

## Comparative chemical compositions of aqueous extracts from representative clays

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### ABSTRACT

Aqueous extracts from 31 samples, representative of deposits of kaolinite (weathered and hydrothermal), flint clay, halloysite, dickite, high-alumina minerals, illite, smectite, and Paleozoic shales and underclays, were prepared in the laboratory to simulate the seep and run-off waters from those rocks into the natural environment. The centrifuged extracts were analyzed by inductively-coupled-plasma spectrography and ion chromatography for 36 elements and radicals. Despite the traditionally known low solubility of clay in water, even low-mobility Al was found in 13 of the extracts, e.g., in amounts up to 18.5  $\mu\text{g}/\text{mL}$  from the illitic Fithian Shale.

The concentration of a “dissolved element” in an extract depends not only on the amount present in the sample but also on its aqueous solubility, the pH and Eh of the system, its possible combination with other ions present, the effect of organic matter as a combinant and complexer, the ion-exchange effect, and dispersibility of colloidal clay particles too small to settle out. The data on comparative amounts extracted are discussed from the viewpoint of individual elements and radicals, in terms of the clay mineral or rock deposits furnishing the extracts, and the relation of the extracted material to the genesis and geologic environment of the sample.

### INTRODUCTION

Water held in, or passing through, geologic deposits of clay or shale will dissolve or extract from the clay and associated minerals a kinetic solution load characteristic of the clay deposit. These aqueous extracts, not so barren of solute as conventional wisdom might suggest, represent the contribution of the effluent from the clay or shale deposit to a stream or other drainage, hence to the aqueous environment of the region. The extracts also represent the soluble chemical load available to plants growing in or on the clay deposit. It is speculatively possible that the compositions of the extracts also may reflect the environment(s) of genesis and diagenesis of the deposit.

The purpose of this report is to furnish comparative chemical-compositional data on aqueous extracts from a variety of representative clays, shales, underclays, and high-alumina materials. Although the experiment is done in the laboratory, geologic field conditions are simulated in the preparation of the specimens and solutions in the hope that they will be representative.

### MATERIALS AND METHODS

Thirty-one clays representing well-known geologic deposits were studied. They included six from commercial kaolin deposits, four kaolinitic refractory clays, two hydrothermal kaolins, and one dickite, three halloysites, three illites, one smectite, and eight shales and underclays, as listed in Table 1. Ten grams of each specimen

were crushed to particles about 2 mm in diameter, thereby preserving in part the inherent lithology and natural consolidation of the clay (exceptions are the Clay Minerals Society Source Clays, a reference-type clay collection, which had been pulverized). To these solids were added 100 mL of deionized, distilled water in a polyene beaker, stirred, and stored at room temperature, 20–22 °C. They were stirred again after 4 days and then once a week for 1 month. Visual clearing of the supernatant liquid apparently speeded after the third stirring, which was interpreted as being due to more rapid flocculation of the suspension as the solution became more concentrated. From earlier experiments on dissolution of clay minerals, it was observed that the rate of dissolution slows very significantly after about 10 day’s contact (Huang and Keller, 1971); hence, extraction for a month’s time should be adequate to determine what is naturally extractable.

The supernatant clear liquids were then centrifuged at 10000 rpm for 30 min whereby all particles less than 0.2- $\mu\text{m}$  equivalent spherical diameter should be deposited. A 25-mL portion of the clear centrifugate was analyzed by the Trace Substances Laboratory (Environmental Trace Substances Center, University of Missouri–Columbia) using ion chromatography for anions and inductively-coupled-plasma spectrography for other elements. The pH was determined colorimetrically (with ColorpHast), thereby eliminating errors inherent in electrometric, glass-electrode instrumentation with colloidal clay soils.

## RESULTS, INTERPRETATIONS, AND SPECULATIONS

Analyses of the extract solutions are recorded in Table 1. Although 36 elements were sought, 18 of them were below the concentration limit of detection, or barely detectable in a few nondistinctive occurrences. These 18—Ag, As, Be, Br, Bi, Cd, Co, Cr, Mo, Ni, P, Pb, Sb, Se, Sn, Tl, V, and W—are omitted from Table 1 to conserve space. The concentrations reported are expressed in microgram per milliliter. Because the volume of solution extracted was 100 mL, the amount of each element dissolved from the 10 g of clay sample would be, in micrograms, the analysis number multiplied by 100. For comparative compositions of the extracts, which is the main purpose of this experiment, the numerical amounts in micrograms may be contrasted, one with another.

The amount of an element that is dissolved may depend upon several factors: (1) the amount of it present in the clay or shale, including pore water, (2) the nature of its chemical combination in mineral form, e.g., as a low-solubility aluminum or iron silicate in contrast to a higher-solubility aluminum or iron sulfate, (3) ion exchange from the clay, (4) hydrolytic susceptibility of the minerals present, (5) dispersibility of the clay in water, and (6) effects of organic compounds, in terms of both their individual chemical compositions and their abilities to serve as complexing agents. These variables, although operative individually, also are functional in combination, and thus serve as a part of the comparative solution environment similar to that which occurs in nature.

Comparisons between extracts may be organized (1) by the elements that are found by analysis to be relatively highest or lowest (or nil), (2) in terms of the mineral contents of the clay rocks extracted, and (3) by the mode of origin and/or the geologic environment in which the argillaceous materials were formed, were deposited, or underwent diagenesis.

### Elemental ionic concentrations

**Aluminum.** Reference to Table 1 reveals that Al was extracted in highest concentration from the Fithian Shale (18.5  $\mu\text{g}$ ), from halloysite at the Dragon mine (2.83  $\mu\text{g}$ ), and from the Pennsylvanian Drywood Underclay (1.7  $\mu\text{g}$ ). A potential and probable anion that combined with the Al to stabilize its solubility is  $\text{SO}_4$ , which is present in amounts of 1500, 70, and 1300  $\mu\text{g}/\text{mL}$ , respectively, also high in those samples. It is interpreted that sulfuric acid generated by oxidation of pyrite known to be abundant in the Fithian Shale and Drywood Underclay dissolved and extracted the Al. The pH of 4 in the extract from the Fithian Shale supports this interpretation. The Crowe-burg Underclay contains the minerals kaolinite, illite, smectite, quartz, and alunite in decreasing amount (Keller, 1986). The alunite may be a source of, and/or likewise a product of, soluble aluminum sulfate in the underclay. Halloysite, as from the Dragon mine, is commonly formed in a sulfuric acid environment (Keller et al., 1966); indeed, it is surprising that the Gardner Ridge halloysite

does not yield a higher concentration of Al and  $\text{SO}_4$  in solution than was found.

**Boron.** B was detected in all extracts (including the distilled-water blank) except in the bauxite from Weipa, Australia. Because borosilicate glassware was used to contain the extracts after separation from the clay or shale, it is possible that minor concentrations of B may have been dissolved from the glass. On the other hand, clay minerals are effective sorbers of B (Spivack et al., 1987), especially in a marine depositional environment (Degens et al., 1957), so it is expected that B will be present in argillaceous rocks. Extracts yielding B concentrations in excess of 0.20  $\mu\text{g}/\text{mL}$  included the Georgia kaolins of the Source Clays, the Ordovician Maquoketa Shale, and the Pennsylvanian Crowe-burg Shale and Underclay, which are marine deposits or derivatives (Crowe-burg Under-clay). High B in the dickite from a hydrothermal deposit in Mexico and the Dragon mine halloysite are consistent with elevated B end-member fluids in hydrothermal solutions (Spivack et al., 1987). The lack of B in the extract from the Weipa bauxite is consistent with the observation of Spivack et al. (1987) who found partial mobilization and removal of B in formation of an oxisol from granite in the Guyana shield.

**Barium.** Ba was found in minor quantities in the extracts of all the samples. Ba has long been known to be widely distributed in small quantities in both igneous and sedimentary rocks (e.g., Clarke, 1924) and, among the divalent alkaline earths, is held most strongly by ion exchange (Blatt et al., 1980). It is not outstandingly higher or lower in any one of the aqueous extracts.

**Calcium.** Ca, as with its alkaline-earth partner Ba, was found in the concentrates of all the specimens. This is not unexpected because most sedimentary rocks were deposited in a Ca-containing environment and/or were weathered from Ca-containing parent rock. Secondary kaolin (Georgia kaolin) and halloysite deposits yielded extracts relatively low in Ca, whereas shales commonly associated with limestones in their stratigraphic section or cyclothem yielded the highest concentrations, e.g., the Cambrian Davis Shale, Pennsylvanian Fithian Shale, Ordovician Maquoketa Shale, and Pennsylvanian Crowe-burg Underclay.

**Copper.** Cu is scanty in the extracts. It is more likely to occur in shales where it may be complexed with organic matter, than in residually leached deposits.

**Iron.** Fe, having relatively low solubility in an oxidizing environment, is in low concentration in most extracts except in the sulfate solutions from the Dragon mine halloysite and pyritiferous Fithian Shale and Crowe-burg Underclay.

**Potassium.** K is present in all extracts except those from the Tertiary Georgia kaolins, (GaK-2 and the Purvis pit), which were genetically highly leached. Illitic shales have high K outputs, as might be expected because of the K content of illite.

**Lithium.** Li, a relatively soluble, small-ion alkali metal, occurring in small amounts in nearly all igneous rocks

**TABLE 1.** Analyses of aqueous extracts from clays and shales, using inductively-coupled-plasma spectroscopy and ion chromatography

	Al	B	Ba	Ca	Cu	Fe	K	Li	Mg	Mn	Na
<b>Dionized distilled water</b>											
Blank run		0.03	0.001	2.0	0.003	0.024			0.21	0.007	0.7
<b>Kaolin</b>											
Zettlitz, Czechoslovakia	0.523	0.078	0.015	1.7	0.006	0.015	6.6	0.09	0.652	0.006	14.1
Purvis pit, Georgia		0.17	0.007	0.60	0.004	0.01		0.007	0.110		0.79
GaK-2, Source Clays		0.28	0.018	1.2		0.008		0.006	0.114		1.47
GaK-1, Source Clays		0.086	0.016	1.3		0.008	2.0		0.083		2.06
Meeks pit, Georgia		0.14	0.010	0.45		0.17	2.0		0.078		0.71
Cornwall, Imperial pit		0.15	0.02	0.74			2.0	0.004	0.532		3.59
<b>Refractory clay</b>											
Plastic Cheltenham, Missouri	0.73	0.33	0.026	7.1		0.057	6.6	0.041	1.25		5.54
Flint clay, Missouri	0.02	0.11	0.018	1.4		0.008	2.0	0.015	0.403		1.31
Flint clay, Olliers, France		0.3	0.024	5.7	0.007		2.0		3.59		1.2
Hammanskraal flint clay, Africa		0.30	0.008	0.46			3.0	0.017	0.82		1.1
<b>Hydrothermal kaolin</b>											
Sombrerete, Mexico		0.12	0.024	10.9		0.008	2.0	0.002	0.148		1.1
San Luis Potosi, Mexico		0.088	0.027	11.6		3.0	0.035	1.97	4.98	11.7	0.073
Dickite, Nayarit, Mexico	0.02	0.088	0.016	0.70		0.036	2.0		0.50		1.68
<b>Halloysite</b>											
Gardner Ridge, Indiana	1.8	0.15	0.02	1.20		0.030	2.0		0.051		4.3
Spruce Pine, North Carolina		0.24	0.032	0.39	0.002	0.008	2.0		0.07	0.07	15.1
Dragon mine, Utah	2.83	0.092	0.005	16.1	0.01	3.41	4.0	0.015	5.40	0.395	9.12
<b>Illite</b>											
Silver Hill Shale, Source Clays	0.03	0.21	0.03	12.7		0.018	9.2	0.15	11.7		36.3
Fithian Shale, Illinois	18.5	0.75	0.05	265	0.28	12.3	39	0.352	85.3	4.64	10.2
Marblehead, Illinois		0.23	0.041	29.2	0.002		6.7	0.008	14.2		4.82
<b>Smectite-"bentonite"</b>											
SAz, Source Clays	0.58	0.15	0.09	11.0	0.002	0.074	4.0	0.03	1.76	0.017	7.35
<b>High-alumina</b>											
Bauxite, Arizona		0.15	0.25	6.5		0.007	2.0		0.869	0.12	2.26
Bauxite, Weipa			0.001	4.7			3.0		1.44		1.41
Diaspore, Missouri	0.08	0.13	0.023	1.2		0.006	2.0	0.003	0.392		0.62
<b>Shale-underclay</b>											
Bluejacket Shale, Missouri		0.24	0.06	5.1	0.002	0.18	8.1	0.033	1.71	0.16	11.5
Bluejacket Underclay, Missouri		0.23	0.026	2.8		0.009	6.8		0.903		14.6
Croweburg Shale, Missouri	0.48	0.52	0.05	8.2	0.003	0.087	16.0	0.17	1.79	0.04	318
Croweburg Underclay, Missouri	0.94	0.82	0.035	82.8	0.017	2.15	10.0	0.551	45.8	13.3	447
Drywood Shale, Missouri		0.12	0.83	19.6			13	0.096	10.2	0.72	7.89
Drywood Underclay, Missouri	1.7	0.06	0.008	1.3		0.25	5	0.028	0.036	0.047	8.49
Maquoketa Shale, Missouri		0.98	0.08	143	0.006		21	0.081	33		6.9
Davis Shale, Missouri		0.03	0.026	32.3			24	0.076	16.7		1.5

Note: Amounts are reported in  $\mu\text{g}/\text{mL}$ . Blank spaces indicate that quantities were below the limits of detectability.

and in the waters of many mineral springs (Clarke, 1924), correspondingly is present in low concentrations in 21 of the extracts. Those from the Pennsylvanian Fithian Shale and Croweburg Underclay are highest.

**Magnesium.** Mg, in parallel with Ca, is present in all the extracts. It is in highest concentration from illitic shales, possibly from ion-exchangeable Mg-bearing clay or even dolomite, ranging from 85.3  $\mu\text{g}/\text{mL}$  in the Fithian Shale, decreasing to 45 in the Croweburg Underclay, 33 in the Maquoketa Shale, 16.7 in the Davis Shale, 14.2 in the Marblehead Illite, and 11.7 in the Silver Hill Shale (Source Clays). Among the refractory kaolinitic clays, the flint-clay extracts from Missouri and Olliers, France, yielded the highest amounts of Mg, with 4.03 and 3.59  $\mu\text{g}/\text{mL}$ , respectively. The Missouri flint-clay pit is surrounded by dolomite country rock, a possible source of Mg secondarily introduced by ground water, but we do

not have knowledge of the depositional environment of the Olliers clay.

**Manganese.** Mn is most prevalent among extracts from shales, particularly those with high concentrations of sulfate ions. As with Fe, the dissolution of Mn apparently depends largely on its anionic combination, i.e., with  $\text{SO}_4$ , and effective pH.

**Sodium.** Na, the abundant, highly water-soluble alkaline earth, is present in all of the extracts, as might be expected. Highest concentrations are in the Croweburg Underclay and Shale, with 447 and 318  $\mu\text{g}/\text{mL}$ , respectively; an order of magnitude less are the Silver Hill Shale, 36.3, unexpectedly the Zettlitz kaolin, 14, and the Fithian Shale, 10  $\mu\text{g}/\text{mL}$ .

**Silicon.** Si, perhaps more realistically expressed as the silicate anion, is present in all of the extracts. Omnipresence is to be expected because silicate anions are not only

TABLE 1.—Continued

Si	Sr	Ti	SO <sub>4</sub>	NO <sub>3</sub>	Cl	F	pH
0.10	0.009		3.0				5.0
12.0	0.031	0.074	30		0.95	1.0	5.0
3.07	0.003		1.0		0.79	0.52	4.8
4.85	0.003		2.7	3.5	3.2		5.0
3.69	0.003		3.0	2.0	3.6		5.0
2.49	0.003		1.0				5.0
1.29	0.006		6.1	1.0	2.0	0.1	5.0
5.50	0.035	0.018	18.0	7.4	1.0	1.1	5.2
10.0	0.008		1		0.95	0.98	5.0
8.49	0.014		5.4		1.7	0.3	5.0
13.4	0.003		2.1		0.78	1.0	5.0
11.5	0.018		4.5		1.3	0.4	5.0
	30	3.0	3.2	0.62	5.2		
6.12	0.002		3.9	1.0	0.05		5.0
11.0	0.002		0.7	1.0	3.5		5.0
2.31	0.0025		1		20		5.0
16.8	0.041		72		6.0	0.37	4.5
6.35	0.110		27	2.5	20	0.74	5.8
18.5	2.84		1500	5.3	3.9	5.3	4.0
4.90	0.19		4.3		3.5	1.2	7.0
23.0	0.15	0.007	3.7	2	1.2	0.55	5.8
2.05	0.035		22		2.0		5.0
1.58	0.018		7.6		2.4		5.3
4.21	0.018	0.014	3.4		0.61	0.1	5.0
4.98	0.030		38		0.5		5.0
4.47	0.020		47		1.7	0.3	5.0
5.84	0.24	0.008	480		3.6	1.7	7.5
10.4	2.24		1300		9.8	1.0	5.0
1.58	0.021		32		1.3	1.1	5.8
16.9	0.004	0.032	21.1		1.0		5.1
2.71	0.337		520		1.6	0.99	5.7
5.48	0.162		22	11	2.0	0.57	6.5

a dominant part of each clay structure, but are hydrophylic in the aqueous environment of the extract. Another reason for the highest concentration, 23  $\mu\text{g}/\text{mL}$ , in the Arizona smectite (SAZ—Source Clays) is the probable presence in the extract of abundant dispersed colloidal-clay particles smaller than 0.2  $\mu\text{m}$  owing to the high dispersibility of the smectite. The silica from them may not be ionically soluble silicic acid, but is still dispersed within the extract—a valid simulation of what occurs in the natural environment.

The hydrothermal kaolins of Mexico yielded 11.7  $\mu\text{g}/\text{mL}$  of Si from San Luis Potosi, and 11.5 from Sombrette, presumably because the progress of hydrothermal desilication of the volcanic parent rock toward kaolinite was interrupted before completion, owing to cessation of hydrothermal action; i.e., some silica that had been released from the rock by hot water remained available for cold-

water extraction in our experiment. An analogous delay mechanism probably prevailed for the genetic kaolinization of Zettlitz kaolinite (12  $\mu\text{g}/\text{mL}$ ), Missouri flint clay (10), and halloysite from the Dragon mine (16.8) and from Gardner Ridge (11). Shales and underclays presumably contain aluminum silicate compounds in kinetically metastable condition with respect to illite or other clay minerals.

In the real geologic world, many argillaceous kinetic assemblages exist, e.g., in shales that do not meet the stringent, idealized chemical, physical, and crystallographic properties of ideal clay minerals, such as they are often described in the literature [or even long-term metastability as viewed by Lippman (1981) for kaolinite toward stable dickite]. Hence, when natural drainage waters dissolve them, the solutions are more varied and complex than those from relatively pure clay-mineral specimens.

**Strontium.** Sr is present in the extracts of all samples studied, but in low concentrations. The highest concentrations are in the extracts of the Crowburg Underclay and the Fithian Shale, both less than 3  $\mu\text{g}/\text{mL}$ .

**Titanium.** Ti is present in only six of the extracts, being highest in that from the Zettlitz kaolin (but only 0.074  $\mu\text{g}/\text{mL}$ ), second in the Drywood Underclay, and third in Missouri diaspore. We speculate that it was present as tiny TiO<sub>2</sub> particles freed during weathering and held in suspension.

#### Volatile anionic concentrations

Volatile anions present in clays and shales may be reported merely as loss on ignition (LOI), or "Loss Of Information" (Keller, 1986), in conventional chemical analyses, without being specifically identified; these anions include SO<sub>4</sub>, NO<sub>3</sub>, Cl, F, and others. That they are highly abundant and definitive of properties, including genesis and diagenesis of clays and shales, was shown by their distinctive presence in condensates from heated (dehydroxylated) clays and shales (Keller, 1986), some of which are replicate samples of those in this extraction study. Some of these anions may be readily extracted in aqueous solution, but others appear to be tightly held to the clay.

**Sulfate.** The sulfate radical was observed in every extract, attesting to its widespread occurrence in argillaceous materials. The concentration ranges widely, however, from 0.7–1.0  $\mu\text{g}/\text{mL}$  in flint clay and halloysite to 1500 in the Fithian Shale and 1300 in the Crowburg Underclay. High concentration is correlated with pyritiferous rocks, whereas low values occur in residual clays such as those that underwent leaching during genesis.

**Nitrate.** Soluble nitrate was detected in less than half the samples and is quite low in concentration, typically less than 5  $\mu\text{g}/\text{mL}$ .

**Chloride.** The chloride ion occurred in all extracts except that from the kaolinite in the Meeks pit of Georgia. That chloride is, indeed, a typical constituent of clay, though not in the mineral formula, is confirmed by its abundant presence in the dehydroxylate condensates of

all clays and shales studied in a previous experiment (Keller, 1986). Concentrations in the aqueous extracts were low, reaching a maximum of 20  $\mu\text{g}/\text{mL}$  from the Silver Hill Shale and from halloysite at Spruce Pine, North Carolina. No unique correlation with a marine environment of origin or deposition is indicated.

**Fluorine.** The fluoride ion was widespread in occurrence, but low in concentration. Again, as with chloride, fluoride was typically present in the clays examined in the condensate study (Keller, 1986).

#### GENETIC TYPES AND ENVIRONMENTAL GROUPS

Kaolinites, flint clay, halloysites, and high-alumina minerals, including hydrothermally leached kaolins collected from commercial deposits, yield aqueous extracts usually low in Al, which is to be expected from their history of origin, except possibly where sulfate is also high. It is interpreted that the environment either producing sulfate or maintaining it is conducive to solubilizing Al.

Illites, which really signify illitic shales, yield relatively high concentrations of many elements. This response is consistent with their origin, which is characterized as an accumulated mixture (shale) of a variety of rock-forming minerals. Underclays typically contain, in addition to the rock-forming minerals common to shale, a wide variety of organic substances intimately mixed with the inorganics. These range from coal, per se, to decomposed plant residues, organic-rich soil clays and silts, plant nutrients and compounds of translocated plant nutrients, compounds of nitrates and of ammonia, and minerals precipitated during the depositional and diagenetic process that operate typically in a reducing environment. Pyrite especially, and lesser other metal sulfides, are formed and dispersed within the underclay. Possibilities of extracting soluble compounds from the underclay are high, both in variety of type and quantity, as demonstrated by the results of analyses.

Aqueous extracts of smectites typically contain subcolloidal-sized, dispersed clay particles, visible in a bright beam of light (the Tyndall cone effect), in addition to the ionically dissolved elements. Dispersed Wyoming Na-

montmorillonite prepared by the same procedure as were the other clays is incorporated by and with water so effectively and tenaciously that its aqueous "extract" was more of a gel than an extract—hence it was not included in the analyses.

Clay minerals and rocks, although notoriously "insoluble," are actually low in solubility and do furnish a share of mobile constituents, as shown by analyses, to seep water and run-off from those rocks. Likewise when buried, clays and shales also furnish a mobile chemical load to the rock column during compaction, leaching, and diagenesis of the clay stones.

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