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Supporting information for article:

Whole-nanoparticle atomistic modelling of the schwertmannite structure from total scattering data

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S1. RMC-DSE refinement code

In order to study the structure of schwertmannite a specific routine (RMC-DSE) for the refinement of nanoparticles was built. In this routine a starting model was refined by applying an algorithm similar to Reverse Monte Carlo (RMC) [1]. As commonly done in the RMC approach, small atomic displacements were randomly applied simulating the thermal and the surface relaxation disorders. The displacements were accepted or rejected on the basis of the agreement between experimental and calculated structural functions. Structure Factor and their Fourier Transform related Pair Distribution Function (PDF) were simultaneously used in the optimization procedure.
To speed up the calculation the most time-consuming part of the code was allowed to run on a fast graphics processing unit (GPU). The whole (RMC-DSE) routine was written in C/C++/CUDA [2].

The Structure Factor S(Q) of the starting model was calculated through the Debye Scattering Equation (DSE) $I_{coh}(Q)$, which represents the coherent scattering contribution to the X-ray diffraction powder pattern:

$$I_{coh}(Q)=\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}f_i(Q)f_j(Q)\frac{\sin(Qr_{ij})}{Qr_{ij}}$$

$$Q=4\pi\sin(\theta/\lambda)$$

where q is the scattering vector being theta the half scattering angle and lambda the wavelength of the incident radiation; N is the total number of atoms; $f_i(Q)$ is the atomic scattering factor of the i-th atom and r_{ij} is the distance between the atoms i and j.

$$S(Q)=\frac{I_{coh}(Q)-\langle f(Q)^2\rangle}{\langle f(Q)\rangle^2}+1$$

$$\langle f(Q)^2\rangle=\sum_{m=1}^{M}x_m f_m(Q)^2$$

$$\langle f(Q)\rangle^2=\left(\sum_{m=1}^{M}x_m f_m(Q)\right)^2$$

where x_m is the molar fraction of the element m, f_m is the atomic form factor of the element m and M is the number of atomic species.

The PDF function is calculated applying the Fourier Transform to the S(Q), which is damped at Q_{max} by the Hann Function:

The calculated functions were compared with the corresponding experimental functions using the $\chi 2$ parameter:

$$\chi^2 = \frac{W_S}{\sigma^2}\frac{\sum^{NQ}(S_{exp}(Q)-S_{calc}(Q))^2}{NQ} + \frac{W_{PDF}}{\sigma^2}\frac{\sum^{NR}(PDF_{exp}(r)-PDF_{calc}(r))^2}{NR}$$

where W_S and W_{PDF} can balance the weight of the each contribution, ♦ is called the temperature factor, NQ and NR are the number of points of the S(Q) and PDF functions. The temperature factor can be tuned to allow a smaller or a greater number of moves in order to avoid local minimum traps.
The optimization procedure can be summarized as follows:

- One atom is randomly chosen and its coordinates are randomly modified within a maximum displacement value. The new coordinates should satisfy constraints over the minimum and the maximum distance allowed between neighboring atoms. A new atomic configuration is then obtained.
- New S(Q) and their Fourier Transform are calculated.
- In order to reduce the computation time the new S(Q) is calculated as follows:

$$S'(Q) = S(Q) - \frac{2}{N}\sum_j f_k f_j \frac{\sin(Qr_{kj})}{Qr_{kj}} + \frac{2}{N}\sum_j f_k f_j \frac{\sin(Qr'_{kj})}{Qr'_{kj}}$$

where k is the moved atom, r_{kj} and r'_{kj} are the distances between atoms k and j before and after the move, respectively. In this way, only the contributions of the moved atom with the others are taken into account. Furthermore, the two contributions are simultaneously calculated through parallel computing using an Nvidia GeForce gtx 690 GPU.
The Fourier Transform of the S'(Q) provides a new PDF' and a new χ'^2 is calculated. If the new value of the agreement parameter is less than the old value the move is accepted. If not the move could be accepted according with the conditional probability :

$$rnd[0;1] \leq e^{[-(\chi'^2-\chi^2)/2]}$$

The smaller the difference between χ'^2 and χ^2, the higher the probability.

- Another atom is then randomly chosen and moved and the recursive procedure continues until convergence.

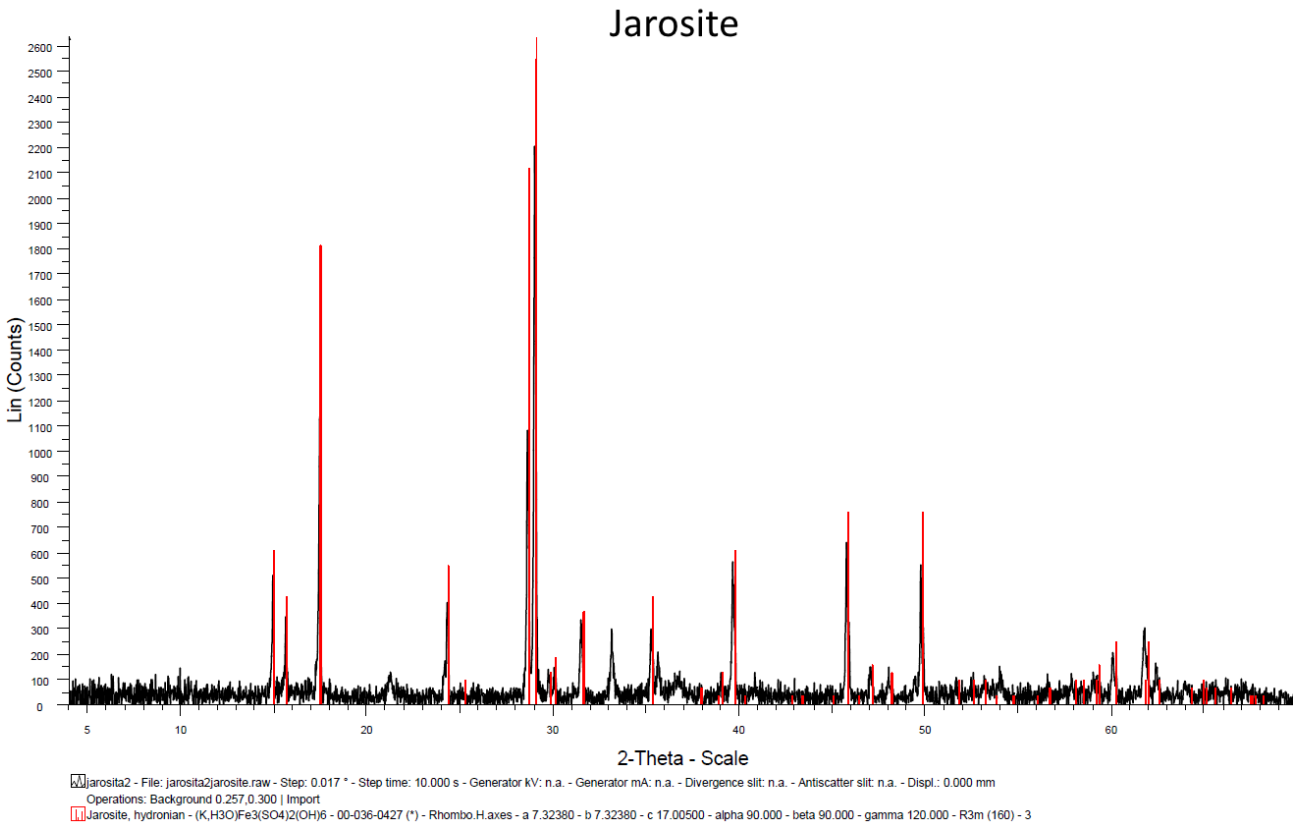
References

[1] McGreevy R.L. and Pusztai L., Molecular Simulation, 1, 359-367, 1988.

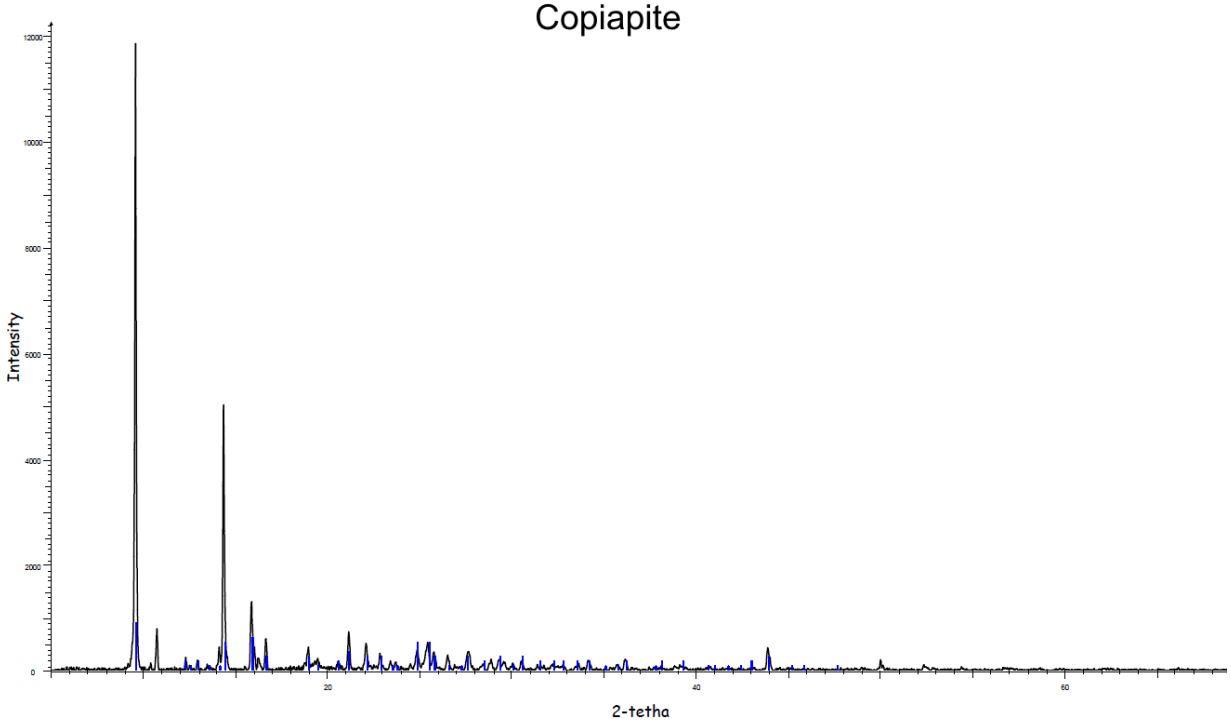
[2] Cuda Programming Guide 2.3 Nvidia Corp.

X-ray diffraction characterization of halotrichite and copiapite samples

The experimental diffraction patterns of jarosite, copiapite and halotrichite samples are shown in Figure S1, together with the reflections for each phase, from PDF files #00-036-0427 (jarosite), #00-039-1387 (halotrichite) and #00-035-0583 (copiapite). A small level of impurities (not identified) has been found in the halotrichite sample. These does not seem to affect the results of the S-XANES analyses, with the halotrichite sample not showing any pre-peak, as expected.

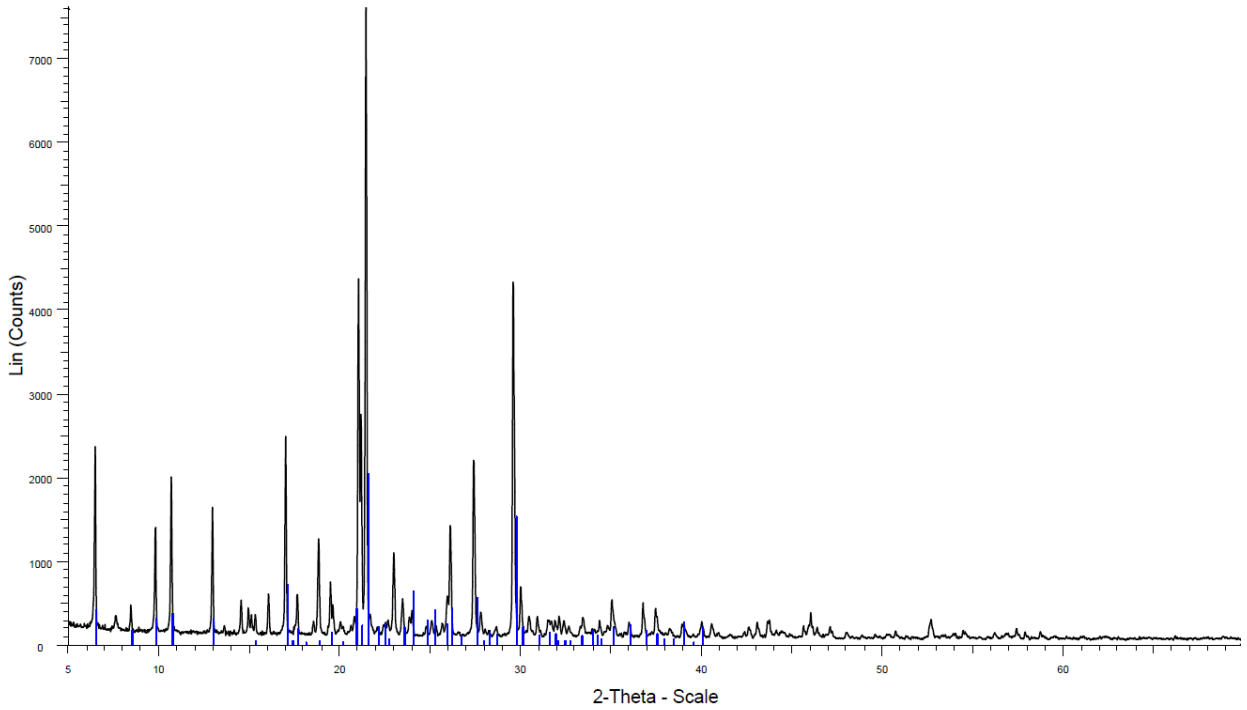


Copiapite



File: copiapite.raw - Step: 0.026 ° - Step time: 6.000 s - Anode: Cu - Generator kV: 40 kV - Generator mA: 40 mA - Divergence slit: 0.298 ° - Antiscatter slit: 0.298 ° - Displ.: 0.000 mm
Copiapite - FeFe4(SO4)6(OH)2·20H2O - 00-035-0583 (I) - Triclinic - a 7.33700 - b 18.76000 - c 7.37900 - alpha 91.460 - beta 102.180 - gamma 98.950 - P-1 (2) - 1

Halotrichite



Halotrichite - File: Halotrichite.raw - Step: 0.026 ° - Step time: 7.000 s - Anode: Co - Generator kV: 40 kV - Generator mA: 39 mA - Divergence slit: n.a. - Antiscatter slit: n.a. - Displ.: 0.000 mm
Operations: Import
Halotrichite - Fe+2Al2(SO4)4·22H2O - 00-039-1387 (I) - Monoclinic - a 6.19540 - b 24.26200 - c 21.26200 - alpha 90.000 - beta 100.300 - gamma 90.000 - P21/c (14) - 4

Schwertmannite S EXAFS

	Fit	Coordination 1	Proportion (%)	χ2	R-factor	Ind. Point	Variable	Ind. Variable	Red. χ2	Model 1	Model 2	F-test	Probability (%)
Sch-Nat	1	b. b. inner sp.	100	11.50	0.007	9.79	6	3.79	3.06	Fit 1	Fit 2	1.62	72.00
	2	b. b. inner sp.	50	21.36	0.013	9.79	4	5.79	3.69	Fit 1	Fit 3	1.26	64.00
	3	outer sp.	100	26.78	0.016	9.79	2	7.79	3.44				
Sch-Syn	1	b. b. inner sp.	75	20.76	0.008	13.10	7	6.10	3.40	Fit 1	Fit 2	43.85	99.99
	2	b. b. inner sp.	50	27.75	0.011	10.15	4	6.15	4.51	Fit 1	Fit3	2.05	83.00
	3	outer sp.	100	35.02	0.008	10.15	2	8.15	4.30				

b.b. inner sp.: bidentate binucleate inner-sphere

outer sp.: outer-sphere

Table S1. Results of the F-tests performed using different hypotheses. Only the inclusion of the fit2 (with two shells) yields a probability of statistical significance higher than 90%.

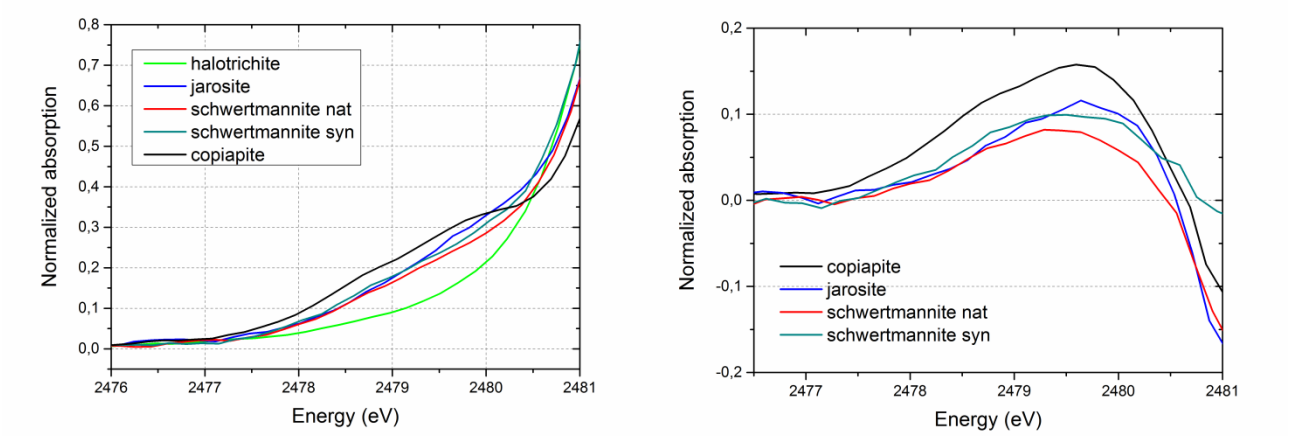


Figure S2. Left: Detail of the pre-edge region of the normalized X-ray absorption spectroscopy spectra of schwertmannite and the references. Right: Difference normalized spectra using the spectrum of halotrichite (free sulfate) as reference.

Rietveld refinement

Goethite starting model CIF file

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_journal_year 1999
_journal_page_first 895
_journal_page_last 904
_publ_section_title
;
 In situ study of the goethite-hematite phase transformation by real time
 synchrotron powder diffraction
 Sample at T = 25 C
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_database_code_amcsd 0002226
_chemical_formula_sum 'Fe H O2'
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_cell_length_b 3.0128
_cell_length_c 4.5800
_cell_angle_alpha 90
_cell_angle_beta 90
_cell_angle_gamma 90
_cell_volume 136.791
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  'x,1/2-y,z'
  '-x,1/2+y,-z'
  '1/2-x,1/2+y,1/2+z'
  '1/2+x,1/2-y,1/2-z'
  '1/2+x,y,1/2-z'
  '1/2-x,-y,1/2+z'
  '-x,-y,-z'
loop_
_atom_site_label
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_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
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H -0.10100 0.25000 -0.39900 0.06000
O1 -0.19900 0.25000 0.28500 0.04600
O2 -0.05170 0.25000 -0.19600 0.04600

Schwertmannite starting model CIF file

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'Timon V'
'Roman-Ross G'
'Cuello G J'
'Daniels J E'
'Ayora C'
_journal_name_full 'American Mineralogist'
_journal_volume 95
_journal_year 2010
_journal_page_first 1312
_journal_page_last 1322
_publ_section_title
;
 The structure of schwertmannite, a nanocrystalline iron oxyhydroxysulfate
 Note: Model 1, positions of sulfate groups not determined
;
_database_code_amcsd 0018670
_chemical_compound_source 'Monte Romero mine (Iberian Pyrite Belt), Spain'
_chemical_formula_sum 'Fe O2'
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_cell_length_b 6.002
_cell_length_c 10.514
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_cell_angle_beta 92.6
_cell_angle_gamma 90.0
_cell_volume 682.157
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_atom_site_fract_z
_atom_site_U_iso_or_equiv
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Fe  0.14000  0.00000  0.64500  0.00200
O  0.28800  0.00000  0.32200  0.00900
O  0.04300  0.00000  0.33600  0.00900
O  0.33500  0.00000  0.69000  0.00900
O  0.32500  0.00000  0.94600  0.00900
Fe  0.85700  0.25000  0.61100  0.00200
Fe  0.70000  0.25000  0.09300  0.00200
O  0.78700  0.25000  0.79600  0.00900
O  0.54000  0.25000  0.81000  0.00900
O  0.86100  0.25000  0.15900  0.00900
O  0.82400  0.25000  0.41900  0.00900
Fe  0.66900  0.00000  0.81100  0.00200
Fe  0.86600  0.00000  0.32000  0.00200
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O  0.95600  0.00000  0.61200  0.00900
O  0.66400  0.00000  0.26000  0.00900
O  0.67400  0.00000  0.00200  0.00900
Fe  0.15100  0.25000  0.35200  0.00200
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O  0.17500  0.25000  0.52700  0.00900
Fe  0.33700  0.50000  0.14200  0.00200
Fe  0.14400  0.50000  0.64800  0.00200
O  0.28800  0.50000  0.32200  0.00900
O  0.04300  0.50000  0.33600  0.00900
O  0.33500  0.50000  0.69000  0.00900
O  0.32500  0.50000  0.94600  0.00900
Fe  0.84600  0.75000  0.60600  0.00200
Fe  0.69600  0.75000  0.09500  0.00200
O  0.78700  0.75000  0.79600  0.00900
```

O 0.54200 0.75000 0.81000 0.00900
O 0.85700 0.75000 0.15700 0.00900
O 0.82400 0.75000 0.41900 0.00900
Fe 0.66600 0.50000 0.80400 0.00200
Fe 0.86500 0.50000 0.32200 0.00200
O 0.71100 0.50000 0.62600 0.00900
O 0.95600 0.50000 0.61200 0.00900
O 0.66400 0.50000 0.26000 0.00900
O 0.67400 0.50000 0.00200 0.00900
Fe 0.15300 0.75000 0.33800 0.00200
Fe 0.36300 0.75000 0.83500 0.00200
O 0.21100 0.75000 0.15000 0.00900
O 0.45600 0.75000 0.13800 0.00900
O 0.16500 0.75000 0.78600 0.00900
O 0.17500 0.75000 0.52800 0.00900

RMC-DSE refinement

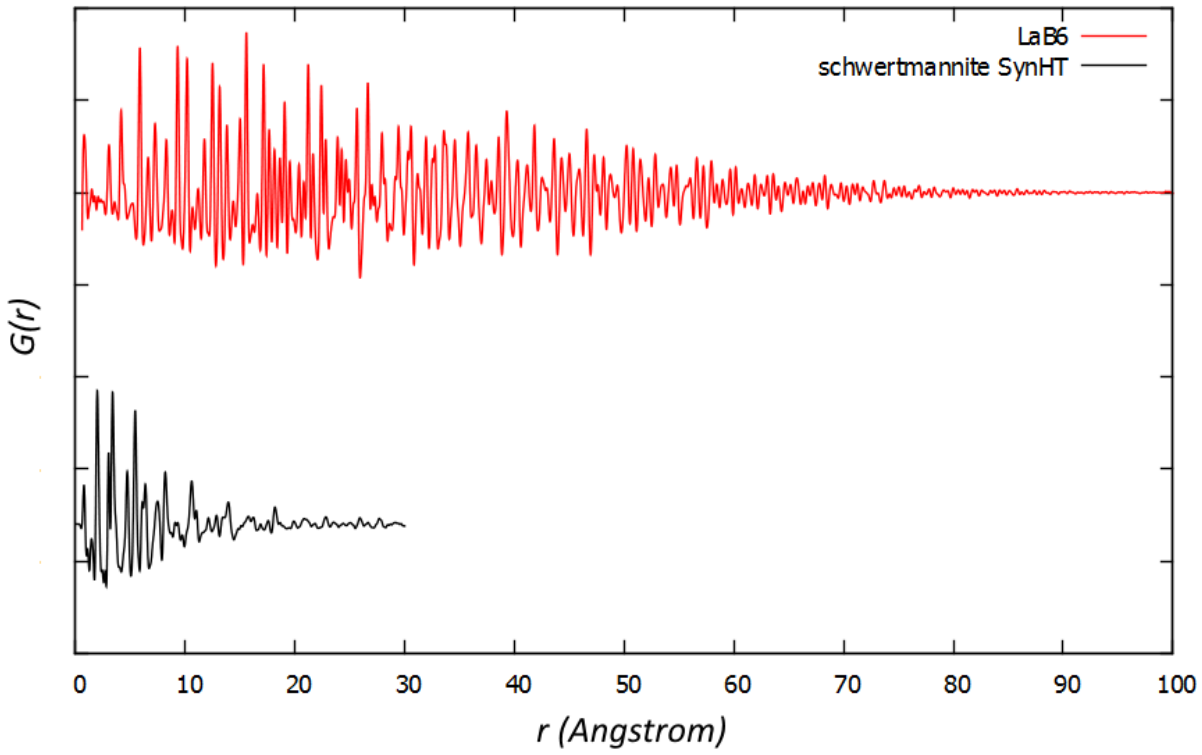

Figure S3. Pair distribution functions of a crystalline standard (LaB_6) and of schwertmannite. The dampening of the LaB6 PDF is purely due to instrumental resolution effects. For schwertmannite, the dampening is dominated by the microstructure. This effect of an exponential decay in the real-space is translated into peak width in the reciprocal space.

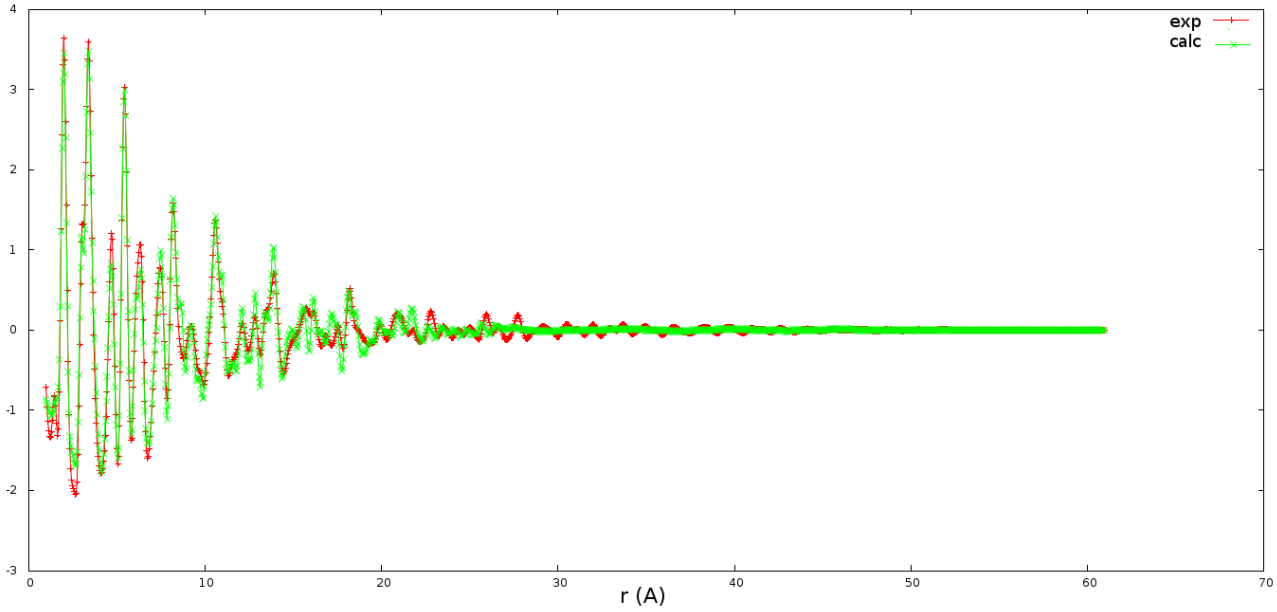

Figure S4. Full experimental and calculated PDFs for the sample SynHT contemplating the presence of goethite so as to appreciate the whole nanoparticle size effect.