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BASELINE STUDIES OF THE CLAY MINERALS SOCIETY SOURCE CLAYS: CHEMICAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY (ICP-MS)

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INTRODUCTION

Inductively coupled plasma-mass spectrometry (ICP-MS) is ideally suited for the rapid and simultaneous analysis of multiple elements in geological materials, including soils, organic substances and most rock types (Eggins *et al.*,1997; Longerich *et al.*, 1990; Jenner *et al.*, 1990). The application to clay minerals is more recent (Jain *et al.*, 1994). This technique is highly sensitive, and is capable of analyzing a wide range of isotopes covering the entire mass spectrum. Consequently, ICP-MS is used to measure directly rare earth and platinum group elements at ppb levels without preconcentration.

Table 1. List of analytes, isotopes, interferences and detection limits.

Element	Isotope	Interferences	Detection limit (ppm)
Co	59		0.073
Ni	60	CaO	0.563
Cu	63	TiO, TiOH	0.293
Zn	66	TiO, TiOH	0.932
Ga	69	Ce^{2+}, ^{142}Nd^{2+}	0.178
Rb	85		0.658
Sr	88	^{86}Kr	0.147
Y	89		0.064
Mo	95		0.377
Cd	114	Sn	0.164
In = Internal Std.	115		NA
Sn	118		0.268
Sb	121		0.200
Cs	133		0.933
Ba	138		0.134
La	139		0.040
Ce	140		0.069
Pr	141		0.075
Nd	146		0.223
Sm	147		0.263
Eu	151	BaO, BaOH	0.045
Gd	157	SmO, NdO, Dy^{145}	0.143
Tb	159	NdO	0.046
Dy	162	NdO	0.050
Ho	165	SmO	0.046
Er	166	EuO	0.045
Tm	169		0.024
Yb	174	GdO	0.014
Lu	175	TbO	0.029
Tl	205		0.113
Pb	208		0.299
Bi = Internal Std.	209		NA
Th	232		0.062
U	238		0.176

NA: not applicable.

Commercial ICP-MS instrumentation was introduced in 1983. Since that time it has become an acceptable tool for geochemical analysis. Like most analytical techniques, however, accurate and precise quantitative measurements require special considerations. For example, mass-dependent matrix effects, mass spectral interferences, and drift must be monitored closely and corrections applied to the data to obtain quantitative analyses. Also, this is a solution-based technique, and therefore solid samples must be digested. Quantitative results require the use of external calibration standards and results can be monitored by analyzing reference materials.

INSTRUMENTATION AND METHODS

Microwave digestion

Samples and a geochemical reference material (USGS G2) were digested in a CEM MDS-2100 laboratory microwave system using a procedure optimized to reduce HF (Lewis and Bruns, 1997). This method has several advantages over traditional microwave digestion methods because it utilizes significantly reduced quantities of HF. This allows for elimination of the neutralization step, requires less dilution, and improves elemental detection limits.

The method consists of placing 0.100 g of oven-dried material into a lined digestion vessel together with 250 μL HF, 2 mL HCl, 2 mL HNO_3 and 2 mL H_2O. The microwave is then heated in three incremental steps to bring the samples completely into solution.

Table 2. Operating parameters.

Parameter	Operating conditions
Forward power	1350 W
Nebulizer gas flow rate	0.829 L min^{-1}
Dwell time	320 μs
Scan region	5.6 to 239.4 m/z (skip 11.5–22.5 m/z, 27.5–41.5 and 79.5–80.5 m/z)

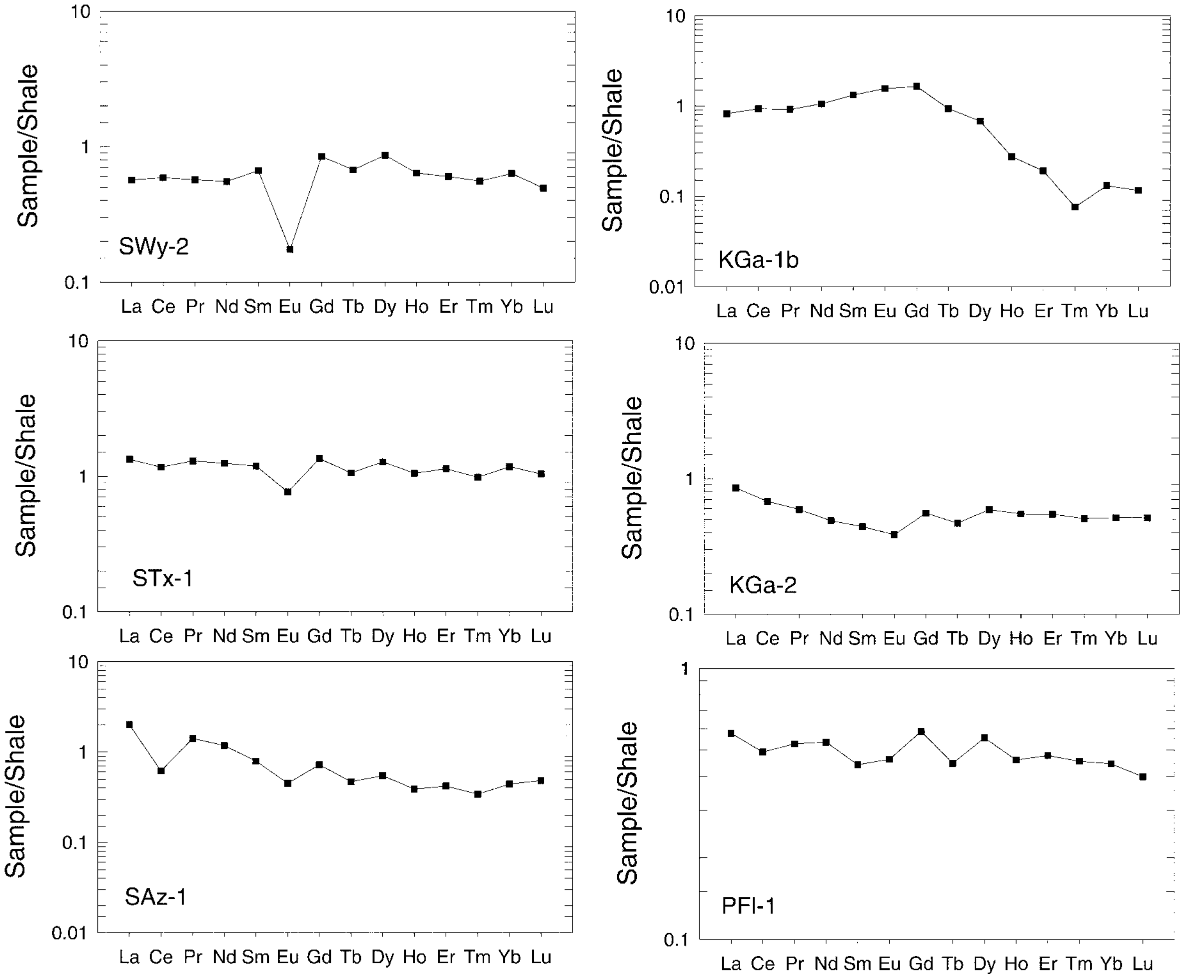

Figure 1. Shale-normalized REE data for CMS Source Clays.

ICP-MS

Abundances of 32 trace and rare earth elements (REE) were determined using a VG Elemental PlasmaQuad II Plus ICP-MS (Table 1). Each sample was digested three times and loaded randomly in the autosampler. This approach was taken to monitor for, and to minimize the effects of, instrumental drift. Average abundances were calculated from the three digestions.

The samples were spiked with internal standards (In and Bi) to correct for matrix effects, and multi-element synthetic external standard solutions were used to make calibration standards for full quantification. Some Al and Si were added to these standard solutions to match the matrix of the digestates and decrease the effects of interferences. Calibration curves were generated for each analyte using a blank and three standard solutions of varying concentration. Table 2 lists the instrumental operating parameters.

RESULTS

Reference materials

To evaluate the quality of the data, a certified reference material (USGS G2 granite) was analyzed and compared with published values (Table 3). For the majority of elements, the measured and recommended values are in close agreement, and the measured values are generally within 2σ of the recommended value (Table 4). Notable exceptions are Zn, Ga, Mo, Cd, Ba, Eu, Gd, Er, Tl and Pb. Interferences (Table 1) and suppression in particular may account for some of the poor results. The Zn, Ga, Cd and Ba were excluded in the final data set owing to the questionable reliability of these data. The remaining elements were included because, although the mean concentration measured for these elements does not fall within 2σ of the recommended value, they are typically very close to 2σ.

Table 3. Results for four replicate analyses of USGS G2 (ppm).

Element	Isotope	Avg. measured concentration	Standard deviation	Recommended values	Standard deviation
Co	Co 59	5.45	0.49	4.6	0.7
Ni	Ni 60	4.07	1.11	5	2.8
Cu	Cu 63	13.40	2.40	11	3
Zn	Zn 64	141.91	64.16	86	8
Cu	Cu 65	17.13	3.57	11	3
Zn	Zn 66	137.34	58.92	86	8
Ga	Ga 69	32.09	8.50	23	2
Ga	Ga 71	32.09	8.50	23	2
Rb	Rb 85	170.91	16.83	170	3
Sr	Sr 88	473.14	39.74	478	2
Y	Y 89	8.37	0.31	11	2
Mo	Mo 95	0.36	0.31	1.5	0.5
Cd	Cd 111	0.27	0.29	0.016	0.0001
Cd	Cd 114	0.09	0.10	0.016	0.0001
Sn	Sn 118	1.58	0.52	1.8	0.8
Sn	Sn 120	1.85	0.48	1.8	0.8
Sb	Sb 121	0.09	0.06	0.07	0.02
Cs	Cs 133	1.49	0.46	1.34	0.16
Ba	Ba 138	1750.82	153.45	1882	23
La	La 139	94.43	6.65	89	8
Ce	Ce 140	168.92	10.03	160	10
Pr	Pr 141	17.56	1.17	18	2
Nd	Nd 146	57.11	8.47	55	6
Sm	Sm 147	7.65	1.09	7.2	0.7
Eu	Eu 151	2.06	0.15	1.4	0.12
Gd	Gd 157	6.12	1.24	4.3	0.8
Tb	Tb 159	0.58	0.11	0.48	0.08
Dy	Dy 162	2.51	0.58	2.4	0.3
Ho	Ho 165	0.38	0.13	0.4	0.06
Er	Er 166	1.44	1.17	0.92	0.18
Tm	Tm 169	0.11	0.03	0.18	0.08
Yb	Yb 174	0.61	0.12	0.8	0.17
Lu	Lu 175	0.08	0.04	0.11	0.02
Tl	Tl 203	1.28	0.48	0.91	0.14
Tl	Tl 205	1.30	0.48	0.91	0.14
Pb	Pb 206	36.38	13.63	30	4
Pb	Pb 207	40.19	15.31	30	4
Pb	Pb 208	40.82	15.17	30	4
Th	Th 232	27.22	6.01	24.7	1.8
U	U 238	2.20	0.73	2.07	0.12

Table 4. Comparison of measured values with recommended values for USGS G2 Granite.

Measured mean within 1σ of the recommended value	Measured mean within 2σ of the recommended value	Measured mean within 3σ of the recommended value	Measured mean $>3\sigma$ of the recommended value
Ni 60, Cu 63, Rb 85, Sn 118, Sn 120, Sb 121, Cs 133, La 139, Ce 140, Pr 141, Nd 146, Sm 147, Dy 162, Ho 165, Tm 169	Co 59, Cu 65, Sr 88, Y 89, Tb 159, Yb 174, Lu 175, Pb 206, Th 232, U 238	Mo 95, Gd 157, Er 166, Tl 203, Tl 205, Pb 207, Pb 208	Zn 64, Zn 66, Ga 69, Ga 71, Cd 111, Cd 114, Ba 138, Eu 151.

Table 5. Concentration (ppm) reported as mean and standard deviation calculated from three experiments.

Analyte	Syn-1		SHCa-1		SWy-2		STx-1		KGa-1b	
	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD
Co 59	0.199	0.074	2.449	0.215	0.73	0.126	1.33	0.35	3.27	0.14
Ni 60	10.34	1.494	5.226	0.225	2.837	0.582	5.02	1.96	17.87	0.96
Cu 63	1.596	0.81	5.439	1.708	4.077	1.102	7.53	3.49	25.24	1.44
Rb 85	1.032	2.128	13.768	3.225	6.611	1.357	3.77	1.4	1.32	0.29
Sr 88	1.974	0.732	714.299	117.499	223.993	49.632	81.73	23.47	41.69	3.19
Y 89	0.303	0.275	0.566	0.186	23.28	5.364	34.71	9.09	6.95	0.74
Mo 95	0.653	0.121	0.971	1.340	0.890	0.077	1.060	0.800	2.020	0.310
Sn 118	nd	nd	1.245	1.652	16.262	3.575	4.18	1.72	5.74	0.73
Sb 121	nd	nd	0.2	0.2	0.436	0.076	0.77	0.235	0.299	0.094
Cs 133	nd	nd	3.763	0.303	−0.933	−0.933	nd	nd	nd	nd
La 139	4.611	2.671	0.865	0.351	23.279	5.442	54.77	11.71	33.73	2.7
Ce 140	1.619	0.774	5.264	1.54	49.057	11.215	96.86	20.61	77.12	5.73
Pr 141	0.693	0.389	0.188	0.078	5.757	1.288	13.11	3.05	9.28	0.68
Nd 146	2.154	1.475	0.899	0.532	21.066	5.329	47.39	10.49	40.07	3.79
Sm 147	nd	nd	nd	nd	4.999	1.563	8.92	2.68	9.91	1.97
Eu 151	nd	nd	nd	nd	0.281	0.116	1.23	0.260	2.510	0.340
Gd 157	nd	nd	nd	nd	5.376	1.215	8.58	1.48	10.43	1.31
Tb 159	nd	nd	nd	nd	0.831	0.298	1.3	0.12	1.15	0.19
Dy 162	0.078	0.066	0.142	0.064	4.747	1.247	7.02	1.72	3.74	0.36
Ho 165	nd	nd	nd	nd	0.857	0.228	1.41	0.19	0.369	0.073
Er 166	nd	nd	nd	nd	2.258	0.578	4.26	0.87	0.717	0.078
Tm 169	nd	nd	nd	nd	0.351	0.074	0.619	0.098	0.048	0.024
Yb 174	0.028	0.022	0.073	0.007	2.238	0.506	4.153	0.811	0.462	0.003
Lu 175	nd	nd	nd	nd	0.302	0.14	0.635	0.075	0.071	0.024
Tl 205	nd	nd	nd	nd	nd	nd	0.3	0.027	nd	nd
Pb 208	nd	nd	nd	nd	20.63	3.14	6.24	0.69	32.5	3.99
Th 232	0.158	0.139	0.97	0.624	26.27	7.83	25.73	3.1	37.15	5.54
U 238	nd	nd	nd	nd	12.41	2.27	6.81	0.9	1.96	0.4

nd: not detected.

Trace-element chemistry

Trace-element chemistry for each Source Clay is reported in Table 5. Concentrations are given in ppm and represent the mean calculated from three digestions. Results from two separate sets of digestions for PFl-1 are also included.

REE chemistry

The REE chemistry is reported in Table 5 and in Figures 1 and 2, where the data are normalized to chondrites and the North American Shale Composite (NASC). Plots were prepared for the six source clays having REE abundances greater than the detection limit (3σ above background).

Normalization reveals subtle enrichments and depletions of elements and groups of elements. This information is useful for understanding clay mineral genesis. For example, SWy-2, which is a Na-rich bentonite from Wyoming, has a pronounced negative Eu anomaly. This REE pattern was probably inherited from the silicic glass that altered to form the benton-

Table 5. Extended.

SAz-1		PFl-1		PFl-1		KGa-2	
Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD
1.06	0.18	8.62	0.79	9.62	0.96	8.75	0.15
2.58	1.21	25.78	1.1	28.58	2.41	44.53	1.76
3.09	1.44	10.43	0.93	12.51	2.04	37.83	5.51
4.19	0.96	50.35	7.54	56.11	6.1	1.58	0.39
304.02	71.87	57.82	11.82	65.65	8.32	36.69	4.09
15.51	2.85	22.24	3.16	24.91	2.64	18.64	5.35
0.478	0.286	0.690	0.170	0.746	0.065	5.140	1.560
3.37	0.65	1.5	0.21	1.4	0.82	5.99	0.55
0.372	0.043	0.236	0.061	0.337	0.085	0.497	0.079
nd	nd	3.09	0.4	3.69	0.34	0.228	0.077
82.36	20.22	23.64	5.22	26.5	2.24	35	5.88
51.16	12.81	40.81	7.54	45.96	4.8	56.43	8.22
14.28	3.78	5.32	1.31	6.15	0.46	5.98	0.93
44.69	11.32	20.33	4.03	22.01	3	18.57	3.46
5.96	1.97	3.31	1.09	4.41	0.38	3.32	0.44
0.726	0.304	0.744	0.191	0.93	0.170	0.622	0.283
4.59	0.99	3.72	0.98	4.23	0.62	3.53	0.61
0.577	0.15	0.55	0.117	0.64	0.074	0.578	0.129
3.01	1.11	3.05	0.47	3.67	0.22	3.25	0.58
0.523	0.174	0.616	0.181	0.72	0.06	0.737	0.167
1.57	0.41	1.79	0.34	2.09	0.33	2.05	0.32
0.215	0.077	0.286	0.016	0.3	0.008	0.32	0.031
1.56	0.31	1.57	0.42	1.87	0.19	1.82	0.35
0.294	0.061	0.243	0.038	0.294	0.022	0.314	0.035
0.178	0.025	0.436	0.036	0.634	0.088	nd	nd
34.79	7.01	9.98	1.62	11.29	1.04	44.31	2.63
24.29	6.81	7.19	1.77	8.32	0.83	11.36	2.1
1.19	0.41	4.14	1.15	4.74	0.48	3.02	0.6

ite (Elzea *et al.*, 1990). Negative Eu anomalies occur in silicic magmas because feldspar and apatite crystallization preferentially removes divalent Eu over trivalent REE, which leaves the melt depleted in Eu. Generally, clay minerals formed in equilibrium with seawater have low total REE concentrations, a depletion of Ce, and an enrichment of heavy REE relative to the light REE (Piper, 1974). The negative Ce anomaly in most seawater is attributed to oxidation of trivalent Ce to the highly insoluble quadrivalent state, and its subsequent precipitation in ferromanganese nodules.

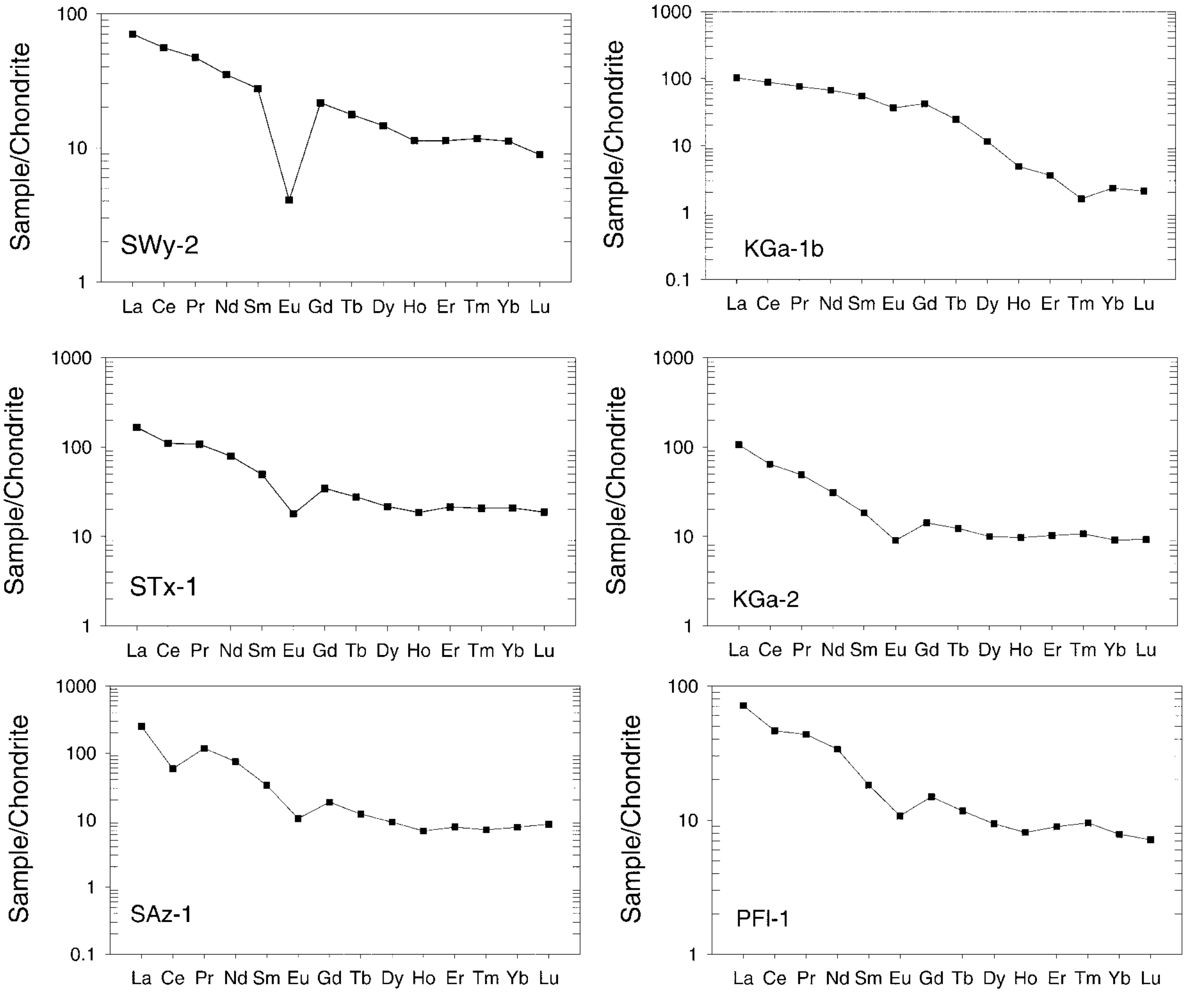

Figure 2. Chondrite-normalized REE data for CMS Source Clays.

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