

COMPARISON OF RAPID METHODS FOR CHEMICAL ANALYSIS OF MILLIGRAM SAMPLES OF ULTRAFINE CLAYS

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Abstract—Two rapid methods for the decomposition and chemical analysis of clays were adapted for use with 20–40-mg size samples, typical amounts of ultrafine products (<0.5- μm diameter) obtained by modern separation methods for clay minerals. The results of these methods were compared with those of “classical” rock analyses. The two methods consisted of mixed lithium metaborate fusion and heated decomposition with HF in a closed vessel. The latter technique was modified to include subsequent evaporation with concentrated H_2SO_4 and re-solution in HCl, which reduced the interference of the fluoride ion in the determination of Al, Fe, Ca, Mg, Na, and K. Results from the two methods agree sufficiently well with those of the “classical” techniques to minimize error in the calculation of clay mineral structural formulae. Representative maximum variations, in atoms per unit formula of the smectite type based on 22 negative charges, are 0.09 for Si, 0.03 for Al, 0.015 for Fe, 0.07 for Mg, 0.03 for Na, and 0.01 for K.

Key Words—Borate fusion, Chemical analysis, Classic rock analysis, HF decomposition, Microanalytical method.

INTRODUCTION

Modern methods of separation have made it possible to obtain nearly monomineralic samples of crypto-crystalline materials from a variety of parent rocks. These ultrafine particle-size materials (<0.5- μm equivalent spherical diameter) are very chemically reactive and, therefore, particularly sensitive to changes in their geochemical environment. Their accurate analysis is thus extremely important to modern investigations of clay mineral genesis and for studying the history of sediments in which they occur. Unfortunately, the paucity of clay-size material in many sediments often produces only very limited quantities of purified products—a few tens of milligrams at best—thereby limiting the accuracy of standard analytical procedures which commonly require several hundred milligrams of sample. The objective of this study was therefore to modify existing analytical techniques to develop for samples weighing no more than 50 mg a reasonably rapid wet chemical procedure which would provide an accuracy comparable to that obtained by “classical” rock analyses. Chemical analyses of purified clays from the Amargosa Desert, Nevada, and Lake Abert, Oregon, obtained from modified lithium meta- and tetraborate fusion and HF-dissolution methods are herein compared with those obtained on the same samples using standard or conventional rock analysis procedures.

EXPERIMENTAL

Sample preparation

The Amargosa Desert and Lake Abert clay samples have been mineralogically characterized and reported on in detail elsewhere (Amargosa Desert: Khoury, 1979; Khoury and Eberl, 1979, 1981; Eberl *et al.*, 1982; Lake Abert: Jones and Weir, 1983). From X-ray powder diffraction and electron optical data, these materials are known to be relatively homogeneous. At the same time, the environment of deposition suggests that the samples are also reasonably free of sesquioxide or organic coatings. Samples P-7 and 12-14 are mixed-layer kerolite/stevensite collected near the Amargosa Flat. Sepiolite and kerolite from the same area were collected by R. L. Hay, and sample H-1 came from the Hectorite-Whiting pit on the California side of the Amargosa Desert. The Kinney bentonite was obtained from a pit near the Ash Meadows portion of the basin. The Lake Abert samples were from fine sediment sample AB21jb at a depth of 0.82 m in the proximal playa at the north end of the lake, and from pyroclastic sample AR 33 in a formerly submerged outcrop at the base of the Abert Rim at the northeast end of the lake.

Bulk samples were dispersed mechanically and then ultrasonically in deionized water and passed through a 37- μm (400-mesh) sieve. This suspension was fractionated by sedimentation in glass columns, and the

<2.0- μm portion was subjected to high-speed centrifugation to obtain suspensions of <0.2- μm or <0.1- μm equivalent spherical diameter. These solids were recovered by flocculation with 0.5 N NaCl and then re-dispersed and centrifuged repeatedly until they were sufficiently salt-free that no chloride could be detected upon the addition of silver nitrate. They were then dried overnight at 90°C, ground in a mortar, and divided for analysis. To minimize sample heterogeneity, more than 100 g of each sample was prepared in this manner.

Analytical procedure

The "classical" rock analysis technique described by Lundell and Hoffman (1938) and Hillebrand *et al.* (1953) has been developed over a period of many years. It is still used today and is the standard against which other methods are measured, but it is very time-consuming and requires painstaking work by a skilled analyst plus sizeable samples. More rapid wet-chemical methods with similar degrees of accuracy have been proposed. One widely used method was developed by Ingamells (1964) and modified by Shapiro (1975) and consists of fusing the sample with a mixture of lithium metaborate and tetraborate. This method is advantageous because it produces a single solution from which all of the common constituents can be determined, although the solution contains a high concentration of salts which can cause matrix problems in atomic absorption determinations. Another "rapid" method involves heating the sample in a closed vessel with HF or a combination of acids (Langmyhr and Paus, 1968; Bernas, 1968). Dissolution of the sample by HF followed by complexing with boric acid produces a salt-free matrix but leaves a high concentration of fluoride and borate ions in the solution. In the present study the fluoroborate ions were volatilized by evaporation with concentrated H_2SO_4 and the residue redissolved in dilute HCl.

An appropriate test of precision was considered to be a reproducibility of better than 0.1 atom per mica or smectite half-unit cell, that is, per $\text{O}_{10}(\text{OH})_2$ formula unit or 22 negative charges.

Lithium metaborate and tetraborate fusion method. A 20–40 mg sample was mixed with 0.2 g of a flux consisting of 1 part lithium metaborate to 2 parts lithium tetraborate and then fused for 1 hr at 900°C in a graphite crucible. The cooled bead was dissolved overnight in about 50 ml of deionized water and 1 ml of concentrated nitric acid and then diluted to 100 ml in a volumetric flask. A further 1/10 dilution was made of the 100-ml solution for use in the silica, aluminum, and iron determinations. All solutions were transferred immediately to plastic bottles to minimize the leaching of silica from glass containers.

Silica was analyzed by the colorimetric ammonium

molybdate method, using 5.0 ml of 1 M HCl, 5.0 ml of 0.1% NaF, 5.0 ml of 4.9% ammonium molybdate, and 10.0 ml of 17% Na_2SO_3 . The resulting molybdate blue complex was allowed to stand at least 1 hr before absorption was measured spectrophotometrically at 700 nm. Aluminum was determined colorimetrically with 5.0 ml of 0.05% ferron (8-hydroxy, 7-iodo-5-quinoline sulfonic acid), 2.0 ml of 1% hydroxylamine HCl, and 2.0 ml of 35% sodium acetate, and the resulting color complex was measured at 370 nm. Iron was determined colorimetrically at 520 nm after the addition of 1.0 ml of 0.2% bipyridine, 2.0 ml of 1% hydroxylamine HCl, and 2.0 ml of 35% sodium acetate. Calcium, magnesium, sodium, and potassium were determined by atomic absorption spectrophotometry. These methods are essentially those described by Skougstad *et al.* (1979).

HF-dissolution method. A 20–40 mg sample and 3 ml 40% HF were heated for 1 hr at 110°C in a 25 ml Parr bomb which is designed so that the sample comes in contact only with a Teflon cup sealed inside the bomb. After cooling, 2.8 g of boric acid and a few milliliters of deionized water were added to the Teflon cup. The solution was diluted to 100 ml and transferred to a plastic bottle. Fifty milliliters of this solution was placed in a platinum dish, evaporated with 1.0 ml of concentrated H_2SO_4 on a steam bath, and then evaporated to complete dryness on a hot plate. The residue was redissolved with a few milliliters of water and 1 ml of concentrated HCl by gently warming on a steam bath. It was then diluted to its original volume of 50 ml and also stored in a plastic bottle.

The remaining portion of the sample solution which was not evaporated was diluted 1:9, and silica was determined in the 1/10 dilution by the same method as that of the lithium borate fusion procedure. Aluminum, iron, calcium, magnesium, sodium, and potassium were determined in the evaporated sample by the same procedures used in the lithium borate fusion method.

Classical or conventional rock analysis. A 0.1-g sample was fused with 1 g of sodium carbonate for 45 min, and the melt was heated to dryness on a steam bath with water and an excess of HCl. The soluble salts were then redissolved in 10% HCl, and the solution was filtered through filter paper to remove the dehydrated silica. The procedure of re-solution and filtration was then repeated. The combined silica precipitates were ignited to constant weight at 1100°C. The silica was then volatilized by digestion in HF and a few drops of H_2SO_4 , and the remaining precipitate was ignited to constant weight at 1100°C. The loss in weight represents the amount of silica in the sample.

The filtrate from the silica determination was heated to near boiling, and the R_2O_3 was precipitated by

the addition of 1:1 ammonium hydroxide at a pH of 6.6–6.7. The solution was filtered through filter paper, the precipitate was washed with hot 2% ammonium chloride, and the filtrate was reserved for the determination of calcium and magnesium. The R_2O_3 precipitate was dissolved off the filter paper with dilute HCl, and the precipitation and filtration process repeated. The precipitate was then ignited at 1100°C to constant weight. After weighing, the precipitate was transferred to a Vycor crucible, fused with 1 g of potassium pyrosulfate, leached with dilute sulfuric acid, and diluted to 100 ml in a volumetric flask. An aliquot of this solution was used to determine total iron spectrophotometrically with o-phenanthroline.

The solution containing calcium and magnesium was made basic with NH_4OH , and heated to boiling. Calcium was precipitated by the addition of ammonium oxalate. After digestion on a steam bath, the precipitate was filtered onto filter paper and redissolved with HCl. The process was then repeated, and the second precipitate was ignited to oxide.

The combined filtrates from the calcium determination were treated with 20% diammonium hydrogen phosphate and made basic with ammonium hydroxide to precipitate magnesium. After standing overnight, the precipitate was filtered on filter paper, redissolved, and the precipitation process repeated. The precipitate was then ignited to constant weight at 1000°–1100°C.

To determine Na and K, a separate sample was put into solution by heating with HF and $HClO_4$ and diluted to 100 ml in a volumetric flask. An aliquot of this solution was used for a sodium determination after sufficient KCl was added to make the concentration of potassium equal to 0.2%. Another aliquot was similarly treated with NaCl and then used to determine potassium. Both determinations were made by atomic absorption spectrophotometry.

Comparative methodology

To evaluate the results of the three methods it was necessary to use a common basis for comparison. Thus, the sum of the major constituents, i.e., SiO_2 , Al_2O_3 , Fe_2O_3 , CaO, MgO, Na_2O , and K_2O for each analysis was multiplied by the appropriate factor to make the sum equal 100%. In the classical rock analysis, FeO was recalculated as Fe_2O_3 and added to the determined Fe_2O_3 to give a total iron value. Tables 1 and 2 show the chemical analyses of the eight clays from the Amargosa Desert, Nevada, and the two from Lake Abert, Oregon.

In the lithium borate fusion and HF-dissolution methods, aluminum was determined colorimetrically by reaction with ferron (8-hydroxy, 7-iodo-5-quinoline sulfonic acid) as described by Skougstad *et al.* (1979). They reported that the presence of fluoride was responsible for low aluminum values. In the lithium bo-

rate fusion method, aluminum values were unaffected because fluorine was complexed as fluoborates. In the HF-dissolution method, however, the aluminum determination was seriously affected even though boric acid was added after the dissolution. Probably some free fluoride ions remained uncomplexed. To ensure the removal of any excess fluoride ion, an aliquot of the sample solution was evaporated to dryness in a platinum dish with 1 ml of concentrated H_2SO_4 and redissolved by gentle warming with dilute HCl. This solution was used for the aluminum determination, and the results agree well with the classical rock analysis values, as can be seen in Tables 1 and 2. The fluoboric acid matrix, however, led to low results for calcium, sodium, and potassium when compared to the lithium borate fusion and the classical rock method. Lee and Güven (1975) reported similar problems of chemical interferences in the HF-dissolution method. They overcame the problem by preparing the standard solutions of calcium, magnesium, and iron with silicon and aluminum concentrations matching those of the sample. We attempted to solve the problem by extending the use of the fluoride-free solution to include every constituent except silica. To answer the question of whether sample inhomogeneity might be responsible for the differences, a few samples were divided into two equal portions after the HF-dissolution and only one was evaporated with H_2SO_4 . Iron, calcium, magnesium, sodium, and potassium were then determined on each portion. Results in Table 3 show that Ca, Na, and K are consistently lower in the portion untreated with H_2SO_4 and therefore the discrepancy was not caused by sample inhomogeneity. Iron values are slightly higher in the untreated portion, and there is no discernible trend for magnesium. The low results for calcium in the fluoboric acid matrix can be readily accounted for by the precipitation of insoluble calcium fluoride, but the lower results for sodium and potassium are harder to explain. If the fluoborate matrix has a depressant effect, why does not the lithium borate matrix have a similar effect? In the HF-dissolution method, some free fluoride ions may remain even after an excess of boric acid has been added. Furthermore, the total amount of HF and boric acid added is greater than the amount of lithium borates used in the fusion method so that the HF-dissolution matrix is more concentrated by a factor of 10.

The results of a study of reagent blanks are expressed in Table 4 as percentages of an assumed sample weight of 30 mg. It can be seen that blank values are lowest for the lithium borate fusion and highest for the HF dissolution followed by evaporation. Surprisingly, it appears that most of the reagent contamination in the HF dissolution is due not to the rather large quantity of boric acid which had to be used to complex the HF, but to the sulfuric and hydrochloric acids used to volatilize the HF and boric acid. Reagent grade acids were

Table 1. Chemical analyses of 20–40-mg samples of clays from the Amargosa Desert, Nevada, by three analytical methods.¹

Sample number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
<i>12-14</i>							
Classical rock anal.	63.7	4.33	1.21	n.d.	28.0	0.77	1.94
Li borate fusion	63.2	3.72	1.79	n.d.	28.7	0.89	1.68
<i>P7</i>							
Classical rock anal.	63.8	1.57	0.51	n.d.	28.4	4.54	1.16
Li borate fusion	62.9	1.30	0.69	n.d.	28.7	5.27	1.14
<i>HEC-1</i>							
Classical rock anal.	64.0	3.08	1.16	n.d.	26.7	4.54	0.51
Li borate fusion	62.8	2.73	1.20	n.d.	26.8	5.43	0.96
	60.5	3.01	1.21	n.d.	28.7	5.40	1.09
<i>Kinney bentonite #1</i>							
Classical rock anal.	67.9	23.0	0.75	n.d.	6.80	1.21	0.31
Li borate fusion	67.9	21.9	1.64	n.d.	6.82	1.50	0.32
<i>Kinney bentonite #2</i>							
Classical rock anal.	67.29	21.01	1.29	1.68	7.22	1.29	0.26
Li borate fusion	68.82	21.06	1.70	0.95	6.85	1.38	0.20
	67.06	21.99	1.67	0.97	6.72	1.40	0.20
HF diss. ²	69.67	18.99	1.99	0.48	7.48	1.23	0.15
	70.45	18.15	1.84	0.56	7.61	1.24	0.17
	70.47	18.58	1.82	0.49	7.25	1.28	0.15
	68.92	19.61	1.83	0.26	8.08	1.16	0.15
	68.59	20.02	1.72	0.28	8.09	1.18	0.13
HF diss. + H ₂ SO ₄ evap.	65.08	22.54	1.70	1.58	7.44	1.43	0.23
	66.47	21.65	1.59	1.58	7.10	1.36	0.21
<i>Kerolite</i>							
Classical rock anal.	63.32	0.86	0.37	0.37	33.88	0.74	0.49
Li borate fusion	64.61	0.52	0.32	1.94	32.15	0.23	0.27
HF diss. + H ₂ SO ₄ evap.	67.07	0.25	0.41	0.41	30.69	0.83	0.33
	65.48	0.17	0.41	0.37	32.62	0.66	0.32
<i>SEP-2</i>							
Classical rock anal.	67.5	1.49	0.62	n.d.	29.1	0.85	0.42
Li borate fusion	66.5	0.95	0.64	n.d.	30.6	0.74	0.57
	66.5	1.33	0.52	n.d.	30.4	0.77	0.42
<i>Sepiolite</i>							
Classical rock anal.	66.70	1.12	0.37	0.37	30.43	0.37	0.62
Li borate fusion	67.83	0.69	0.48	0.05	29.98	0.53	0.47
HF diss. + H ₂ SO ₄ evap.	67.75	0.64	0.71	0.05	30.09	0.49	0.30

¹ All values in anhydrous wt. %; n.d. = not determined.² Aluminum determined in fluoride-free aliquot.

Table 2. Chemical analyses of 20–40-mg samples of clays from Lake Abert, Oregon by three analytical methods.

Sample number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
<i>AB21jb</i>							
Li borate fusion	57.70	13.09	12.64	0.12	10.38	2.64	3.43
HF diss. ¹	59.15	12.39	13.33	0.01	10.87	2.19	2.05
HF diss. + H ₂ SO ₄ evap.	61.32	10.50	12.50	0.16	10.02	2.47	3.02
HF diss. + H ₂ SO ₄ evap.	60.83	11.59	12.48	0.17	9.41	2.55	2.98
<i>AR33 <0.2 μm</i>							
Li borate fusion	62.68	19.59	8.59	0.17	4.54	3.55	0.90
HF diss. ¹	63.94	20.16	8.82	0.04	3.60	2.96	0.48
HF diss. + H ₂ SO ₄ evap.	63.09	19.46	8.25	0.30	4.37	3.50	1.06
HF diss. + H ₂ SO ₄ evap.	64.86	18.40	8.23	0.21	4.18	3.30	0.79
<i>AR33 0.2–2.0 μm</i>							
Classical rock anal.	73.44	13.63	6.11	0.82	3.53	1.18	1.29
Li borate fusion	71.51	15.54	6.72	0.60	3.30	1.22	1.10
HF diss. ¹	72.80	15.70	6.89	0.27	2.53	1.18	0.62
HF diss. + H ₂ SO ₄ evap.	71.69	15.22	6.53	0.91	3.15	1.33	1.19
HF diss. + H ₂ SO ₄ evap.	72.74	14.82	6.48	0.81	2.89	1.19	1.08

¹ All values in anhydrous wt. %; aluminum determined in fluoride-free aliquot.

Table 3. Comparison of methods employing HF dissolution and HF dissolution followed by evaporation with H₂SO₄.

Sample number	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
<i>AB 21jb</i>					
HF diss.	12.78	0.07	10.49	2.20	2.26
HF diss. + H ₂ SO ₄ evap.	12.50	0.16	10.02	2.47	3.02
HF diss.	12.56	0.05	10.40	2.16	2.11
HF diss. + H ₂ SO ₄ evap.	12.48	0.17	9.41	2.55	2.98
<i>AH33 <0.2 μm</i>					
HF diss.	8.55	0.14	3.43	2.99	0.63
HF diss. + H ₂ SO ₄ evap.	8.25	0.30	4.37	3.50	1.06
HF diss.	8.41	0.08	3.77	3.06	0.62
HF diss. + H ₂ SO ₄ evap.	8.23	0.21	4.18	3.30	0.79
<i>AR33 0.2–2.0 μm</i>					
HF diss.	6.70	0.40	2.47	1.06	0.76
HF diss. + H ₂ SO ₄ evap.	6.53	0.91	3.15	1.33	1.19
HF diss.	6.70	0.34	2.56	1.01	0.74
HF diss. + H ₂ SO ₄ evap.	6.48	0.81	2.89	1.19	1.08

All values in anhydrous wt. %.

used in this study; higher-purity acids would be preferable.

DISCUSSION OF RESULTS

Standard deviations from the classical analysis were calculated from the data in Tables 1 and 2 for those samples which were analyzed by all three methods, i.e., Kinney bentonite #2, kerolite, sepiolite, and sample AR33 0.2–2.0 μm. The standard deviations for SiO₂, Al₂O₃, Fe₂O₃, and MgO were calculated from all 18 analyses, but for Na₂O and K₂O, the results of HF dissolution alone were considered erroneous, and their standard deviations were calculated from only 12 analyses. The standard deviations are SiO₂ = 1.83%, Al₂O₃ = 1.49%, Fe₂O₃ = 0.23%, MgO = 0.96%, Na₂O = 0.18%, and K₂O = 0.09%.

The data in Tables 1 and 2 show several rather large

variations in CaO between the different methods. For the Kinney bentonite #2 and the sepiolite, the values for the classical rock analysis are much greater, and for the kerolite sample, the lithium borate fusion value is much larger than the others. Some of this variation may be due to the presence of calcite. The samples in this study were not treated to remove carbonates, and the Amargosa Flat clays are associated with authigenic calcite and dolomite (Eberl *et al.*, 1982). It is also possible that in samples with very low calcium content, the classical rock analysis is less accurate than atomic absorption methods for calcium, especially when magnesium is abundant. Maxwell (1968) noted that the greatest possibility for error in the calcium determination lies in the co-precipitation of magnesium.

The presence of dolomite may also be responsible for some of the variation in SiO₂:Mg ratios in the mixed-layer kerolite/smectites. Serpentine has also been suspected (Eberl *et al.*, 1982), and its higher magnesium content would increase the magnesium levels of samples relative to silica.

The data in Tables 1 and 2 also show that the samples with high aluminum content, such as Kinney bentonite and the Lake Abert clays, have similar inverse ratios between silica and aluminum. As silica increases, aluminum decreases so that combined percentages remain relatively constant. The shift is only between values for silica and aluminum, and other constituents are not noticeably affected. Kinney bentonite may contain mica impurity (Khoury *et al.*, 1982), and the Lake Abert sediments contain fine-grained volcanic plagioclase (Deike and Jones, 1980). The potassium and sodium content, respectively, in these minerals is small relative to silica and alumina so that it would be difficult to detect small amounts in the analyses which had escaped detection by X-ray powder diffraction.

Thus, it appears that some of the discrepancies in Tables 1 and 2 are caused by sample heterogeneity

Table 4. Reagent blanks for Li borate fusion and HF-dissolution methods.

Method of dissolution	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
Li borate fusion	0.00	0.09	0.03	0.14	0.00	0.04	0.02
	0.00	0.09	0.01	0.11	0.00	0.03	0.00
	0.00	0.08	0.01	0.06	0.00	0.04	0.00
	0.08						
	0.05						
HF dissolution	0.05						
			0.00	0.00	0.00	0.04	0.00
		0.00	0.11				
HF dissolution + H ₂ SO ₄ evap.		0.00	0.06	0.17	0.03	0.07	0.00
	0.00	0.30	0.06	0.15	0.05	0.11	0.08
	0.06						
	0.06						
				0.13	0.08	0.15	0.04
			0.13	0.03	0.07	0.02	

All values in wt. %.

exacerbated by the use of very small samples. Nevertheless, both the lithium borate fusion and the HF-dissolution methods provide a rapid and convenient means of analyzing small amounts of clays. The analyses have proved sufficiently reproducible to minimize error in the calculation of clay mineral formulae. Representative maximum variations, in atoms per unit formula of the smectite type based on 22 negative charges are as follows: 0.09 for Si, 0.03 for Al, 0.015 for Fe, 0.07 for Mg, 0.03 for Na, and 0.01 for K.

It should be kept in mind that some error has been introduced through determination of only the major constituents which have been assumed to constitute 100% of the sample. If other elements, such as titanium or manganese, are present in significant amounts, they can easily be appraised. The presence of significant quantities of anions other than oxygen or hydroxyl presents a greater problem, however, and the techniques for such analyses in very small samples were not investigated in this study.

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Резюме—Два быстрые метода для разложения и химического анализа глин были адаптированы при использовании образцов размером 20–40 мг, типичных количеств ультрамелких продуктов (диаметром <0,5 μm), полученных при помощи современных методов сепарации для глинистых минералов. Результаты этих методов сравнивались с результатами “классических” анализ пород. Два метода состояли из реакции синтеза метабората и последующего разложения при подогреве в присутствии HF в замкнутом сосуде. Последняя техника была модифицирована и содержала последующие степени: испарение с концентрированной H_2SO_4 и пере растворение в HCl, что уменьшало вмешательство флюоридового иона при определении Al, Fe, Ca, Mg, Na, и K. Результаты обоих методов довольно хорошо соглашаются с результатами “классических” техник и уменьшают ошибку вычисления структурной формулы глинистого минерала. Характерные максимальные вариации в единицах атом на формулу типа смектита, определенные на основании 22 отрицательных зарядов, равны 0,09 для Si, 0,03 для Al, 0,015 для Fe, 0,07 для Mg, 0,03 для Na, и 0,01 для K. [E.G.]

Resümee—Zwei schnelle Methoden für die Aufbereitung und chemische Analyse von Tonen wurden auf Probenmengen von 20–40 mg zugeschnitten, da dies der typischen Probenmenge von extrem kleinen Produkten ($<0,5 \mu\text{m}$ Durchmesser) entspricht, die bei der Trennung von Tonmineralen mittels moderner Methoden entstehen. Die Ergebnisse dieser schnellen Methoden wurden mit denen klassischer Gesteinsanalysen verglichen. Die zwei Methoden bestehen aus der Herstellung einer Lithium-Metaboratschmelze und der Auflösung in HF in einem geschlossenen Behälter. Die letzte Methode wurde dahingehend abgewandelt, daß sie eine anschließende Verdampfung mit konzentrierter H_2SO_4 und Wiederauflösung in HCl beinhaltet, wodurch die Beeinflussung durch das F-Ion bei der Bestimmung von Al, Fe, Ca, Mg, Na, und K verringert wurde. Die Ergebnisse dieser zwei Methoden stimmen recht gut überein mit den Ergebnissen von klassischen Methoden zur Minimierung der Fehler bei der Berechnung von Strukturformeln von Tonmineralen. Repräsentative Maximalabweichungen betragen in Atomen pro Formeleinheit eines Smektittyps, basierend auf 22 negativen Ladungen, 0,09 für Si; 0,03 für Al; 0,15 für Fe; 0,07 für Mg; 0,03 für Na; und 0,01 für K. [U.W.]

Résumé—Deux méthodes rapides pour la décomposition et l'analyse chimique d'argiles ont été adoptées pour être employées avec des échantillons de taille 20–40 mg, quantités typiques de produits ultra-fins ($<0,5 \mu\text{m}$ de diamètre) obtenus par des méthodes de séparation modernes pour des minéraux argileux. Les résultats de ces deux méthodes ont été comparés avec ceux d'analyses "classiques" de roches. Les deux méthodes consistaient de fusion mélangée de lithium métaborate et décomposition échauffée avec HF dans un vaisseau fermé. Cette dernière technique a plus tard été modifiée pour inclure l'évaporation subséquente avec H_2SO_4 concentré et la re-solution dans HCl, ce qui a réduit l'interférence de l'ion fluorure dans la détermination d'Al, Fe, Ca, Mg, Na, et K. Les résultats de ces deux méthodes s'accordent suffisamment bien avec ceux des techniques "classiques" pour minimiser l'erreur dans le calcul des formules de structures de minéraux argileux. Des variations représentatives maximum exprimées en atomes par unité de formule du type smectite, basées sur 22 charges négatives, sont 0,09 pour Si, 0,03 pour Al, 0,15 pour Fe, 0,07 pour Mg, 0,03 pour Na, et 0,01 pour K. [D.J.]