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Time-resolved structural analysis of K-, Ba-, and Cs-exchange in synthetic birnessite using synchrotron X-ray diffraction

C.L. LOPANO¹, P.J. HEANEY¹, J.E. POST², J. HANSON³,
AND S. KOMARNENI⁴

¹ Dept. of Geosciences, Pennsylvania State University,
University Park, PA 16802 (clopano@geosc.psu.edu;
heaney@geosc.psu.edu)

² Dept. of Mineral Sciences, Smithsonian Institution
(post.jeffrey@nmnh.si.edu)

³ Dept. of Chemistry, Brookhaven National Laboratory
(hanson1@bnl.gov)

⁴ Dept. of Crop and Soil Sciences and Materials Research
Institute, Pennsylvania State University
(komarneni@geosc.psu.edu)

Birnessite is an abundant layer-structure Mn-oxide phase in soils, desert varnishes, and ocean nodules that plays a significant role in soil and groundwater chemistry. In this study, aqueous K⁺, Cs⁺, and Ba²⁺ cations were exchanged for interlayer Na⁺ in synthetic birnessite using a simple flow-through cell, and the exchange products were monitored via time-resolved X-ray powder diffraction at the National Synchrotron Light Source. Powder X-ray diffraction patterns were collected every 2-3 minutes.

The starting structure for Na-birnessite was based on a triclinic unit cell [1]. Rietveld analyses (using the GSAS program) of the X-ray diffraction patterns for K- and Ba-exchanged birnessite revealed decreases in the *a*, *c*, and β unit-cell parameters, with a decrease of 1.4% and 0.5% respectively in the overall unit-cell volume relative to Na-birnessite. In contrast, the exchange of Cs⁺ into the birnessite structure led to a decrease in the *a* and β parameters but an increase in the length of *c*, generating an overall increase of 0.9% in the total unit-cell volume. This structural expansion can be attributed to the larger size of Cs²⁺ relative to Na⁺ and to the lower charge of Cs⁺ in comparison with Ba²⁺.

Fourier electron difference syntheses revealed that the structural changes were a function of the configuration of the interlayer species. Split electron density maxima with centroids at (0 0.5 0.5) were present for both Na and K end-members; however, with increased substitution of K for Na, the axis connecting the split-site maxima rotated from an orientation parallel to the *b*-axis to along the *a*-axis. The split electron density maxima of interlayer Ba, on the other hand, exhibited no rotation, but splitting was more pronounced. The exchanged interlayer Cs cations revealed yet another arrangement, with positional disorder over four proximal sites.

Reference

[1] Post J.E., Heaney P.J., and Hanson J.C. (2002) *Powder Diffraction* **17**(3), 218-221.

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Pattern of minor element enrichment in columbites: A SRXRF study

J.P. MIRÃO¹ AND M.O. FIGUEIREDO²

¹ Geophys. C., Univ. of Évora, Portugal (jmirao@uevora.pt)

² Cryst. Miner. C., ICT, Lisboa, Portugal (crysmin@clix.pt)

Columbites have the general formula A²⁺B⁵⁺₂O₆, where A is Mn or Fe and B is Nb or Ta. Typical of pegmatites that are economically important as Nb and Ta ores, the physical properties of these oxide minerals make them convenient as prototypes for technologically relevant materials.

Their crystal structure is based on a hexagonal closest packing of oxygen anions with cations filling half of the available octahedral sites. Occupied octahedra share two opposite edges defining zigzag chains along [001] with only one kind of metal (A or B). Closest packed planes are parallel to (100) and contain A- or B-type cations in a sequence [ABB]. The presence of metal ions with valences 2+ and 5+ and different radii in the structure constrains the relative volume of filled octahedra. According to the so-called Bond Valence Theory [1], cations A are overbonded while B are underbonded, a situation that is partially counterbalanced by the off-centring of Nb and Ta in B-type octahedra.

The low level of incorporation of minor elements renders difficult to understand the role of geochemical constrains vs. crystal structure hindrance factors in columbites. With the purpose of disclosing a pattern for minor element enrichment in columbites, a crystal chemical study was undertaken on minerals sampled at the pegmatite province of Zambezia in Mozambique. Major element concentrations were determined by electron microprobe analysis and trace elements were analysed using the LURE photon microprobe [2]. The unique properties of synchrotron radiation allow for focusing the beam on a very small spot and select the excitation energy according to the elements to analyse. Very low figures may then be attained for the detection limits of trace elements and informative topochemical mappings can be traced.

The plot of analysed samples in the quadrilateral FeNb₂O₆-MnNb₂O₆-MnTa₂O₆-FeTa₂O₆ is representative of a wide compositional range and suggests an evolution trend due to the increment of Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios.

Although minor element concentrations depend on geochemical features (such as the abundance in the fluid), obtained data show that the incorporation of trace elements (e.g. Ti, U, Zr, Y, W) in columbites is mainly constrained by the presence of Nb. A topological approach to columbite crystal structure based on bond valence calculations was developed, showing that minor elements that decrease or, at least, do not increase, the stress in the crystal structure are preferentially incorporated.

References

[1] Brown I.D. (1992) *Acta Cryst. B* **48**, 553-572.

[2] Chevallier P. et al. (1996) *J. Trace Microprobe Tech.* **14**, 517-539.