Table S1. X-ray powder diffraction data for fluorcarletonite and carletonite.

Fluorcarletonite			**Carletonite (Chao, 1971)**			*hkl*
I_{meas}	d_{meas}	$d_{calc.}$	I_{meas}	d_{meas}	$d_{calc.}$	
22	16.92	16.77	40	16.705	16.695	001
7	9.419	9.361	30	9.319	9.3185	110
76	**8.417**	**8.386**	**100**	**8.353**	**8.3476**	**002**
3	6.643	6.619	20	6.583	6.5892	200
6	5.942	5.921	10	5.890	5.8935	210
8	5.597	5.590	25	5.563	5.5650	003
3	5.196	5.196	10	5.173	5.1720	202
10	4.843	4.837	40	4.816	4.8145	212
14	4.684	4.681	30	4.659	4.6592	220
3	4.288	4.271	10	4.250	4.2516	203
100	**4.190**	**4.187**	**100**	**4.171**	**4.1672**	**310**
18	4.072	4.065	**50**	**4.053**	**4.0462**	**213**
8	3.585	3.589	5	3.573	3.5725	223
15	3.418	3.422	25	3.405	3.4061	214
20	3.358	3.354	40	3.337	3.3357	005
			10	3.236	3.2322	401
3	3.216	3.211	5	3.202	3.1962	410
3	3.160	3.154	5	3.139	3.1391	411
4	3.125	3.123	10	3.109	3.1088	224
18	3.069	3.069	40	3.057	3.0550	323
8	2.965	2.960	25	2.945	2.9468	420
28	2.917	2.915	**90**	**2.903**	**2.9018**	**421**
7	2.847	2.848	15	2.835	2.8350	403
27	2.790	2.791	40	2.777	2.7787	422
20	2.758	2.762	15	2.750	2.7497	324
14	2.723	2.725	20	2.713	2.7122	333
3	2.674	2.678	5	2.667	2.6662	116
15	2.614	2.616	40	2.604	2.6042	423
			5	2.584	2.5844	510
6	2.548	2.549	15	2.540	2.5376	414
			10	2.466	2.4652	325
3	2.431	2.432	5	2.421	2.4212	521
22	2.393	2.396	**60**	**2.384**	**2.3850**	**007**
			10	2.329	2.3296	440
			5	2.265	2.2600	530
7	2.245	2.250	10	2.239	2.2396	531
10	2.216	2.220	15	2.209	2.2094	425
4	2.174	2.176	10	2.165	2.1665	610
4	2.155	2.159	10	2.149	2.1485	443
6	2.130	2.133	15	2.121	2.1230	227
7	2.094	2.096	20	2.086	2.0869	008
4	2.073	2.077	5	2.065	2.0676	621
11	2.042	2.046	10	2.037	2.0364	118
			5	2.022	2.0216	622
5	2.005	2.006	10	1.966	1.9974	327
			10	1.971	1.9738	525
12	1.918	1.921	30	1.912	1.9135	632
15	1.897	1.900	15	1.890	1.8917	337
6	1.870	1.872	10	1.860	1.8636	550
7	1.858	1.861				711
4	1.843	1.846				526
			5	1.836	1.8340	605

8	1.818	1.821	40	1.813	1.8122	328
3	1.790	1.794	5	1.786	1.7852	446
			5	1.766	1.7672	553
			10	1.748	1.7474	418
3	1.736	1.738	10	1.731	1.7304	730
3	1.726	1.717	10	1.710	1.7094	616
			5	1.679	1.6788	651
3	1.658	1.660	5	1.653	1.6523	733
			10	1.636	1.6345	438
10	1.608	1.610	30	1.603	1.6031	645
4	1.573	1.576	15	1.568	1.5692	743
4	1.553	1.560	15	1.553	1.5530	660
3	1.537	1.540	5	1.533	1.5332	538
6	1.521	1.524				832
			15	1.517	1.5177	439
4	1.456	1.458				842
4	1.353	1.355				836
4	1.245	1.249				71.10
6	1.230	1.233				72.10

Table S2. Selected bond distances (Å) and angles (º) of the framework terahedra for fluorcarletonite.

	Fluorcarletonite	**Carletonite (Chao, 1972)**		**Fluorcarletonite**	**Carletonite (Chao, 1972)**
Si1-O1	1.5968(5)	1.590(3)	Si2-O1	1.6278(5)	1.625(3)
Si1-O2	1.5990(5)	1.588(3)	Si2-O2	1.6303(5)	1.627(3)
Si1-O5	1.6217(4)	1.612(4)	Si2-O3	1.5774(5)	1.567(3)
Si1-O6	1.6157(3)	1.613(3)	Si2-O4	1.6320(5)	1.623(4)
<Si1-O>	**1.608(1)**	**1.601(7)**	**<Si2-O>**	**1.617(1)**	**1.611(7)**
O1-Si1-O2	112.81(3)	112.8(2)	O1-Si2-O2	104.93(3)	104.7(2)
O1-Si1-O5	110.58(3)	110.0(2)	O1-Si2-O3	111.79(2)	112.2(2)
O1-Si1-O6	108.24(3)	107.9(2)	O1-Si2-O4	108.77(3)	108.4(2)
O2-Si1-O5	105.47(3)	106.3(2)	O2-Si2-O3	114.38(2)	114.2(2)
O2-Si1-O6	109.95(3)	109.8(2)	O2-Si2-O4	105.09(3)	105.1(2)
O5-Si1-O6	109.76(3)	110.2(2)	O3-Si2-O4	111.41(3)	111.7(2)
<O-Si1-O>	**109.47(7)**	**109.5(5)**	**<O-Si2-O>**	**109.40(6)**	**109.4(5)**

Table S3. Selected bond distances (Å) and angles (º) for polyhedra and C-triangles for fluorcarletonite.

	Fluorcarletonite	**Carletonite (Chao, 1972)**		**Fluorcarletonite**	**Carletonite (Chao, 1972)**
			Polyhedra		
K-O2 (×4)	3.1824(4)	3.215(3)	Na1-O3 (×4)	2.3313(5)	2.345(4)
K-O5 (×2)	2.9430(5)	2.925(4)	Na1-F13	2.651(1)	2.630(4)
K-O10 (×4)	2.7902(6)	2.773(3)	Na1-O11(w)	2.339(2)	2.342(8)
<K-O>	**2.978(1)**	**2.98(1)**	**<Na1-O,F>**	**2.386(2)**	**2.39(1)**
Na2-O4	2.4489(8)	2.464(7)	Na3-O7 (×4)	2.5371(6)	2.544(6)
Na2-O7 (×2)	2.3868(6)	2.376(5)	Na3-O8 (×2)	2.3879(7)	2.386(7)
Na2-O10 (×2)	2.3263(7)	2.349(5)	Na3-O9 (×2)	2.5297(8)	2.558(6)
Na2-O12(w)	2.755(1)	2.86(5)	**<Na3-O >**	**2.498(1)**	**2.51(2)**
<Na2-O>	**2.438(2)**	**2.46(5)**			
			Ca-O3	2.3672(5)	2.371(3)
	C-triangles		Ca-O3’	2.4292(5)	2.434(3)
C1-O7 (×2)	1.2882(6)	1.288(7)	Ca-O7	2.5098(4)	2.527(3)
C1-O9	1.290(1)	1.268(7)	Ca-O7’	2.5417(4)	2.541(3)
			Ca-O8	2.4482(5)	2.450(5)
O7-O7’	2.2512(7)	2.252(4)	Ca-O9	2.4327(2)	2.430(5)
O7-O9 (×2)	2.2226(8)	2.202(5)	Ca-O10	2.4101(5)	2.405(3)
			Ca-F13	2.5031(2)	2.500(4)
O7-C1-O7’	121.80(7)	122.0(2)	**<Ca-O,F>**	**2.455(1)**	**2.46(1)**
O7-C1-O9	119.09(4)	119.0(2)			
C2-O10 (×2)	1.2820(6)	1.266(7)			
C2-O8	1.3039(8)	1.298(9)			
O10-O10’	2.2493(7)	2.230(4)			
O8-O10 (×2)	2.2243(7)	2.201(6)			
O10-C2-O10’	122.64(7)	123.4(2)			
O8-C2-O10	118.67(4)	118.3(2)			

Table S4. Band position (cm^{-1}) and assignment for the H_2O, OH^- and CO_3^{2-} absorption bands of the studied fluorcarletonite and literature selected chemically related phyllosilicates.

Specimen	Occurence	Chemical formula	Band position	Band assignment	References
Fluorcarletonite	Murun (Russia)	$KNa_4Ca_4Si_8O_{18}(CO_3)_4F{\cdot}H_2O$	662, 690, 728, 782, 875 1393, 1450, 1477, 1525 1623 3436 3555	CO_3^{2-} bending CO_3^{2-} stretching H_2O bending H_2O stretching OH^- stretching	This study
Carletonite	Mont Saint-Hilaire (Canada)	$KNa_4Ca_4Si_8O_{18}(CO_3)_4(OH){\cdot}H_2O$	650, 685, 694, 697 860, 868 1388, 1400, 1408, 1442, 1472, 1520 1715, 1760 3580, 3640	CO_3^{2-} planar bending CO_3^{2-} bending CO_3^{2-} asymmetric stretching H_2O bending OH^- stretching	Chao, 1971
Carletonite	Mont Saint-Hilaire (Canada)	$KNa_4Ca_4Si_8O_{18}(CO_3)_4(OH){\cdot}H_2O$	1020, 1046, 1071 1395, 1449, 1479, 1522 1602, 1623 2998, 3126, 3398, 3624	CO_3^{2-} stretching CO_3^{2-} stretching H_2O stretching H_2O stretching	Frost et al., 2013
Apophyllite-(KF)	Pune District (India)	$KCa_4Si_8O_{20}F{\cdot}8H_2O$	2682, 2934, 3003, 3133, 3417 3538, 3553	H_2O bonds OH^- stretching	Frost and Xi, 2012
Apophyllite-(KF)	Palabora Open Pit (South Africa)	$KCa_4Si_8O_{20}F{\cdot}8H_2O$	2808, 3003, 3073, 3419 3540, 3554	H_2O bonds OH^- stretching	Frost and Xi, 2012
Apophyllite-(KOH)	Christmas Mine (USA)	$KCa_4Si_8O_{20}(F,OH){\cdot}8H_2O$	2637, 3837, 3989, 3083, 3414 3547, 3559	H_2O bonds OH^- stretching	Frost and Xi, 2012
Delhayelite	Khibiny (Russia)	$K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$	1020 1640 3450	Si-OH stretching H_2O bending H_2O stretching	Pekov et al., 2009

Hydrodelhayelite	Khibiny (Russia)	$KCa_2AlSi_7O_{17}(OH)_2 \cdot 6H_2O$	1040 3200-3210	Si-OH stretching Si-OH silanol group	Pekov et al., 2009
Rhodesite	Bultfontein (South Africa)	$KNa_2Ca_2Si_8O_{19}(OH) \cdot 6H_2O$	1040 3200-3210	Si-OH stretching Si-OH silanol group	Pekov et al., 2009
Surite	Cruz del Sur (Argentina)	$Pb(Pb,Ca)_{1.17}(Al,Fe,Mg)_2(Si_{3.6}Al_{0.4})O_{10}(CO_3)_2(OH)_2$	690, 840, 1430	CO_3^{2-} bonds	Hayase et al., 1978

Table S5. Crystallographic data for the studied fluorcarletonite and literature selected structurally related phyllosilicates.

Mineral	Chemical formula	Sp. gr.	Parameters of unit cell	References
Fluorcarletonite	$KNa_4Ca_4Si_8O_{18}(CO_3)_4F{\cdot}H_2O$	Tetragonal *P4/mbm*	a = 13.1808(5) Å, c = 16.6980(8) Å	This study
Carletonite	$KNa_4Ca_4Si_8O_{18}(CO_3)_4(OH){\cdot}H_2O$	Tetragonal *P4/mbm*	a = 13.178(3) Å, c = 16.695(4) Å	Chao, 1971
Delhayelite	$K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$	Orthorhombic *Pmmn*	a = 24.86(1) Å, b = 7.07(2) Å, c = 6.53(1) Å	Cannillo *et al.*, 1969
Hydrodelhayelite	$KCa_2AlSi_7O_{17}(OH)_2{\cdot}6H_2O$	Orthorhombic $Pnm2_1$	a = 6.648 Å, b = 23.846 Å, c = 7.073 Å	Dorfman and Chiragov, 1979
Rhodesite	$KNa_2Ca_2Si_8O_{19}(OH){\cdot}6H_2O$	Orthorhombic *Pman*	a = 23.42 Å, b = 6.55 Å, c = 7.01 Å	Hesse and Liebau, 1992
Macdonaldite	$BaCa_4Si_{16}O_{36}(OH)_2{\cdot}10H_2O$	Orthorhombic *Cmcm*	a = 14.06 Å, b = 23.52 Å, c = 13.08 Å	Cannillo *et al.*, 1968
Monteregianite-(Y)	$Na_4K_2Y_2Si_{16}O_{38}{\cdot}10H_2O$	Monoclinic $P2_1/n$	a = 9.512(2) Å, b = 23.956(4) Å, c = 9.617(2) Å, β = 93.85(1)°	Ghose et al., 1987

Figure S1. Curves of thermal effects (TG, DSC) and mass spectra (dependences of ion current *I* on temperature *T*) of gaseous thermolysis products: release of H_2O (m.n. 18) upon sample heating from fluorcarletonite crystal structure

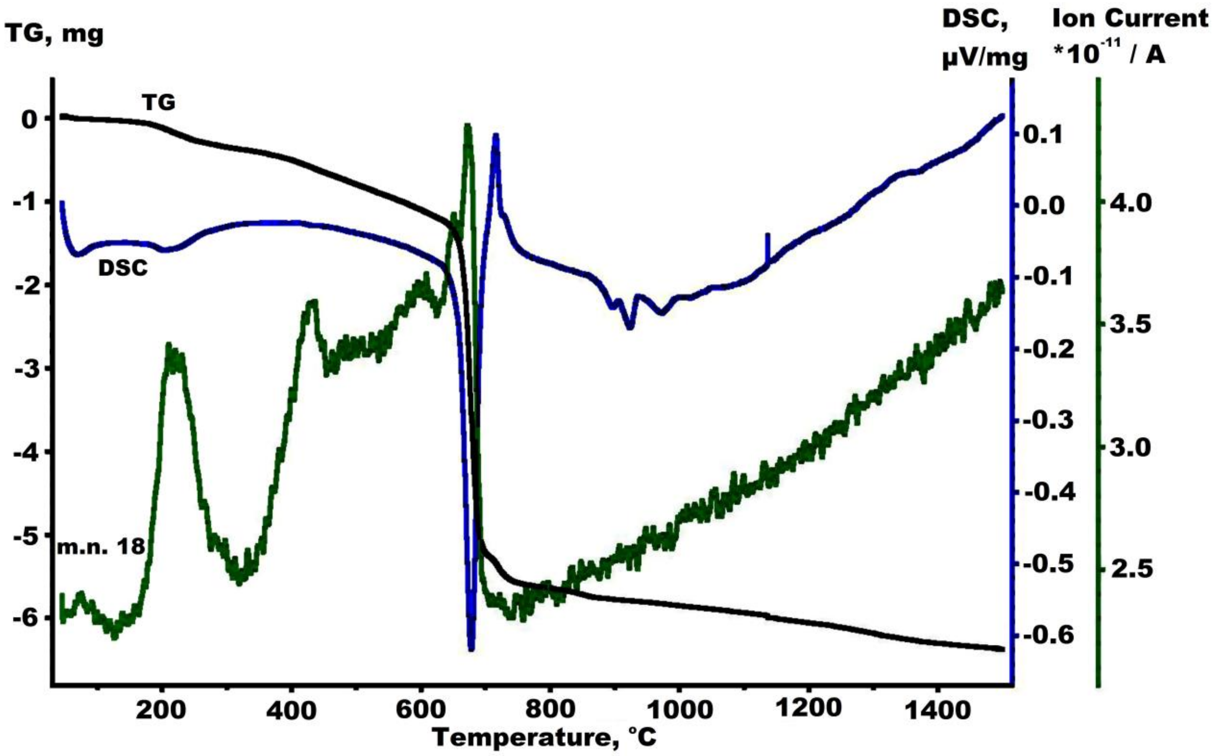


Figure S2. Curves of thermal effects (TG, DSC) and mass spectra (dependences of ion current *I* on temperature *T*) of gaseous thermolysis products: release of F (m.n. 19) upon sample heating from fluorcarletonite crystal structure

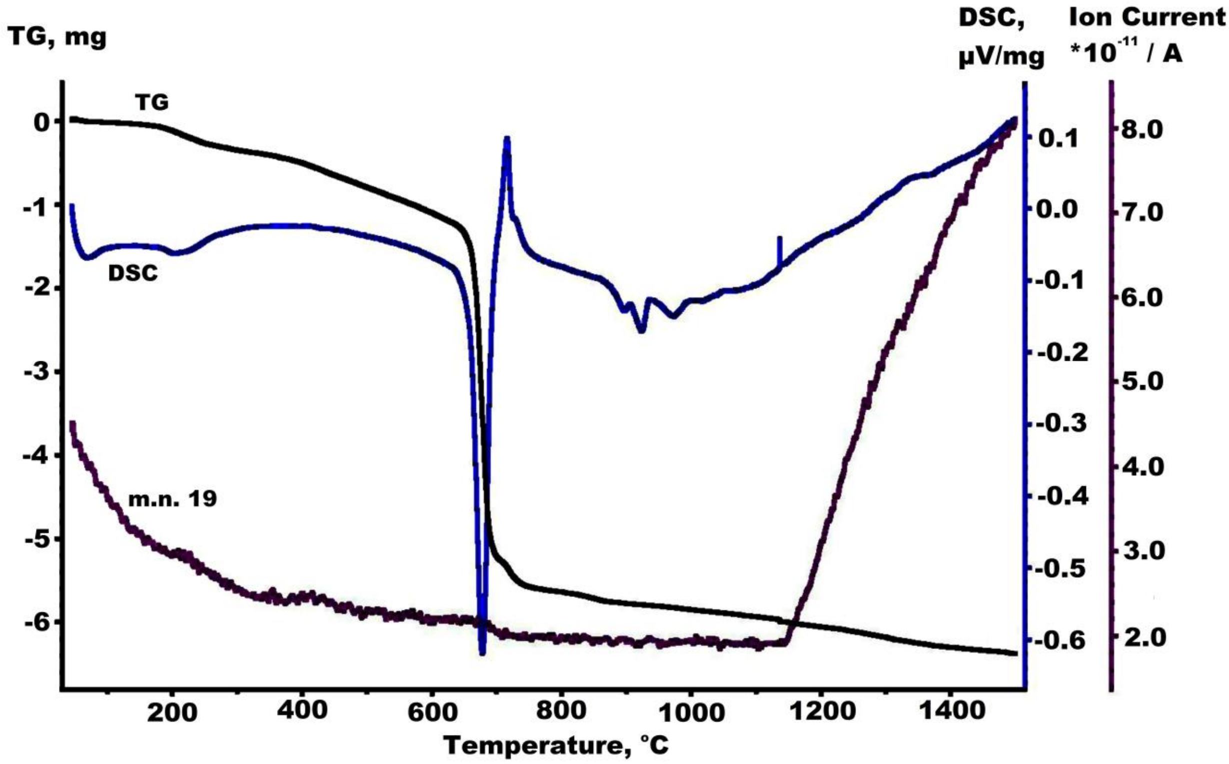
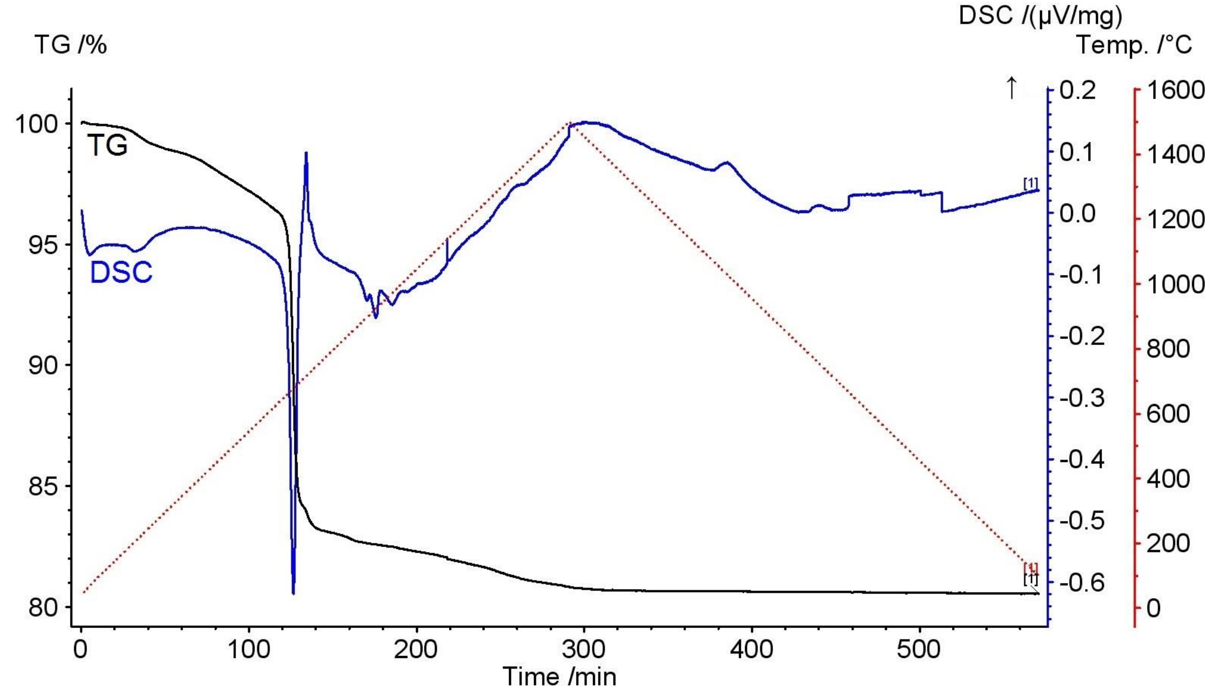


Figure S3. Curves of thermal effects (TG, DSC) upon fluorcarletonite sample heating and cooling



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