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Supplementary materials

Nataliakulikite, $Ca_4Ti_2(Fe^{3+},Fe^{2+})(Si,Fe^{3+},Al)O_{11}$, a New Perovskite-Supergroup Mineral from Hatrurim Basin, Negev Desert, Israel

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Table S1. Chemical composition (WDS, wt.%) of nataliakulikite from larnite-gehlenite rock (W11-3), Nahal Morag Canyon, Hatrurim Basin, Israel.

Area	S-1	S-1	S-4	S-4	S-4	S-4	S-5	S-5	S-5	S-6	S-6	S-8a	S-8a	S-8b	S-8b	S-9a	S-10	S-10
SiO_2	4.59	5.26	4.32	5.71	4.93	5.40	5.47	5.49	6.87	4.91	5.66	4.32	4.00	5.15	4.03	4.93	5.40	4.53
TiO_2	30.53	28.54	30.66	26.91	26.63	25.83	26.01	27.77	25.48	29.06	27.65	29.68	30.77	29.94	31.34	27.90	27.95	29.02
ZrO_2	0.64	0.61	0.64	0.63	0.71	0.64	0.64	0.59	0.58	0.61	0.67	0.65	0.74	0.56	0.71	0.70	0.73	0.73
Nb_2O_5	0.04	0.02	0.07	0.01	0.03	0.04	0.02	0.08	0.02	0.06	0.00	0.04	0.05	0.10	0.06	0.00	0.06	0.02
Cr_2O_3	0.06	0.17	0.09	0.12	0.10	0.09	0.12	0.12	0.10	0.08	0.12	0.10	0.02	0.07	0.05	0.09	0.07	0.07
Al_2O_3	1.28	1.24	1.47	1.55	2.05	2.39	2.22	1.41	1.85	1.40	2.58	1.94	2.00	1.46	1.76	1.99	1.72	2.05
Fe_2O_3	12.87	16.23	12.76	17.53	18.99	19.62	19.51	16.34	17.36	15.12	14.85	14.36	12.74	13.02	12.09	17.00	15.75	15.32
FeO	6.14	5.38	6.06	3.89	3.05	2.75	3.19	4.33	4.27	5.11	4.81	5.11	5.92	6.34	6.26	4.32	5.20	5.01
MnO	0.13	0.19	0.05	0.15	0.04	0.06	0.06	0.16	0.07	0.12	0.08	0.00	0.00	0.05	0.03	0.03	0.04	0.02
CaO	41.90	41.89	41.87	42.29	42.18	42.37	42.27	42.34	42.25	42.09	42.19	42.04	41.91	42.09	42.06	42.08	41.86	41.92
SrO	0.24	0.27	0.23	0.29	0.20	0.22	0.22	0.28	0.28	0.26	0.29	0.23	0.22	0.28	0.23	0.24	0.28	0.26
UO_2	0.11	0.12	0.19	0.14	0.23	0.11	0.17	0.14	0.17	0.23	0.14	0.21	0.25	0.12	0.20	0.10	0.14	0.21
Sum	98.53	99.90	98.40	99.23	99.14	99.52	99.91	99.05	99.30	99.05	99.05	98.68	98.62	99.18	98.82	99.38	99.20	99.16

Formula based on 8 cations and 11 oxygens																		
Si	0.411	0.465	0.387	0.506	0.438	0.476	0.481	0.488	0.606	0.437	0.500	0.386	0.357	0.457	0.359	0.437	0.479	0.403
Al	0.135	0.129	0.155	0.162	0.215	0.249	0.231	0.148	0.192	0.147	0.269	0.204	0.210	0.152	0.185	0.208	0.180	0.215
Fe^{3+}	0.454	0.406	0.458	0.332	0.347	0.275	0.288	0.364	0.202	0.416	0.231	0.410	0.432	0.391	0.456	0.356	0.341	0.382
Sum T	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ti	2.054	1.896	2.066	1.793	1.779	1.713	1.721	1.855	1.689	1.946	1.836	1.992	2.068	1.997	2.102	1.858	1.865	1.939
Zr	0.028	0.026	0.028	0.027	0.031	0.028	0.027	0.025	0.025	0.026	0.029	0.028	0.032	0.024	0.031	0.030	0.032	0.031
Nb	0.001	0.001	0.003	0.001	0.001	0.001	0.001	0.003	0.001	0.002	0.000	0.002	0.002	0.004	0.002	0.000	0.002	0.001
Cr	0.004	0.012	0.006	0.008	0.007	0.006	0.009	0.009	0.007	0.006	0.008	0.007	0.002	0.005	0.003	0.006	0.005	0.005
Fe^{3+}	0.412	0.673	0.403	0.838	0.923	1.027	1.003	0.727	0.949	0.597	0.755	0.554	0.424	0.478	0.356	0.777	0.711	0.642
Fe^{2+}	0.459	0.397	0.454	0.288	0.227	0.203	0.235	0.322	0.315	0.381	0.355	0.381	0.443	0.470	0.467	0.320	0.386	0.372
Mn	0.010	0.014	0.004	0.012	0.003	0.004	0.004	0.012	0.005	0.009	0.006	0.000	0.000	0.004	0.002	0.002	0.003	0.002
Sum B	2.969	3.019	2.964	2.967	2.970	2.983	3.001	2.953	2.991	2.967	2.991	2.964	2.971	2.983	2.964	2.993	3.003	2.992
Ca	4.016	3.965	4.020	4.015	4.015	4.004	3.985	4.029	3.991	4.015	3.992	4.020	4.013	4.000	4.020	3.992	3.979	3.991
Sr	0.012	0.014	0.012	0.015	0.010	0.011	0.011	0.014	0.014	0.014	0.015	0.012	0.011	0.014	0.012	0.012	0.014	0.013
U	0.002	0.002	0.004	0.003	0.005	0.002	0.003	0.003	0.003	0.004	0.003	0.004	0.005	0.002	0.004	0.002	0.003	0.004
Sum A	4.031	3.981	4.036	4.033	4.030	4.017	3.999	4.047	4.009	4.033	4.009	4.036	4.029	4.017	4.036	4.007	3.996	4.008
End members (mole %)																		
$Ca_4Ti_2Fe^{3+}Fe^{3+}O_{11}$	45.42	40.62	45.78	33.18	34.71	27.52	28.82	36.44	20.25	41.61	23.14	41.02	43.23	39.09	45.58	35.57	34.08	38.24
$Ca_4Ti_2Fe^{3+}AlO_{11}$	13.52	12.91	15.51	16.22	21.50	24.85	23.05	14.79	19.18	14.68	26.87	20.43	21.02	15.22	18.47	20.77	18.02	21.51
$Ca_4Ti_2Fe^{2+}SiO_{11}$	41.07	46.47	38.71	50.60	43.80	47.63	48.13	48.76	60.57	43.71	49.98	38.55	35.75	45.68	35.95	43.66	47.91	40.25

MgO, CuO, NiO and ZnO are below detection limits (<0.005 wt.%). Ntk – nataliakulite; Ntk-TEM – grain used for HRTEM study (see Figure 10); Ntk-1-2 – grains used for EBSD and Raman studies (see Figures 9 and 11); FeO and Fe_2O_3 are calculated on charge balance.

Table S1. *Cont.*

Area	S-11	S-11	S-11	S-11	S-12	S-12	S-12	S-12	S-13a	S-13a	S-14a	S-14a	S-14a	S-14a	refl 4	refl 4	Ntk-TEM	Ntk-TEM	Ntk-TEM
SiO_2	4.99	4.60	5.99	5.47	4.44	4.07	4.69	4.24	3.71	4.63	6.09	4.06	5.05	5.60	5.63	5.93	4.38	5.84	5.11
TiO_2	27.61	31.20	28.00	26.66	30.47	31.00	29.27	31.13	32.64	28.45	29.34	31.85	29.86	27.79	26.37	26.01	30.33	28.69	29.51
ZrO_2	0.67	0.69	0.70	0.64	0.69	0.70	0.73	0.76	0.70	0.76	0.64	0.81	0.76	0.72	0.54	0.50	0.75	0.68	0.71
Nb_2O_5	0.01	0.04	0.04	0.05	0.01	0.07	0.06	0.03	0.08	0.04	0.05	0.05	0.10	0.00	0.04	0.04	0.00	0.06	0.03
Cr_2O_3	0.09	0.08	0.06	0.09	0.06	0.06	0.07	0.10	0.06	0.09	0.06	0.08	0.04	0.07	0.08	0.08	0.08	0.10	0.09
Al_2O_3	2.25	2.76	2.08	2.76	2.03	2.14	2.10	1.92	2.02	2.30	2.03	1.85	1.53	2.08	1.61	1.70	2.04	2.25	2.14
Fe_2O_3	17.02	10.67	14.35	17.62	13.26	12.42	14.48	11.85	9.93	16.15	11.44	10.79	12.92	15.56	18.60	18.69	13.31	13.04	13.17
FeO	4.01	6.66	5.51	3.89	5.88	6.08	5.30	6.39	7.07	4.48	7.02	6.84	6.40	5.05	3.80	3.74	6.13	6.22	6.18
MnO	0.04	0.03	0.05	0.06	0.03	0.02	0.00	0.02	0.00	0.00	0.06	0.00	0.07	0.07	0.21	0.25	0.00	0.07	0.04
CaO	42.17	42.50	42.35	42.23	42.28	42.07	42.13	42.07	42.08	42.20	42.18	42.06	41.91	42.10	41.82	41.91	41.90	42.12	42.01
SrO	0.24	0.22	0.26	0.28	0.23	0.28	0.27	0.22	0.27	0.24	0.23	0.25	0.30	0.27	0.32	0.32	0.23	0.25	0.24
UO_2	0.14	0.24	0.14	0.19	0.19	0.19	0.20	0.19	0.21	0.20	0.13	0.17	0.07	0.17	0.28	0.28	0.19	0.08	0.13
Sum	99.23	99.69	99.52	99.94	99.58	99.08	99.29	98.91	98.79	99.54	99.26	98.81	99.01	99.48	99.30	99.44	99.33	99.39	99.36
Formula based on 8 cations and 11 oxygens																			
Si	0.442	0.404	0.527	0.480	0.392	0.362	0.416	0.377	0.331	0.409	0.537	0.362	0.449	0.494	0.500	0.525	0.388	0.514	0.451
Al	0.235	0.286	0.215	0.286	0.212	0.224	0.219	0.202	0.212	0.240	0.211	0.194	0.161	0.216	0.168	0.177	0.213	0.233	0.223
Fe^{3+}	0.323	0.310	0.257	0.234	0.396	0.415	0.366	0.421	0.457	0.351	0.253	0.444	0.390	0.289	0.332	0.298	0.398	0.253	0.325
Sum T	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ti	1.838	2.061	1.853	1.759	2.025	2.071	1.951	2.083	2.188	1.891	1.944	2.135	1.997	1.844	1.761	1.732	2.022	1.900	1.961
Zr	0.029	0.030	0.030	0.027	0.030	0.030	0.032	0.033	0.030	0.033	0.028	0.035	0.033	0.031	0.023	0.022	0.032	0.029	0.031
Nb	0.000	0.002	0.001	0.002	0.000	0.003	0.002	0.001	0.003	0.002	0.002	0.002	0.004	0.000	0.002	0.002	0.000	0.003	0.001
Cr	0.006	0.005	0.004	0.006	0.004	0.004	0.005	0.007	0.004	0.006	0.004	0.006	0.003	0.005	0.006	0.006	0.005	0.007	0.006
Fe^{3+}	0.811	0.395	0.693	0.929	0.486	0.416	0.600	0.373	0.209	0.724	0.506	0.280	0.474	0.744	0.911	0.947	0.489	0.611	0.551
Fe^{2+}	0.297	0.489	0.405	0.285	0.435	0.452	0.393	0.476	0.527	0.331	0.517	0.510	0.476	0.373	0.282	0.277	0.455	0.458	0.456
Mn	0.003	0.002	0.004	0.005	0.002	0.001	0.000	0.001	0.000	0.000	0.004	0.000	0.005	0.005	0.016	0.019	0.000	0.005	0.003
Sum B	2.985	2.984	2.991	3.013	2.982	2.977	2.982	2.974	2.963	2.987	3.005	2.967	2.991	3.002	3.000	3.003	3.004	3.013	3.009
Ca	4.001	4.000	3.993	3.969	4.003	4.005	4.000	4.012	4.019	3.997	3.981	4.017	3.992	3.981	3.978	3.975	3.980	3.973	3.977
Sr	0.012	0.011	0.013	0.014	0.012	0.014	0.014	0.011	0.014	0.012	0.011	0.013	0.015	0.014	0.016	0.016	0.012	0.013	0.012
U	0.003	0.005	0.003	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.002	0.003	0.001	0.003	0.006	0.006	0.004	0.001	0.003
Sum A	4.015	4.016	4.009	3.987	4.018	4.023	4.018	4.026	4.037	4.013	3.995	4.033	4.009	3.998	4.000	3.997	3.996	3.987	3.991

End members (mole %)																			
$Ca_4Ti_2Fe^{3+}Fe^{3+}O_{11}$	32.35	31.04	25.74	23.44	39.60	41.47	36.56	42.10	45.70	35.10	25.27	44.40	39.03	28.94	33.17	29.77	39.85	25.27	32.53
$Ca_4Ti_2Fe^{3+}AlO_{11}$	23.47	28.55	21.54	28.58	21.17	22.37	21.88	20.17	21.23	23.97	21.08	19.41	16.07	21.63	16.85	17.74	21.32	23.32	22.32
$Ca_4Ti_2Fe^{2+}SiO_{11}$	44.18	40.41	52.72	47.99	39.23	36.16	41.56	37.73	33.07	40.93	53.65	36.19	44.90	49.42	49.98	52.50	38.84	51.42	45.15

MgO, CuO, NiO and ZnO are below detection limits (<0.005 wt.%). Ntk – nataliakulite; Ntk-TEM – grain used for HRTEM study (see Figure 10); Ntk-1-2 – grains used for EBSD and Raman studies (see Figures 9 and 11); FeO and Fe_2O_3 are calculated on charge balance.

Table S1. *Cont.*

Area	**Ntk-1**	**Ntk-1**	**Ntk-1**	**Ntk-1**	**Ntk-1**	**Ntk-1**	**Ntk-2**	**Ntk-2**	**Ntk-2**	**Ntk-2**	**Ntk-2**	**Ntk-2**	**Ntk-2**
						n=5							**n=6**
SiO_2	4.92	5.54	5.24	4.90	4.96	5.11	5.11	5.26	5.28	5.31	4.66	5.37	5.17
TiO_2	30.33	29.02	29.02	30.03	30.03	29.69	28.64	29.29	29.04	28.39	32.13	29.17	29.44
ZrO_2	0.66	0.77	0.80	0.76	0.74	0.75	0.65	0.74	0.59	0.53	0.84	0.77	0.69
Nb_2O_5	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Cr_2O_3	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Al_2O_3	2.17	2.29	2.63	2.55	2.23	2.37	2.31	2.44	2.40	3.02	1.91	2.72	2.47
Fe_2O_3	12.19	12.98	13.03	12.37	12.23	12.56	14.08	12.68	13.29	14.17	9.24	13.08	12.76
FeO	6.71	6.02	5.79	6.31	6.60	6.29	5.10	6.03	5.94	4.99	8.07	5.91	6.01
MnO	0.05	0.05	0.05	0.05	0.05	0.05	0.14	0.14	0.14	0.14	0.14	0.14	0.14
CaO	42.01	42.29	42.15	42.19	41.91	42.11	41.99	42.06	41.87	42.31	41.91	42.37	42.09
SrO	0.30	0.30	0.32	0.30	0.31	0.31	0.32	0.30	0.32	0.31	0.34	0.33	0.32
UO_2	0.28	0.28	0.27	0.24	0.33	0.28	0.28	0.28	0.28	0.32	0.28	0.24	0.28
Sum	99.74	99.66	99.43	99.82	99.51	99.63	98.74	99.34	99.27	99.61	99.64	100.22	99.47
Formula based on 8 cations and 11 oxygens													
Si	0.434	0.488	0.462	0.431	0.438	0.450	0.454	0.464	0.467	0.466	0.412	0.469	0.456
Al	0.225	0.238	0.273	0.264	0.232	0.247	0.242	0.254	0.250	0.313	0.199	0.280	0.256
Fe^{3+}	0.341	0.275	0.265	0.305	0.330	0.303	0.304	0.282	0.283	0.221	0.389	0.250	0.288
Sum T	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ti	2.010	1.920	1.924	1.985	1.995	1.967	1.915	1.945	1.930	1.875	2.135	1.918	1.953
Zr	0.028	0.033	0.034	0.033	0.032	0.032	0.028	0.032	0.025	0.023	0.036	0.033	0.030
Nb	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Cr	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
Fe^{3+}	0.468	0.584	0.600	0.514	0.484	0.530	0.638	0.561	0.601	0.716	0.225	0.610	0.559
Fe^{2+}	0.495	0.443	0.427	0.464	0.488	0.463	0.379	0.445	0.439	0.366	0.596	0.432	0.443
Mn	0.004	0.004	0.004	0.004	0.004	0.004	0.011	0.010	0.010	0.010	0.010	0.010	0.010

Sum B	3.012	2.992	2.997	3.006	3.010	3.003	2.978	3.000	3.013	2.997	3.010	3.010	3.001
Ca	3.967	3.987	3.982	3.974	3.968	3.976	4.000	3.979	3.965	3.981	3.967	3.968	3.977
Sr	0.015	0.015	0.016	0.015	0.016	0.016	0.016	0.015	0.016	0.016	0.017	0.017	0.016
U	0.005	0.005	0.005	0.005	0.006	0.005	0.006	0.006	0.006	0.006	0.006	0.005	0.005
Sum A	3.988	4.008	4.003	3.994	3.990	3.997	4.022	4.000	3.987	4.003	3.990	3.990	3.999
End members (mole %)													
$Ca_4Ti_2Fe^{3+}Fe^{3+}O_{11}$	34.09	27.50	26.47	30.50	32.95	30.30	30.37	28.17	28.33	22.11	38.94	25.03	28.81
$Ca_4Ti_2Fe^{3+}AlO_{11}$	22.54	23.75	27.33	26.42	23.22	24.65	24.20	25.39	25.00	31.26	19.89	28.02	25.64
$Ca_4Ti_2Fe^{2+}SiO_{11}$	43.36	48.75	46.20	43.08	43.83	45.04	45.43	46.44	46.67	46.63	41.17	46.94	45.55

MgO, CuO, NiO and ZnO are below detection limits (<0.005 wt.%). Ntk – nataliakulite; Ntk-TEM – grain used for HRTEM study (see Figure 10); Ntk-1-2 – grains used for EBSD and Raman studies (see Figures 9 and 11); FeO and Fe_2O_3 are calculated on charge balance.

Table S2. Chemical composition (WDS-EDS, wt.%) of Fe^{3+}-rich perovskite from larnite-gehlenite rocks (W11-3, W11-2-2), Nahal Morag Canyon, Hatrurim Basin, Israel.

Sample	**W11-3**					**W11-2-2**				
Area	**S-8a**	**S-9a**	**S-12**	**S-13a**	**S-14a**	**Refl-2**	***n*=6**	**s2**	**s2**	***n*=2**
SiO_2	3.13	3.70	3.61	3.71	4.04	4.66	3.81	2.85	3.02	2.94
TiO_2	34.98	33.69	33.60	32.64	33.10	32.13	33.36	38.70	38.53	38.62
ZrO_2	0.79	0.77	0.73	0.70	0.61	0.84	0.74	0.46	0.36	0.41
Nb_2O_5	0.12	0.04	0.04	0.08	0.02	0.04	0.06	0.00	0.00	0.00
Cr_2O_3	0.03	0.07	0.11	0.06	0.05	0.08	0.07	0.19	0.26	0.23
Al_2O_3	1.51	1.62	2.10	2.02	1.64	1.91	1.80	1.28	1.27	1.28
Fe_2O_3	17.58	17.51	16.85	17.79	18.04	18.20	17.66	13.87	14.13	14.00
MnO	0.00	0.00	0.00	0.00	0.02	0.14	0.03	0.14	0.14	0.14
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	41.91	41.96	41.94	42.08	42.07	41.91	41.98	41.38	41.17	41.28
SrO	0.24	0.21	0.26	0.27	0.27	0.34	0.27	0.20	0.20	0.20
UO_2	0.23	0.22	0.22	0.21	0.21	0.28	0.23	0.00	0.00	0.00
Sum	100.52	99.79	99.46	99.58	100.07	100.53	99.99	99.07	99.08	99.07
Formula based on 2 cations										
Si	0.070	0.082	0.081	0.083	0.090	0.103	0.085	0.064	0.068	0.066
Al	0.039	0.043	0.055	0.053	0.043	0.050	0.047	0.034	0.034	0.034
Ti	0.585	0.565	0.564	0.547	0.553	0.534	0.558	0.655	0.652	0.654
Zr	0.009	0.008	0.008	0.008	0.007	0.009	0.008	0.005	0.004	0.005
Nb	0.001	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000
Cr	0.000	0.001	0.002	0.001	0.001	0.001	0.001	0.003	0.005	0.004
Fe^{3+}	0.294	0.294	0.283	0.298	0.301	0.303	0.296	0.235	0.239	0.237
Mn	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.003	0.003	0.003
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.998	1.002	1.003	1.005	1.001	0.992	1.000	0.998	0.993	0.996
Sr	0.003	0.003	0.003	0.004	0.003	0.004	0.003	0.003	0.003	0.003
U	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000
$CaFeO_{2.5}$	0.40	0.42	0.42	0.44	0.44	0.46	0.43	0.34	0.34	0.34

The molar fraction of $CaFeO_{2.5}$ was calculated as $(Fe^{3+} + Al + Cr + Si)/(Fe^{3+} + Al + Cr + Ti + Si + Zr + Nb)$. Photo of Fe^{3+}-rich perovskite from sample W11-2-2 is given in Figure 13 of the manuscript.