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Compositions of condensates from heated clay minerals and shales

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ABSTRACT

The analytical fraction termed H_2O+, or LOI, of clay minerals and shales contains, in addition to OH, numerous chemical elements and compounds, such as F, Cl, B, Br, NO_2, NO_3, SO_3, SO_4, NH_4, and C. The pH of liquids condensed from such volatiles ranges from approximately 1 to 10.

The sources of these ions and compounds, driven off at temperatures above the critical temperature of water, may include inheritances from the parent rock and from processes of argillation, diagenesis, and also re-exposure of the clay to surface agents that include the phytosphere and its products. Clay minerals, because of their complex structures, ion exchange on interlayer and surface sites, and varied bonding properties are prime candidates (as zeolites also should be) for holding accessories to OH as important parts of their chemical compositions.

Alternatively, it is possible that some of the volatile elements in the specimen may be non–clay mineral impurities in minor quantity; if they were significantly abundant the specimen would be termed a "clay rock." These diverse volatile ions and compounds potentially may be used as fingerprints to help interpret the geologic history of the clay minerals and the mud rocks in which they are dominant.

INTRODUCTION

An essential part of the composition of clay minerals and shales, as shown by their chemical analyses, is the fraction that volatilizes at the so-called dehydroxylation temperatures of the clays, typically above 500°C, at which the OH^- in the crystal structure reacts to form H_2O and bonded oxygens. This fraction is traditionally reported in the chemical composition of the clay as, for example, H_2O above 110°C, H_2O+, (OH,F), or LOI (loss on ignition, at about 950°C). Ceramists refer to it as the "water-smoking" stage of clay firing. Intuitively, it might be expected that the water of dehydroxylation, upon condensation, would be relatively pure; however, as experiments show, rarely is that water from clays pure, or even neutral in pH. For example, the volatiles driven off by dehydroxylation of halloysites from the Brushy Basin mines at Spruce Pine, North Carolina, and from Gardner Ridge, Indiana, yield, upon cooling and condensation, liquids having pH values in the range of 1 to 2. In contrast, the condensate of the LOI from the Silver Hill, Montana, illitic shale (a Clay Minerals Society Source Clay for illite) yields a pH of about 10. Furthermore, during dehydroxylation of some clay or shale samples, strong odors of ammonia, nitriles (?), sulfides, or other compounds not easily identifiable by odor, may be detected in the volatiles, indicating that substances other than H_2O are present.

The purpose of this paper is to present data obtained with qualitative to semiquantitative, but geologically meaningful, analytical procedures of the LOI fraction from various clay minerals and shales, and to infer and interpret possible relationships between these data and the geologic environments under which the clay minerals and clay rocks originated and/or were later modified. This investigation is exploratory, using representative bulk geologic materials; it invites further, higher-precision analytical research on clay-mineral specimens that are more nearly ideal in chemical composition and crystal structure.

MATERIALS AND METHODS

Clay samples differing in mineralogy, collected from diverse, well-known geologic occurrences, different types of genetic environments, and widely separated geographic localities, were selected for this study. Many of the samples were personally collected while investigating clay deposits, some were taken as "grab samples" while attending field excursions at organized geologic meetings, and others were sent to me by experienced geologists (sources acknowledged). Except for the Clay Minerals Society Source Clays, which have been pulverized and thereby presumably also homogenized, the samples represent lump-size crude-ore specimens, and hence are free from any possible artifacts of processing. They are thus geologically representative of the deposit named, but it is likewise recognized that if the specimen had been collected 1 m vertically or laterally distant, it might have varied slightly in composition, but still be geologically representative of that part of the deposit. Data from such samples, although only semiquantitative in terms of highest laboratory precision, are therefore fully meaningful in terms of natural occurrence. Indeed, clay minerals whose compositions are nearly that of ideal formulas, or whose crystals are without significant defect in structure, are so rare that comparative studies of clay minerals are necessarily made of sets called "Reference" or "Source Clays" rather than "pure" clay minerals.

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Table 1. Analyses of condensates by ion chromatography

Clay	Location	pH	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_3^{2-}-SO_4^{2-}	NH_4^+
Halloysite	Spruce Pine, North Carolina	1–1.5	13	393					15	22
	Gardner Ridge, Indiana	1.5–2	44	131	54					9.5
	Dragon Mine, Utah	1–1.5	375	1700					115	70
	Japan spherical	3.5–4	100	90					38	27
Dickite	Ouray, Colorado	1.5–2	1400	65	5					100
	Chon, Mexico, slick fracture	1.5–2	n.d.							
	Chon, Mexico, grainy fracture	1.5	n.d.							
Illite	IMT-1, Source Clays	10	55	39	57				23	580
	Marblehead shale	9–9.5	4	140	24				13	950
	Fithian, Illinois, shale	4–5	30	280		34			3750	1350
High alumina	First-grade diaspore, Missouri	1–1.5	71	218					5	70
	Super-select diaspore, Missouri	1.5–2	n.d.							
	Weipa bauxite	4		52					250	165
	Arkansas bauxite	6.5–7	32	17					130	160
Flint clay	Schaefferkoetter pit, Missouri	5.5–6.5	80	52					46	110
	Matthews pit, Missouri	7–7.5	n.d.							
	Maher pit, Missouri	6–7	36	54					46	100
	New Florence pit, Missouri	4.5–5	n.d.							
Kaolinite	Zettlitz, Czechoslovakia	5–5.5	28	55		20	10		44	55
	Cornwall, United Kingdom	9–9.5	46	47	18				26	170
	Jari River, Brazil	4–4.5	12	62			14		220	90
	Huber Mine, Georgia	3.5–4	19	23					85	33
	Chambers no. 3 mine, Georgia	4.5–5	10	19					30	46
	Meeks mine, Georgia	4–5.5	n.d.							
	Hodges mine, Georgia	4–5	n.d.							
	Murfreesboro, Arkansas	8.5	n.d.							
	GaK-1, well-crystallized Source Clays, old	4–5.5	18	20					80	95
	GaK-1, well-crystallized Source Clays, new	5.5–6.5	10	20					95	100
	GaK-2, poorly crystallized Source Clays	2–3		42			19		200	70
	Thiele Hinton mine, gray, Georgia	3.5–4.5	n.d.							
	Thiele Hinton mine, tan, Georgia	3.5–4	24	50					130	95
	Purvis mine, Georgia	3.5–4.5	n.d.							
Smectite	SWy-1, Source Clays	8–8.5		62	25		12	2.3	1.9	72
	SAz-1, Source Clays	5–6	8	60	37					20
Hydrothermal origin	Sombrerete, Mexico	2–2.5	350	190						
	Chon, Mexico	3–3.5	n.d.							

Note: Amounts are expressed as parts per million. Blank spaces indicate that quantities, if present, were below the limits of detectibility, or not determined (n.d.) in a few specimens.

Portions of the experimental samples, usually 50 to 60 g, were crushed (minimal grinding) to particles about 4 mm in diameter plus fines, which were then dried at 110°C and stored in a desiccator. To dehydroxylate, a dried sample was poured into a fused silica tube, closed at one end and about 410 mm long, with a 30-mm outside diameter and a 26-mm inside diameter. This tube was placed horizontally, closed-end inward, in an electrically heated, combustion-type furnace. The furnace temperature was raised to 650°C (700°C for dickite and nacrite), thereby heating the furnace wall and sample to a glowing red temperature. The open end of the tube, which extended 130 mm out of the furnace, was loosely stoppered with a Pyrex test tube whose outside diameter was about 2 mm smaller than the inside diameter of the silica tube and which was kept cool by a water-soaked sponge inside the test tube. Thus, the vaporized products traveled outward to the cool, open end of the silica tube outside the furnace and there condensed (at about 50–55°C and down to room temperature) to a liquid that dripped from the end of the silica tube into a small Pyrex beaker. Usually about 6 to 10 mL of liquid was condensed and collected, but the amounts were somewhat variable. The amounts were less from samples such as sandy shale or incompletely argillized granite (Cornwall granite) that also contain nonargillaceous rock-forming minerals.

The pH of the liquid condensate was measured in drop-size quantity (too small for glass-electrode measurement) where it first condensed at the end of the silica tube using colorimetric test papers. Two different brands, pHydrion and ColorPHast, were used as counterchecks, yielding a precision of measurement of about 0.2 to 0.5 pH units. The condensate in the collection beaker, again tested for pH, was stored in a Pyrex glass vial with a screw cap until it was chemically analyzed. A glass electrode was not used to measure the pH of the liquid before chemical analysis in order to avoid possible contamination of the liquid by electrolyte that might have diffused from the electrode. After analyses, if sufficient liquid remained, it was tested for pH with a glass electrode, thereby confirming the earlier measurement by test paper.

During the heating cycle of the clay, slight vapor condensation usually began to appear when the clay had been heated to about 450°C, followed by vigorous volatilization and condensation that continued to about 650°C, or higher. These temperatures are consistent with temperatures of dehydroxylation as identified with differential thermal analyses of the clays. Volatilization and condensation reactions appeared to be completed after about 15 min of heating at 650°C.

ANALYTICAL DATA

Thirty-six samples of clay were heated and tested for condensate pH as listed in Table 1. Of these, 25 were further analyzed by ion chromatography at the Trace Substances Research Laboratories, University of Missouri–

Table 2. Analyses of condensates by inductively coupled plasma-spectrography

	Spruce Pine halloysite	Indiana halloysite	IMT-1 Source Clays	First-grade diaspore	Cornwall kaolin	GaK-1 Source Clays	GaK-2 Source Clays	SWy-1 Source Clays	SAz-1 Source Clays
Al	27	45	0.94	10	1.7	0.85	0.53	1.4	1.6
B	1.7	1.7	0.54	4.1	3.7	1.4	1.3	2.0	1.9
Ba	0.12	0.12	0.099	0.13	0.11	0.016	0.016	0.024	0.076
Ca	1.8	1.7	2.3	0.51	1.3	0.82	0.79	1.3	7.5
Cu	1.1	0.06							
Fe	0.66	0.90	0.1	0.84	0.1	0.04	0.04	0.32	0.20
Mg	0.11	0.25	0.81	0.35	0.51	0.24	0.22	0.70	1.6
Mn									0.11
Na	2.7	3.3	2.3	4.9	4.8	4.4	4.3	6.7	5.3
Ni	0.3								
Pb	0.7								
Si	20	42	3.0	43	2.8	1.2	0.99	4.9	11
Sr	0.013	0.013	0.020	0.091	0.007	0.006	0.006	0.013	0.11
Ti	0.036	0.02	0.035	0.069	0.02	0.03	0.02	0.02	0.03
Zn	3.0	0.23		0.12		0.040	0.034	0.02	0.033
C	2700	550	30 000	340	1700	200	120	370	200

Note: Amounts expressed as μg/mL. Other elements looked for, but not found in detectible amounts, include Ag, As, Be, Bi, Cd, Co, Cr, K, Li, Mo, P, Sb, Se, Sn, Tl, and V.

Columbia, for anions and NH_4^+. Further analyses for 32 elements were made of 9 samples by inductively coupled plasma spectrography (Table 2). Although insufficient funds were available for complete analysis of all of the samples, those samples selected represent the different types of clay minerals examined.

COMMENTS ON THE CONDENSATES AND THEIR COMPOSITIONS

The samples listed in Table 1 are divided into groups according to certain common properties such as mineralogy or mode of genesis. For example, the first four listed are halloysites. Chemical similarities and/or dissimilarities within these groups are discussed in consideration of properties that may be characteristic of the samples, their changing environments, or geneses.

Halloysites and kaolin

The mineral halloysite generally tends to yield a highly acidic condensate as shown in Table 1. The Spruce Pine and Dragon mine condensates predominate in HCl with lesser HF, as indicated by Cl^- and F^- (Table 1), whereas that of the Indiana halloysite contains almost as much HF as HCl calculated in micromoles. F^- is commonly present in silicates and is lost on ignition (El-Attar et al., 1972), but because Cl^- has a radius almost 30% larger than OH^-, it is problematical whether Cl^- substitutes for OH^- in the clay-mineral crystals or is present in other forms. Noting also from Table 2 that appreciable Al and Si are in solution in the dehydroxylates from the Spruce Pine and Indiana halloysites, it appears that the acidic aqueous vapor at high temperature dissolves Al and Si from halloysite corresponding to the original 1:1 mole ratio. At dehydroxylation temperatures, which are significantly above the critical temperature for water, such "water vapor" is characteristically a more powerful solvent and reactive with mineral elements than if it remained in the liquid state, as was pointed out by Eugster (1986). Geologists and geochemists must recognize more fully the important possibilities of intensified dissolution, corrosion, transportation, and deposition of chemical elements and minerals from aqueous vapors at supercritical temperatures. Note that B and C are present in determinable quantity in both hydroxylates listed in Table 2. Their occurrence invites questions, such as (1) where did the B reside in these nonmarine clays that are characteristically B poor (Degens et al., 1957), or may B have been dissolved from the Pyrex glass, and (2) may C have been introduced into the clay as humic compounds by surface groundwater migrating through the clay?

Acidity in halloysite is not solely a laboratory-generated property; it is possibly inherited from the natural field environment. When the Spruce Pine clay was collected in 1963, the moist clay face in the mine yielded a pH of 3.5–4 (colorimetric test paper), and a pool of water standing in the clay had a pH of 3.5. Whether that acidity originated in the clay or from organic acids contributed by the Holocene phytosphere is undetermined. When the Indiana halloysite was collected in 1963, the wet mine face had a pH of 4.5–5.0. Acid water that migrated downward from the overlying Mansfield Shale, which contained oxidizing iron sulfide, presumably contributed acidity to the halloysite.

The abundance of SO_4^{2-} in the Dragon mine clay may reflect the environment of genesis that was described by Kerr and Kulp (1949) as follows: "Clay mineral formation in the wall rock was evidently one phase of the general mineralization associated with the sulphate deposition."

The Japan spherical halloysite, which yielded a dehydroxylate with less acid than those from the American clays, was altered from pumice, debatedly by a weathering process or "by rising solutions" (Minato, 1975). A small amount of unaltered but reactive pumice glass might remain in the clay, which could contribute to the lesser acidity of its dehydroxylate, as field studies have shown (Keller, 1960).

Dickite and kaolin

The Ouray dickite is high in F^-; hence, HF is present in the dehydroxylate. Two dickites from Mexico, one showing a "slick," flinty fracture and the other a coarse granular texture, also yielded highly acid condensates. Although S-rich vapors are commonly present in hydrothermally altered areas, such as contain alunite, the sulfate ion was not found in the Ouray condensates.

Illite and illitic shale

Judging from the condensate of the well-crystallized illite in the Silver Hill Shale, dehydroxylates from illite (rocks?) apparently tend to be high in pH except where they are accompanied by acid-forming sulfate, as in the Fithian shale samples. The Silver Hill Shale gives off a noticeable odor of ammonia when heated to dehydroxylation. The location of the NH_4^+ in the illite of this shale may be acocunted for by some interlayer NH_4^+, and probably additional, admixed organic compounds. The chemical analysis of the Silver Hill Shale reported by Hower and Mowatt (1966) shows 8.04% H_2O of which 6.4% is H_2O+, but NH_4^+ is not listed and presumably was not determined. Hower and Mowatt noted that "all illites and mixed-layer illites contain H_2O+ in excess of the 'normal' 4.5% of aluminum dioctahedral micas." Hence, 1.9% "excess H_2O+" may in part be NH_4^+. It is encouraging that currently more chemical analyses of minerals (especially clay minerals and feldspar) include determination of NH_4^+, which is probably more widespread in rock-forming minerals than hitherto identified. Presumably, NH_4^+ remains in excess of F^-, Cl^-, and SO_4^{2-} in the condensate from the Silver Hill sample and maintains a high alkalinity in the dehydroxylates. Note that 57 ppm of NO_2^-, and 30 000 ppm dissolved, or volatile, C compounds are present in the condensate of the Silver Hill sample, suggesting that accessory organic CN compounds were pyrolyzed from the shale. The Marblehead Shale yields a condensate only slightly less alkaline than the Silver Hill rock. Marblehead condensate contains more Cl^- than does that from Silver Hill, but is compensated by a much larger content of NH_4^+. The condensate of the Fithian Shale is strongly acid, caused probably by the higher concentration of Cl^- and especially by the significant amount of SO_4^{2-} derived from parent iron sulfide in the shale. The Fithian sample was collected from the exposed type section of the shale where oxidation of iron sulfide would generate effective sulfur-containing acids.

Although the Fithian sample was collected from the type locality for illite, and the Silver Hill sample is crystallographically standard illite, apparently neither of these clays is "compositionally pure" illite, nor free from a chemical imprint of its geologic environment of formation. Where does an illite having an "ideal" chemical composition occur, if such a mineral specimen actually exists; would it be either authigenically crystallized, or of hydrothermal origin?

High-alumina "clay" minerals

First-grade diaspore (Al_2O_3 content above 68%) from the Missouri Schaefferkoetter pit (Keller and Stevens, 1983) yields a condensate that is highly acidic in HCl and HF, but also contains NH_4^+ in about the same micromolar concentration as each acid. If the derivation of the N compound yielding NH_4^+ is organic, was it present during genesis of the diaspore, or was it introduced while Tertiary and/or Holocene erosion removed the strata of Pennsylvanian age covering the diaspore? As in the halloysite dehydroxylates, the acid vapor of this diaspore dehydroxylate dissolved both Al and Si, the latter presumably from the relatively small amount of kaolin still present with the diaspore. This corrosive vapor was present at temperatures above the critical temperature for H_2O. B, source unknown (Pyrex glass?), is relatively high in the diaspore condensate. Weipa, Australia, bauxite yields a condensate that is only moderately acid, presumably because Cl^- and SO_4^{2-} are moderate in concentration and NH_4^+ is high. The condensate of Arkansas bauxite is essentially neutral in pH; its content of F^-, Cl^-, and SO_4^{2-} is low, but neutralizing(?) NH_4^+ is almost as high in concentration as that from Weipa.

Flint clay, Missouri

Flint clay, which is composed of kaolinite that typically is well crystallized (Keller, 1981), yields condensate ranging from weakly acid to neutral. F^- and SO_4^{2-} are moderate in concentration and apparently balanced, in effect, by NH_4^+.

Kaolinite and kaolin

Relatively pure kaolinites yield condensates that are usually moderately acid, i.e., in the range of 3.5 to 5. They are similar in this respect to the aqueous suspensions of kaolinite and to the water standing in pools in kaolinite mines or draining kaolinite deposits.

The Zettlitz kaolin, a one-time recommended standard for kaolinite, contains a variety of anions in its condensate, notably Br^- in addition to F^-, Cl^-, NO_3^-, SO_3^{2-}-SO_4^{2-}, and NH_4^+.

Kaolin from the Cornwall district of England containing megascopically visible kaolinite, incompletely kaolinized feldspar, mica flakes, and quartz, yields a condensate that is higher in pH than those of most kaolins, probably because of the relatively high content of NH_4^+. NO_2^- is also present. The source of such relatively abundant N is not known. Bristow (1977) and Durrance et al. (1982) have suggested that the Cornwall kaolin has undergone both magmatic hydrothermal alteration and significant further kaolinization by resurgent water that was circulated by heat from radioisotopes in the granite. The N may be from surface waters that have been active since erosional exposure of the clay, but magmatic sources must not be overlooked. It is possible that the NH_4^+ may be present in the mica and/or feldspar.

Table 3. Condensates from heated Paleozoic shales of Missouri

Formation—Member	Age	pH of condensate*		Mineralogy**
		Lower *T*	Higher *T*	
Calhoun Shale	Penn.	2	9	I, K, Ch, Al, Q
Oread—Heebner	Penn.	2	9.5	I, K, Ch, Ma, Si, Q
Stanton—Eudora	Penn.	2	9.5	K, I, Ch, Sml, Q
Bluejacket Shale	Penn.	4.5	N.C.	I, K, Sml, Q, Di
Bluejacket Underclay	Penn.	3.5	N.C.	K, I, Sml, Q, Al
Drywood Shale	Penn.	8	N.C.	K, I, Sml, Q, Py
Drywood Underclay	Penn.	2	N.C.	K, I, Sml, Q, Al
Croweburg Shale	Penn.	8	N.C.	K, I, Sml, Q
Croweburg Underclay	Penn.	5	N.C.	I, K, Sml, Q
Fern Glen Shale	Miss.	8	N.C.	I, Ca, D (?), Q
Maquoketa Shale	Ord.	2	9.5	I, K, D, Q
Decorah Shale	Ord.	2	8.5	I, Sml, K, Q, Ca, D
Davis Shale	Cam.	3	N.C.	I, Sml, K, D, Pa (?)

* "Lower *T*" refers to first-condensed liquid volatilized at about 425°C; "Higher *T*" refers to condensates from highest-temperature, last-stage volatilization; "N.C." indicates no change.

** Mineral abbreviations: I, illite; Sml, smectite mixed layer; K, kaolinite; Ch, chlorite; Q, quartz; Al, alunite; Si, siderite; Ma, marcasite; Ca, calcite; D, dolomite; Py, pyrite; Di, diadochite; Pa, palygorskite. The most prominent clay mineral as determined by X-ray reflection is listed first in the shale-mineral sequences. Shales were collected by A. Rueff, Missouri Geological Survey.

Kaolinite from Brazil, in a tropical environment, yields a condensate typical of kaolinite in acidity with relatively abundant F^-, Cl^-, NO_3^-, SO_3^{2-}-SO_4^{2-}, and NH_4^+.

Kaolinites of Cretaceous age from Georgia yield typical acid condensates in which Fe^-, Cl^-, and SO_3^{2-}-SO_4^{2-} exceed NH_4^+. Murfreesboro, Arkansas, kaolinite evolves a strong organic and ammoniacal odor when heated.

Well-crystallized Cretaceous Georgia kaolinite was examined in two samples of GaK-1 from the Source Clays Repository, one from an "old" barrel container nearly empty from which many samples of clay had been disbursed, and another from a "newly opened" barrel. The "old' clay yielded a slightly more acid condensate than did the "new," but other components, such as B, Al, Si, and C, were closely comparable.

Poorly crystallized Tertiary Georgia kaolinite, GaK-2 of the Source Clays, and three other samples from the Wrens-area mines produced condensates that were slightly more acid than those from the Cretaceous kaolins, possibly owing to a higher content of Cl^- and/or SO_3^{2-}-SO_4^{2-}.

Smectite and bentonite

The condensate of Wyoming bentonite, SWy-1, is slightly alkaline, whereas that of Arizona bentonite, SAz-1, is slightly acid; the difference is possibly because the NH_4^+ content of the former is 3.5 times that of the latter. Consistent with the compositions of Arizona Ca-bentonite and Wyoming Na-bentonite, more Ca and less Na are present in the Arizona condensate than in the Wyoming condensate.

Hydrothermal clays

Two kaolin-dominant hydrothermal clays from Mexico were examined in addition to the two dickite-dominant Mexico Chon clays previously described. Both these kaolinitic clays yielded condensates that are acid, but less so than those from "pure" Ouray dickite. The Sombrerete deposit contains alunite in some parts, but SO_4^{2-} was not detected in the dehydroxylate; F^- and Cl^- are the main acid anions.

CONDENSATES FROM SHALES AND UNDERCLAY

Thirteen Paleozoic shales and underclays, ranging from Cambrian to Pennsylvanian age and collected from representative localities in Missouri, were processed in the same way as were the previously described clay specimens, yielding the data in Table 3. With the exception of the Cambrian Davis Shale, all gave off organic to tarry odors of varying intensity during heating above about 500°C, indicating some pyrolytic action in addition to dehydroxylation of chemically bound water.

The first liquid to condense from five of the shales, starting from a temperature of about 400 to 425°C, was quite acid at a pH of about 2. As the temperature continued to rise to 600°C over a period of about 10 min, the pH of the condensing liquid rose to 8.5 to 9.5, during which time the strong organic (ammoniacal?) odors were evolved.

On the other hand, condensates of the Drywood, Croweburg, and Fern Glen shales were alkaline, pH 8, at low temperatures of heating and remained so as the temperature was raised. The Bluejacket shale and underclay produced acid condensate, presumably because of respective contents of diadochite and alunite. The Drywood underclay contained alunite. The cause for acidity from the Croweburg underclay and the Davis shale is not apparent, although underclays may contain humic compounds originating within the environment of the superjacent coal.

The conclusion is inescapable that the portion "LOI" in a chemical analysis of mud rocks such as these listed in Table 3 must include compositionally much more than "H_2O+."

CHEMICAL ANALYSES AND THEIR IMPLICATIONS IN CLAY MINERAL–ROCK RELATIONSHIPS

Increased sensitivity in chemical analyses of minerals and rocks reveals the presence of many more elements in the specimens than those designated by the ideal formulas of the minerals. Such chemical information not only enhances knowledge about the composition of the minerals, but it likewise provokes questions about which of those lesser elements are essential components of the minerals, and which may be impurities held either physically or chemically. Impurities are especially likely to taint clay minerals because their compositions are easily and significantly modified owing to their relatively large capacity for ion exchange, substitution of framework ions, defects in ordering within the crystal structure, and occlusion by sorption forces and in physical pore spaces of both inorganic and organic compounds. Furthermore, the geologic history of most clay deposits includes modifying effects of diverse biogeochemical environments during stages of genesis, burial, and re-exposure of the clays at the Earth's surface. Although clay minerals are notable for their variations in minor quantities or trace elements, it is salutary to recall that even quartz, upon sensitive chemical analysis, is commonly found to contain trace amounts of Al, presumably substituting for Si, that are stoichiometrically balanced in charge by identifiable K or Na.

It is concluded from this exploratory analysis of condensates from clay minerals and rocks that their LOI content in a conventional analysis may be lightly paraphased also as "loss of information" or "lots of information."

Furthermore, a highly quantitative chemical analysis, supported by sensitive structural analyses, with techniques such as IR, NMR, and spin resonance, is necessary to determine which chemical elements in a clay sample are essential in the mineral structure and which are alien accessories. On the whole, the essential trace-element content (both volatile and nonvolatile) appears to vary widely among clay minerals. Among the volatile elements to be especially looked for in clay minerals is NH_4^+, which may possibly be essential (exchangeable or fixed) or physically admixed and in associated organic compounds.

Strict differentiation, therefore, between a clay-mineral sample and a clay-rock specimen is not easy. Because the LOI content of clay minerals and clay rocks commonly represents a summation of a complex environmental history ranging from the time of genesis through burial to re-exposure at the surface of the Earth, potentially much of the geologic history of the clay may be inferred from a comprehensive analysis of its LOI. More extensive research is invited on the study of the LOI fraction, not only of clay minerals and rocks, but of other rocks and minerals in which the amount of LOI is significant.

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