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Representative sampling - a geo-analytical laboratory praxis testK. ESBENSEN¹ H.-D. ZIMMERMAN² AND S. GRUNDTVIG²¹ ACACSRG (Applied Chemometrics, Analytical Chemistry & Sampling Research Group, Aalborg University, Esbjerg (AUE), Denmark² Geologisk Institut, Aarhus Universitet, Denmark

The Rønne granite, Bornholm belongs to the oldest parts of the island's Proterozoic basement. It is a dark medium grained rock, occurring in two varieties distinguished by their uniform textures throughout and by their very homogeneous appearance in the field. Particularly with rocks of such homogeneous appearance, representative sampling for chemical and mineralogical analyses should seem straightforward - but is it? "How well do the laboratory analyses reflect the average composition of the rock sampled in the field?" is only addressed reluctantly in most geological curricula, if at all. Is there a theory, or better a practical protocol, which can be used to assure optimum sample representativity? Thanks to its accessibility and distinguishing relative homogeneity, the Rønne granite appears most suited for a praxis test of sampling representativity. There does indeed exist such a theory (TOS, the Theory of Sampling) – in fact it has existed for 50+ years, but it has never been invoked in geology and geochemistry in the same period. Why? At the Geological Institute, University of Aarhus we have recently conducted an extensive evaluation of the acknowledged standard sample preparation procedures which consists of rather complex multi-stage sub-sampling/mass reductions. It will be shown that these procedures in general are not in agreement with the Theory of Sampling (TOS) – in fact that they are fraught with several severe principal breaches, based on a bench-mark reference procedure. The result of such incorrect laboratory sampling is analytical results which can be shown to be very far removed from being representative of the true average concentration of the field outcrop. We expose the details of such deviations and their principal causes, as basis for delineating what simple remedies must be invoked etc.

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In situ synchrotron X-ray diffraction study of the dehydration behaviors of Na- and K-birnessitesJ.E.POST¹, P.J. HEANEY² AND J. HANSON³¹ Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560-0119 (post.jeffrey@nmnh.si.edu)² Department of Geosciences, 309 Deike, Pennsylvania State University, University Park, PA 16802³ Chemistry Department, Brookhaven National Laboratory, Upton, NY 11793

Manganese oxide minerals having the birnessite-type layer structure occur in a wide variety of geological settings, including soils, sediments, Mn crusts and nodules, and rock varnish. They readily participate in cation-exchange and oxidation-reduction reactions, and synthetic birnessite-like phases are extensively being studied as possible catalysts and cation-exchange agents. The interlayer region is occupied by H₂O molecules and in natural samples various cations such as Na⁺, Ca²⁺, K⁺, etc; synthetic birnessite phases have been synthesized having a wide assortment of other interlayer cations. The chemical activity exhibited by birnessite is, at least in part, due to the apparent ease by which the structure adjusts to accommodate a range of interlayer water and cation compositions.

In situ, temperature-resolved synchrotron X-ray diffraction and the Rietveld method was used to investigate the dehydration behaviors of synthetic Na- and K-birnessites as they were heated from room temperature to 300 °C. The X-ray diffraction data were collected in air at beam line X7B of the National Synchrotron Light Source, Brookhaven National Laboratory, using a wavelength of 0.9370 Å and a MAR345 full imaging plate detector.

Na- and K-birnessite exhibit complex dehydration behaviors when heated from room temperature to 300 °C, accompanied by three distinct structural changes: at 70-80 °C, 100 °C, and 140-150 °C. The changes are most significant for Na-birnessite. For Na-birnessite, the first dehydration step is accompanied by increases in the α and β unit-cell parameters (C-centered triclinic cell), and decrease in a ; above 100 °C, β increases sharply and a and c decrease; from 140-180 °C, γ increases and a , c , and β decrease until the structure is fully dehydrated and collapses. The unit-cell volume decreases at each dehydration step but most dramatically above 140 °C. As K-birnessite is heated, α increases slightly and c and volume start to decrease at ~70 °C; from 100 °C to 140 °C, a increases, c and volume continue to get smaller, and β and γ start to decrease; above 140 °C, α , β , and γ increase and a , c and volume decrease sharply. At ~175 °C K-birnessite transforms to an anhydrous layer structure with a layer spacing of 6.69 Å, that persists to at least 300 °C. Upon cooling in air this phase rehydrates.