Supplementary information

Whewellite, $CaC_2O_4 \cdot H_2O$: structural study by a combined NMR, crystallography and modelling approach

Hélène Colas,[a] Laure Bonhomme-Coury,[a] Cristina Coelho Diogo,[b] Frederik Tielens,[a] Florence Babonneau,[a] Christel Gervais,[a] Dominique Bazin,[a] Danielle Laurencin[c], Mark E. Smith,[d,e] John V. Hanna,[e] Michel Daudon,[f] and Christian Bonhomme*[a]

Figure S1. Powder XRD patterns of: a) synthetic whewellite, $CaC_2O_4 \cdot H_2O$. b) a mixture of whewellite, $CaC_2O_4 \cdot H_2O$ and wedellite, $CaC_2O_4 \cdot 2H_2O$ (obtained by precipitation).

Figure S2. Calculated powder XRD patterns for various models of $CaC_2O_4 \cdot H_2O$: non relaxed data (see Daudon *et al*., 2009)[5], in blue; all atoms relaxed, in red; and all atoms and cell relaxed, in green.

Table S1. Cell parameters after DFT optimization of the whewellite structure (from: Daudon *et al*., *J. Appl. Crystallogr.*, 2009, **42**, 109).

Table S2. Comparison of bond lengths after DFT relaxation.

Table S3. GIPAW data for all structural models.

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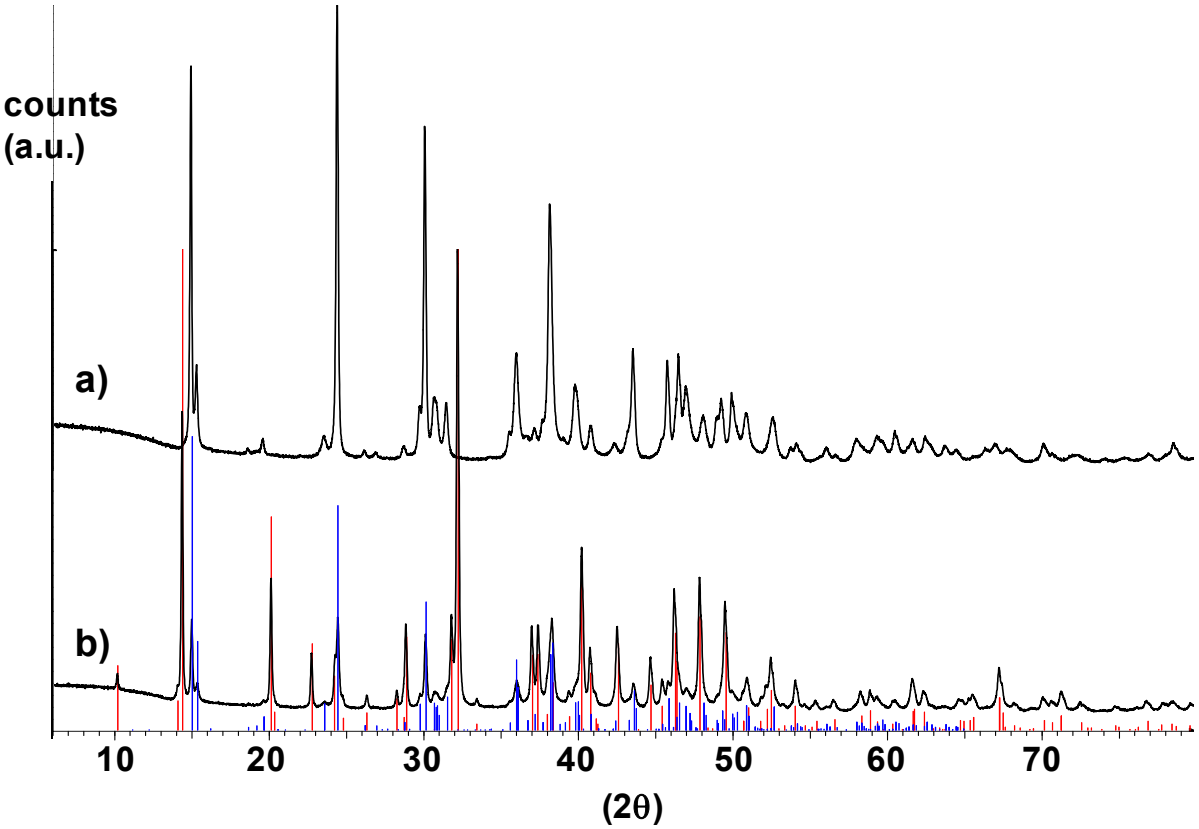

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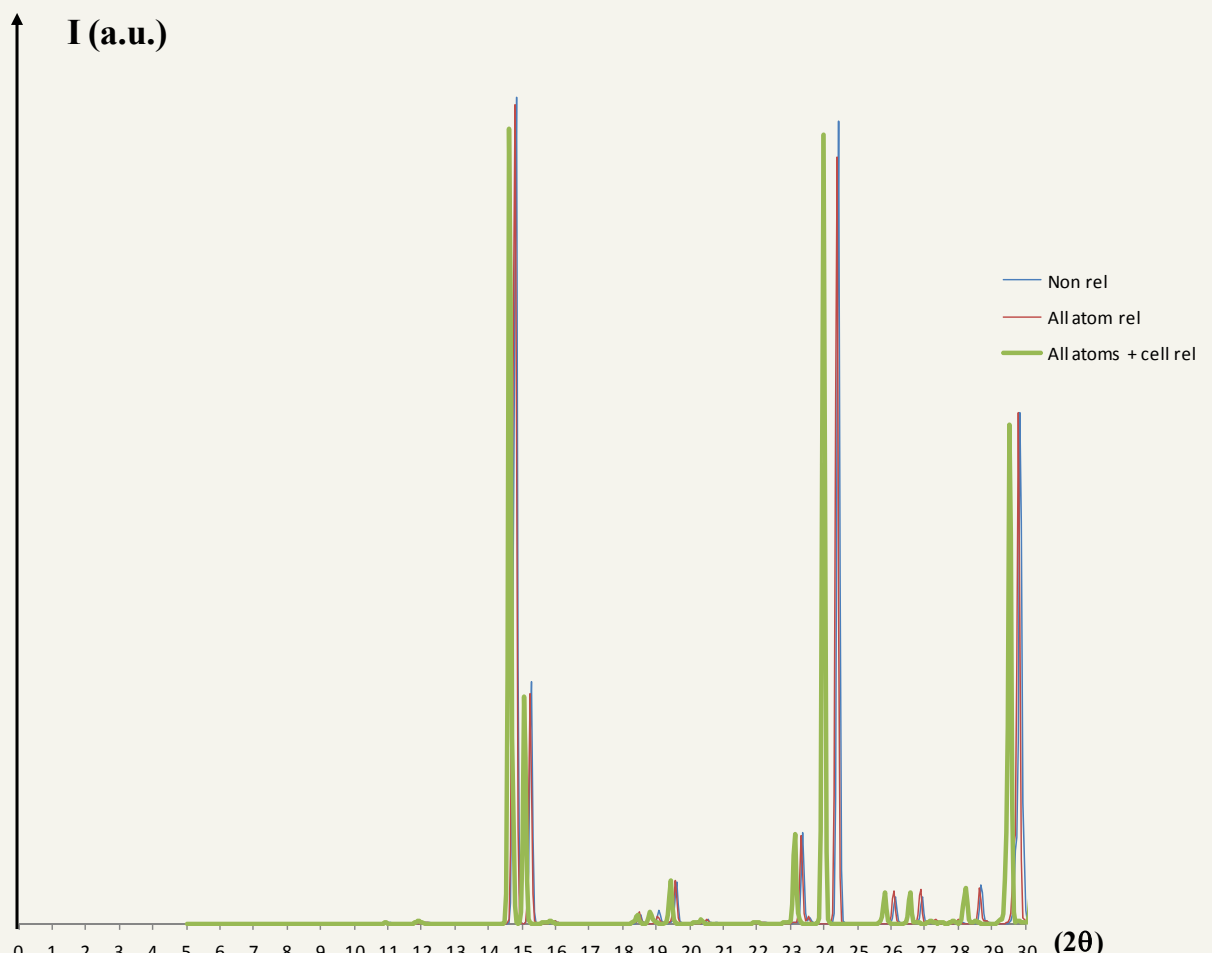


Table S1. Cell parameters after DFT optimization of the whewellite structure (from: Daudon *et al*., *J. Appl. Crystallogr.*, 2009, **42**, 109).

	Optimized cell parameters	**Experimental cell parameters**
	(this work)	**(Daudon, 2009)** **monoclinic, $P2_1/c$**
a/Å	6.3664	6.316 (2)
b/Å	14.7597	14.541 (3)
c/Å	10.1451	10.116 (5)
β/°	109.2977	109.1 (3)
vol./Å^3	899.7437	878.2 (16)

Table S2. Comparison of bond lengths after DFT relaxation.

d : bond length in Å , $\Delta d = d_{rel} - d_{non\ rel}$

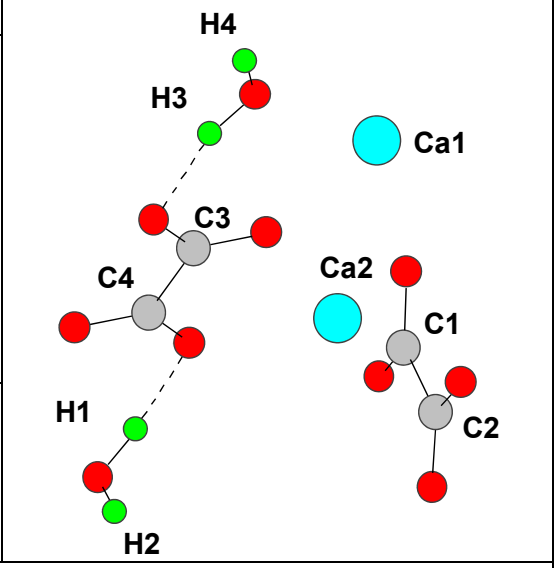
from: Daudon *et al*., *J. Appl. Crystallogr.*, 2009, **42**, 109.

	Non relaxed		All atoms relaxed		All atoms + cell relaxed	
Oxalate group						
	d		d	Δd	d	Δd
C1-C2	1.5657		1.5584	-0.0073	1.5735	0.0078
C3-C4	1.5411		1.5382	-0.0029	1.5484	0.0073
Calcium polyhedra						
Ca1-W2	2.4205		2.4370	0.0165	2.4249	0.0044
Ca1-O1	2.4270		2.4171	-0.0099	2.4610	0.0340
Ca1-O4	2.4311		2.4165	-0.0146	2.4350	0.0039
Ca1-O6	2.4331		2.4136	-0.0195	2.4565	0.0234
Ca1-O4	2.4622		2.4265	-0.0357	2.4846	0.0224
Ca1-O3	2.4622		2.4547	-0.0075	2.4684	0.0062
Ca1-O5	2.4639		2.5163	0.0524	2.5218	0.0579
Ca1-O7	2.4951		2.5081	0.0130	2.5006	0.0055
<Ca1-O>	2.4494		2.4487		2.4691	0.0197
Ca2-O2	2.4160		2.3995	-0.0165	2.4163	0.0003
Ca2-O2	2.4196		2.3998	-0.0198	2.4454	0.0258
Ca2-O7	2.4274		2.4096	-0.0178	2.4493	0.0219
Ca2-O3	2.4323		2.4168	-0.0155	2.4710	0.0387
Ca2-O8	2.4409		2.4737	0.0328	2.4777	0.0368
Ca2-O1	2.4530		2.4431	-0.0099	2.4631	0.0101
Ca2-O6	2.4624		2.4643	0.0019	2.4488	-0.0136
Ca2-W1	2.5623		2.5711	0.0088	2.5893	0.0270
<Ca2-O>	2.4517		2.4472		2.4701	0.0184
Hydrogen bonding	D-H	H…A	D-H	H…A	D-H	H…A
W1-H1…O8	0.9902	1.6815	1.0252	1.6244	1.0085	1.6474
W1-H2…O5	0.9424	2.0454	0.9986	1.8853	0.9837	1.9573
W2-H3…O5	0.9669	1.7546	1.0046	1.7528	0.9908	1.7542
W2-H4…W1	0.9592	1.8829	1.0060	1.7797	0.9897	1.7542

Table S3. GIPAW data for all structural models.

Tazzoli et al. (American Mineralogist 1980)

	H_2O relaxed			All atoms relaxed		
	δ_{iso}			δ_{iso}		
C1	168.4			169.1		
C2	170.2			168.2		
C3	170.6			170.8		
C4	169.1			169.2		
H1	8.9			9.1		
H2	1.9			2.8		
H3	6.1			6.0		
H4	5.3			5.7		
	δ_{iso}	C_Q	η	δ_{iso}	C_Q	η
Ca1	6.2	1.38	0.73	7.2	-1.43	0.70
Ca2	10.7	-1.62	0.74	12.8	-1.78	0.67



Daudon et al. (Journal of Applied Crystallography 2009)

	Non relaxed			H atoms relaxed			All atoms relaxed			All atoms + cell relaxed		
	δ_{iso}			δ_{iso}			δ_{iso}			δ_{iso}		
C1	168.9			168.9			168.9			168.1		
C2	168.3			168.3			167.9			167.6		
C3	171.1			171.3			170.8			169.9		
C4	170.9			170.9			169.2			168.2		
H1	7.2			8.8			9.1			8.2		
H2	-0.1			1.8			2.6			1.7		
H3	5.1			6.7			6.1			5.8		
H4	3.0			4.9			5.6			4.6		
	δ_{iso}	C_Q	η	δ_{iso}	C_Q	η	δ_{iso}	C_Q	η	δ_{iso}	C_Q	η
Ca1	5.5	1.25	0.77	5.9	1.23	0.79	6.0	-1.33	0.58	-1.7	1.34	0.99
Ca2	10.6	-1.50	0.73	10.8	-1.47	0.74	12.1	-1.72	0.70	4.2	-1.68	0.59