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pXRF Measurements on Soil Samples for the Exploration of an Antimony Deposit: Example from the Vendean Antimony District (France)

Supplementary file 1: pXRF data processing results on raw data

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ALL	As	Ba	Ca	Cr	Cu	Fe	K	Mn	Mo	Ni	Pb	Rb	S	Sb	Sr	Th	Ti	V	Zn	Zr
nb	160	166	192	98	46	192	192	178	30	5	192	192	28	**60**	192	178	192	187	186	192
min	7	62	958	27	19	5188	8811	68	7	46	9	42	523	**19**	49	5	2672	49	11	170
max	486	497	69043	98	183	49077	22665	4177	9	71	60	113	3252	**515**	137	15	9184	170	330	433
avg	28	248	4103	45	34	19175	15152	441	7	57	22	66	1193	**95**	80	8	5482	90	33	297
med	18	243	2662	42	25	17991	14860	353	7	49	21	65	929	**45**	78	8	5457	85	25	290

Figure S1. pXRF measurements with over 20% observations above LOD, B horizon soils (pXRF, in mg/kg).

	Fe	V	Cr	S	Ba	Zn	K	Rb	Mn	Pb	Sb	Ca	As	Cu	Sr	Ti	Th	Zr
Fe	1.000	0.718	0.715	0.692	0.743	0.481	0.534	0.327	0.517	0.292	0.395	0.349	0.454	0.311	0.387	0.054	-0.092	-0.710
V	0.718	1.000	0.599	0.519	0.604	0.491	0.453	0.415	0.335	0.291	0.131	0.336	0.267	0.192	0.296	0.378	-0.037	-0.546
Cr	0.715	0.599	1.000	0.471	0.629	0.442	0.477	0.417	0.372	0.271	0.160	0.220	0.306	0.224	0.225	0.137	0.066	-0.445
S	0.692	0.519	0.471	1.000	0.414	0.634	0.430	0.264	0.347	0.276	0.331	0.657	0.314	0.232	0.296	0.025	-0.091	-0.610
Ba	0.743	0.604	0.629	0.414	1.000	0.358	0.658	0.405	0.395	0.145	0.278	0.230	0.220	0.212	0.315	0.048	-0.010	-0.578
Zn	0.481	0.491	0.442	0.634	0.358	1.000	0.437	0.361	0.155	0.371	0.108	0.491	0.221	0.102	0.198	0.066	-0.048	-0.490
K	0.534	0.453	0.477	0.430	0.658	0.437	1	0.577	0.123	0.080	0.065	0.507	0.209	0.244	0.047	-0.060	-0.073	-0.624
Rb	0.327	0.415	0.417	0.264	0.405	0.361	0.577	1.000	0.093	0.493	0.058	0.054	0.094	0.138	-0.123	0.039	0.504	-0.068
Mn	0.517	0.335	0.372	0.347	0.395	0.155	0.123	0.093	1.000	0.336	0.626	0.003	0.204	0.285	0.151	0.051	0.047	-0.239
Pb	0.292	0.291	0.271	0.276	0.145	0.371	0.080	0.493	0.336	1.000	0.263	-0.039	0.143	0.185	-0.156	0.185	0.345	0.000
Sb	0.395	0.131	0.160	0.331	0.278	0.108	0.065	0.058	0.626	0.263	1.000	-0.038	0.531	0.140	0.035	-0.117	-0.030	-0.085
Ca	0.349	0.336	0.220	0.657	0.230	0.491	0.507	0.054	0.003	-0.039	-0.038	1.000	0.099	0.240	0.350	0.044	-0.341	-0.614
As	0.454	0.267	0.306	0.314	0.220	0.221	0.209	0.094	0.204	0.143	0.531	0.099	1.000	0.165	-0.108	0.019	-0.272	-0.327
Cu	0.311	0.192	0.224	0.232	0.212	0.102	0.244	0.138	0.285	0.185	0.140	0.240	0.165	1.000	0.162	0.038	-0.087	-0.287
Sr	0.387	0.296	0.225	0.296	0.315	0.198	0.047	-0.123	0.151	-0.156	0.035	0.350	-0.108	0.162	1.000	0.105	-0.088	-0.341
Ti	0.054	0.378	0.137	0.025	0.048	0.066	-0.060	0.039	0.051	0.185	-0.117	0.044	0.019	0.038	0.105	1.000	0.004	-0.011
Th	-0.092	-0.037	0.066	-0.091	-0.010	-0.048	-0.073	0.504	0.047	0.345	-0.030	-0.341	-0.272	-0.087	-0.088	0.004	1.000	0.479
Zr	-0.710	-0.546	-0.445	-0.610	-0.578	-0.490	-0.624	-0.068	-0.239	0.000	-0.085	-0.614	-0.327	-0.287	-0.341	-0.011	0.479	1

Figure S2. Pearson correlations on pXRF raw data for B horizon soils (as heat map). The use of colour shading and its interpretation is described in [1].

	F1	F2	F3	F4	F5	F6
As	3.113	0.008	15.084	7.414	7.971	11.854
Ba	9.512	0.202	0.116	0.096	15.849	5.195
Ca	4.870	12.837	3.638	0.852	4.384	9.600
Cr	8.870	1.469	0.389	0.796	1.952	4.057
Cu	2.335	0.023	1.160	0.280	0.236	4.038
Fe	13.236	0.015	1.238	0.526	1.673	0.403
K	7.844	0.152	6.139	12.800	3.764	2.414
Mn	3.948	3.759	16.811	4.773	2.197	2.671
Pb	2.008	19.042	0.000	0.083	14.064	4.442
Rb	3.400	16.431	10.835	5.341	0.317	0.108
S	9.868	0.643	0.014	0.266	4.253	12.042
Sb	2.176	3.059	32.399	0.733	0.010	1.509
Sr	2.009	6.028	0.134	24.913	8.302	8.962
Th	0.209	25.632	5.350	0.712	3.793	6.224
Ti	0.255	0.371	1.773	32.414	19.664	14.012
V	9.676	0.247	1.501	6.309	0.808	5.942
Zn	7.170	0.006	3.398	1.095	10.732	5.827
Zr	9.498	10.076	0.020	0.596	0.033	0.699

Figure S3. Contribution of each element to the 6 main factors for B horizon observations, pXRF raw data. Coloured cells indicate meaningful positive contributions.

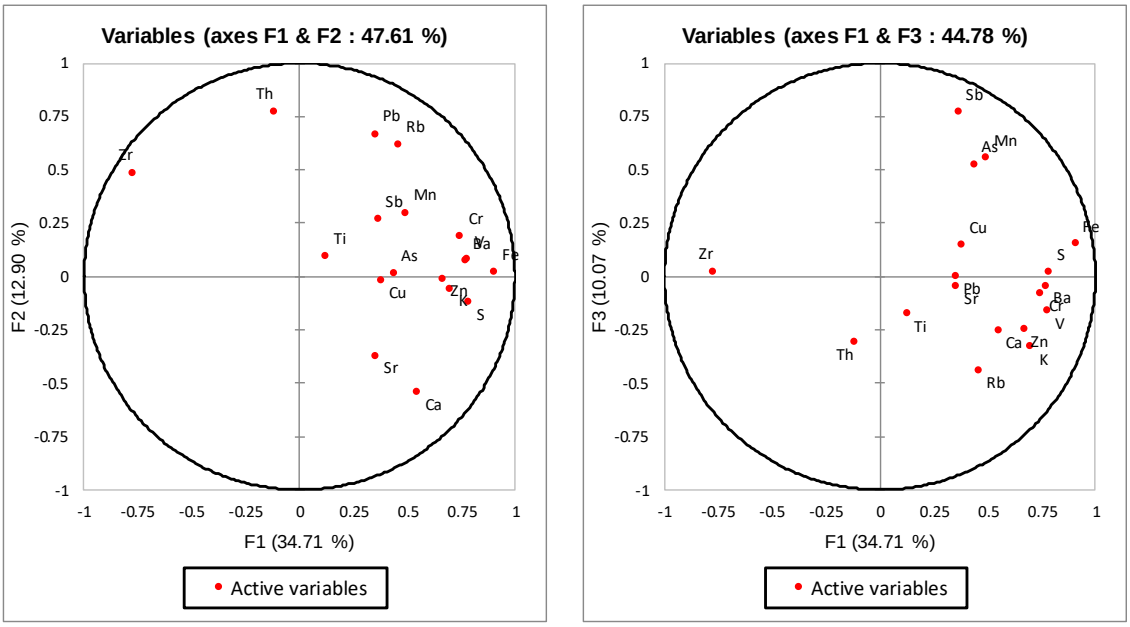

Figure S4. PCA factor diagrams for F1, F2 (**a**) and F3 (**b**). Samples from B horizon, pXRF raw data.

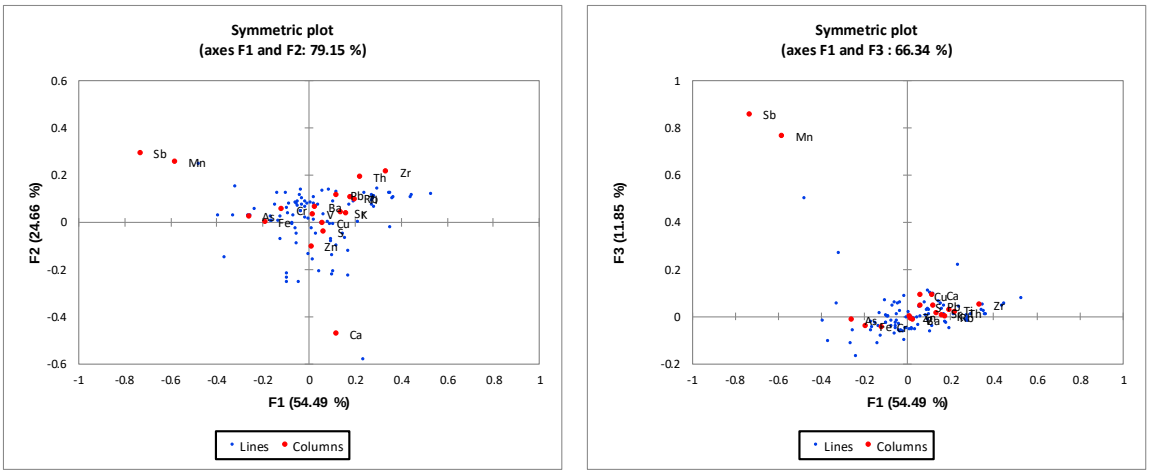

Figure S5. CA symmetric plots for F1, F2 (**a**) and F3 (**b**). Samples from B horizon, pXRF raw data.

	Rb	K	Ti	Sr	Th	Zr	S	Pb	Ba	V	Ca	Cu	Zn	Cr	Fe	Mn	Sb	As
Rb	1.000	0.813	0.777	0.525	0.774	0.800	0.377	0.684	0.251	0.204	-0.046	0.134	-0.158	-0.094	-0.531	-0.742	-0.428	-0.705
K	0.813	1.000	0.690	0.506	0.484	0.577	0.416	0.358	0.419	0.170	0.298	0.131	-0.109	-0.155	-0.413	-0.661	-0.501	-0.560
Ti	0.777	0.690	1.000	0.727	0.602	0.883	0.441	0.587	0.163	0.224	0.064	0.152	-0.235	-0.288	-0.602	-0.649	-0.433	-0.650
Sr	0.525	0.506	0.727	1.000	0.476	0.626	0.477	0.277	0.247	0.209	0.217	0.175	-0.123	-0.267	-0.290	-0.452	-0.478	-0.673
Th	0.774	0.484	0.602	0.476	1.000	0.735	0.264	0.674	0.143	0.132	-0.257	0.091	-0.162	-0.023	-0.426	-0.529	-0.354	-0.711
Zr	0.800	0.577	0.883	0.626	0.735	1.000	0.325	0.681	0.067	0.060	-0.178	0.144	-0.293	-0.275	-0.712	-0.655	-0.227	-0.650
S	0.377	0.416	0.441	0.477	0.264	0.325	1	0.226	-0.015	0.105	0.432	0.003	0.096	-0.240	-0.088	-0.338	-0.398	-0.470
Pb	0.684	0.358	0.587	0.277	0.674	0.681	0.226	1.000	-0.078	0.073	-0.200	0.090	-0.095	-0.117	-0.442	-0.517	-0.197	-0.593
Ba	0.251	0.419	0.163	0.247	0.143	0.067	-0.015	-0.078	1.000	0.268	-0.030	-0.025	-0.145	0.236	0.204	-0.126	-0.380	-0.327
V	0.204	0.170	0.224	0.209	0.132	0.060	0.105	0.073	0.268	1.000	0.039	-0.153	-0.004	0.072	0.144	-0.125	-0.395	-0.236
Ca	-0.046	0.298	0.064	0.217	-0.257	-0.178	0.432	-0.200	-0.030	0.039	1.000	0.102	0.178	-0.251	-0.008	-0.169	-0.313	0.006
Cu	0.134	0.131	0.152	0.175	0.091	0.144	0.003	0.090	-0.025	-0.153	0.102	1.000	-0.236	-0.154	-0.166	-0.131	-0.207	-0.204
Zn	-0.158	-0.109	-0.235	-0.123	-0.162	-0.293	0.096	-0.095	-0.145	-0.004	0.178	-0.236	1.000	0.119	0.266	0.068	-0.208	0.059
Cr	-0.094	-0.155	-0.288	-0.267	-0.023	-0.275	-0.240	-0.117	0.236	0.072	-0.251	-0.154	0.119	1.000	0.309	0.184	-0.218	-0.029
Fe	-0.531	-0.413	-0.602	-0.290	-0.426	-0.712	-0.088	-0.442	0.204	0.144	-0.008	-0.166	0.266	0.309	1.000	0.523	-0.119	0.292
Mn	-0.742	-0.661	-0.649	-0.452	-0.529	-0.655	-0.338	-0.517	-0.126	-0.125	-0.169	-0.131	0.068	0.184	0.523	1.000	0.122	0.395
Sb	-0.428	-0.501	-0.433	-0.478	-0.354	-0.227	-0.398	-0.197	-0.380	-0.395	-0.313	-0.207	-0.208	-0.218	-0.119	0.122	1.000	0.502
As	-0.705	-0.560	-0.650	-0.673	-0.711	-0.650	-0.470	-0.593	-0.327	-0.236	0.006	-0.204	0.059	-0.029	0.292	0.395	0.502	1

Figure S6. Pearson correlations on clr data for B horizon Group B observations, pXRF measurements. The use of colour shading and its interpretation is described in [1].

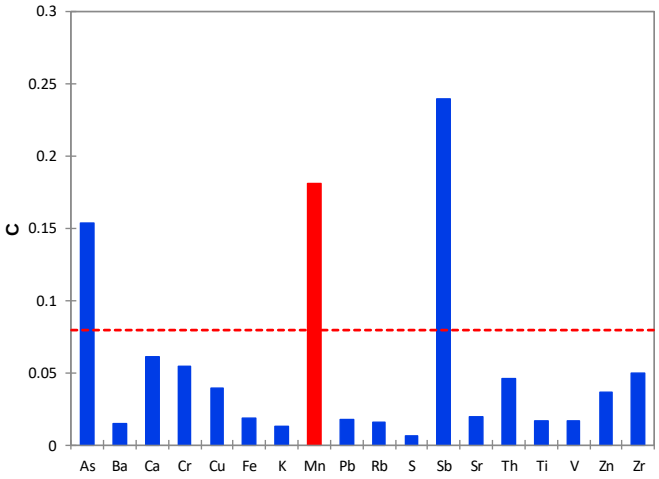

Figure S7. Cochran's C test. Samples from B horizon, pXRF data. The C test detects one exceptionally large variance value at a time.

AH	As	Ba	Ca	Cr	Cu	Fe	K	Mn	Mo	Ni	Pb	Rb	S	Sb	Sr	Th	Ti	V	Zn	Zr
nb	81	70	96	38	19	96	96	91	13	0	96	96	27	**27**	96	84	96	93	94	96
min	7	62	1297	27	19	6837	8811	78	7		12	43	523	**20**	52	5	2672	49	13	170
max	486	409	69043	86	183	32732	21678	1992	8		60	113	3252	**436**	137	12	6667	156	330	390
avg	29	169	5511	42	41	17982	14865	409	7		23	64	1204	**80**	79	8	5326	87	38	284
med	16	163	3329	40	24	16921	14442	334	7		21	64	979	**44**	76	8	5282	83	26	280

Figure S8. Elementary statistics for Ah horizon observations, pXRF measurements (in mg/kg).

	Mn	Fe	Cr	V	Rb	Zn	Ba	K	Ca	Sb	Sr	Cu	As	S	Pb	Th	Ti	Zr
Mn	1.000	0.579	0.635	0.541	0.392	0.344	0.353	0.290	0.284	0.186	0.370	0.246	0.095	0.084	0.200	-0.053	0.297	-0.483
Fe	0.579	1.000	0.730	0.753	0.459	0.203	0.640	0.619	0.136	0.080	0.337	0.041	0.130	-0.028	0.194	-0.059	0.114	-0.661
Cr	0.635	0.730	1.000	0.653	0.560	0.102	0.573	0.542	0.094	0.018	0.217	-0.018	0.019	-0.071	0.106	0.068	0.247	-0.488
V	0.541	0.753	0.653	1.000	0.541	-0.128	0.402	0.495	-0.172	-0.042	0.064	-0.255	0.026	-0.195	0.296	0.061	0.460	-0.465
Rb	0.392	0.459	0.560	0.541	1.000	-0.082	0.445	0.535	-0.186	-0.052	-0.136	-0.206	-0.052	-0.158	0.224	0.446	0.314	-0.076
Zn	0.344	0.203	0.102	-0.128	-0.082	1.000	-0.020	0.021	0.912	0.503	0.473	0.937	0.261	0.764	-0.063	-0.285	-0.596	-0.456
Ba	0.353	0.640	0.573	0.402	0.445	-0.020	1.000	0.642	-0.014	-0.043	0.215	-0.133	-0.016	-0.364	-0.081	0.118	0.218	-0.274
K	0.290	0.619	0.542	0.495	0.535	0.021	0.642	1.000	0.037	-0.063	0.012	-0.128	0.050	-0.115	-0.085	-0.017	0.035	-0.514
Ca	0.284	0.136	0.094	-0.172	-0.186	0.912	-0.014	0.037	1.000	0.434	0.526	0.910	0.204	0.690	-0.169	-0.344	-0.611	-0.451
Sb	0.186	0.080	0.018	-0.042	-0.052	0.503	-0.043	-0.063	0.434	1.000	0.116	0.426	0.855	0.498	-0.097	-0.191	-0.186	-0.214
Sr	0.370	0.337	0.217	0.064	-0.136	0.473	0.215	0.012	0.526	0.116	1.000	0.426	0.034	0.222	-0.102	-0.227	-0.063	-0.372
Cu	0.246	0.041	-0.018	-0.255	-0.206	0.937	-0.133	-0.128	0.910	0.426	0.426	1.000	0.111	0.703	-0.152	-0.259	-0.645	-0.310
As	0.095	0.130	0.019	0.026	-0.052	0.261	-0.016	0.050	0.204	0.855	0.034	0.111	1.000	0.373	-0.042	-0.215	-0.063	-0.243
S	0.084	-0.028	-0.071	-0.195	-0.158	0.764	-0.364	-0.115	0.690	0.498	0.222	0.703	0.373	1.000	0.022	-0.298	-0.577	-0.355
Pb	0.200	0.194	0.106	0.296	0.224	-0.063	-0.081	-0.085	-0.169	-0.097	-0.102	-0.152	-0.042	0.022	1.000	0.057	0.213	-0.099
Th	-0.053	-0.059	0.068	0.061	0.446	-0.285	0.118	-0.017	-0.344	-0.191	-0.227	-0.259	-0.215	-0.298	0.057	1.000	0.358	0.560
Ti	0.297	0.114	0.247	0.460	0.314	-0.596	0.218	0.035	-0.611	-0.186	-0.063	-0.645	-0.063	-0.577	0.213	0.358	1.000	0.201
Zr	-0.483	-0.661	-0.488	-0.465	-0.076	-0.456	-0.274	-0.514	-0.451	-0.214	-0.372	-0.310	-0.243	-0.355	-0.099	0.560	0.201	1

Figure S9. Pearson correlations on raw data for Ah horizon, pXRF raw measurements (as heat map). The use of colour shading and its interpretation is described in [1].

	F1	F2	F3	F4	F5	F6
As	3.279	0.010	41.390	4.914	1.435	1.257
Ba	0.063	10.796	2.382	3.686	9.993	2.242
Ca	15.841	0.624	2.472	1.123	0.831	0.097
Cr	1.051	14.091	0.162	0.436	0.220	0.031
Cu	13.931	1.774	2.594	5.484	1.050	0.000
Fe	2.457	14.491	0.071	0.522	0.334	0.129
K	0.449	10.362	0.964	9.565	6.526	9.774
Mn	3.328	8.388	0.113	7.476	1.972	6.549
Pb	0.172	1.133	3.415	15.667	27.118	9.385
Rb	0.224	10.297	0.735	8.868	8.680	7.892
S	11.100	2.256	1.826	2.805	0.125	6.559
Sb	6.654	0.255	30.932	0.149	3.972	2.425
Sr	5.709	0.400	6.697	0.274	1.559	32.173
Th	4.368	0.517	0.097	25.204	20.632	0.062
Ti	6.167	4.918	4.302	1.823	2.052	18.492
V	0.004	14.854	1.234	0.081	4.254	0.342
Zn	16.585	0.368	0.492	4.155	0.826	0.162
Zr	8.616	4.465	0.122	7.769	8.420	2.429

Figure S10. Contribution of each element to the 6 main factors for Ah horizon, pXRF measurements. Coloured cells indicate meaningful positive contributions.

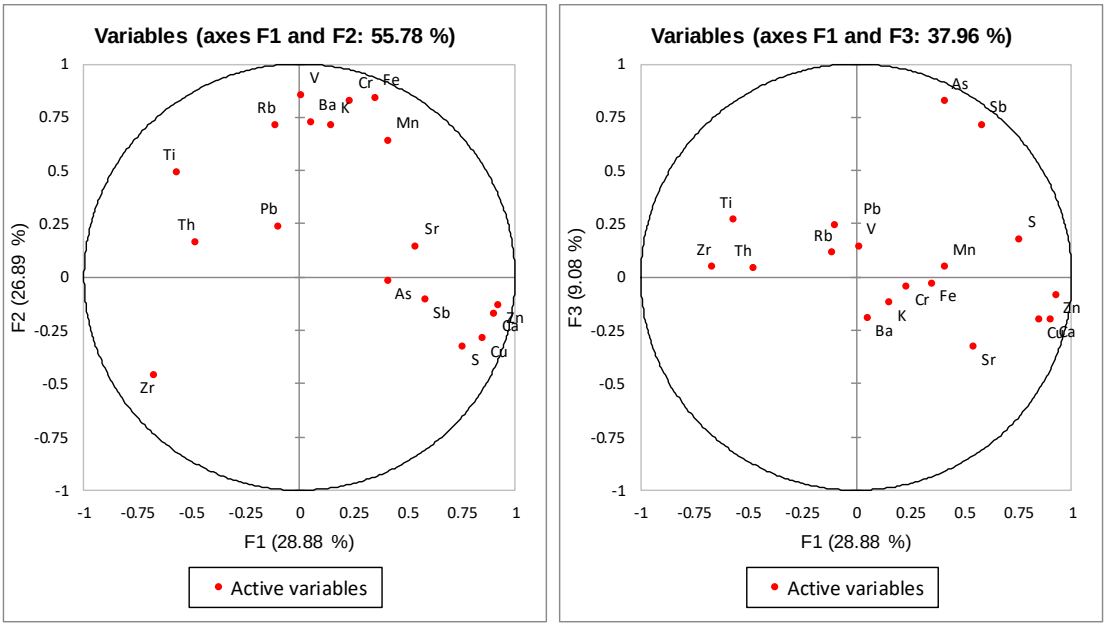

Figure S11. PCA factor diagrams for F1, F2 (**a**) and F3 (**b**). Samples from group Ah, pXRF raw data.

Reference

1. Reimann, C.; Filzmoser, P.; Hronc, K.; Kynčlová, P.; Garrett, R.G. A new method for correlation analysis of compositional (environmental) data—A worked example. *Sci. Total Environ.* **2017**, *607–608*, 965–971.