ-MnO₂ crystal structure. The structural changes may modify band gap energy of δ-MnO₂ and accordingly its photochemical reduction properties that affect Mn cycling in euphotic zones in oceans and lakes.