

SUPPLEMENTARY FOR

Nanostructure reveals REE mineral crystallization mechanisms in granites from heavy-REE deposit, South China

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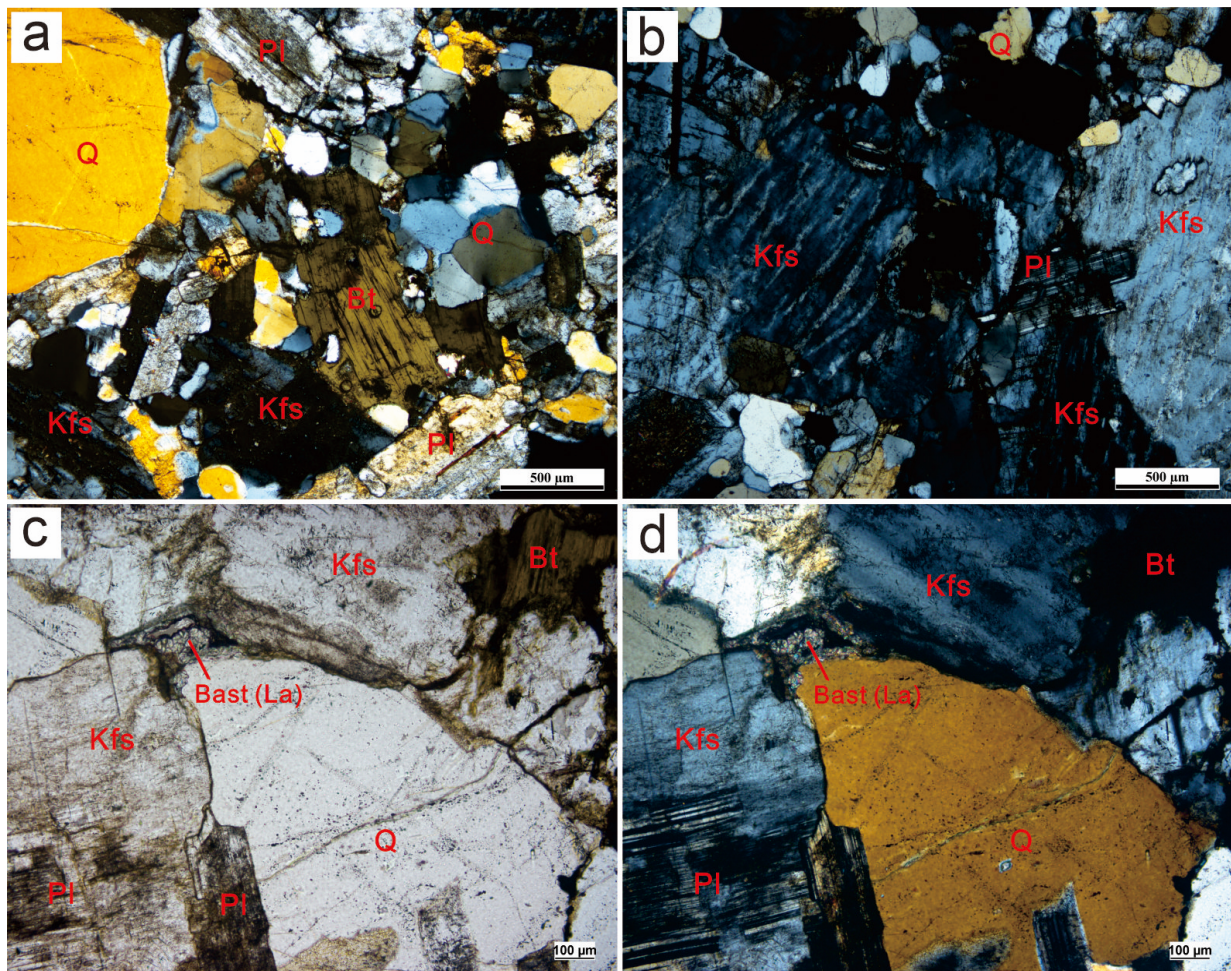
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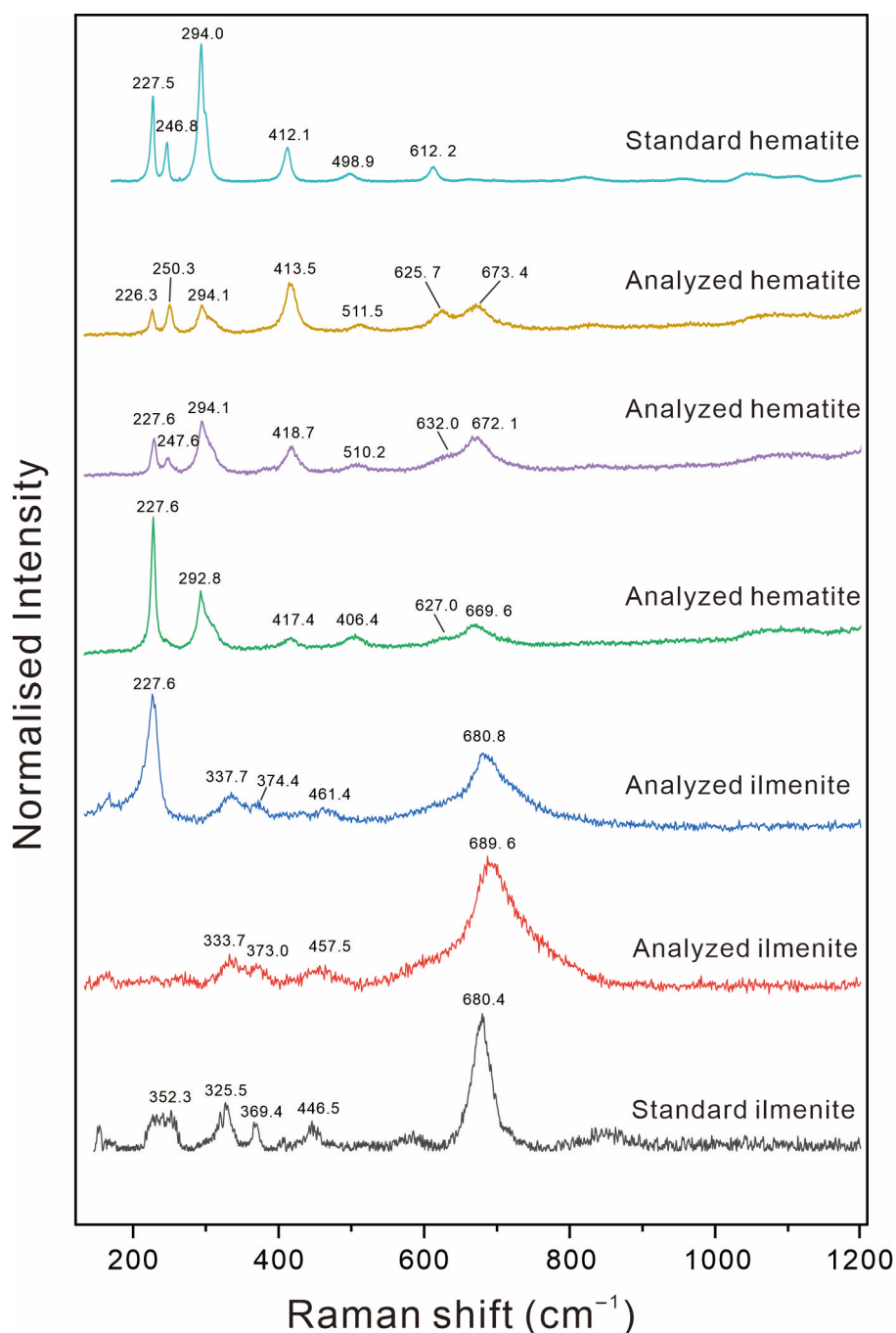
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Supplementary figures S1 to S4

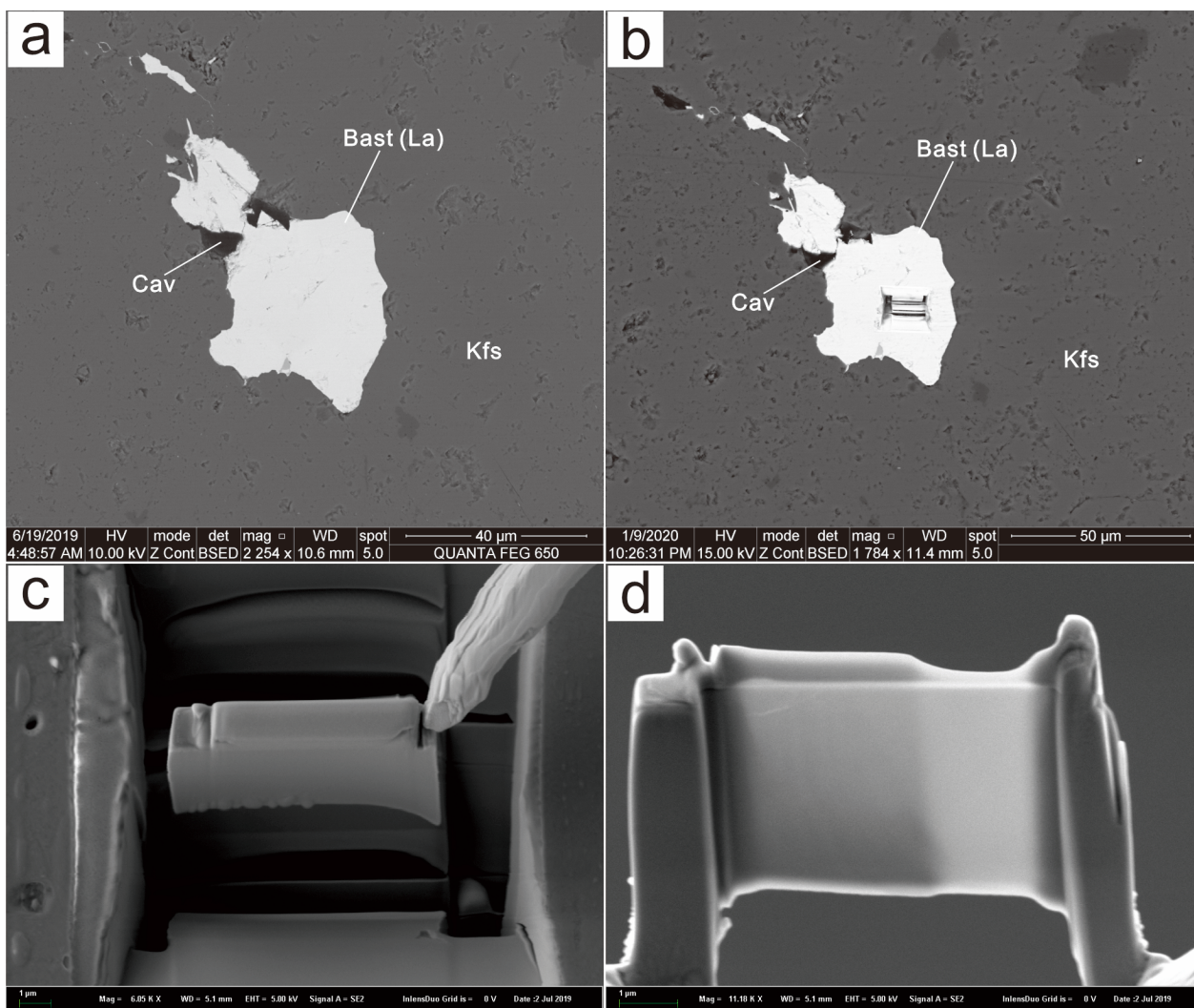
Supplementary tables S1 and S2



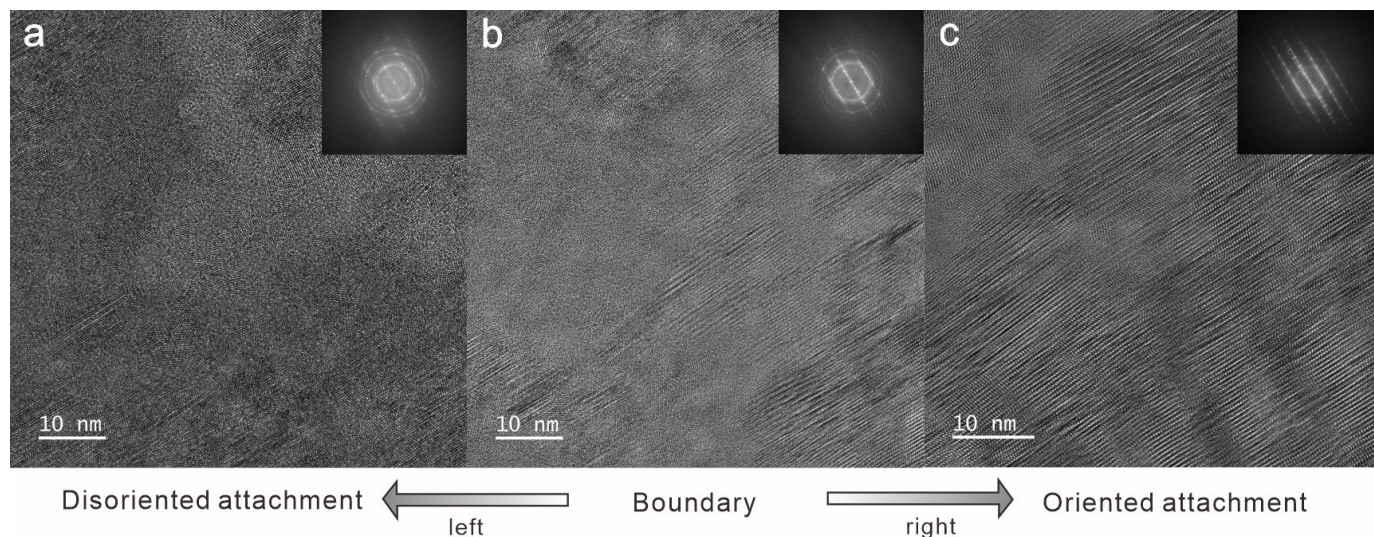
Supplementary Figure S1. Characteristic textures and mineral assemblage observed in the relatively fresh parental granites of the Zhaibei REE-rich clays. (a, b) Petrographic features of the parental granites suggest only incipient feldspar and biotite alteration. (c, d) Big grain of Ce-poor, Nd-Y-rich bastnäsite-(La) which is intimately associated with quartz. Pl, plagioclase; Kfs, K-feldspar; Q, quartz; Bt, biotite; Bast (La), Ce-poor, Nd-Y-rich bastnäsite-(La).



Supplementary Figure S2. Raman spectra of analyzed ilmenite and hematite compared with standard spectra. The Raman spectra in the bottom and the top of the figure are standard spectra for ilmenite and hematite, respectively. From the bottom to the top of the figure, the intensity of Raman signals at 680.4, 446.5, 369.4, 325.5, and 352.3 cm^{-1} gradually diminishes, and the intensity of Raman signals at 612.2, 498.9, 412.1, 294.0, 246.8, and 227.5 cm^{-1} gradually increases. This transition indicates a gradual increase in the proportion of hematite with increasing oxidation. Raman data for standard ilmenite and hematite are from <https://rruff.info/>.



Supplementary Figure S3. The preparation process of the electron-transparent foil by focused ion beam technique (FIB). **(a)** The Ce-poor, Nd-Y-rich bastnäsite-(La) grain used to prepare the electron-transparent FIB foil. **(b)** The same grain after the electron-transparent foil has been taken out. **(c)** Lift-out of the electron-transparent foil cut away from substrate. **(d)** The prepared electron-transparent foil after final thinning and polishing. Kfs, K-feldspar; Bast (La), Ce-poor and Nd-Y-rich bastnäsite-(La); Cav, cavity.



Supplementary Figure S4. The gradual transition from disoriented attachment to oriented attachment between nanoparticles of Ce-poor, Nd-Y-rich bastnäsite-(La) observed in the HRTEM foil. The nanoparticles aggregated randomly (**a**), in the left side of the boundary (**b**), while most of them are aligned in the right side (**c**). Insets are fast Fourier-transformed (FFT) patterns.

Supplementary Table S1. Compositions (wt.%) of minerals in granites

Sample	K-feldspar					plagioclase				
	1	2	3	4	5	1	2	3	4	5
SiO ₂	65.31	65.74	65.25	65.91	65.95	69.81	67.96	67.69	68.27	69.24
Al ₂ O ₃	18.23	18.30	18.23	18.13	18.34	19.77	20.91	20.92	19.88	20.49
CaO	bdl	bdl	bdl	bdl	bdl	0.46	1.68	2.08	0.84	0.50
FeO	0.10	0.04	0.03	bdl	0.05	bdl	0.10	0.10	0.08	bdl
Na ₂ O	0.71	0.26	0.21	0.46	0.25	10.73	9.67	9.89	10.61	10.48
K ₂ O	16.10	16.64	16.79	16.54	16.14	0.11	0.14	0.17	0.21	0.09
Total	100.45	100.98	100.51	101.04	100.73	100.88	100.46	100.85	99.89	100.80
Formulae based on 8 oxygens										
Si	3.005	3.010	3.006	3.015	3.016	3.010	2.951	2.937	2.983	2.987
Al	0.989	0.988	0.990	0.978	0.989	1.005	1.070	1.070	1.024	1.042
Ca	0.000	0.000	0.000	0.000	0.000	0.021	0.078	0.097	0.039	0.023
Fe	0.004	0.002	0.001	0.000	0.002	0.000	0.004	0.004	0.003	0.000
Na	0.063	0.023	0.019	0.041	0.022	0.897	0.814	0.832	0.899	0.877
K	0.945	0.972	0.987	0.965	0.942	0.006	0.008	0.009	0.012	0.005
Mol.% end-members										
An	0.00	0.00	0.00	0.00	0.00	2.30	8.68	10.31	4.14	2.55
Ab	6.28	2.32	1.87	4.06	2.30	97.05	90.45	88.69	94.63	96.90
Or	93.72	97.68	98.13	95.94	97.70	0.65	0.86	1.00	1.23	0.55

Supplementary Table S1. Continued

Sample	biotite									
	1	2	3	4	5	6	7	8	9	10
SiO ₂	36.12	36.38	35.34	35.77	36.00	35.11	36.27	36.50	36.29	36.54
TiO ₂	3.55	3.31	3.38	3.63	3.15	3.30	3.74	3.52	3.05	3.36
Al ₂ O ₃	12.81	13.10	14.15	12.27	13.23	13.17	12.25	12.64	13.39	12.67
MgO	3.86	3.56	3.11	3.80	3.70	3.70	4.01	4.02	3.59	3.51
MnO	0.67	0.70	0.58	0.69	0.75	0.66	0.64	0.67	0.63	0.54
FeO	30.94	29.79	30.52	31.14	30.62	30.37	30.47	30.24	29.90	30.77
Na ₂ O	0.03	0.04	0.05	0.04	0.06	0.05	0.10	0.05	0.02	0.03
K ₂ O	9.12	9.23	9.35	9.26	9.30	9.17	8.90	9.35	9.57	9.20
Total	97.10	96.11	96.48	96.60	96.81	95.53	96.38	96.99	96.44	96.62
Formulae based on 11 oxygens										
Si	2.873	2.907	2.828	2.873	2.872	2.843	2.899	2.899	2.896	2.916
Ti	0.212	0.199	0.204	0.219	0.189	0.201	0.225	0.210	0.183	0.202
Al	1.201	1.234	1.335	1.162	1.244	1.257	1.154	1.183	1.259	1.192
Mg	0.458	0.424	0.371	0.455	0.440	0.447	0.478	0.476	0.427	0.418
Mn	0.045	0.047	0.039	0.047	0.051	0.045	0.043	0.045	0.043	0.036
Fe ²⁺	2.058	1.991	2.043	2.092	2.043	2.057	2.037	2.009	1.995	2.053
Na	0.005	0.006	0.008	0.006	0.009	0.008	0.015	0.008	0.003	0.005
K	0.926	0.941	0.955	0.949	0.947	0.947	0.908	0.947	0.974	0.937

Supplementary Table S1. Continued

cerianite													
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
P ₂ O ₅	3.57	3.77	3.10	3.83	2.32	2.98	3.21	3.29	2.13	3.05	1.00	1.01	0.98
Nb ₂ O ₅	0.01	bdl	0.04	bdl	bdl	bdl	0.03	0.03	0.04	bdl	bdl	bdl	bdl
Ta ₂ O ₅	0.23	0.06	bdl	bdl	bdl	bdl	bdl	0.12	bdl	bdl	bdl	bdl	bdl
SiO ₂	4.66	4.42	3.39	4.31	4.98	4.43	4.30	3.96	6.09	6.66	8.75	9.28	8.34
ThO ₂	0.04	0.03	0.04	0.04	0.22	bdl	bdl	bdl	0.31	0.03	0.84	0.58	0.85
UO ₂	0.18	0.14	0.13	0.12	0.09	0.22	0.25	0.12	0.15	0.12	0.16	0.17	0.08
Al ₂ O ₃	0.98	1.09	1.01	1.38	2.62	4.42	1.64	1.19	2.77	1.98	0.83	1.15	1.15
Y ₂ O ₃	bdl	0.04	0.02	bdl	bdl	0.04	0.11	0.05	0.07	0.03	0.07	0.03	0.02
La ₂ O ₃	bdl	bdl	0.07	0.12	0.10	bdl	0.07	0.18	0.39	0.19	bdl	0.03	bdl
Ce ₂ O ₃	86.04	86.74	83.74	84.46	80.19	86.29	82.79	83.70	71.04	76.58	77.66	75.97	77.44
Nd ₂ O ₃	0.65	0.59	0.86	0.87	0.67	0.70	0.70	0.79	1.13	0.77	0.50	0.47	0.51
Dy ₂ O ₃	1.12	1.24	1.45	1.51	1.72	1.01	1.43	1.33	2.70	2.17	0.37	0.31	0.25
Er ₂ O ₃	bdl	bdl	bdl	bdl	bdl	0.15	bdl	0.10	0.11	0.09	bdl	0.07	0.14
Yb ₂ O ₃	bdl	bdl	0.19	bdl	0.04	0.03	bdl	0.04	0.03	bdl	bdl	bdl	bdl
CaO	0.43	0.75	0.60	0.40	0.36	0.31	0.48	0.36	1.19	1.01	0.42	0.44	0.45
MnO	2.43	2.60	3.07	3.43	3.55	1.93	2.65	2.98	5.25	4.84	0.62	0.77	0.76
FeO	1.15	1.22	1.48	1.35	1.85	1.23	1.13	1.16	2.91	2.16	5.40	5.41	5.97
PbO	0.39	bdl	bdl	bdl	bdl	bdl	0.02	bdl	0.46	0.40	bdl	bdl	bdl
F	1.92	2.00	1.56	1.83	1.10	1.68	1.65	1.87	1.09	1.88	1.26	1.33	1.19
O=F	-0.81	-0.84	-0.66	-0.77	-0.46	-0.71	-0.69	-0.79	-0.46	-0.79	-0.53	-0.56	-0.50
Total	102.99	103.85	100.09	102.88	99.35	104.71	99.77	100.48	97.40	101.17	97.35	96.46	97.63
Formulae based on 2 oxygens													
P	0.086	0.089	0.078	0.091	0.056	0.068	0.079	0.082	0.051	0.070	0.024	0.024	0.024
Nb	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Ta	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Si	0.132	0.124	0.101	0.121	0.143	0.119	0.125	0.116	0.171	0.180	0.249	0.262	0.237
Th	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.002	0.000	0.005	0.004	0.006
U	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001
Al	0.033	0.036	0.036	0.046	0.088	0.140	0.056	0.041	0.091	0.063	0.028	0.038	0.039
Y	0.000	0.001	0.000	0.000	0.000	0.001	0.002	0.001	0.001	0.000	0.001	0.000	0.000
La	0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.002	0.004	0.002	0.000	0.000	0.000
Ce	0.892	0.889	0.915	0.867	0.840	0.849	0.881	0.898	0.729	0.756	0.810	0.784	0.806
Nd	0.007	0.006	0.009	0.009	0.007	0.007	0.007	0.008	0.011	0.007	0.005	0.005	0.005
Dy	0.010	0.011	0.014	0.014	0.016	0.009	0.013	0.013	0.024	0.019	0.003	0.003	0.002
Er	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.001	0.000	0.001	0.001
Yb	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.013	0.022	0.019	0.012	0.011	0.009	0.015	0.011	0.036	0.029	0.013	0.013	0.014
Mn	0.058	0.062	0.078	0.081	0.086	0.044	0.065	0.074	0.125	0.111	0.015	0.018	0.018
Fe	0.027	0.029	0.037	0.032	0.044	0.028	0.027	0.028	0.068	0.049	0.129	0.128	0.142
Pb	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.000

Supplementary Table S1. Continued

Sample	cerianite										Al-Fe-rich silicate in		
	14	15	16	17	18	19	20	21	22	23	1	2	3
P ₂ O ₅	1.13	0.92	1.04	1.16	1.26	1.07	1.25	1.06	1.09	1.19	0.43	0.42	0.37
Nb ₂ O ₅	bdl	0.06	bdl	0.05	bdl	0.08	bdl	bdl	0.04	bdl	0.06	0.01	0.06
Ta ₂ O ₅	bdl	bdl	bdl	bdl	0.00	0.01	bdl	bdl	0.19	bdl	0.04	0.08	0.12
SiO ₂	10.56	8.44	9.80	12.28	13.04	11.11	12.47	9.62	10.2	11.29	14.69	14.35	14.12
ThO ₂	0.78	0.65	0.67	0.44	0.49	0.41	0.46	0.64	0.29	0.53	0.17	0.03	0.08
UO ₂	0.28	0.07	0.05	0.04	0.18	0.16	0.20	0.18	0.22	0.29	bdl	0.07	bdl
Al ₂ O ₃	1.79	1.39	1.50	2.83	2.96	1.19	2.03	1.13	1.15	1.15	6.77	5.79	6.31
Y ₂ O ₃	0.03	0.01	bdl	0.05	bdl	0.01	0.05	bdl	0.03	bdl	0.04	bdl	bdl
La ₂ O ₃	bdl	0.04	bdl	0.12	0.04	0.02	bdl	0.01	bdl	bdl	bdl	bdl	0.05
Ce ₂ O ₃	77.25	75.8	74.0	77.05	75.78	79.46	78.70	75.4	76.2	76.63	4.79	2.52	6.09
Nd ₂ O ₃	0.54	0.52	0.51	0.51	0.46	0.62	0.60	0.50	0.53	0.53	0.12	0.06	bdl
Dy ₂ O ₃	0.27	0.15	0.39	0.50	0.43	0.40	0.35	0.43	0.54	0.44	0.27	0.30	0.36
Er ₂ O ₃	0.02	bdl	bdl	0.02	bdl	bdl	bdl	bdl	0.02	0.08	0.32	0.30	0.46
Yb ₂ O ₃	0.13	bdl	bdl	0.03	bdl	bdl	bdl	bdl	0.09	bdl	bdl	bdl	bdl
CaO	0.41	0.35	0.53	0.98	0.85	1.16	1.04	0.41	1.23	1.20	0.25	0.21	0.18
MnO	0.71	0.75	0.71	1.01	0.90	0.99	0.89	0.69	1.15	0.95	0.48	0.41	0.44
FeO	6.47	6.75	6.84	4.58	3.97	4.49	5.12	5.29	3.66	5.83	55.79	57.62	54.44
PbO	bdl	bdl	bdl	bdl	0.08	bdl	bdl	bdl	bdl	bdl	0.14	0.07	bdl
F	1.51	1.10	1.22	1.57	1.78	1.71	1.51	1.41	1.35	2.59	bdl	bdl	bdl
O=F	-0.63	-0.4	-0.5	-0.66	-0.75	-0.72	-0.63	-0.5	-0.5	-1.09	-	-	-
Total	101.2	96.6	96.8	102.5	101.4	102.1	104.0	96.2	97.5	101.6	84.36	82.24	83.08
Formulae based on 2 oxygens											Formulae based on 1		
P	0.025	0.02	0.02	0.024	0.026	0.024	0.026	0.02	0.02	0.026	0.008	0.008	0.007
Nb	0.000	0.00	0.00	0.001	0.000	0.001	0.000	0.00	0.00	0.000	0.001	0.000	0.001
Ta	0.000	0.00	0.00	0.000	0.000	0.000	0.000	0.00	0.00	0.000	0.000	0.001	0.001
Si	0.276	0.24	0.26	0.303	0.320	0.289	0.306	0.27	0.28	0.293	0.317	0.317	0.313
Th	0.005	0.00	0.00	0.002	0.003	0.002	0.003	0.00	0.00	0.003	0.001	0.000	0.000
U	0.002	0.00	0.00	0.000	0.001	0.001	0.001	0.00	0.00	0.002	0.000	0.000	0.000
Al	0.055	0.04	0.04	0.082	0.086	0.036	0.059	0.03	0.03	0.035	0.172	0.151	0.165
Y	0.000	0.00	0.00	0.001	0.000	0.000	0.001	0.00	0.00	0.000	0.000	0.000	0.000
La	0.000	0.00	0.00	0.001	0.000	0.000	0.000	0.00	0.00	0.000	0.000	0.000	0.000
Ce	0.739	0.78	0.74	0.697	0.682	0.756	0.708	0.77	0.76	0.728	0.038	0.020	0.049
Nd	0.005	0.00	0.00	0.004	0.004	0.006	0.005	0.00	0.00	0.005	0.001	0.000	0.000
Dy	0.002	0.00	0.00	0.004	0.003	0.003	0.003	0.00	0.00	0.004	0.002	0.002	0.003
Er	0.000	0.00	0.00	0.000	0.000	0.000	0.000	0.00	0.00	0.001	0.002	0.002	0.003
Yb	0.001	0.00	0.00	0.000	0.000	0.000	0.000	0.00	0.00	0.000	0.000	0.000	0.000
Ca	0.011	0.01	0.01	0.026	0.022	0.032	0.027	0.01	0.03	0.033	0.006	0.005	0.004
Mn	0.016	0.01	0.01	0.021	0.019	0.022	0.019	0.01	0.02	0.021	0.009	0.008	0.008
Fe	0.141	0.16	0.15	0.095	0.082	0.098	0.105	0.12	0.08	0.126	1.005	1.066	1.009
Pb	0.000	0.00	0.00	0.000	0.001	0.000	0.000	0.00	0.00	0.000	0.001	0.000	0.000

Supplementary Table S1. Continued

Sample	Al-Fe-rich silicate rim												
	1	2	3	4	5	6	7	8	9	10	11	12	13
P ₂ O ₅	bdl	bdl	bdl	bdl	0.11	bdl	0.07	bdl	bdl	bdl	2.04	2.08	2.06
SiO ₂	22.0	20.85	21.35	18.70	14.66	16.97	15.88	21.34	20.23	20.71	7.07	6.63	6.67
TiO ₂	0.09	bdl	0.09	bdl	bdl	bdl	0.05	0.09	bdl	0.09	0.63	0.75	0.58
Al ₂ O ₃	3.05	2.82	3.10	3.94	4.83	3.40	5.40	3.06	2.82	3.11	10.65	10.76	10.65
Y ₂ O ₃	0.15	0.14	0.17	0.18	0.72	0.13	0.32	0.15	0.14	0.17	0.13	0.08	0.15
La ₂ O ₃	bdl	bdl	bdl	0.20	2.04	0.31	0.90	bdl	bdl	bdl	0.30	0.41	0.22
Nd ₂ O ₃	bdl	bdl	bdl	0.24	1.45	0.18	0.96	bdl	bdl	bdl	0.37	0.42	0.26
CaO	0.11	bdl	0.09	0.12	0.11	0.09	0.12	0.10	bdl	0.09	0.12	0.11	0.06
FeO	62.60	62.94	62.12	64.94	62.15	65.93	64.00	62.48	62.83	62.00	63.58	62.30	63.81
Na ₂ O	0.18	0.20	0.12	0.09	0.03	0.12	0.06	0.18	0.20	0.12	bdl	bdl	bdl
K ₂ O	0.18	0.13	0.06	0.15	0.07	0.05	0.22	0.18	0.13	0.06	0.02	0.01	0.03
F	0.16	0.14	0.10	0.12	0.33	0.16	0.31	0.15	0.14	0.09	0.40	0.38	0.42
O=F	-0.07	-0.06	-0.04	-0.05	-0.14	-0.07	-0.13	-0.06	-0.06	-0.04	-0.17	-0.16	-0.18
Total	88.45	87.16	87.16	88.63	86.36	87.27	88.16	87.67	86.43	86.40	85.14	83.77	84.73
Formulae based on 1 cation													
P	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.000	0.000	0.000	0.038	0.039	0.038
Si	0.430	0.418	0.424	0.376	0.316	0.355	0.329	0.423	0.411	0.417	0.154	0.146	0.146
Ti	0.001	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.001	0.010	0.012	0.010
Al	0.070	0.067	0.073	0.093	0.123	0.084	0.132	0.071	0.068	0.074	0.273	0.280	0.275
Y	0.002	0.001	0.002	0.002	0.008	0.001	0.004	0.002	0.002	0.002	0.002	0.001	0.002
La	0.000	0.000	0.000	0.001	0.016	0.002	0.007	0.000	0.000	0.000	0.002	0.003	0.002
Nd	0.000	0.000	0.000	0.002	0.011	0.001	0.007	0.000	0.000	0.000	0.003	0.003	0.002
Ca	0.002	0.000	0.002	0.003	0.003	0.002	0.003	0.002	0.000	0.002	0.003	0.003	0.001
Fe	1.022	1.056	1.032	1.093	1.121	1.152	1.108	1.035	1.068	1.044	1.156	1.151	1.170
Na	0.007	0.008	0.005	0.004	0.001	0.005	0.002	0.007	0.008	0.005	0.000	0.000	0.000
K	0.004	0.003	0.002	0.004	0.002	0.001	0.006	0.005	0.003	0.002	0.001	0.000	0.001

bdl, below determination limits of microprobe. Formulae for the Al-Fe-rich silicate is calculated as goethite.

Ab, An, and Or stand for the albite, anorthite and orthoclase end-members, respectively.

Supplementary Table S2. Comparison of *d*-spacings (Å) between Ce-poor, Nd-Y-rich bastnäsite-(La) and typical Y-poor bastnäsite-(La)

<i>d</i> -spacings	1	2	3	4	5	6	7	8	9	10
Ce-poor,	4.8471	3.5110	3.3353	2.8387	2.5706	2.4186	2.2351	2.2117	2.0749	2.0265
Y-poor bastnäsite	4.8590	3.5470	3.0718	2.8649	2.5965	2.4295	-	-	-	2.0479

Supplementary Table S2. Continued.

<i>d</i> -spacings	11	12	13	14	15	16	17	18	19	20
Ce-poor,	1.9910	1.8702	1.8423	1.8086	1.7551	1.6498	1.6122	1.5534	1.4649	1.4218
Y-poor bastnäsite	2.0044	1.8871	-	-	1.7735	1.6660	1.6197	1.5658	1.4733	1.4324

Supplementary Table S2. Continued.

<i>d</i> -spacings	21	22	23	24	25	26	27	28	29	30
Ce-poor,	1.3723	1.3262	1.2799	1.2617	1.2081	1.1872	1.1671	1.1635	1.1391	1.1373
Y-poor bastnäsite	-	1.3406	1.2924	1.2704	1.2148	1.1960	1.1823	1.1738	1.1492	1.1488

d-spacings data of typical Y-poor bastnäsite-(La) are from <http://rruff.geo.arizona.edu/AMS/amcsd.php>