

Supplementary Information for

Mechanistic and thermodynamic insights into anion exchange by green rust

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Contents:

Supplementary text

Figs. S1 to S7

Tables S1 to S4

References for SI reference citations

Supplementary Information Text

Scherrer equation

Scherrer equation is:¹

$$D = \frac{k \lambda}{FWHM \cos(\theta)}$$

in which D is the crystallite size (\AA), k is a shape constant (equal to 1), λ is the X-ray wavelength (\AA), FWHM is the full width at half-maximum of the diffraction peak (rad) and θ is the Bragg angle (rad).

Calculation of XRD patterns (Fig. S6)

XRD patterns were calculated using micro-GR(Cl) as a starting structure model (Fig. S6, black line: micro-GR(Cl)) and working with the software CALCIPOW.² Mean and maximum number of layers were set to 12 and 15 respectively (lognormal distribution). Radius of crystallite in the **a-b** plane was fixed to 50 \AA . The amount of stacking defects were set to: 0 % - 3D-ordered structure (micro-GR(Cl) in this case, black line on Fig. S6), 50 % (light blue line on Fig. S6A) and 100 % - turbostratism (red line on Fig. S6). The model from micro-GR(Cl) was also modified to obtain a green rust with two coherently stacked sheets on average (purple line on Fig. S6B).

Supplementary Figures

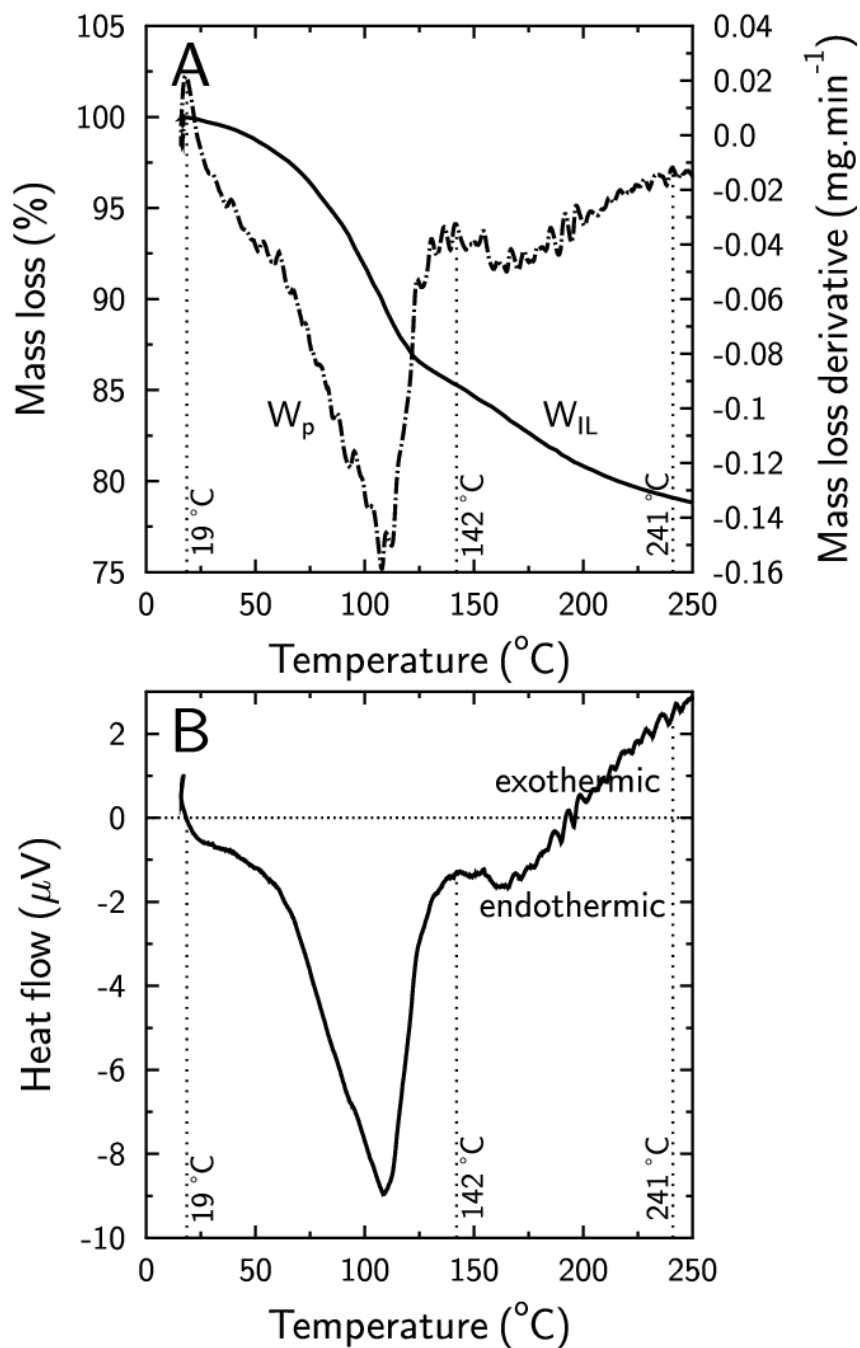


Fig. S1. A: TGA results for micro-GR(Cl). Full line: mass loss (%); Dash line: mass loss derivative (mg·min⁻¹); W_p= interparticle (capillary) pore water; W_{IL}= interlayer water. B: DSC results.

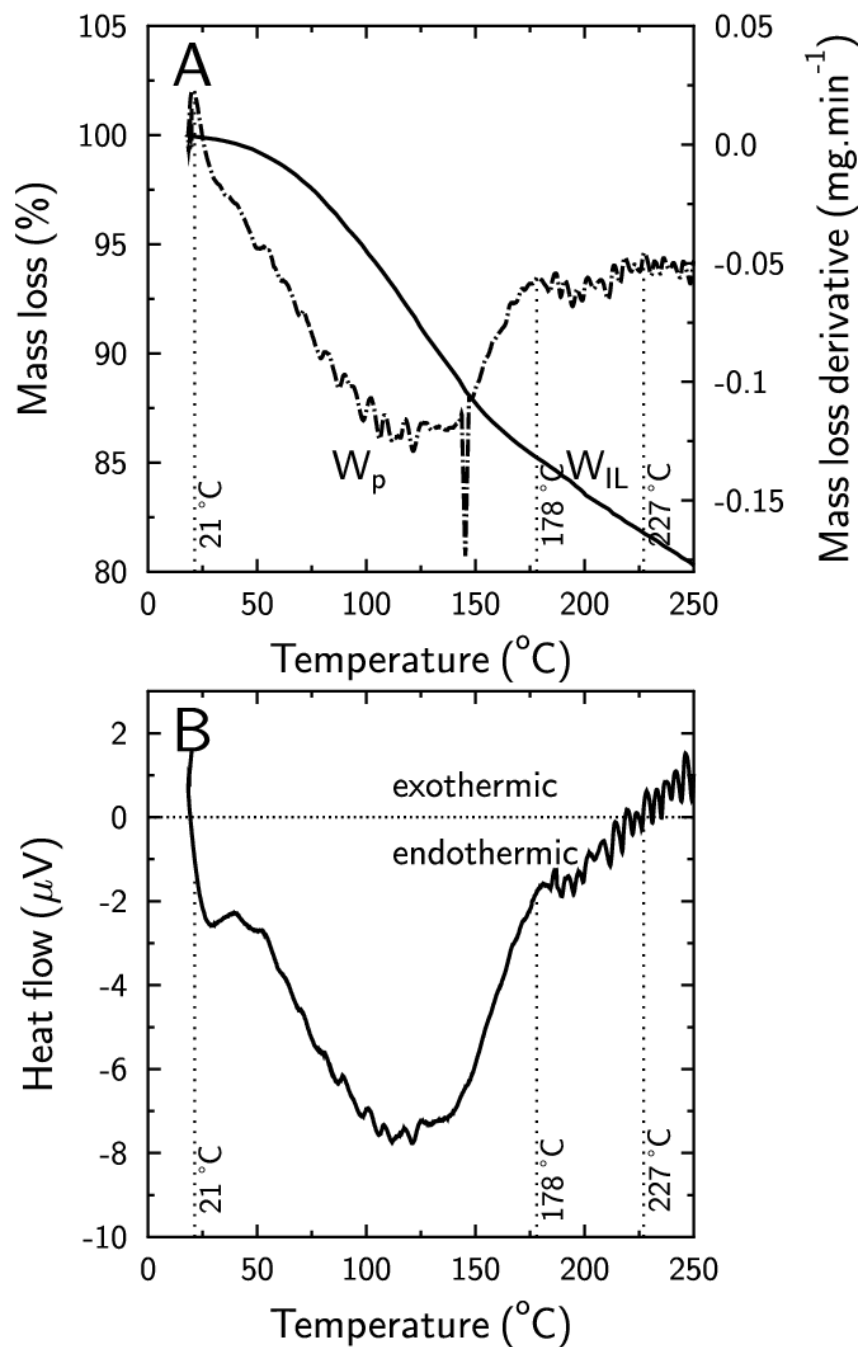


Fig. S2. A: TGA results for nano-GR(SO₄). Full line: mass loss (%); Dash line: mass loss derivative (mg·min⁻¹); W_P= interparticle (capillary) pore water; W_{IL}= interlayer water. B: DSC results

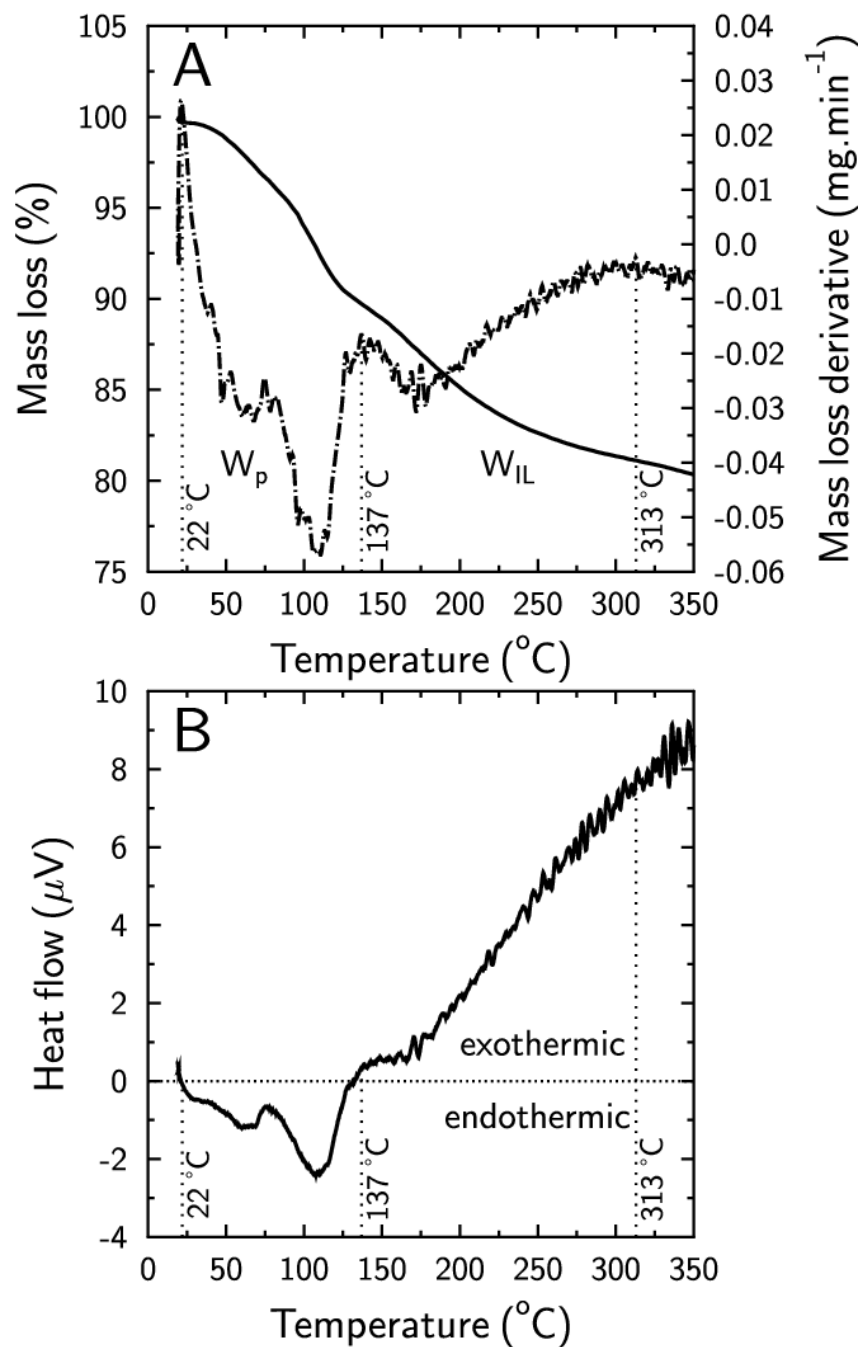


Fig. S3. A: TGA results for micro-GR(SO₄). Full line: mass loss (%); Dash line: mass loss derivative (mg·min⁻¹); W_P= interparticle (capillary) pore water; W_{IL}= interlayer water. B: DSC results

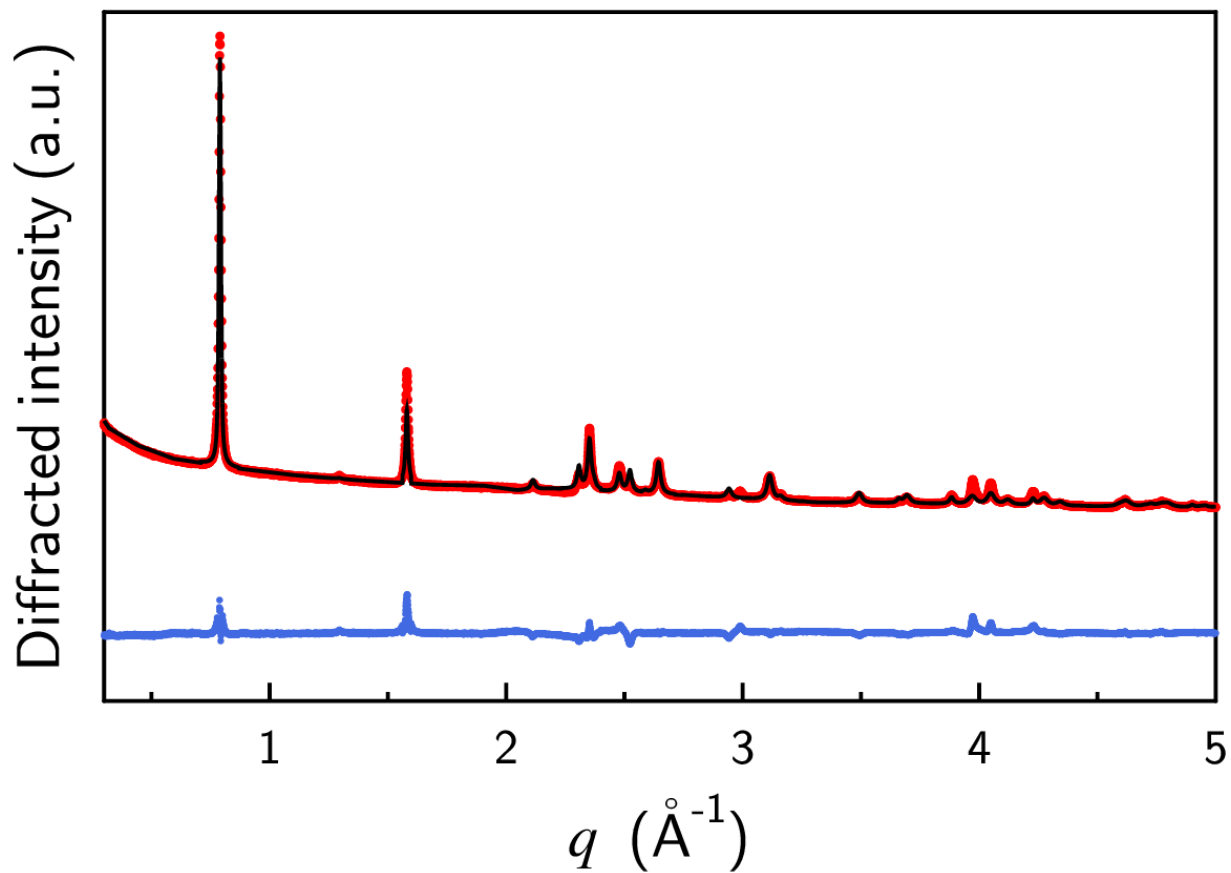


Fig. S4: Rietveld refinement results (black line) on micro-GR(Cl) XRD pattern (red line). Blue line is the residue between the data and the refinement results.

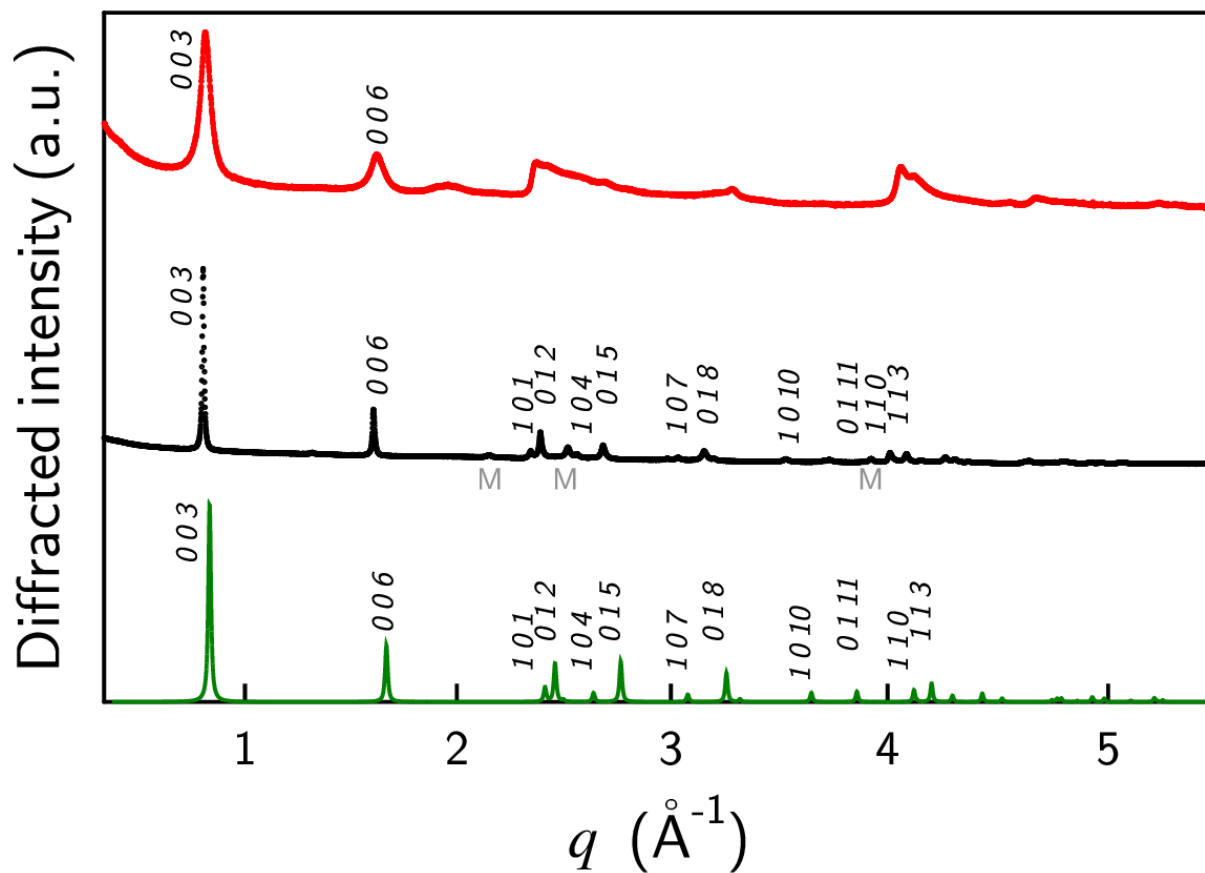


Fig. S5: XRD patterns of Fougerite³ (green line), micro-GR(Cl) (black line) and nano-GR(Cl) (red line). M: magnetite impurities in micro-GR(Cl). Intensities were normalized to the maximum intensity of 003 reflection.

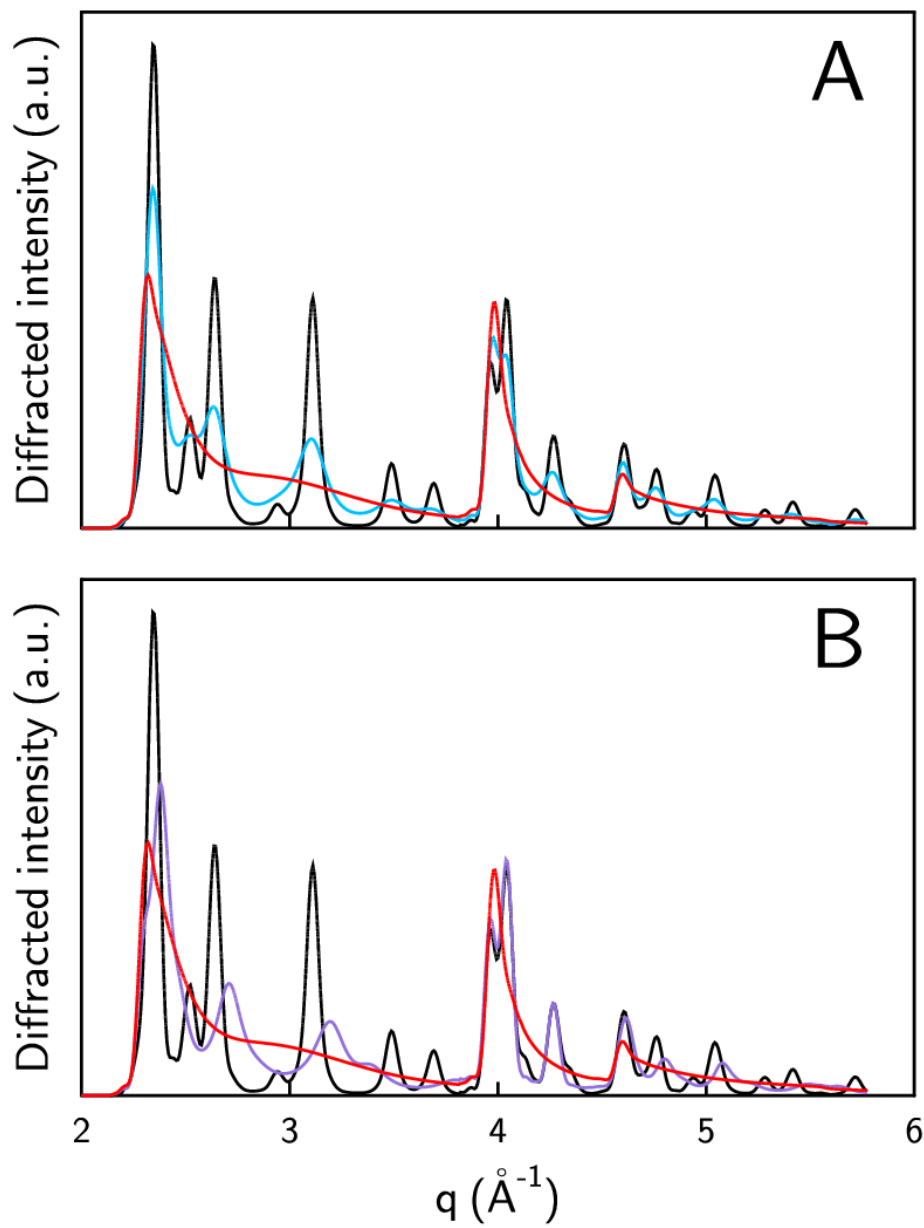


Fig. S6: Influence of stacking defects on micro-GR(Cl). Black line: initial micro-GR XRD pattern – 0 % stacking defects (A and B). Red line: 100 % stacking defects = turbostraticity (A and B). Light blue line: 50 % stacking defects in the micro-GR(Cl) model (A). Purple line: two coherently stacked green rust sheets on average, assuming a lognormal distribution (B).

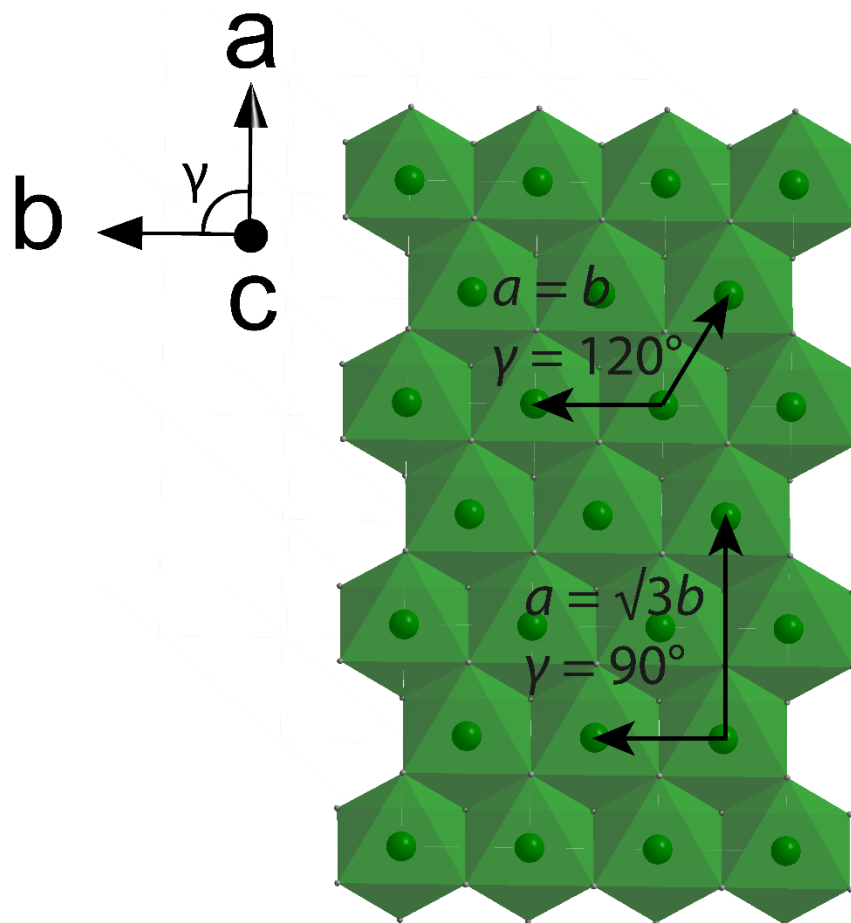


Fig. S7: Two equivalent hexagonal layer symmetries. If the layer symmetry is lowered, a becomes different from $\sqrt{3} \times b$ and the layer would not be hexagonal anymore.

Table S1. Nomenclature and concentrations of solutions used for batch experiments

Name	Concentration NaCl (mmol.L⁻¹)	Concentration Na₂SO₄ (mmol.L⁻¹)
Cl50	50	0
S25	0	25
S15	0	15
S5	40	5
S2.4	45	2.4
S1	48	1
S0.5	49	0.5

Table S2. Protocol for the batch exchange experiments of micro-GR (see Table S1 for nomenclature of solutions, AEC = anionic exchange capacity, K_{ex} = selectivity coefficient, E= Surface equivalent fraction)

Protocol	Exp S25	Exp S5	Exp S2.4	Exp S1	Exp S0.5
Equilibrium phase	200 mL Cl50				
Rinsing 1	30-40 mL Milli-Q Water Direct Filtration				
Exchange phase 1 - 1	200 mL S25	200 mL S5	20 mL S2.4	200 mL S1	200 mL S0.5
2	200 mL S25	200 mL S5	40 mL S2.4	200 mL S1	200 mL S0.5
3	200 mL S25	200 mL S5	60 mL S2.4	200 mL S1	200 mL S0.5
4	<i>End of this experiment</i>	200 mL S5	100 mL S2.4	200 mL S1	200 mL S0.5
5		200 mL S5	200 mL S2.4	200 mL S1	200 mL S0.5
6			200 mL S2.4		
Rinsing 2	30-40 mL Milli-Q Water Direct Filtration				
Exchange phase 2 - 1		200 mL S25	200 mL S15	200 mL S25	200 mL S25
2			200 mL S15	200 mL S25	
Obtained parameters	Exchange stoichiometry + AEC	Log K_{ex} + E			

Table S3. Protocol for the batch exchange experiments of nano-GR (see Table S1 for nomenclature of solutions, AEC = anionic exchange capacity, K_{ex} = selectivity coefficient, E= Surface equivalent fraction)

Protocol	Exp S25	Exp S5	Exp S2.4
Equilibrium phase	200 mL Cl50		
Rinsing 1	30-40 mL Milli-Q Water Direct Filtration		
Exchange phase 1 - 1	200 mL S25	200 mL S5	10 mL S2.4
2	200 mL S25	200 mL S5	10 mL S2.4
3	200 mL S25	200 mL S5	10 mL S2.4
4	<i>End of this experiment</i>	200 mL S5	15 mL S2.4
5		200 mL S5	20 mL S2.4
6			20 mL S2.4
Rinsing 2	30-40 mL Milli-Q Water Direct Filtration		
Exchange phase 2 - 1		200 mL S25	200 mL S15
2			200 mL S15
Obtained parameters	Exchange stoichiometry + AEC	Log K_{ex} + E	

Table S4. Stoichiometries of Fe, Co, Cl and S contents in studied samples determined by EPMA (on the basis of Fe+Co = 1). Each number is an average on the number of independent measurements (n; \pm standard deviation). Fe(III) stoichiometry is inferred from Cl stoichiometry or SO₄ stoichiometry times 2 and Fe(II)=Fe - Fe(III).

Sample	n	Fe	Co	Fe(III)	Fe(II)	Cl	S
Micro-	61	0.67 \pm	0.33 \pm	0.25 \pm	0.42 \pm	0.25 \pm	0 \pm 0
GR(Cl)		0.04	0.04	0.04	0.08	0.04	
Micro-	49	0.66 \pm	0.34 \pm	0.22 \pm	0.44 \pm	0 \pm 0	0.11 \pm
GR(SO₄)		0.02	0.02	0.02	0.04		0.01
Nano-	35	0.49 \pm	0.51 \pm	0.2 \pm	0.29 \pm	0.2 \pm	0 \pm 0
GR(Cl)		0.05	0.05	0.03	0.06	0.03	
Nano-	53	0.52 \pm	0.48 \pm	0.16 \pm	0.37 \pm	0 \pm 0	0.08 \pm
GR(SO₄)		0.03	0.03	0.02	0.05		0.01

References

- (1) Muniz, F. T.; Aurélio, M.; Miranda, R.; Morilla, C.; Santos, D.; Sasaki, J. M. The Scherrer equation and the dynamical theory of X-ray diffraction. *Acta Crystallogr.* **2016**, *72*, 385–390.
- (2) Plançon, A. CALCIPOW: a program for calculating the diffraction by disordered lamellar structures. *J. Appl. Crystallogr.* **2002**, *35*, 377–377.
- (3) Trolard, F.; Bourrié, G.; Abdelmoula, M.; Refait, P.; Feder, F. Fougerite, a new mineral of the pyroaurite-iowaite group: Description and crystal structure. *Clays Clay Miner.* **2007**, *55*, 323–334.