Supplementary Information

Table A1. Output of *SVDdiagnostic* for problematic cases of Rietveld refinements of ellestadite $Ca_{10}[(SiO_4)_x(PO_4)_{6-2x}(SO_4)_x]Cl_2$ for the models in which the Ca(1) and Ca(2) sites were refined simultaneously. (a) $x = 2.5$, (b) $x = 2$, (c) $x = 1$, (d) $x = 0.5$, and (e) $x = 0$.

Table A2. Bond lengths in monoclinic structure ($P2_1/m$) for selected compositions.

Table A3. Composition of ellestadite obtained by EPMA.

Figure A1. FTIR spectra of $Ca_{10}(SiO_4)_{2.5}(PO_4)(SO_4)_{2.5}Cl_2$ (a) before and (b) after treatment in dilute acid.

Figure A2. NPD $P6_3/m$ Rietveld profiles (a) $x = 3$, (b) $x = 1$ and (c) $x = 0$. (x in $Ca_{10}[(SiO_4)_x(PO_4)_{6-2x}(SO_4)_x]Cl_2$)

Table A1

(a). Output of *SVDdiagnostic* for problematic cases of Rietveld refinements of $Ca_{10}(SiO_4)_{2.5}(PO_4)(SO_4)_{2.5}Cl_2$.

PRECONDITIONED normal matrix

Condition number for matrix of normal equations = 0.642E+02

Error propagation is likely to spoil 2 trailing decimal digits out of probably 14.

Problem well conditioned for double-precision matrix inversion.

Eigenvectors for P1.out ranked according to eigenvalues are printed as columns below

Eigenvector #		1 ..	26	27	28	29	30	31	32	33
bkg1	1	-0.341 ..	0.26	-0.185	0.153	0.295	0.058	-0.248	0.531	-0.034
bkg2	2	-0.045 ..	-0.041	0.001	-0.006	-0.034	-0.011	-0.282	0.059	0.007
bkg3	3	0.265 ..	0.162	-0.37	0.396	-0.108	-0.043	-0.112	-0.219	0.015
bkg4	4	-0.011 ..	-0.189	-0.03	0.032	0.174	0.025	0.021	0.147	0
bkg5	5	0.011 ..	0.176	-0.235	0.213	-0.04	-0.029	-0.146	-0.074	0.004
zeroerror	6	0.003 ..	0.003	0.017	-0.018	0.049	-0.749	0.031	0.082	0.001
peaktype	7	0.078 ..	0.059	0.057	0.103	-0.024	0.021	-0.192	-0.263	0.019
Ascale	8	-0.351 ..	0.068	-0.015	-0.122	0.092	-0.097	-0.331	-0.687	0.085
Aalta	9	-0.012 ..	-0.032	-0.487	-0.305	-0.113	-0.005	0.009	0.019	-0.045
Ablta	10	-0.019 ..	-0.003	0.565	0.43	0.14	-0.028	-0.049	-0.023	0.028
Aclta	11	-0.011 ..	0.067	-0.113	-0.117	-0.079	-0.045	-0.019	0.078	-0.006
peaktyep	12	0.15 ..	-0.121	-0.078	0.3	-0.4	-0.02	0.338	-0.032	-0.025
P1scale	13	-0.41 ..	0.045	0.127	0.105	-0.753	-0.017	-0.25	0.176	-0.048
P1atla	14	-0.01 ..	-0.011	-0.031	0.016	-0.009	-0.628	0.033	0.055	0.011
P1ctla	15	0.015 ..	0.007	0.043	-0.032	0.064	-0.15	-0.009	0.019	-0.001
Ca1z	16	-0.004 ..	0.103	0.113	-0.027	-0.027	-0.02	0.025	0.006	0
Ca1occ	17	-0.286 ..	0.109	-0.055	0.039	0.007	0.016	0.037	0.047	0.709
Ca2x	18	0.027 ..	0.106	0.192	-0.354	-0.138	-0.001	0.091	-0.032	-0.03
Ca2y	19	0.013 ..	0.197	0.202	-0.349	-0.149	0.005	0.1	-0.012	-0.034
Ca2occ	20	-0.283 ..	0.128	-0.032	0.09	0.095	-0.009	-0.001	-0.088	-0.692
Cabeq	21	0.372 ..	0.734	0.068	-0.068	0.002	-0.004	-0.119	0.051	0.024
Px	22	0.013 ..	0.004	0.013	-0.012	-0.006	-0.001	-0.013	-0.019	0
Py	23	0.005 ..	-0.031	0.013	0.045	0.019	-0.004	0	0.005	0.008
Pocc	24	0.16 ..	0.174	0.088	0.046	-0.143	0.003	-0.026	0.063	-0.003
O1x	25	-0.045 ..	0.025	0.095	-0.031	0.06	0.015	0.006	0.001	-0.006
O1y	26	0.04 ..	-0.033	-0.019	0.017	0.046	0.01	0.006	-0.001	-0.002
Obeq	27	0.388 ..	-0.352	0.092	-0.15	-0.063	-0.024	-0.677	0.162	-0.014
O2x	28	-0.017 ..	-0.013	-0.011	-0.006	0.035	-0.001	0.016	0.017	-0.004
O2y	29	-0.008 ..	-0.044	-0.131	-0.007	-0.005	0	0.004	0.008	0.009
O3x	30	0.018 ..	0.068	0.086	0.046	0.012	-0.02	0.023	-0.003	0.015
O3y	31	0.001 ..	0.014	0.105	0.101	0.022	-0.001	0.03	-0.014	-0.018
O3z	32	-0.006 ..	0.114	0.015	-0.09	-0.047	0	0.025	0.067	-0.021
Clz	33	-0.091 ..	0.056	0.119	-0.21	0.037	-0.011	0.035	0.002	-0.017
Eigenvalues		4.35E+03 ..	3.36E-01	3.15E+02	2.87E-01	1.60E-01	1.44E-01	1.06E-01	6.33E-02	3.33E-02

Table A1

(b). Output of *SVDdiagnostic* for problematic cases of Rietveld refinements of $Ca_{10}(SiO_4)_2\ (PO_4)_2(SO_4)_2\ Cl_2$.

PRECONDITIONED normal matrix

Condition number for matrix of normal equations = 0.136E+03

Error propagation is likely to spoil 2 trailing decimal digits out of probably 14.

Problem well conditioned for double-precision matrix inversion.

Eigenvectors for P2.out ranked according to eigenvalues are printed as columns below

Eigenvector #		1 ..	26	27	28	29	30	31	32	33
bkg1	1	-0.354 ..	-0.325	-0.217	-0.097	-0.203	0.339	-0.051	-0.541	-0.035
bkg2	2	-0.085 ..	0.23	0.043	-0.07	0.052	-0.044	-0.019	-0.309	-0.021
bkg3	3	0.268 ..	-0.306	-0.582	0.181	0.101	-0.142	-0.003	0.007	0.004
bkg4	4	0.021 ..	0.103	0.093	0.187	-0.079	0.188	-0.027	-0.061	-0.018
bkg5	5	0.008 ..	-0.237	-0.355	0.06	0.048	-0.059	-0.013	-0.077	-0.002
zeroerror	6	0.001 ..	0.014	0.025	0.041	-0.158	-0.156	-0.705	0.016	-0.013
peaktype	7	0.047 ..	0.029	-0.09	-0.188	0.491	0.035	-0.136	0.061	-0.008
Ascale	8	-0.258 ..	0.06	-0.102	-0.24	0.653	0.063	-0.207	0.123	-0.013
Aalta	9	0.008 ..	0.081	-0.035	0.031	0.054	0.02	0.022	0.007	0.005
Ablta	10	-0.004 ..	-0.01	0.039	-0.044	-0.055	0.007	-0.011	-0.003	0
Aclta	11	-0.001 ..	-0.048	0.012	0.01	-0.03	-0.021	-0.041	-0.019	-0.004
peaktyep	12	0.139 ..	0.066	-0.182	0.166	-0.075	-0.351	0.089	0.202	0.025
P1scale	13	-0.412 ..	0.142	-0.03	-0.111	-0.009	-0.752	0.177	-0.263	0.025
P1atla	14	-0.007 ..	-0.047	0.017	0.012	-0.167	-0.17	-0.61	0.008	-0.028
P1ctla	15	0.011 ..	0.068	0.016	0.063	-0.029	0.008	-0.117	-0.004	0.001
Ca1z	16	-0.009 ..	-0.143	0.043	-0.062	0	-0.042	0.006	0.024	0.004
Ca1occ	17	-0.299 ..	-0.091	-0.097	-0.019	-0.001	0.011	0.026	0.053	-0.709
Ca2x	18	0.026 ..	-0.433	0.342	-0.102	0.1	-0.13	0.021	0.094	0.036
Ca2y	19	0.02 ..	-0.477	0.311	-0.17	0.039	-0.137	0.039	0.092	0.039
Ca2occ	20	-0.295 ..	-0.054	-0.145	-0.036	-0.008	0.073	-0.034	-0.007	0.698
Cabeq	21	0.014 ..	0.041	0.002	-0.028	0.035	-0.016	0.001	0.002	0.003
Px	22	0.007 ..	0.024	0.006	0.043	-0.034	0.016	-0.006	-0.008	-0.009
Py	23	0.174 ..	-0.204	0.017	-0.106	-0.099	-0.124	0.046	-0.039	-0.006
Pocc	24	-0.055 ..	0.03	0.091	-0.064	-0.026	0.056	0	0.004	0.005
O1x	25	0.05 ..	0.104	-0.032	0.024	0.009	0.039	-0.006	-0.006	0.003
O1y	26	-0.013 ..	0.157	0.001	-0.016	-0.044	0.042	-0.004	0.016	0
Obeq	27	-0.008 ..	0.139	-0.061	0.031	-0.019	0.008	-0.014	-0.006	-0.02
O2x	28	0.4 ..	0.022	0.239	0.206	0.343	-0.095	-0.056	-0.66	-0.014
O2y	29	0.018 ..	0.131	-0.023	-0.069	-0.03	-0.001	-0.024	0.018	-0.016
O3x	30	0.005 ..	0.235	-0.027	-0.049	-0.038	0.011	0.006	0.034	0.021
O3y	31	0.001 ..	0.067	0.078	-0.117	-0.12	-0.02	0.011	-0.013	0.008
O3z	32	-0.1 ..	-0.019	0.233	-0.149	-0.059	0.034	-0.02	0.024	0.018
Clz	33	0.392 ..	0.111	-0.206	-0.789	-0.196	-0.004	0.006	-0.107	-0.028
Eigenvalues		4.36E+03 ..	3.56E-01	2.90E+02	2.71E-01	2.06E-01	1.38E-01	1.21E-01	7.40E-02	3.22E-02

Table A1

(c). Output of *SVDdiagnostic* for problematic cases of Rietveld refinements of $Ca_{10}(SiO_4)\ (PO_4)_4(SO_4)\ Cl_2$.

PRECONDITIONED normal matrix

Condition number for matrix of normal equations = 0.663E+02

Error propagation is likely to spoil 2 trailing decimal digits out of probably 14.

Problem well conditioned for double-precision matrix inversion.

Eigenvectors for P2.out ranked according to eigenvalues are printed as columns below

Eigenvector #		1 ..	26	27	28	29	30	31	32	33
bkg1	1	-0.393 ..	0.268	-0.167	0.054	-0.014	-0.044	-0.402	-0.05	0.55
bkg2	2	-0.111 ..	-0.181	-0.007	0.055	0.097	-0.082	-0.012	0.124	0.331
bkg3	3	0.267 ..	0.361	-0.438	-0.256	0.147	-0.071	0.188	0.176	0.071
bkg4	4	0.056 ..	-0.105	-0.111	-0.171	-0.122	0.022	-0.172	-0.003	0.072
bkg5	5	0.01 ..	0.304	-0.298	-0.144	0.027	-0.023	0.087	0.107	0.077
zeroerror	6	0.022 ..	-0.044	-0.057	-0.016	0.161	0.713	0.008	0.14	0.047
peaktype	7	0.065 ..	0.049	0.013	0.114	0.091	-0.122	0.175	0.352	-0.074
Ascale	8	-0.335 ..	0.066	0.066	0.199	0.147	-0.129	0.231	0.673	-0.145
Aalta	9	-0.009 ..	-0.05	-0.075	0.04	-0.033	0.034	0.022	-0.059	0.011
Ablta	10	0.009 ..	-0.181	-0.088	0.04	-0.005	0.004	0.039	0.006	0.005
Aclta	11	-0.008 ..	0.219	0.079	-0.066	0.075	0.026	-0.018	-0.044	0.047
peaktyep	12	0.12 ..	-0.068	-0.218	-0.261	0.028	0.008	0.274	-0.208	-0.192
P1scale	13	-0.432 ..	-0.048	-0.047	0.085	0.264	0.003	0.639	-0.403	0.244
P1atla	14	-0.014 ..	0.064	0.056	0.026	0.138	0.616	-0.031	0.117	0.048
P1ctla	15	-0.028 ..	-0.145	-0.13	-0.062	0.018	0.134	0.075	0.025	0.012
Ca1z	16	0 ..	0.191	0.077	-0.078	0.012	0.017	0.017	-0.015	-0.013
Ca2x	17	-0.01 ..	0.195	0.451	-0.022	-0.095	0.061	0.131	-0.079	-0.072
Ca2y	18	0.028 ..	0.39	0.391	-0.045	-0.046	0.026	0.087	-0.105	-0.062
Px	19	-0.009 ..	-0.084	0.047	0.034	-0.003	0	0.027	0.027	-0.009
Py	20	0.015 ..	-0.035	-0.016	-0.034	0.006	-0.005	-0.022	0	0.002
Pocc	21	0.247 ..	0.186	0.003	0.111	0.081	0.021	0.107	-0.149	0.038
O1x	22	-0.046 ..	0.015	0.103	0.132	-0.018	-0.005	-0.051	0.001	-0.021
O1y	23	0.042 ..	-0.015	-0.038	0.035	-0.023	-0.012	-0.014	0.013	0.007
Obeq	24	0.006 ..	-0.018	-0.03	-0.018	0.019	0.002	-0.038	0.011	-0.006
O2x	25	0.001 ..	-0.049	-0.079	-0.033	0.035	-0.004	-0.012	0.003	0
O2y	26	0.429 ..	-0.183	0.337	-0.166	-0.067	-0.066	0.232	0.214	0.647
O3x	27	-0.01 ..	-0.313	0.003	0.051	0.05	0.007	0.016	0	-0.018
O3y	28	0.008 ..	-0.318	-0.062	0.054	-0.038	0.009	0.036	0.005	-0.024
O3z	29	-0.014 ..	0.053	0.037	0.133	0.014	0.041	-0.014	-0.099	0.015
Cl1z	30	-0.027 ..	0.055	0.182	0.003	0.434	-0.059	-0.174	-0.065	-0.04
Cl1occ	31	-0.166 ..	0.101	-0.116	0.175	-0.652	0.119	0.167	0.063	0.019
Clbeq	32	0.397 ..	0.094	-0.175	0.767	0.154	-0.027	-0.016	-0.118	0.064
Cl2z	33	0.059 ..	0.086	-0.044	0.16	-0.368	0.124	0.181	-0.015	0.072
Eigenvalues		4.18E+03 ..	3.74E-01	0.3	0.00E+00	2.61E-01	1.96E-01	1.68E-01	1.18E-01	1.07E-01	6.31E-02

Table A1

(d). Output of *SVDdiagnostic* for problematic cases of Rietveld refinements of $Ca_{10}(SiO_4)_{0.5}(PO_4)_5(SO_4)_{0.5}Cl_2$.

PRECONDITIONED normal matrix

Condition number for matrix of normal equations = 0.564E+02

Error propagation is likely to spoil 2 trailing decimal digits out of probably 14.

Problem well conditioned for double-precision matrix inversion.

Eigenvectors for P2.out ranked according to eigenvalues are printed as columns below

Eigenvector #		1 ..	26	27	28	29	30	31	32	33
bkg1	1	-0.377 ..	0.27	0.222	-0.036	-0.014	0.172	0.191	0.306	0.519
bkg2	2	-0.132 ..	-0.229	-0.043	-0.025	-0.049	-0.075	0.011	0.07	0.353
bkg3	3	0.244 ..	0.335	0.391	0.359	-0.127	-0.224	-0.086	-0.047	0.127
bkg4	4	0.071 ..	-0.127	0.007	0.203	0.046	0.096	0.052	0.147	0.078
bkg5	5	0.011 ..	0.276	0.28	0.23	-0.021	-0.11	-0.063	0.007	0.09
zeroerror	6	0.009 ..	-0.029	0.034	0.009	-0.319	0.399	-0.555	0.003	0.043
peaktype	7	0.044 ..	0.023	0.024	-0.142	0.034	-0.408	-0.309	0.058	-0.039
Ascale	8	-0.255 ..	0.032	0.034	-0.2	0.038	-0.55	-0.458	0.101	-0.052
Aalta	9	0.004 ..	0.016	0.005	0.002	0.009	0.06	-0.008	-0.015	-0.017
Ablta	10	0.006 ..	-0.076	0.026	0.016	0.01	-0.039	-0.009	-0.045	-0.002
Aclta	11	0.001 ..	0.062	-0.015	0.015	-0.037	0.013	0.032	0.004	0.034
peaktyep	12	0.153 ..	-0.119	0.131	0.366	-0.072	-0.015	0.039	-0.336	-0.241
P1scale	13	-0.447 ..	-0.039	0.063	-0.09	-0.274	-0.098	0.089	-0.747	0.207
P1atla	14	0.005 ..	0.097	-0.065	-0.033	-0.235	0.34	-0.439	0.036	0.041
P1ctla	15	-0.029 ..	-0.161	0.094	0.087	-0.09	0.151	-0.163	-0.076	0.015
Ca1z	16	-0.006 ..	0.139	-0.035	0.052	-0.005	0.02	-0.011	-0.015	-0.011
Ca2x	17	-0.03 ..	0.335	-0.415	-0.079	0.076	0.067	-0.027	-0.16	-0.068
Ca2y	18	0.046 ..	0.493	-0.366	-0.058	0.057	0.027	0.019	-0.112	-0.071
Px	19	-0.021 ..	-0.091	-0.037	-0.027	0.004	-0.027	-0.034	-0.011	0.003
Py	20	0.024 ..	-0.072	0.008	0.057	-0.009	0.007	0.016	0.021	-0.001
Pocc	21	0.267 ..	0.249	0.109	-0.174	-0.09	0.039	0.06	-0.175	0.02
O1x	22	-0.053 ..	-0.026	-0.038	-0.147	0.031	0.026	0.023	0.028	-0.02
O1y	23	0.042 ..	-0.057	0.036	-0.02	0.014	-0.001	0.017	0.014	0.003
Obeq	24	0.003 ..	-0.043	-0.001	0.042	-0.002	-0.003	-0.007	0.037	-0.004
O2x	25	0.003 ..	-0.058	0.028	0.059	-0.038	-0.005	0.016	0.014	0
O2y	26	0.439 ..	-0.136	-0.394	0.097	0.055	-0.173	-0.105	-0.132	0.661
O3x	27	-0.012 ..	-0.231	-0.066	-0.043	-0.044	0.012	0.005	-0.018	-0.015
O3y	28	0.01 ..	-0.255	-0.026	-0.01	0.046	0.019	-0.024	-0.034	-0.02
O3z	29	-0.001 ..	0.028	0.011	-0.126	0	0.087	0.038	-0.032	0
Cl1z	30	-0.027 ..	0.077	-0.127	-0.134	-0.416	-0.065	0.156	0.151	-0.065
Cl1occ	31	-0.196 ..	0.034	0.145	-0.015	0.633	0.188	-0.19	-0.154	0.045
Clbeq	32	0.398 ..	-0.036	0.383	-0.664	-0.04	0.059	0.089	-0.085	0.061
Cl2z	33	0.121 ..	0.039	0.109	-0.06	0.357	0.149	-0.133	-0.193	0.085
Eigenvalues		3.95E+03 ..	3.91E-01	0 3.29E+02	2.88E-01	2.30E-01	1.97E-01	1.58E-01	1.27E-01	7.01E-02

(e). Output of *SVDdiagnostic* for problematic cases of Rietveld refinements of $Ca_{10}(PO_4)_6Cl_2$.

PRECONDITIONED normal matrix

Condition number for matrix of normal equations = 0.374E+02

Error propagation is likely to spoil 2 trailing decimal digits out of probably 14.

Problem well conditioned for double-precision matrix inversion.

Eigenvectors for P2.out ranked according to eigenvalues are printed as columns below

Eigenvector #		1 ..	20	21	22	23	24	25	26	27
bkg1	1	-0.349 ..	-0.032	-0.3	0.018	0.114	0.062	0.074	0.367	-0.478
bkg2	2	-0.161 ..	-0.029	0.081	0.033	0.004	-0.073	0.036	0.052	-0.335
bkg3	3	0.235 ..	0.162	-0.383	-0.085	0.552	-0.105	0.021	-0.046	-0.137
bkg4	4	0.097 ..	0.003	0.1	-0.094	0.151	0.084	0.006	0.13	-0.076
bkg5	5	-0.002 ..	0.1	-0.307	-0.047	0.344	-0.012	0.007	0.003	-0.105
zeroerror	6	-0.008 ..	-0.234	0.013	0.1	0.091	-0.052	-0.737	0.043	-0.039
peaktype	7	0.226 ..	0.005	-0.008	-0.042	0.365	-0.079	-0.02	-0.369	0.326
P6scale	8	-0.479 ..	0.102	-0.029	0.221	-0.013	-0.398	-0.006	-0.654	-0.211
P6a	9	0.019 ..	0.417	-0.031	-0.009	-0.087	-0.03	-0.642	0.104	-0.052
P6c	10	-0.014 ..	-0.722	0.053	0.085	0.198	-0.023	-0.131	-0.08	0.003
Ca1z	11	0 ..	0.017	-0.053	-0.032	0.021	-0.02	-0.026	-0.016	0.007
Ca2x	12	-0.018 ..	-0.049	-0.298	-0.414	-0.33	0.041	-0.077	-0.184	0.065
Ca2y	13	0.047 ..	-0.049	-0.453	-0.382	-0.292	-0.069	-0.041	-0.122	0.073
Cabeq	14	0.453 ..	0.016	-0.37	0.684	-0.281	-0.065	0.059	-0.004	-0.077
Px	15	-0.043 ..	-0.025	0.062	0.011	-0.038	0.011	-0.003	-0.031	-0.007
Py	16	0.036 ..	0.023	0.071	0.031	0.032	-0.02	0.013	0.024	0.007
Pbeq	17	0.494 ..	-0.076	0.284	-0.272	-0.132	-0.054	0.003	-0.239	-0.66
O1x	18	-0.053 ..	-0.141	-0.076	0.091	-0.144	0.013	0.025	0.034	0.021
O1y	19	0.032 ..	-0.041	-0.104	0.085	-0.017	0.035	0.024	-0.024	-0.011
O2x	20	-0.031 ..	0.032	-0.043	0.001	0.01	-0.045	0.005	0.013	-0.009
O2y	21	0.015 ..	0.042	-0.016	-0.015	0.051	-0.03	0.005	-0.012	0
O3x	22	-0.022 ..	0.258	0.186	0.056	-0.038	-0.075	-0.011	-0.005	0.021
O3y	23	0.022 ..	0.272	0.205	0.08	-0.005	0.024	0.001	-0.037	0.018
O3z	24	0.017 ..	-0.098	-0.079	0.081	-0.124	0.009	-0.027	-0.006	0.013
Cl1z	25	-0.035 ..	-0.119	-0.08	-0.052	-0.134	-0.486	0.02	0.204	0.067
Cl1occ	26	-0.202 ..	0.018	-0.105	0.07	-0.01	0.629	-0.044	-0.228	-0.055
Cl2z	27	0.055 ..	-0.027	-0.073	0.103	-0.035	0.383	-0.063	-0.236	-0.094
Eigenvalues		3.28E+03 ..	4.17E-01	0.4 1.00E+01	3.42E-01	2.94E-01	2.67E-01	2.02E-01	1.67E-01	8.76E-02

Table A2. Bond lengths in monoclinic structure ($P2_1/m$). Note that in all tetrahedra some B-O bond lengths refine to non-physical values. A reasonable spread of B-O distances would be 1.49 – 1.61 Å.

x	bond lengths (Å)					
3	B(1)-O(1)	1.43(3)	B(2)-O(2)	1.52(2)	B(3)-O(3)	1.49(2)
	B(1)-O(4)	1.69(3)	B(2)-O(5)	1.81(4)	B(3)-O(6)	1.69(3)
	B(1)-O(7) × 2	1.63(2)	B(2)-O(8) × 2	1.63(2)	B(3)-O(9) × 2	1.57(2)
	B(1)-O	1.59	B(2)-O	1.64	B(3)-O	1.58
2.5	B(1)-O(1)	1.22(3)	B(2)-O(2)	1.30(2)	B(3)-O(3)	1.17(4)
	B(1)-O(4)	1.73(2)	B(2)-O(5)	1.83(2)	B(3)-O(6)	1.88(4)
	B(1)-O(7)	1.71(1)	B(2)-O(8) × 2	1.62(2)	B(3)-O(9) × 2	1.83(3)
	B(1)-O	1.59	B(2)-O	1.59	B(3)-O	1.67

Table A3. Atomic proportions of selected ellestadites obtained by EPMA. A statistically significant deficit of Ca appears for (Si/S) rich ellestadites. Chlorine is underestimated due to volatilization under the electron beam. Chlorine content derived from neutron diffraction (see Table 2) are more reliable.

	Ca	Si	P	S	Cl	O
$x = 3$	9.88	2.96	0.02	3.06	1.65	24.27
error	0.06	0.07	0.01	0.05	0.09	0.10
$x = 2.5$	9.84	2.41	1.09	2.56	1.58	24.25
error	0.07	0.10	0.07	0.17	0.04	0.16
$x = 1.0$	9.97	0.68	4.51	0.82	1.28	24.12
error	0.09	0.04	0.14	0.06	0.04	0.08
$x = 0$	9.95		5.94		1.26	24.33
error	0.04		0.03		0.08	0.14

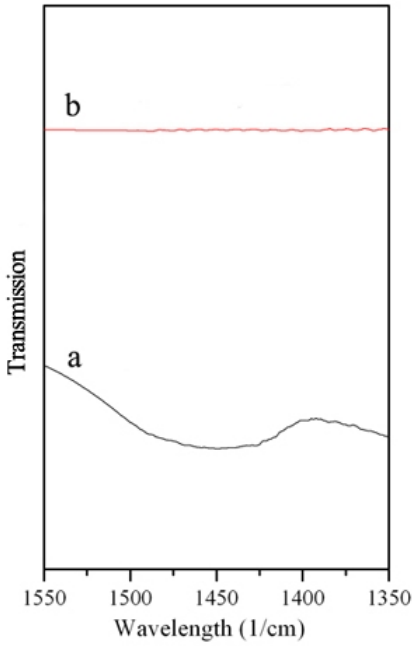

Fig. A1. FTIR spectra of $Ca_{10}(SiO_4)_{2.5}(PO_4)(SO_4)_{2.5}Cl_2$ (a) before and (b) after treatment in dilute acid.

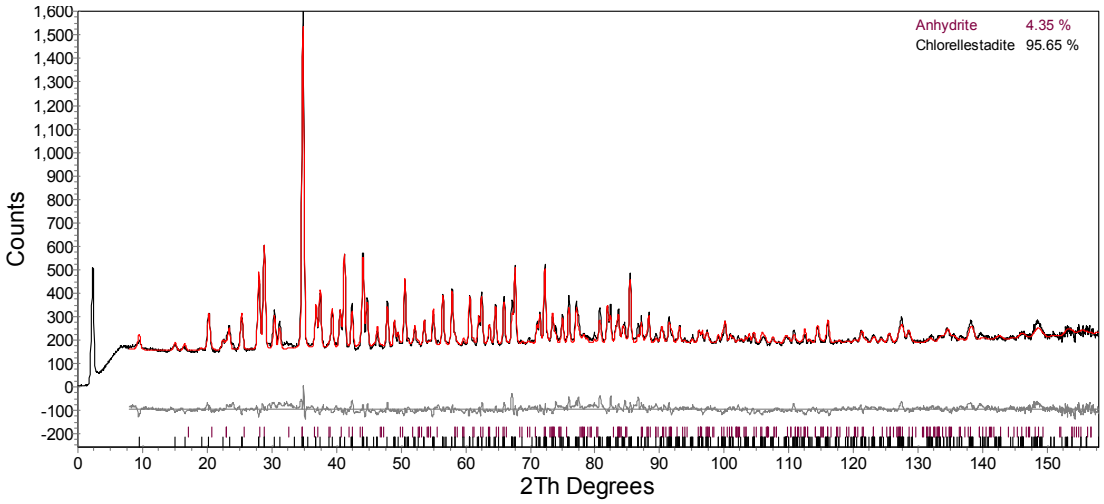

Fig. A2-(a). Neutron data and Rietveld refinement of $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$

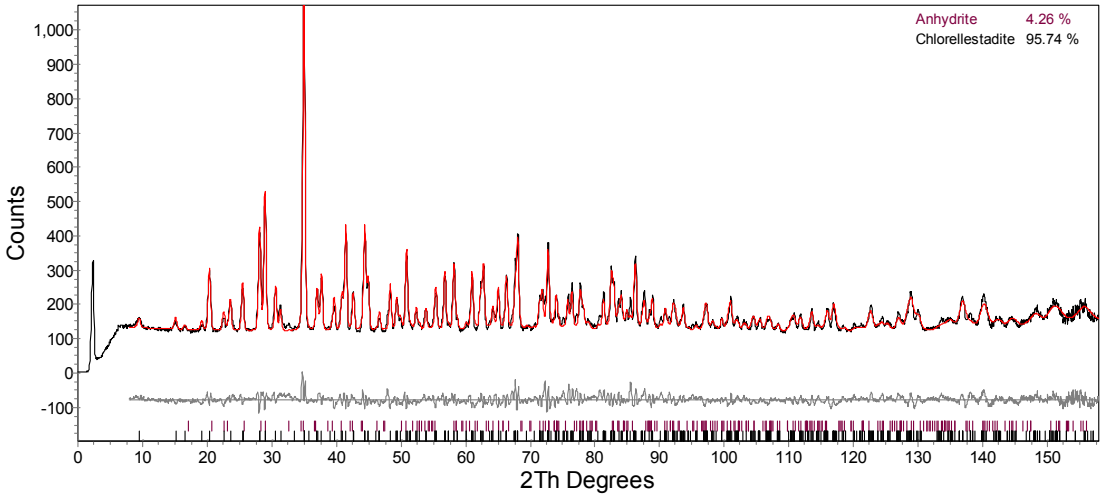

Fig. A2-(b). Neutron data and Rietveld refinement of $Ca_{10}(SiO_4)(PO_4)_4(SO_4)Cl_2$

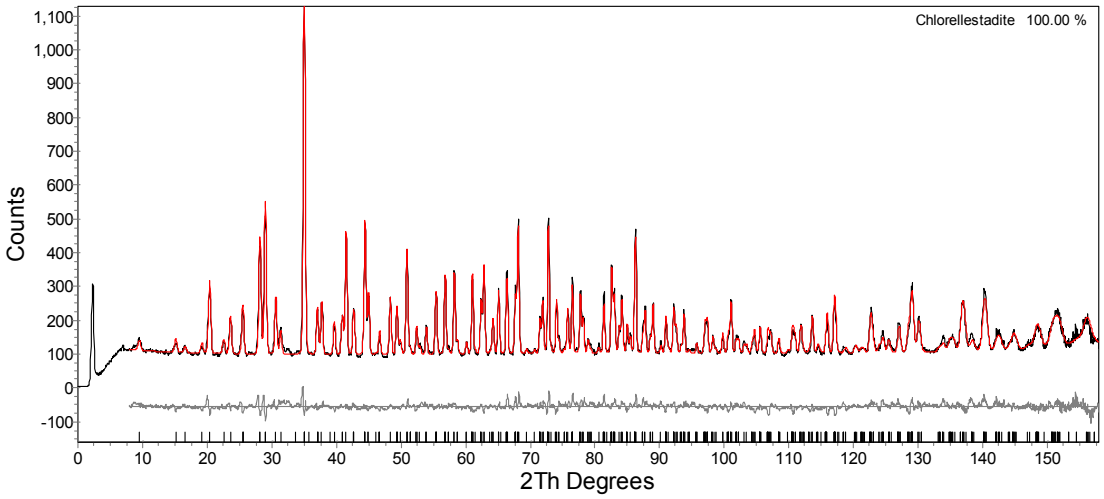

Fig. A2-(c). Neutron data and Rietveld refinement of $Ca_{10}(PO_4)_6Cl_2$