

Incorporation of Monovalent Cations in Sulfate Green Rust

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SUPPORTING INFORMATION FOR PUBLICATION

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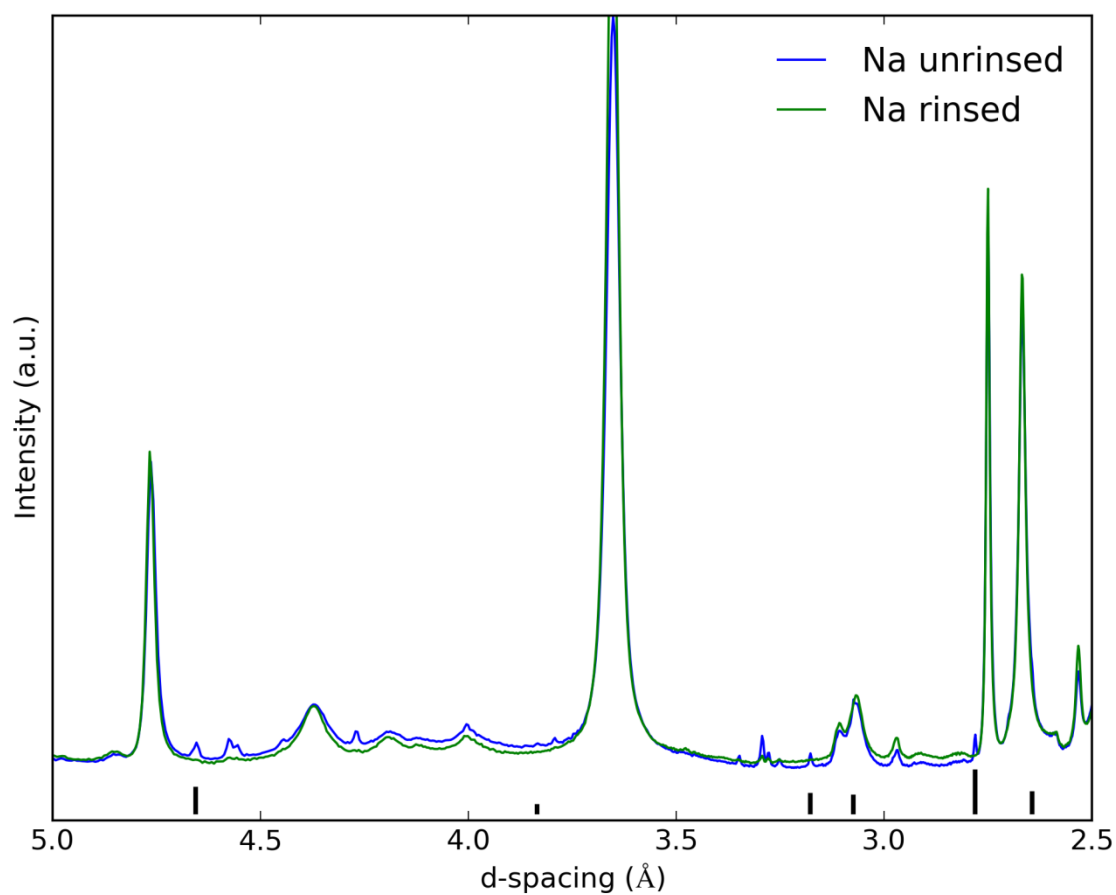


Figure S1: Comparison of X-ray powder diffraction patterns for unrinsed and rinsed GR_{Na₂SO₄}. The black marks show the d-spacings of thenardite, Na₂SO₄. It is evident that thenardite is present before rinsing the material.

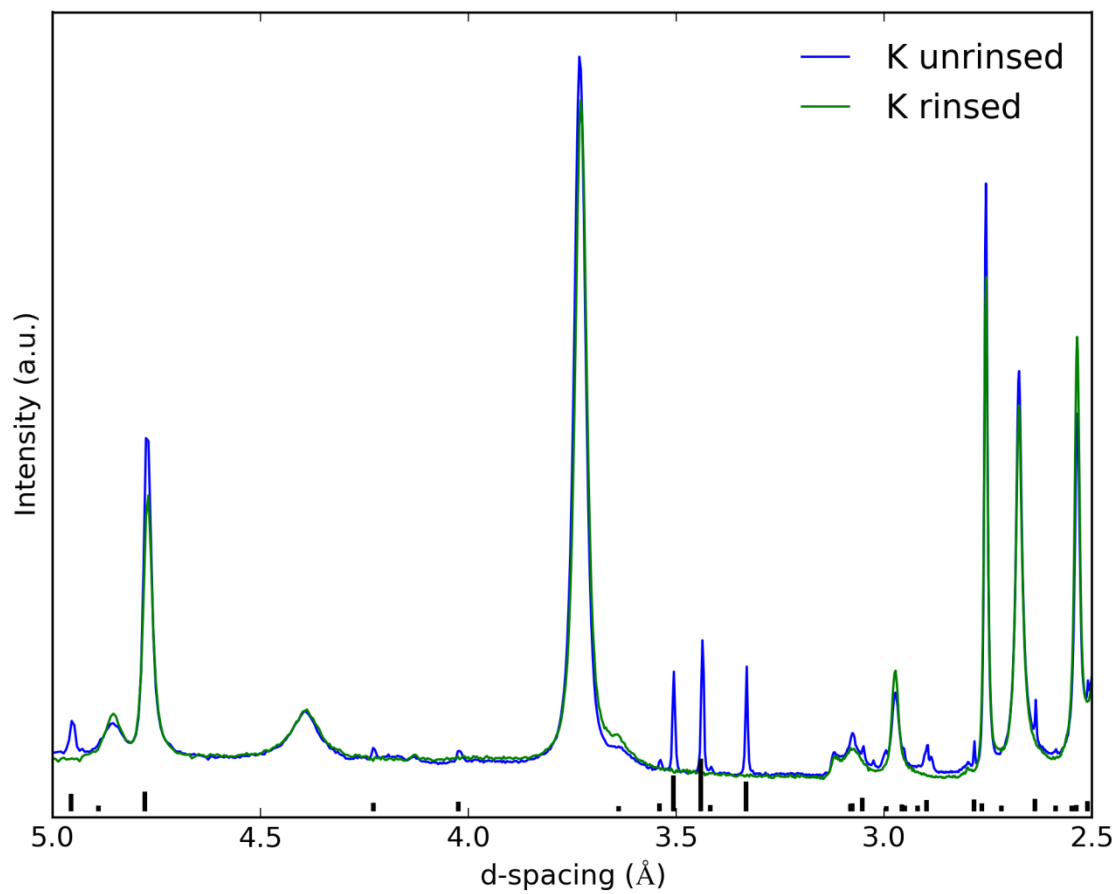


Figure S2: Comparison of X-ray powder diffraction patterns for unrinsed and rinsed GR_{K,SO_4} . The black marks show the d-spacings of mereiterite, $K_2Fe(SO_4)_2 \cdot 4H_2O$. It is evident that mereiterite is present before rinsing the material.

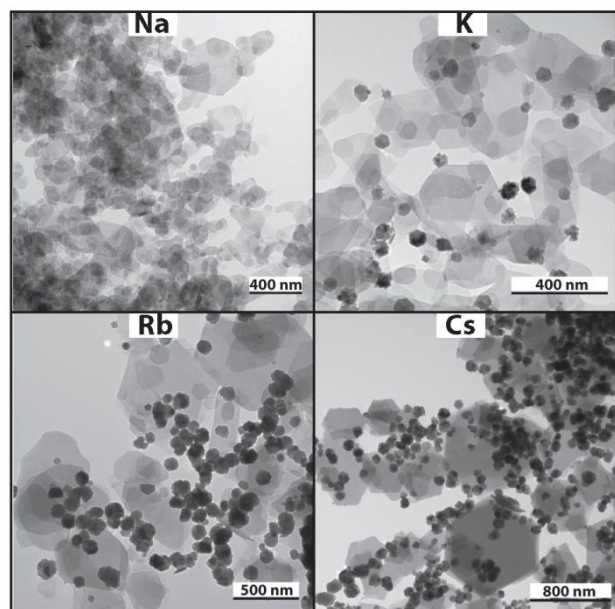


Figure S3: TEM images of $\text{GR}_{\text{Na},\text{SO}_4}$, $\text{GR}_{\text{K},\text{SO}_4}$, $\text{GR}_{\text{Rb},\text{SO}_4}$ and $\text{GR}_{\text{Cs},\text{SO}_4}$. The small black particles are magnetite nanocrystals.

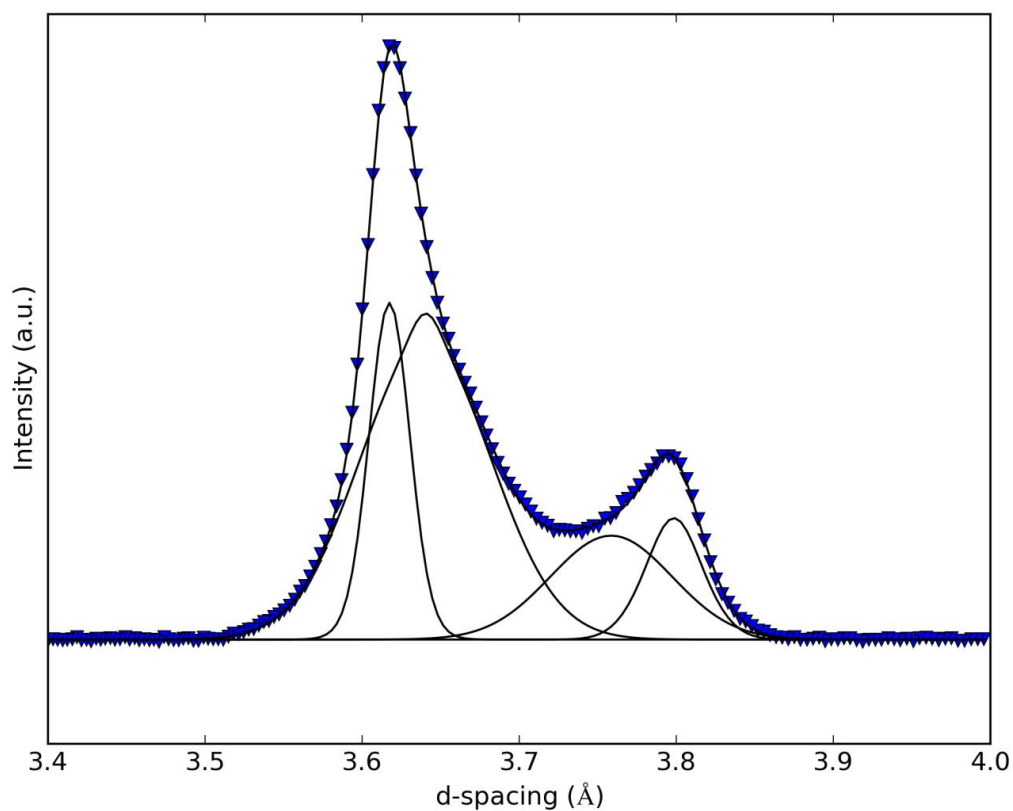


Figure S4: Background corrected X-ray powder diffraction patterns of the 003 peak for $\text{GR}_{\text{CsSO}_4}$. Three pairs of Gauss functions and one single Gauss function are used to fit the experimental 003 reflection. Every pair of Gauss functions are constrained to have the same position, but width and intensity are fitted independently. The four fitted centers are located at 3.617, 3.640, 3.759, and 3.799 Å. This results in basal plane (001) distances of 10.85, 10.92, 11.28 and 11.40 Å. The four individual peaks (double Gaussian peaks) are shown as well as the total fit to the experimental points.

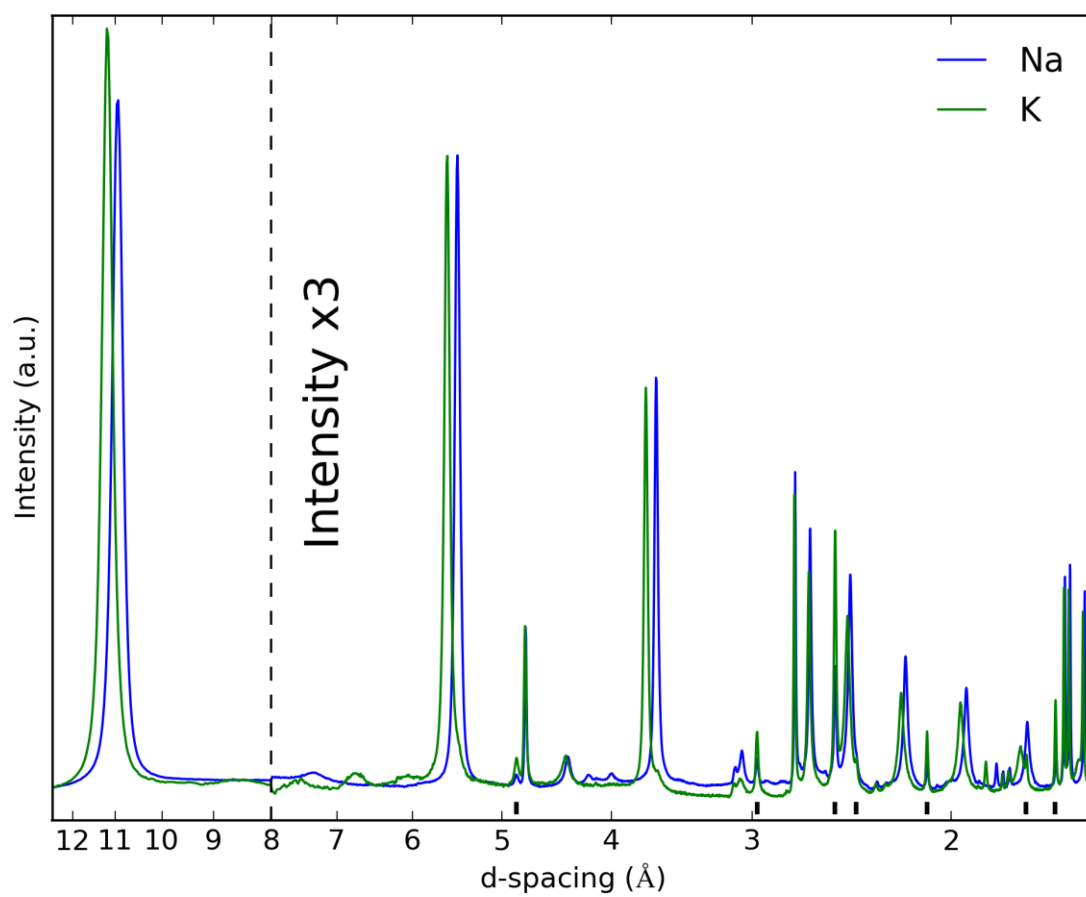


Figure S5: X-ray powder diffraction patterns for rinsed $\text{GR}_{\text{Na},\text{SO}_4}$ and $\text{GR}_{\text{K},\text{SO}_4}$. The black marks show the d -spacings of magnetite.

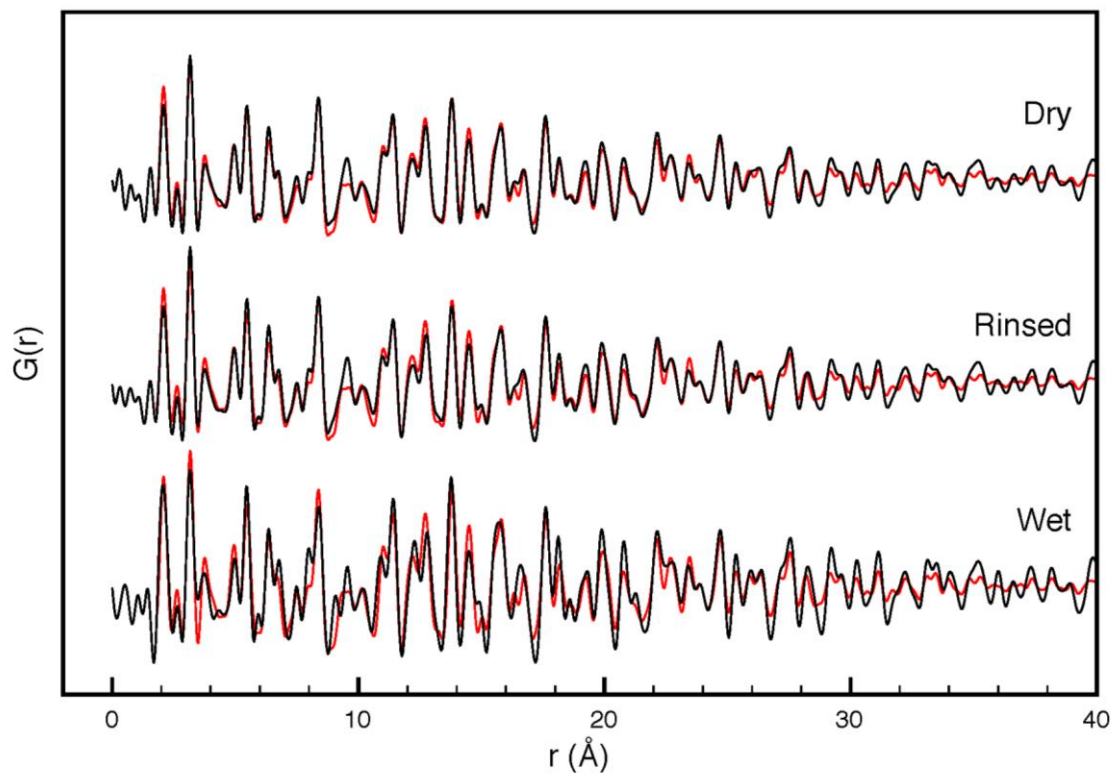


Figure S6: PDFgui fitting. Experimental PDFs are in black, whereas the fitted PDF is in red. Initially, the PDFs for the dry material were fitted using a Qdamp of 0.049 \AA^{-1} determined from natural magnetite, allowing variation of the parameters: scaling, unit cell dimension, size of coherent scattering domains ($\sim 70 \text{ \AA}$), correlated atomic motion (δ_2 , 3.3 \AA^2) and isotropic atomic displacement for Fe (0.008 \AA^2) and O (0.028 \AA^2). Using these fitted values, the PDFs for the rinsed and wet sample were subsequently fitted allowing variation of only scaling and unit cell dimensions. The resulting residual parameters (Rw) were 0.28 for the dry sample, 0.33 for the rinsed sample and 0.45 for the wet sample. Most peaks are fitted well, but there are notable misfits at 1) high r -values, presumably because coherent scattering domains are not spherical as assumed in the fitting and 2) at $\sim 9.5 \text{ \AA}$. Because the r -value of the latter peak corresponds to the unit cell a -axis dimension, it has contributions from atomic pairs of all the GR constituents, making analysis of the discrepancy highly complicated.

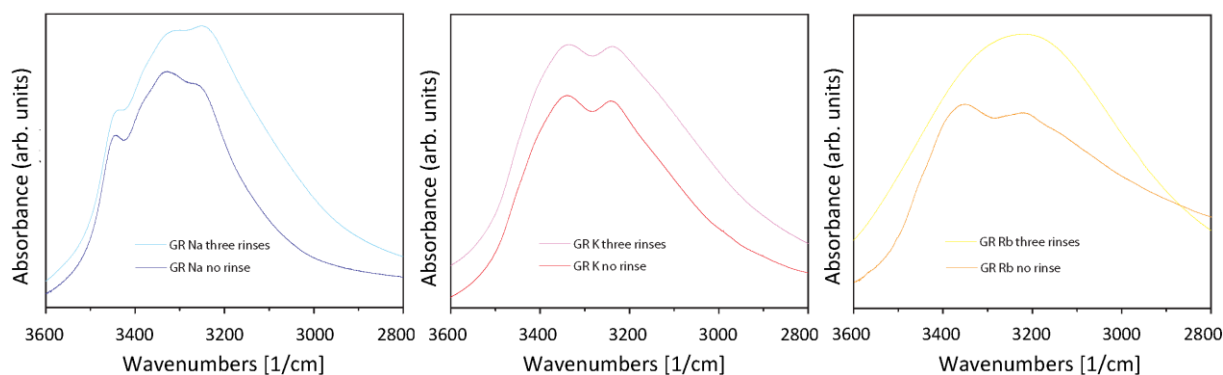


Figure S7: IR spectra in the OH stretch region for $\text{GR}_{\text{Na},\text{SO}_4}$, $\text{GR}_{\text{K},\text{SO}_4}$ and $\text{GR}_{\text{Rb},\text{SO}_4}$ unrinsed and rinsed three times. The spectra for are very similar for rinsed and unrinsed $\text{GR}_{\text{Na},\text{SO}_4}$ and $\text{GR}_{\text{K},\text{SO}_4}$. The band splitting disappears when the $\text{GR}_{\text{Rb},\text{SO}_4}$ sample is rinsed three times.