ESRF	**Experiment title:** Wöhlerite or marianoite?: Feasability of X-ray resonant powder diffraction for minerological challenges	**Experiment number**: A31-1-149
Beamline: BM01	**Date of experiment**: from: 13th September 2021 to: 14th September 2021	**Date of report**:
Shifts: 6	**Local contact(s)**: Dmitry Chernyshov	*Received at ESRF:*

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This experiment was carried our remotely by the beamline scientist, according to the submitted and approved detailed experimental plan.

Report:

Series of wöhlerite samples have been investigated by X-ray resonant powder diffraction (XRPD) to determine the distribution of Nb and Zr atoms over two different *2a* crystallographic sites in the mineral crystal structure. Zr and Nb present a particularity of having both similar atomic numbers (Z_{Nb}= 41, Z_{Zr}= 40) and neutron scattering lengths (b_{Nb}= 7.054 fm, b_{Zr}= 7.16 fm). This makes them indistinguishable by standard X-ray/neutron powder diffraction techniques and requires employment of other scattering methods with the resonant powder diffraction being the first choice technique.

Only 5 (sample ID: W1_A, W2_A, W3_A, W5_A and W8_A) out of 9 samples have been investigated. The powders were measured at room temperature, at the following wavelengths: 0.70848, 0.67018, 0.63582 and 0.60480 Å. During the experiments specimens were sealed in boron-glass capillaries (d = 0.3 mm).

The obtained SR-PXD data have been analyzed by Rietveld refinements that were carried out jointly, for all datasets, for a given composition. The powder diffraction patterns were fitted against the crystal structure model taken from (1). So far, the refinements have been performed with two various software packages: GSAS (2) and Fullprof (3). For all samples, a very good agreement between the observed and calculated SR-PXD data have been observed. The preliminary results suggest the mixed occupancy of Zr and Nb at both $2a_{Zr}$ and $2a_{Nb}$, with no atom ordering. This would suggest that the approach to distinguish wöhlerite from marianoite should be based on *so called* the disordered model approach, according to which the occupancy of Zr and Nb at both $2a_{Zr}$ and $2a_{Nb}$ shall exceed 50 %, in case of the former.

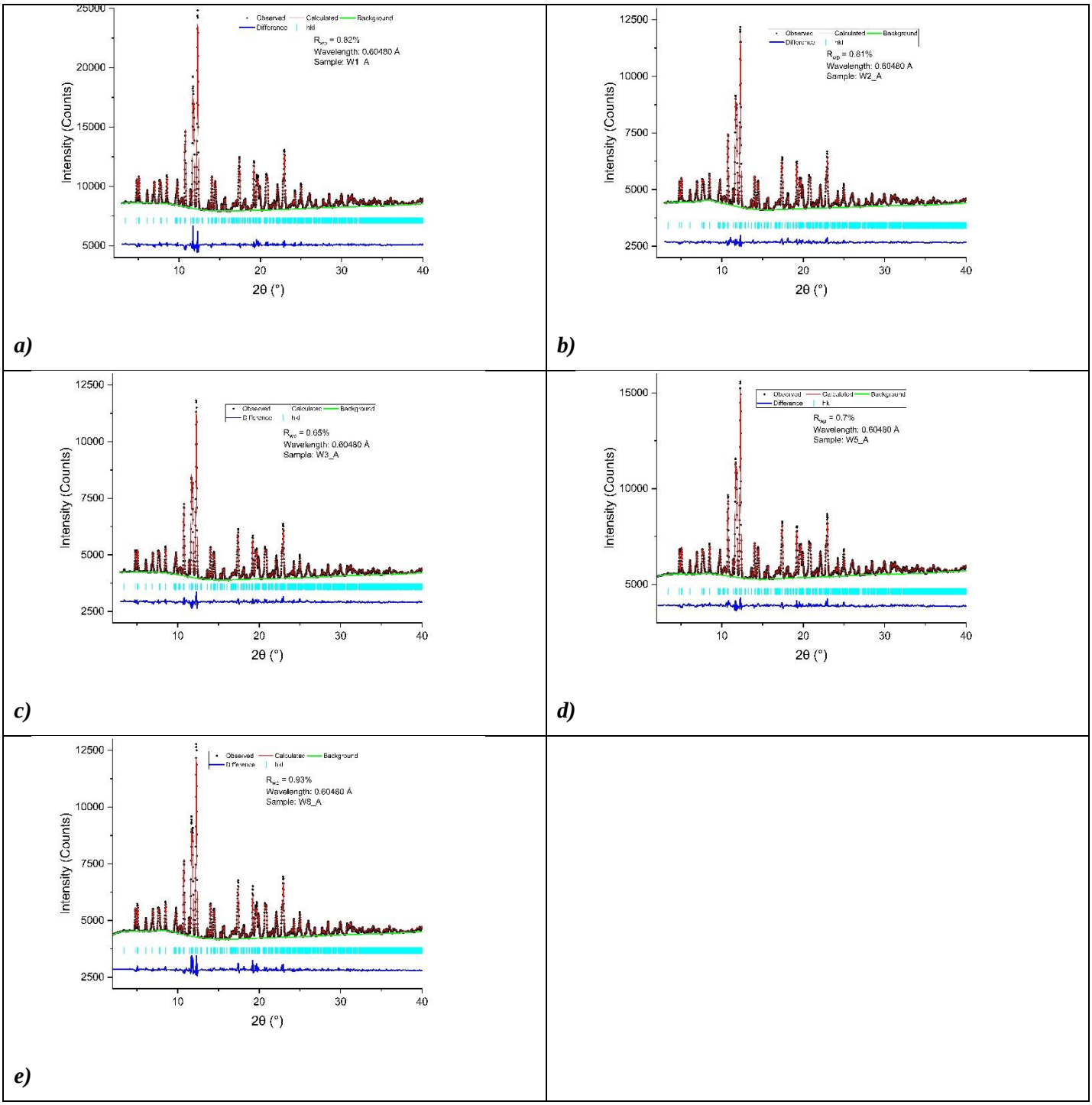

Figure 1. Observed (black), calculated (red) and difference (blue) high resolution diffraction profiles (λ = 0.60480 Å) obtained for **W1_A** (***a***), **W2_A** (***b***), **W3_A** (***c***), **W4_A** (***d***) and **W5_A** (***e***); vertical bars indicate Bragg peak positions of the crystalline wöhlerite phase with the nominal chemical composition of $Na_2Ca_4ZrNb(Si_2O_7)_2O_3F$ (space group: $P2_1$).

Unfortunately, some of the samples reveal problem with a proper line profile refinements that affected strongly the obtained occupancy and estimated standard deviation values. Thus, in the next step, the Rietveld refinements for all samples will be carried out with the TOPAS (4) software and the proposed hypothesis will be reevaluated.

References

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