



Supplement of

Cation and anion ordering in synthetic lepidolites and lithian muscovites: influence of the OH / F and Li / Al ratios on the mica formation studied by NMR (nuclear magnetic resonance) spectroscopy and X-ray diffraction

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Table S1 Lattice metric of the polytype 1M compared to a natural lepidolite from 1) Radkovice, Czechoslovakia (Guggenheim 1981) and a natural Li-free 2M₁ mica from 2) Tetttenhorst and Corbató (1993).

<i>x</i>	2.0	1.9	1.8	1.7	1.6	1.5	1)
<i>y</i>	0.0	0.2	0.2	0.2	0.2	1.0	
<i>a</i> (Å)	5.1856(1)	5.1961(2)	5.1989(2)	5.2039(2)	5.2043(2)	5.1938(4)	5.209(2)
<i>b</i> (Å)	8.9632(2)	8.9839(2)	8.9889(2)	8.9995(2)	8.9962(3)	8.9877(4)	9.011(5)
<i>c</i> (Å)	10.0338(2)	10.0720(3)	10.0758(3)	10.0965(5)	10.1421(3)	10.1895(4)	10.149(5)
β (°)	100.303(2)	100.263(3)	100.265(3)	100.388(4)	100.708(3)	100.192(4)	100.77(4)
<i>Vol</i> (Å ³)	458.83(2)	462.65(2)	463.33(2)	465.20(3)	466.58(2)	468.15(4)	
χ^2	3.76	7.83	5.09	6.24	3.96	1.56	
<i>R_F</i> (<i>IM</i>)	3.43	3.33	2.64	2.98	4.74	3.26	
<i>x</i>	1.2	0.9	0.6	0.3	0.3	0.0	2)
<i>y</i>	0.8	1.0	1.0	1.4	1.6	1.6	
<i>a</i> (Å)	5.1960(6)	5.1955(6)	5.1899(4)	5.1846(11)	5.1929(6)	5.1967(4)	5.220(8)
<i>b</i> (Å)	8.9925(11)	8.9934(7)	8.9800(8)	8.9581(12)	8.9764(6)	8.9517(4)	8.983(10)
<i>c</i> (Å)	10.1481(22)	10.1747(8)	10.1521(14)	10.1847(23)	10.2224(11)	10.2708(9)	10.176(18)
β (°)	99.63(2)	99.89(1)	99.49(3)	99.75(3)	100.58(1)	101.71(1)	101.15(0)
<i>Vol</i> (Å ³)	467.49(13)	468.35(8)	466.66(8)	466.19(15)	468.40(8)	467.85(6)	
χ^2	9.06	10.1	7.51	4.47	6.94	3.06	
<i>R_F</i> (<i>IM</i>)	3.09	3.24	2.87	2.80	2.20	3.93	

20 Table S2 Lattice metric of the polytype 2M₁ compared to 2M₁ lepidolite from 1) Fleet et al. (2003) and a natural Li-free 2M₁ mica from 2) Tettenhorst and Corbató (1993).

<i>x</i>	2.0	1.9	1.8	1.7	1.6	1.5	1)
<i>y</i>	0.0	0.2	0.2	0.2	0.2	0.0	
<i>a</i> (Å)	5.1790(13)	5.1898(8)	5.1955(13)	5.2000(9)	5.1982(4)		5.2
<i>b</i> (Å)	8.9723(22)	8.9963(6)	8.9981(8)	9.0059(8)	9.0077(5)		9.03
<i>c</i> (Å)	19.8617(77)	19.9245(34)	19.9216(49)	19.9385(32)	20.0231(15)		19.97
β (°)	95.541(29)	95.484(25)	95.286(26)	94.994(28)	95.363(5)		95.4
<i>Vol</i> (Å ³)	918.6(5)	926.0(2)	927.4(3)	932.2(2)	933.5(1)		933.6
χ^2	3.76	7.83	5.09	6.24	3.98		
<i>R_F</i> (2M ₁)	4.83	3.66	3.37	3.18	6.03		
<i>x</i>	1.2	0.9	0.6	0.3	0.3	0.0	2)
<i>y</i>	0.8	1.0	1.0	1.4	1.6	1.6	
<i>a</i> (Å)	5.1948(19)	5.1911(4)	5.2051(6)	5.1789(9)	5.1852(4)	5.1886(8)	5.205(4)
<i>b</i> (Å)	8.9972(18)	9.0022(17)	8.9948(12)	8.9734(8)	8.9923(10)	8.9793(17)	9.021(6)
<i>c</i> (Å)	20.0920(32)	20.1733(20)	20.1609(36)	20.1380(28)	20.1701(14)	20.2073(51)	20.078(18)
β (°)	93.29(6)	95.19(4)	95.70(2)	95.02(1)	95.26(2)	95.70(2)	95.67(0)
<i>Vol</i> (Å ³)	937.5(4)	938.9(2)	939.3(2)	932.3(2)	936.5(1)	936.8(3)	
χ^2	9.06	10.1	7.51	4.47	6.94	3.06	
<i>R_F</i> (2M ₁)	2.20	3.36	3.22	3.05	2.64	3.60	

25 Table S3 Quadrupolar coupling parameters of the ^{27}Al MAS NMR tetrahedral and octahedral mica resonances with selected nominal compositions of $\text{K}(\text{Li}_x\text{Al}_{2-x/3}\square_{1-2x/3}[\text{AlSi}_3\text{O}_{10}](\text{OH})_y\text{F}_{2-y})$ with $0.0 \leq x \leq 1.5$; $0.0 \leq y \leq 2.0$ and $\text{K}(\text{Li}_x\text{Al}_{3-x})[\text{Al}_{4-2x}\text{Si}_{2x}\text{O}_{10}](\text{OH})_y\text{F}_{2-y}$ with $1.5 \leq x \leq 2.0$; $0.0 \leq y \leq 2.0$

		^{6}Al / Mica				^{4}Al / Mica			
x	y	pos. ¹⁾	FWHM	C_Q ³⁾	A ⁴⁾	pos. ¹⁾	FWHM	C_Q ³⁾	A ⁴⁾
		[ppm]	CS ²⁾ [ppm]	[MHz]	[%]	[ppm]	[ppm]	[MHz]	[%]
0.0	0.2	1.1	1.7	2.3	65	70.6	4.1	1.5	18
0.0	0.4	1.0	1.1	2.3	64	71.0	3.5	1.4	18
0.6	0.0	1.2	0.0	2.4	67	70.7	3.8	1.4	18
0.6	0.2	1.1	2.0	2.0	59	70.7	2.1	1.5	23
0.6	0.4	2.0	1.0	2.3	55	70.7	3.0	1.6	33
0.9	0.4	8.3	6.1	3.8	64	73.2	3.1	2.6	36
0.9	0.6	7.8	3.8	4.0	62	73.0	3.6	2.4	35
0.9	1.0	9.0	7.0	4.2	61	73.5	5.1	2.3	39
1.2	0.4	7.8	3.7	4.0	64	72.9	3.7	2.4	36
1.2	0.6	7.7	3.7	3.7	59	72.9	3.6	2.4	37
1.2	1.0	7.2	3.5	2.5	42	73.0	3.9	2.5	34
1.5	0.6	8.3	4.8	4.2	59	73.4	5.1	2.5	41
1.5	1.0	8.3	5.3	3.8	56	74.1	5.0	2.7	44
1.5	1.6	6.6	1.6	3.7	25	72.7	5.0	3.7	34
1.6	0.6	6.4	0.0	4.6	59	72.8	3.8	2.6	32
1.6	1.0	7.1	1.3	4.3	46	73.0	3.3	2.4	29
1.6	1.6	6.8	2.3	3.5	24	72.4	4.8	3.7	34
1.8	0.4	5.6	2.6	2.2	65	73.1	0.0	3.2	30
1.8	0.8	5.6	3.4	1.9	36	73.4	0.0	3.9	22
1.8	1.0	4.9	2.2	1.7	49	72.9	0.0	3.5	10
2.0	1.2	4.7	2.1	1.6	75				
2.0	1.6	3.6	0.6	1.3	51				
2.0	1.8	4.0	1.1	1.3	28				

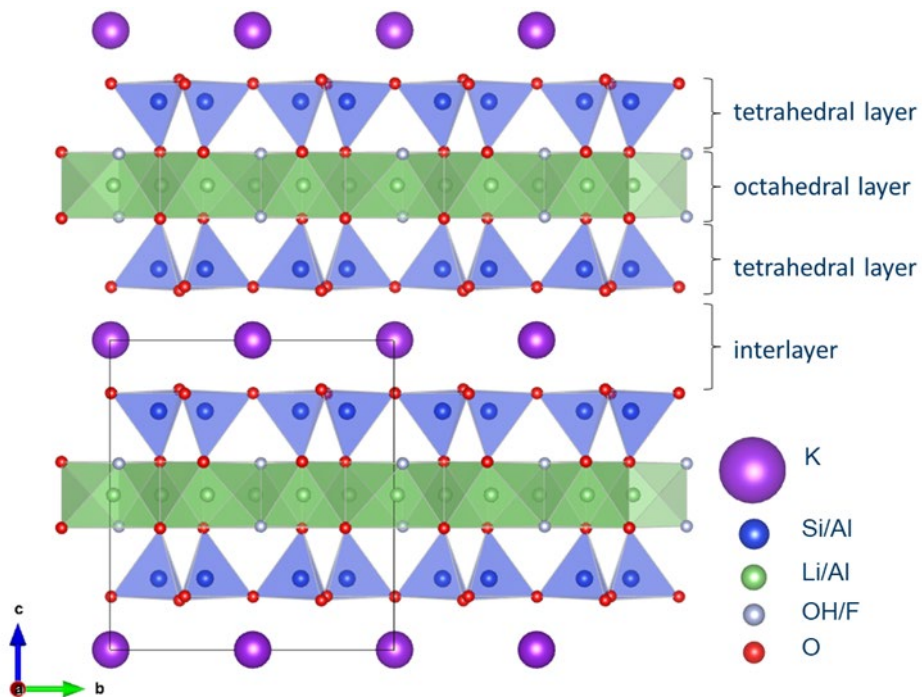
1) pos. = Signal position. Error range: ± 0.5 ppm.

2) FWHM CS = Full width at half maximum of the Gaussian chemical shift distribution.
Error range: ± 0.5 ppm.

3) C_Q = Quadrupole coupling constant. Error range: ± 0.3 MHz

4) A = Relative signal area. Error range is ± 3 %.

30 **Figure S1** Structure of the lepidolites of the polytype 1M. The TOT-layers are stacked along the c-axis and separated by an interlayer cation potassium. The unit cell is emphasized by the black lines (Structure: Brigatti et al. 2000).



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Figure S2 Overview over eight synchrotron powder diffraction diagrams recorded with $\lambda = 1.378 \text{ \AA}$. These samples have been measured using synchrotron radiation at the beamline P08 at PETRA III, DESY, Hamburg, Germany. The Li-content varies between 1.5 and 2. And the OH-content between 0.0 and 0.8. Small additional peaks, which may refer to an additional mica polytype or to stacking disorder are marked with arrows.

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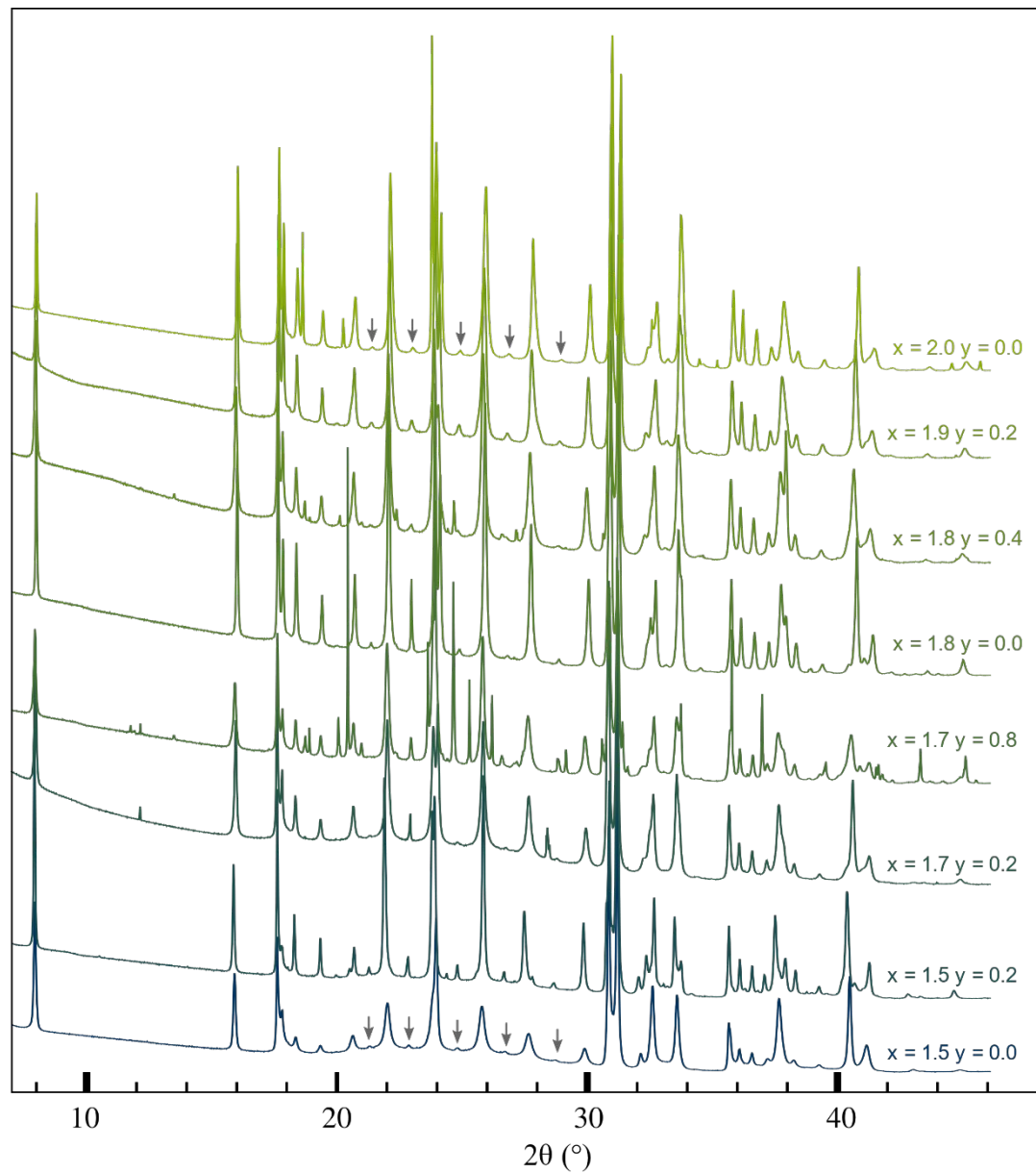
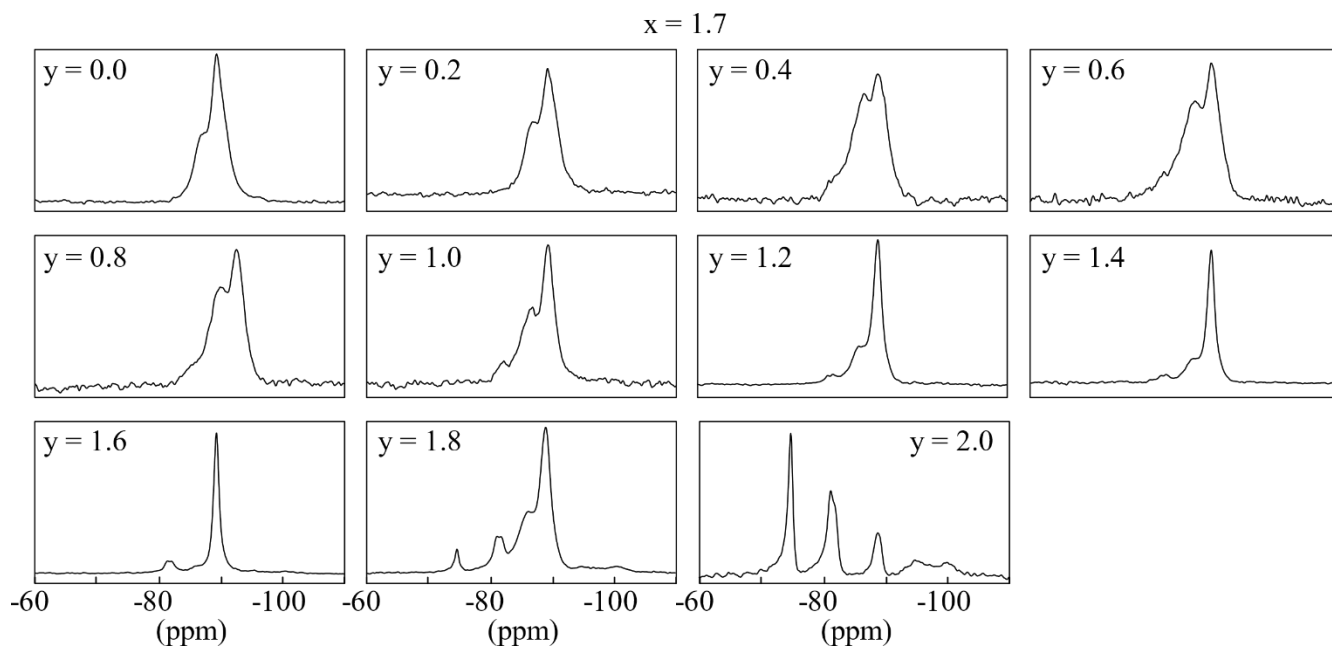


Figure S3 ^{29}Si MAS NMR spectra of lepidolites with $x = 1.7$ and variable OH/F content. The ratio of the three mica signals changes depending on the OH/F content and new signals appear referring to impurity phases.

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References:

Brigatti, M.F., Lugli, C., Poppi, L., Foord, E.E., and Kile, D.E. (2000) Crystal chemical variations in Li- and Fe-rich micas from Pikes Peak batholith (central Colorado). *American Mineralogist*, 85, 1275–1286.