Supplementary Materials

A two-stage particle attachment mechanism for phyllosilicate crystallization in geological processes

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Table S1. Chemical compositions of the muscovite from a pegmatite[a]

Testing spots	1	2	3	4	5	Avg.[b]
SiO_2	49.38	50.18	50.06	49.80	49.46	49.78
Al_2O_3	36.23	36.02	35.80	36.52	36.72	36.26
Fe_2O_3	2.00	1.76	1.63	1.75	1.84	1.80
MgO	0.52	0.57	0.62	0.45	0.49	0.53
K_2O	11.02	10.82	11.27	10.90	10.83	10.97
Na_2O	0.49	0.38	0.32	0.37	0.50	0.41
CaO	-	-	-	-	-	-
TiO_2	0.32	0.24	0.27	0.17	0.12	0.22
MnO	0.52	0.03	0.03	0.03	0.04	0.13
Cl	-	-	-	-	-	-
F	-	-	-	-	-	-

[a]The major element oxides (*wt*.%) by EPMA.

[b]Chemical formula: $(K_{0.889}Na_{0.060})_{\Sigma=0.949}(Al_{1.811}Mg_{0.049}Ti_{0.015}Fe_{0.095}Mn_{0.028})_{\Sigma=1.998}(Al_{0.881}Si_{3.119})_{\Sigma=4}O_{10}(OH)_2$

- below the detection limit.

Table S2. Chemical compositions of the biotite from granite[a]

Testing spots	1	2	3	4	5	Avg.[b]
SiO_2	35.59	36.19	36.00	35.92	36.14	35.97
Al_2O_3	17.32	16.94	16.98	17.12	16.84	17.04
Fe_2O_3	21.42	21.57	21.83	21.53	21.61	21.59
MgO	7.96	7.69	7.78	8.11	7.81	7.87
K_2O	9.53	9.39	9.34	9.53	9.65	9.49
Na_2O	0.09	0.11	0.08	0.08	0.11	0.09
CaO	-	-	0.03	-	-	0.01
TiO_2	2.34	2.41	2.18	1.89	2.04	2.17
MnO	0.53	0.55	0.55	0.53	0.57	0.55
Cl	0.03	0.03	0.03	0.03	0.05	0.03
F	0.28	0.27	0.30	0.36	0.28	0.30

[a]The major element oxides (*wt*.%) by EPMA.

[b]Chemical formula: $(K_{0.930}Na_{0.012}Ca_{0.001})_{\Sigma=0.943}(Ti_{0.125}Mn_{0.036}Fe_{1.387}Mg_{0.901}\ Mn_{0.036}\square_{0.515})_{\Sigma=3}(Si_{2.533}Al_{1.414}Fe_{0.053})_{\Sigma=4}O_{10}(OH,F)_2$

- below the detection limit.

Table S3. Chemical compositions of the metamorphic muscovite[a]

Testing spots	1	2	3	4	5	Avg.[b]
SiO_2	48.87	47.83	49.20	47.44	47.40	48.15
Al_2O_3	33.85	34.81	34.01	35.69	35.71	34.82
Fe_2O_3	4.21	4.55	4.41	4.12	4.21	4.30
MgO	0.77	0.65	0.57	0.70	0.69	0.68
K_2O	11.00	11.09	10.69	11.00	10.98	10.95
Na_2O	0.49	0.38	0.41	0.53	0.47	0.46
CaO	-	-	-	-	-	-
TiO_2	0.79	0.68	0.69	0.50	0.50	0.63
MnO	0.02	0.01	0.01	-	-	0.01
Cl	-	-	-	-	-	-
F	-	-	-	-	-	-

[a]The major element oxides (*wt*. %) by EPMA.

[b]Chemical formula: $(K_{0.900}Na_{0.057})_{\Sigma=0.957}(Al_{1.742}Mg_{0.065}Ti_{0.031}Fe_{0.231})_{\Sigma=2.069}(Al_{0.900}Si_{3.100})_{\Sigma=4}O_{10}(OH)_2$

- below the detection limit.

Table S4. Chemical compositions of the metamorphic biotite[a]

Testing spots	1	2	3	4	5	Avg.[b]
SiO_2	39.71	39.78	39.56	39.74	39.81	39.72
Al_2O_3	18.41	18.38	18.33	18.40	18.32	18.37
Fe_2O_3	14.46	14.43	14.51	14.45	14.54	14.48
MgO	14.57	14.42	14.32	14.45	14.25	14.40
K_2O	9.60	9.88	10.02	9.85	9.92	9.86
Na_2O	0.21	0.19	0.23	0.21	0.20	0.21
CaO	-	-	-	-	-	-
TiO_2	2.78	2.75	2.73	2.73	2.74	2.74
MnO	0.14	0.08	0.14	0.09	0.13	0.12
Cl	0.07	0.06	0.07	0.06	0.05	0.06
F	0.04	0.05	0.13	-	0.07	0.06

[a]The major element oxides (*wt*. %) by EPMA.

[b]Chemical formula: $(K_{0.883}Na_{0.029})_{\Sigma=0.912}(Al_{0.320}Ti_{0.145}Fe_{0.853}Mg_{1.512}Mn_{0.007}\square_{0.163})_{\Sigma=3}(Si_{2.796}Al_{1.204})_{\Sigma=4}O_{10}(OH,F)_2$

- below the detection limit.

Table S5. Chemical compositions of the fluorophlogopite synthesized at 1450 °C[a]

Testing spots	1	2	3	4	5	6	7	8	Avg.[b]
SiO_2	39.64	39.73	39.77	40.06	39.82	40.08	39.58	40.37	39.88
Al_2O_3	18.75	18.65	18.31	18.06	18.34	18.12	18.83	17.58	18.33
FeO	0.03	0.06	0.03	0.02	0.03	0.01	0.02	0.03	0.03
MgO	25.47	25.55	26.08	26	25.41	25.75	25.49	26.01	25.72
CaO	-	-	-	-	-	0.01	0.01	0.01	-
Na_2O	0.12	0.13	0.15	0.09	0.11	0.09	0.08	0.11	0.11
K_2O	10.94	10.98	11.11	10.79	10.98	11.11	10.93	10.85	10.96
F	8.97	8.98	9.13	9.22	9.05	9.09	8.95	9.13	9.07

[a]The major element oxides (*wt*. %) by EPMA.

[b]Chemical formula: $(K_{0.970}Na_{0.011})_{\Sigma=0.981}(Mg_{2.672}Al_{0.271})_{\Sigma=2.943}(Si_{2.768}Al_{1.232})_{\Sigma=4}O_{10}F_{2.00}$

- below the detection limit.

Table S6. Chemical compositions of the fluorophlogopite synthesized at 900 °C[a]

Testing spots	1	2	3	4	5	6	7	8	Avg.[b]
SiO_2	41.41	40.96	41.27	41.19	40.98	41.10	41.48	41.88	41.28
Al_2O_3	15.86	15.77	15.63	15.49	15.92	15.48	15.72	15.28	15.64
FeO	0.02	-	0.01	0.01	0.02	0.03	0.01	0.03	0.02
MgO	26.93	27.10	26.77	27.41	26.98	27.22	27.00	27.12	27.07
CaO	-	-	0.02	-	0.01	0.03	-	-	0.01
Na_2O	0.07	0.07	0.09	0.06	0.10	0.08	0.09	0.08	0.08
K_2O	11.16	11.51	11.12	11.38	11.37	11.26	11.38	11.13	11.29
F	9.20	9.09	8.73	9.03	9.22	9.16	9.13	9.02	9.07

[a]The major element oxides (*wt*.%) by EPMA.

[b]Chemical formula: $(K_{1.00}Na_{0.012})_{\Sigma=1.012}(Mg_{2.811}Al_{0.160})_{\Sigma=2.971}(Si_{2.882}Al_{1.118})_{\Sigma=4}O_{10}F_{2.00}$

- below the detection limit.

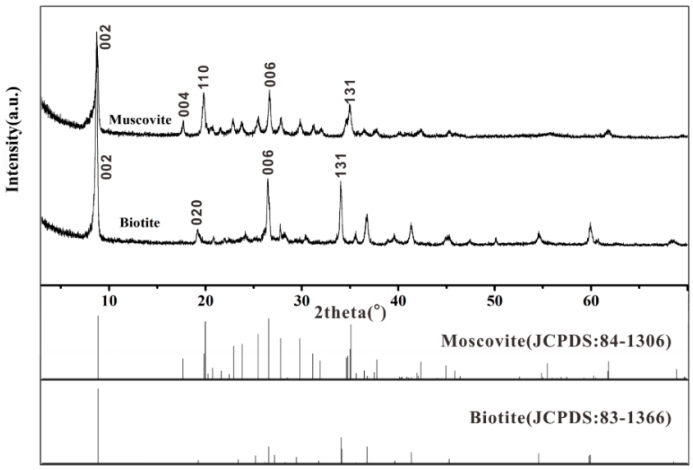

Figure S1. XRD patterns of the biotite from a granite and muscovite from a pegmatite.

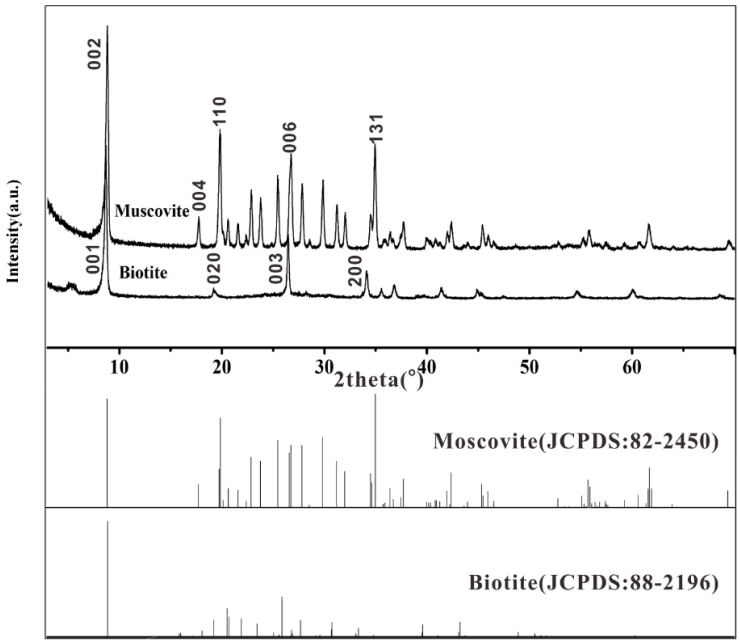

Figure S2. XRD patterns of the metamorphic biotite and muscovite.

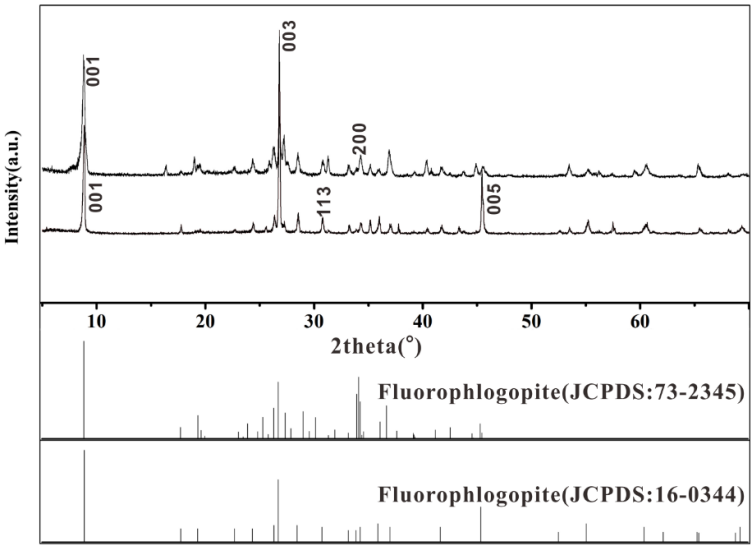

Figure S3. XRD patterns of the synthetic fluorophlogopite. The upper pattern corresponds to the synthetic fluorophlogopite at 900°C, while the lower one corresponds to that at 1450°C.

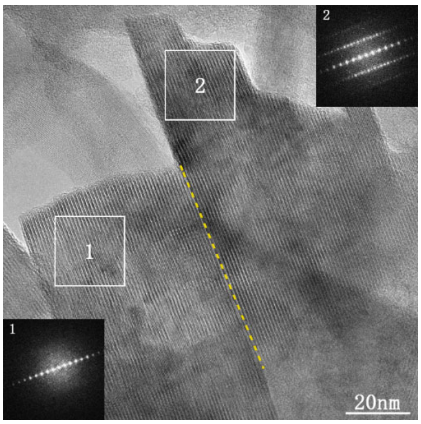

Figure S4. HRTEM image and FFT patterns of metamorphic muscovite. The metamorphic muscovite grain is comprised of 2 nano-flake domains with different crystallographic directions.

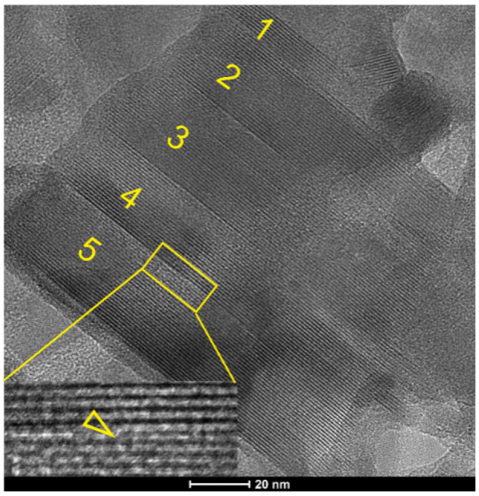

Figure S5. HRTEM image of metamorphic biotite. The biotite grain is comprised of 5 nano-flake domains via oriented attachment. A dislocation is observed at the interface between domain 4 and domain 5 (inset, the enlarged HRTEM image of the area marked with the yellow square).

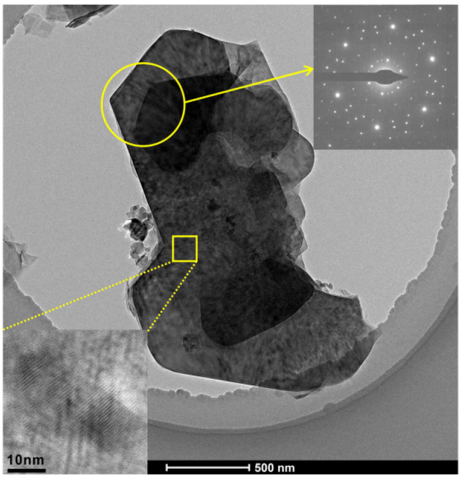

Figure S6. **(HR)TEM images and SAED pattern of synthetic fluorophlogopite (synthesized at 900 ºC).** Both the (HR)TEM images and SAED pattern show that the single-crystal-morphological crystal is comprised of more than one (nano-)flake of fluorophlogopite. The smaller nano-particles were lying on the larger one along the *c* axis. The enlarged HRTEM image (inset, bottom) shows the occurrence of moire fringe of the single-crystal-morphological crystal.