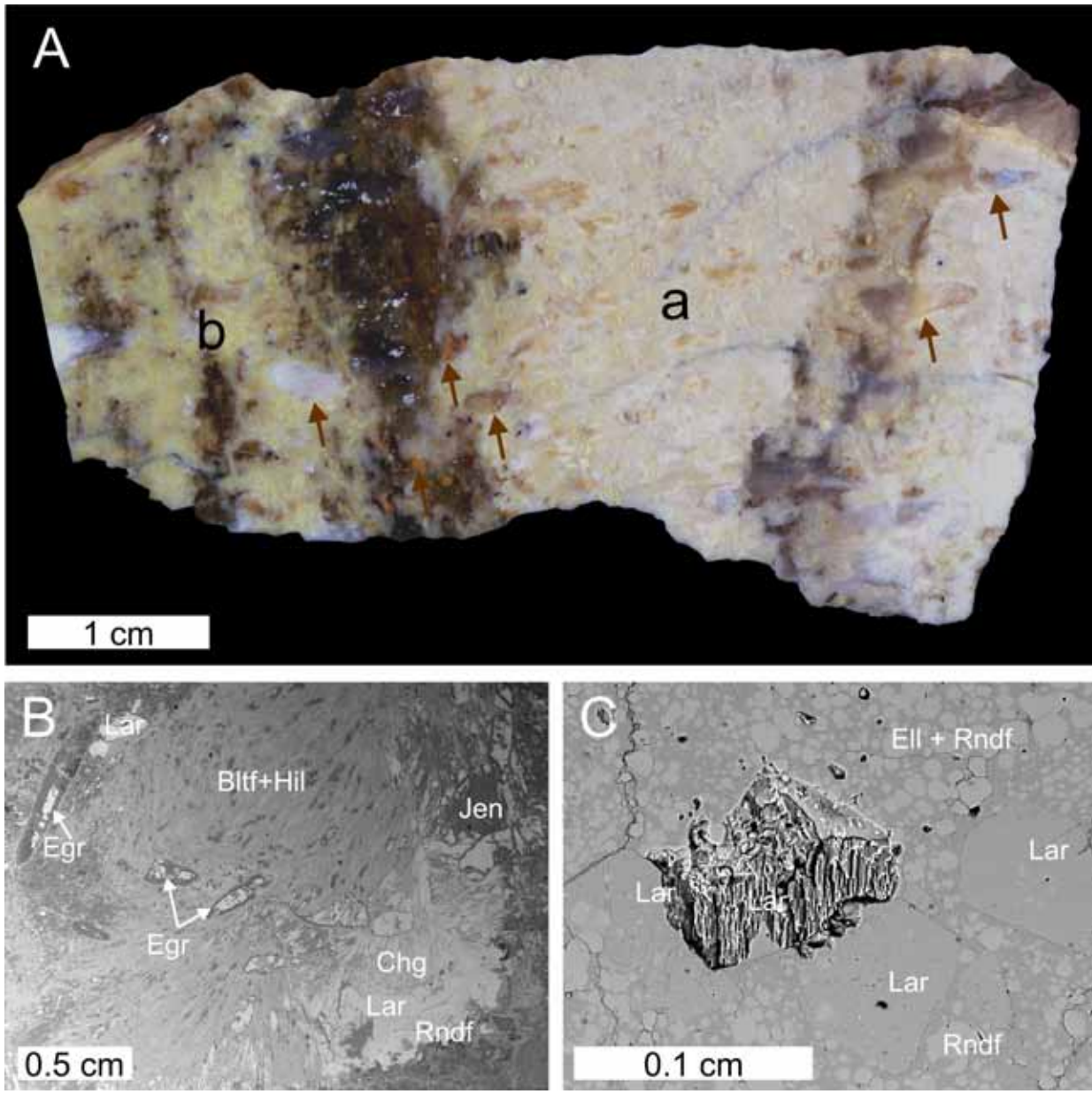

Figure 1. (supplementary materials). A. Altered larnite skarn comprising a cream-colored zone (**a**) containing edgrewite (Fig. 1B) and a yellowish zone (**b**) commonly stained brown-dark by iron hydroxides and sulfates. Arrows point to lenticular aggregates with larnite relics (e.g., Fig. 1C) and to yellow and light-brown "hydrogarnet" pseudomorphs with shapes resembling mafic phenocrysts (pyroxene, amphibole, biotite) in ignimbrite. (**b**) Backscattered electron image of an area in the cream-colored zone showing altered skarn with larnite and rondorfite relics and characteristic atoll-like microstructure with edgrewite. (**c**) Backscattered electron image of a primary skarn relic with larnite and rondorfite crystals in hydroxylellestadite. Bltf = bultfonteinite, Chg = chegemite-fluorchegemite, Egr = edgrewite, Ell = hydroxylellestadite, = jennite, Lar = larnite, Hil = hillebrandite, Rndf = rondorfite, Trb = trabzonite.

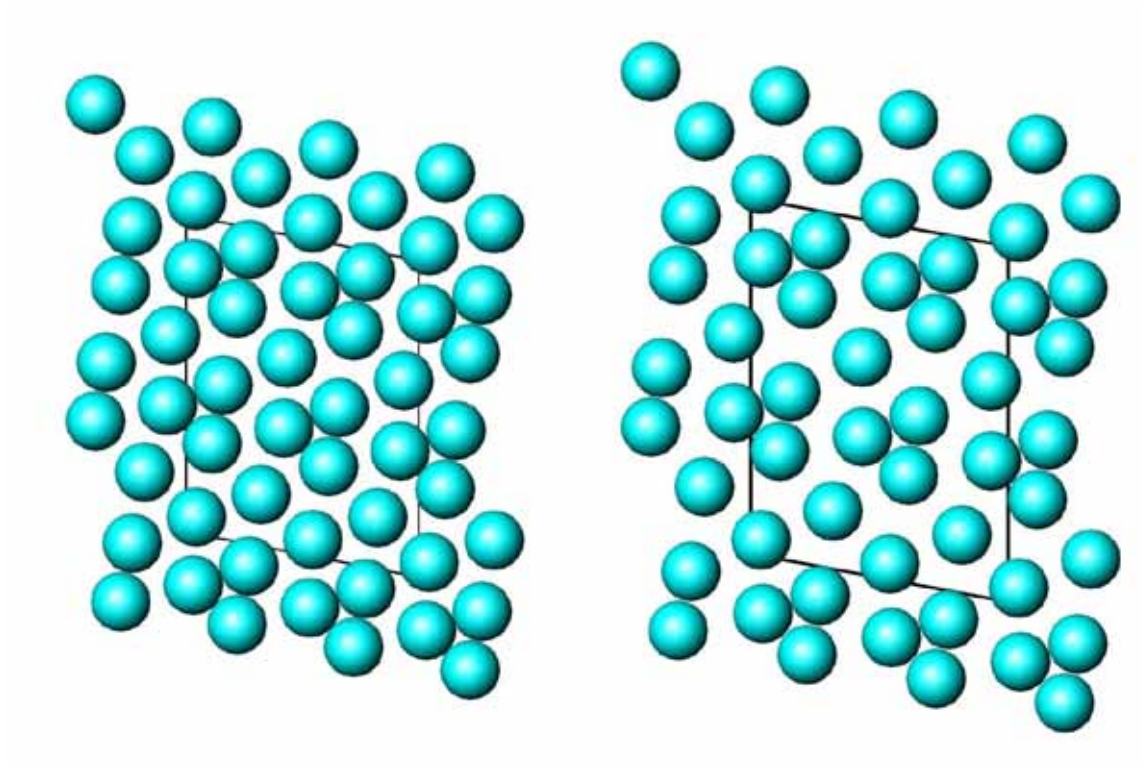

FIGURE 7. (supplementary materials). Left: Anion arrangement in clinohumite $Mg_9(SiO_4)_4(F,OH)_2$ viewed along the short **a** axis ($P2_1/c11$ setting); each oxygen is represented as a sphere of 1.3 Å radius. Right: corresponding anion arrangement in the structure of edgrewite $Ca_9(SiO_4)_4(F,OH)_2$. The large Ca at octahedral sites stretches the close-packed anion arrangement.

Table 2. (supplementary materials) Calculated powder diffraction pattern of edgrewite (Cu$K\alpha_{1+2}$ = 1.540598, 1.544426; geometry: Debye-Scherrer, fixed slit, no anomalous dispersion;
condition: $I > 4$)

h	*k*	*l*	2Theta	d_{hkl}	I_{rel}	*h*	*k*	*l*	2Theta	d_{hkl}	I_{rel}
0	0	1	5.834	15.1377	4	2	1	2	38.755	2.3217	7
0	2	-1	15.866	5.5811	21	1	1	-7	44.878	2.0181	9
0	2	1	17.905	4.9501	5	1	5	1	45.759	1.9813	6
0	2	-2	17.912	4.9482	11	2	2	4	47.652	1.9069	53
1	0	2	21.078	4.2116	16	2	2	-5	47.661	1.9065	54
0	2	2	21.430	4.1432	18	1	1	7	47.744	1.9034	5
0	2	-3	21.440	4.1413	14	2	4	-1	48.083	1.8908	36
1	1	2	23.306	3.8137	42	2	4	1	49.655	1.8345	11
0	0	4	23.489	3.7844	8	2	4	-3	49.663	1.8343	7
1	2	0	23.691	3.7525	10	0	6	1	50.465	1.8070	12
1	2	-1	23.693	3.7522	5	0	6	-4	50.479	1.8065	12
1	1	-3	25.119	3.5424	33	1	3	6	50.566	1.8036	14
1	2	-3	27.796	3.2070	4	1	5	3	50.919	1.7919	10
1	1	-4	29.336	3.0420	28	1	5	-6	52.640	1.7373	8
1	3	-1	29.461	3.0294	100	0	4	6	53.185	1.7208	9
0	0	5	29.480	3.0275	11	0	4	-8	53.211	1.7200	8
1	3	0	29.759	2.9997	24	1	3	-8	53.226	1.7196	9
0	2	4	30.864	2.8949	16	2	4	-5	54.191	1.6912	5
0	2	-5	30.877	2.8937	14	0	0	9	54.513	1.6820	34
1	3	1	31.219	2.8627	29	3	1	0	54.917	1.6705	6
0	4	-1	31.481	2.8395	7	0	6	3	55.658	1.6501	21
1	1	4	31.669	2.8231	79	0	6	-6	55.682	1.6494	21
1	3	-3	32.354	2.7648	65	3	1	2	56.710	1.6219	7
0	4	1	33.680	2.6590	11	1	7	-2	59.820	1.5448	19
0	4	-3	33.691	2.6581	9	3	3	-1	59.923	1.5424	5
1	3	2	33.705	2.6570	31	3	1	4	61.212	1.5130	5
1	1	-5	34.133	2.6247	55	3	3	-3	61.626	1.5038	5
2	0	0	35.389	2.5344	11	1	3	8	61.661	1.5030	6
1	2	4	35.689	2.5138	17	3	1	-5	62.729	1.4800	4
1	2	-5	35.700	2.5130	18	3	2	4	63.725	1.4592	7
1	4	-1	36.233	2.4773	24	3	2	-5	63.733	1.4591	7
2	1	0	36.321	2.4715	12	3	4	-1	64.081	1.4520	4
1	1	5	36.688	2.4476	5	1	3	-10	64.677	1.4400	5
1	3	3	37.036	2.4254	8						

Table 3. (supplementary materials) Calculated powder diffraction pattern of hydroxyledgrewite (Cu$K\alpha_{1+2}$ = 1.540598, 1.544426; geometry: Debye-Scherrer, fixed slit, no anomalous dispersion; condition: $I > 4$)

h	*k*	*l*	2Theta	d_{hkl}	I_{rel}	*h*	*k*	*l*	2Theta	d_{hkl}	I_{rel}
0	0	1	5.836	15.1320	4	0	4	-5	39.677	2.2698	4
0	2	-1	15.872	5.5792	20	2	1	-3	39.941	2.2554	4
0	2	1	17.909	4.9490	4	1	1	-7	44.897	2.0173	9
0	2	-2	17.919	4.9461	10	1	5	1	45.771	1.9808	6
1	0	2	21.084	4.2102	16	2	2	4	47.667	1.9063	52
0	2	2	21.434	4.1422	18	2	2	-5	47.680	1.9058	53
0	2	-3	21.449	4.1394	14	1	1	7	47.760	1.9028	5
1	1	2	23.312	3.8126	41	1	3	-7	48.063	1.8915	4
0	0	4	23.498	3.7830	7	2	4	-1	48.099	1.8902	35
1	2	0	23.698	3.7515	9	2	4	1	49.670	1.8340	11
1	2	-1	23.701	3.7510	5	2	4	-3	49.681	1.8336	7
1	1	-3	25.129	3.5410	32	0	6	1	50.478	1.8066	12
1	2	1	25.132	3.5405	3	0	6	-4	50.499	1.8059	12
1	2	-3	27.807	3.2057	4	1	3	6	50.580	1.8031	14
1	1	-4	29.348	3.0409	27	1	5	3	50.931	1.7915	10
1	3	-1	29.471	3.0285	100	1	5	-6	52.663	1.7366	8
0	0	5	29.491	3.0264	11	0	4	6	53.199	1.7204	9
1	3	0	29.768	2.9989	24	0	4	-8	53.237	1.7192	7
0	2	4	30.872	2.8941	16	1	3	-8	53.250	1.7188	8
0	2	-5	30.891	2.8924	14	2	4	-5	54.213	1.6906	5
1	3	1	31.227	2.8620	28	0	0	9	54.535	1.6813	33
0	4	-1	31.491	2.8386	7	3	1	0	54.935	1.6701	5
1	1	4	31.679	2.8222	78	0	6	3	55.672	1.6497	20
1	3	-3	32.367	2.7638	65	0	6	-6	55.707	1.6487	21
0	4	1	33.688	2.6583	11	3	1	2	56.728	1.6214	6
0	4	-3	33.704	2.6571	9	1	3	-9	58.804	1.5690	4
1	3	2	33.714	2.6564	31	1	7	-2	59.841	1.5443	18
1	1	-5	34.147	2.6236	55	3	3	-1	59.943	1.5419	5
2	0	0	35.400	2.5336	11	3	1	4	61.232	1.5125	5
1	2	4	35.699	2.5131	17	3	3	-3	61.648	1.5033	5
1	2	-5	35.715	2.5120	17	1	3	8	61.681	1.5026	6
1	4	-1	36.244	2.4765	24	3	1	-5	62.751	1.4795	4
2	1	0	36.332	2.4707	12	3	2	4	63.746	1.4588	7
1	1	5	36.700	2.4468	5	3	2	-5	63.757	1.4586	6
1	3	3	37.045	2.4248	8	3	4	-1	64.103	1.4515	4
2	1	2	38.766	2.3210	7	1	3	-10	64.708	1.4394	5

Table 5. (supplementary materials) Comparison of optical properties of Ca-humites

	Kumtyubeite	Chegemite	Chegemite	Edgrewite	Hydroxyledgrewite
	xenolith 1	xenolith 1	xenolith 7	xenolith 1	xenolith 1
X ^ c	15(2)°	0°	0°	12(2) °	12(2)°
Sign	–	–	–	+	+
2V	40-55°	72-88°	76-86	75-85°	75-85°
α	1.594(2)	1.621(2)	1.630(2)	1.621(2)	1.625(2)
β	1.605(2)	1.626(3)	1.636(2)	1.625(2)	1.629(2)
γ	1.608(2)	1.630(2)	1.640(2)	1.631(2)	1.635(2)
Δ	0.014	0.009	0.010	0.010	0.010

Table 6. (supplementary materials) Comparison of chemical compositions of Ca-humites

wt%	Kumtyubeite	Chegemite	Edgrewite
SiO_2	28.44	30.00	30.95
TiO_2	0.06	0.02	0.09
CaO	66.58	65.49	65.23
F	4.84	3.57	2.83
H_2O*	1.98	1.32	0.99
	101.90	100.39	100.09
O=F+Cl	2.04	1.50	1.19
	99.86	98.89	98.89
Ca	5.003	7.004	9.004
Si	1.994	2.994	3.987
Ti^{4+}	0.003	0.001	0.009
OH	0.926	0.876	0.846
F	1.074	1.126	1.154
Ca/Si	~2.5	~2.33	~2.25

formula calculated on 18(O+F+OH), * - calculated on charge balance

Table 8a. (supplementary materials) Anisotropic atomic displacement parameters (Å^2) for edgrewite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.0044(2)	0.0098(3)	0.0075(3)	0.0039(2)	-0.0010(2)	0.0002(2)
Ca2	0.00458(18)	0.0082(2)	0.00785(19)	0.00066(15)	0.00088(13)	0.00077(13)
Ca3	0.00553(18)	0.00596(19)	0.00842(19)	0.00282(15)	-0.00017(14)	0.00040(14)
Ca4	0.00513(18)	0.00561(19)	0.00779(19)	0.00211(14)	-0.00006(14)	-0.00014(14)
Ca5	0.00614(19)	0.0075(2)	0.00770(18)	0.00270(14)	-0.00082(14)	0.00003(14)
Si1	0.0017(2)	0.0053(3)	0.0064(2)	0.0024(2)	-0.00003(18)	-0.00007(18)
Si2	0.0023(2)	0.0052(3)	0.0070(3)	0.0026(2)	0.00012(19)	0.00021(18)
O1	0.0032(6)	0.0092(7)	0.0101(7)	0.0027(6)	-0.0005(5)	-0.0002(5)
O2	0.0054(6)	0.0047(7)	0.0092(7)	0.0035(5)	0.0004(5)	-0.0003(5)
O3	0.0059(7)	0.0082(7)	0.0078(7)	0.0038(5)	0.0004(5)	-0.0007(5)
O4	0.0054(6)	0.0090(7)	0.0077(6)	0.0016(6)	0.0001(5)	0.0002(5)
O5	0.0044(7)	0.0077(7)	0.0113(7)	0.0041(6)	-0.0001(5)	0.0000(5)
O6	0.0071(7)	0.0041(7)	0.0100(7)	0.0031(5)	0.0011(5)	0.0002(5)
O7	0.0061(6)	0.0078(7)	0.0087(7)	0.0033(5)	-0.0002(5)	0.0007(5)
O8	0.0059(6)	0.0079(7)	0.0065(6)	0.0023(5)	-0.0002(5)	0.0001(5)

Note: The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, \mathbf{a}^{*2}\, U_{11} + ... + 2\, h\, k\, \mathbf{a}^*\, \mathbf{b}^*\, U_{12}]$

Table 8b. (supplementary materials) Anisotropic atomic displacement parameters (Å^2) for hydroxyledgrewite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.00786(15)	0.01119(14)	0.00793(14)	0.00293(11)	-0.00111(10)	0.00046(10)
Ca2	0.00786(11)	0.01000(11)	0.00823(11)	-0.00042(8)	0.00119(7)	0.00077(7)
Ca3	0.00902(11)	0.00734(10)	0.00887(11)	0.00193(8)	-0.00022(7)	0.00047(7)
Ca4	0.00870(11)	0.00686(10)	0.00835(11)	0.00133(8)	-0.00018(7)	-0.00025(7)
Ca5	0.00966(11)	0.00912(11)	0.00793(10)	0.00165(8)	-0.00081(7)	0.00025(7)
Si1	0.00570(14)	0.00672(13)	0.00670(13)	0.00109(10)	-0.00008(10)	0.00009(10)
Si2	0.00596(14)	0.00678(13)	0.00712(13)	0.00099(10)	0.00019(10)	0.00000(10)
O1	0.0063(4)	0.0113(3)	0.0104(3)	0.0021(3)	-0.0003(3)	0.0003(3)
O2	0.0083(4)	0.0068(3)	0.0097(3)	0.0016(3)	0.0000(3)	-0.0002(3)
O3	0.0087(4)	0.0100(3)	0.0083(3)	0.0030(3)	0.0002(3)	-0.0005(3)
O4	0.0089(4)	0.0092(3)	0.0089(3)	0.0003(3)	-0.0002(3)	-0.0005(3)
O5	0.0068(3)	0.0104(3)	0.0117(3)	0.0019(3)	-0.0005(3)	0.0000(3)
O6	0.0097(4)	0.0070(3)	0.0105(3)	0.0014(3)	0.0003(3)	0.0001(3)
O7	0.0093(4)	0.0099(3)	0.0083(3)	0.0024(3)	0.0000(3)	0.0006(3)
O8	0.0087(4)	0.0091(3)	0.0086(3)	-0.0002(3)	0.0001(3)	0.0001(3)

Note: The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, \mathbf{a}^{*2}\, U_{11} + ... + 2\, h\, k\, \mathbf{a}^*\, \mathbf{b}^*\, U_{12}]$

Table 9. (supplementary materials)
Bond lengths (Å) for edgrewite and hydroxyledgrewite

Atom1	Atom2	Bond lengths F-dominant	Bond lengths OH-dominant
Ca1	O2	2.3106(14) (2x)	2.3096(7) (2x)
	O1	2.3734(15) (2x)	2.3727(7) (2x)
	O4	2.3955(15) (2x)	2.3957(7) (2x)
	Mean	2.360	2.359
Ca2	O6	2.3078(16)	2.3064(8)
	O2	2.3287(15)	2.3292(8)
	O5	2.3759(15)	2.3754(8)
	O3	2.3794(15)	2.3824(8)
	O1	2.3970(15)	2.3951(8)
	O7	2.3989(15)	2.4015(8)
	Mean	2.365	2.365
Ca3	F9	2.278 (4)	2.281(2)
	O3	2.3087(16)	2.3077(8)
	O6	2.3222(15)	2.3203(7)
	O9	2.365(5)	2.345(2)
	O7	2.4126(15)	2.4123(8)
	O8	2.4417(16)	2.4382(8)
	O5	2.4685(16)	2.4678(8)
	Mean[1]	2.386	2.382
	Mean[2]	2.371	2.371
Ca4	O2	2.3146(15)	2.3105(7)
	O4	2.3557(15)	2.3557(8)
	O7	2.3727(16)	2.3686(7)
	O3	2.4306(15)	2.4282(8)
	O4	2.4596(16)	2.4588(8)
	O1	2.4635(15)	2.4611(8)
	Mean	2.399	2.397
Ca5	F9	2.272(4)	2.262(3)
	O8	2.2783(15)	2.2788(8)
	O9	2.299(4)	2.3036(19)
	F9	2.321(4)	2.312(2)
	O9	2.332(5)	2.329(2)
	O8	2.3641(16)	2.3646(8)
	O5	2.4061(16)	2.4072(8)
	O6	2.4396(15)	2.4404(8)
	Mean[1]	2.353	2.354
	Mean[2]	2.347	2.344
Si1	O1	1.6230(15)	1.6239(8)
	O3	1.6440(16)	1.6431(8)
	O4	1.6446(15)	1.6434(8)
	O2	1.6482(15)	1.6520(7)
	Mean	1.640	1.641
Si2	O5	1.6250(15)	1.6230(8)
	O6	1.6442(16)	1.6458(8)
	O7	1.6458(17)	1.6460(8)
	O8	1.6462(15)	1.6456(8)
	Mean	1.640	1.640
F9	Ca5	2.272(4)	2.262(3)
	Ca3	2.278(4)	2.281(2)
	Ca5	2.321(4)	2.312(2)
	Mean	2.290	2.285

[1]considering O9 but not F9;
[2]considering F9 but not O9.

Table 10. (supplementary materials)
Tetrahedral angles (°) for edgrewite and hydroxyledgrewite

O	T	O	F-dominant	OH-dominant
O3	Si1	O1	113.60(8)	113.56(4)
O4	Si1	O1	114.79(8)	114.79(4)
O4	Si1	O3	105.38(8)	105.28(4)
O2	Si1	O1	112.83(8)	112.80(4)
O2	Si1	O3	104.25(8)	104.43(4)
O2	Si1	O4	105.00(8)	105.00(4)
O6	Si2	O5	113.52(8)	113.48(4)
O7	Si2	O5	114.39(8)	114.33(4)
O7	Si2	O6	105.38(8)	105.48(4)
O8	Si2	O5	112.88(8)	112.92(4)
O8	Si2	O6	104.30(8)	104.36(4)
O8	Si2	O7	105.45(8)	105.35(4)