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PYROPHYLLITE DETERMINATION IN MINERAL MIXTURES

Key Words—Acid treatment, Dissolution, Pyrophyllite, Quantitative mineralogy, Rutile.

Most minerals of silicate rocks can be readily decomposed by mixtures of acids. Abbey (1967) and Belt (1967) described schemes for the decomposition of silicates using a hydrofluoric-perchloric-nitric acid procedure, and Bennet and Reed (1971) described a decomposition method using a hydrofluoric-sulfuric-nitric acid mixture. The dissolution of silicates with hydrofluoric acid in a pressure vessel has also been described (Bernas, 1968). All clay minerals are not, however, attacked to the same extent and this can be used for the separation of some silicates; for example, micas and most other layer silicates are removed by potassium pyrosulfate and quartz and feldspars are thereby concentrated, so that they can be more easily identified (Kiely and Jackson, 1964). Talc, pyrophyllite, and tremolite are partially resistant to the pyrosulfate fusion (Jackson, 1975).

Pyrophyllite is common in mixtures with other clay minerals and resists acid attack. A method for the quantitative estimation of pyrophyllite, based on the selective dissolution of other silicates by hydrofluoric-perchloric-nitric and hydrofluoric-sulfuric-nitric acid mixtures is described below.

MATERIALS AND METHODS

Materials

The samples studied were from four deposits of clay minerals near Almuradiel (Ciudad Real), Hinojosa del Duque (Córdoba), Zalamea la Real, and Cabeza del Buey (Badajoz), Spain. The deposits are in pelitic rocks, ranging in age from Ordovician to Carboniferous, in the southern and southwestern part of the Iberian massif (Iberian plateau). Pyrophyllite (Hillsboro, North Carolina) and illite (Fithian, Illinois, API 35) both supplied by Ward's Natural Science Establishment Inc., Rochester, New York; kaolinite (well crystallized, Washington County, Georgia, KGa-1), and Ca-montmorillonite (Gonzalez County, Texas, STx-1), both obtained from the Source Clays Repository of The Clay Minerals Society; plagioclase feldspar (Ojén (Málaga), Spain); alkali feldspar (Monesterio (Badajoz), Spain), and quartz "pro analisi" supplied by Merck were used as reference materials.

Methods

Selective dissolution. Two methods of selective dissolution were used based on the dissolution techniques for silicates reported by Bennet and Reed (1971) and Bennet *et al.* (1962).

Method 1. Finely ground samples (0.25 g) were treated with a mixture containing 5 ml of HNO_3 (1 + 4), 5 ml of $HClO_4$ (1 + 4), and 10 ml of HF (40% w/w) and evaporated to dryness. To the cooled residue, 5 ml of $HClO_4$ (1 + 4) were added and evaporated to dryness again. The residue was digested with diluted HCl, separated by centrifugation or filtration, washed several times with distilled water, and dried overnight in an oven at 60°C.

Method 2. Finely ground samples (0.25 g) were treated with 10 ml of H_2SO_4-HNO_3 acid mixture (650 ml of H_2O, 100 ml of H_2SO_4 (1 + 1) and 250 ml of HNO_3) and 10 ml of HF (40% w/w) and evaporated to dryness. A second treatment was carried out with 5 ml of the H_2SO_4-HNO_3 acid mixture. The residue from this attack was treated as in method 1.

Chemical analysis. Samples (0.20 g) of the residues were treated for 60 min in a Teflon-lined pressure vessel at 140°C with a mixture of 5 ml of HF (40% w/w), 0.25 ml of HNO_3 (65%), and 0.75 ml of HCl (37%). The vessel was cooled to room temperature, 5 g of boric acid was added, and the vessel was heated at 60°C until a clear solution was obtained. The solution was transferred to a plastic volumetric flask, and the concentration of the elements was determined by atomic absorption spectrometry.

X-ray powder diffraction. X-ray powder diffraction (XRD) diagrams were obtained using a Siemens diffractometer with Ni-filtered CuKα radiation at a goniometer speed of 1°2θ/min and a chart speed of 1 cm/min. Random oriented samples were prepared using a side-packed holder and tapping the holder gently to consolidate the powder (Niskanen, 1964). The best results were obtained using the side-packed holder with the window covered by a piece of filter paper between the sample and the glass slide. Oriented specimens were prepared by smearing the clay paste onto a glass slide (Gibbs, 1965). The semiquantitative estimation of minerals was made using characteristic reflections and their relative intensities, as described by Schultz (1964) and Galán and Martín Vivaldi (1973).

RESULTS AND DISCUSSION

The XRD patterns of the samples are shown in Figure 1. Semiquantitative estimates of the minerals present are listed in Table 1. Sample 1 (Figure 1a) consisted of pyrophyllite (d = 9.20, 4.60, 4.26, 3.06, 2.57, 2.41, 2.30, 1.84 Å), mica (d = 9.92, 4.97, 4.43, 3.32, 2.56,

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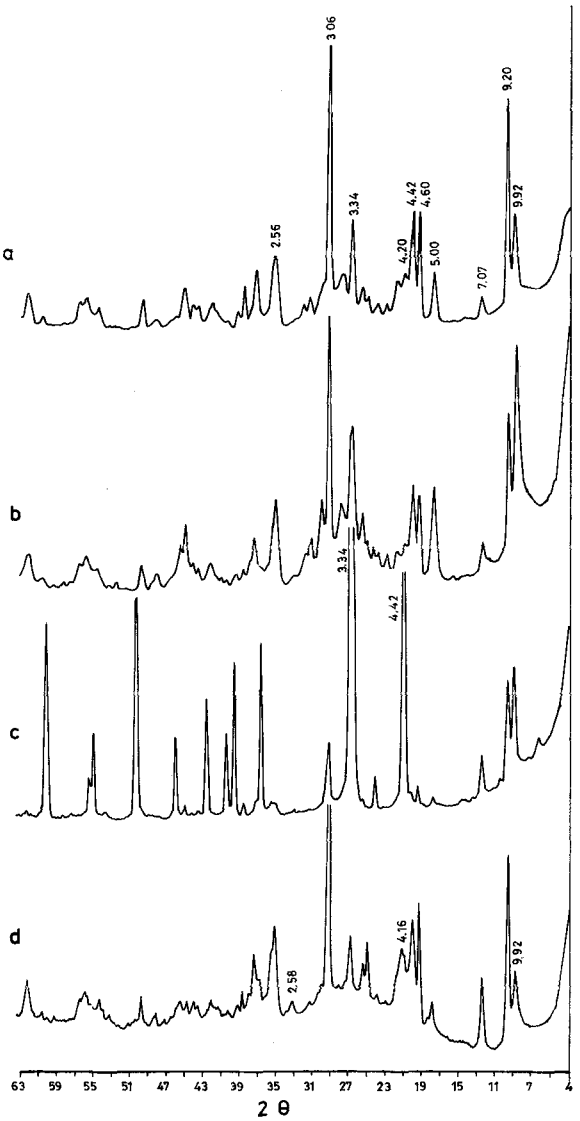


Figure 1. X-ray powder diffraction patterns of clay samples with different proportions of pyrophyllite. (a) Zalamea la Real; (b) Hinojosa del Duque; (c) Almuradiel; (d) Cabeza del Buey (CuKα radiation).

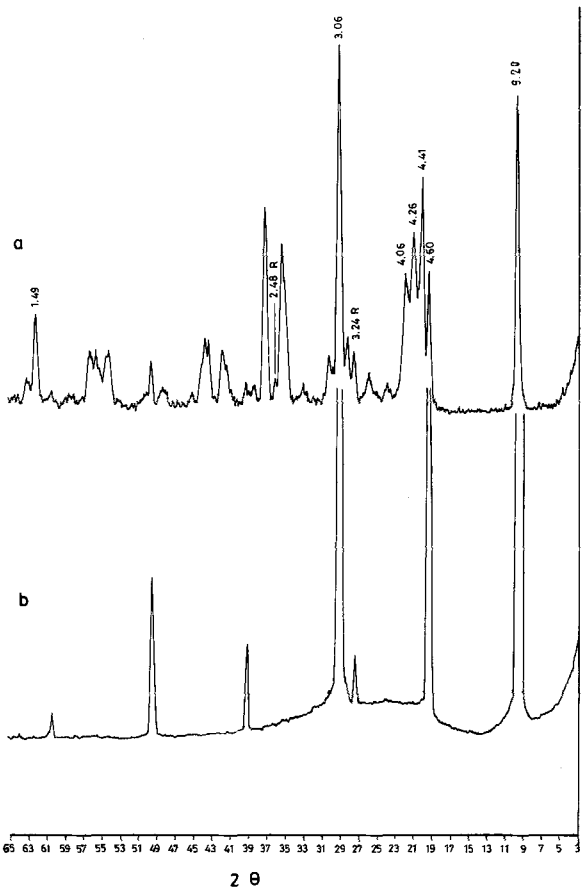


Figure 2. X-ray diffraction patterns of residue from sample from Zalamea la Real, following acid treatment. (a) powder; (b) oriented aggregate (CuKα radiation).

2.00 Å), kaolinite (d = 7.07, 4.43, 3.55, 2.56, 2.49 Å), feldspars (d = 3.64, 3.20 Å), and a regular illite/smectite interstratification (d = 24.00, 12.09, 6.00 Å). Sample 2 (Figure 1b) is similar in composition, but has a lower proportion of mica and kaolinite. Sample 3 (Figure 1c) contains, in addition to pyrophyllite, mica, kaolinite, and feldspars, a large proportion of quartz and small proportion of smectite. Sample 4 (Figure 1d) is similar to sample 1, but has a higher proportion of kaolinite and some goethite.

Chemical analyses of these samples are shown in Table 2. Calcium carbonate in sample 1 was suggested by the chemical analysis but was not detected in the XRD diagrams because of its small proportion and

Table 1. Mineralogical composition and quantitative estimation of pyrophyllite-rich samples.

Sample	Localities	Pyroph.	Mica	Kaol.	Qtz.	Feld.	Smec.	I/S	Goe.
1	Zalamea la Real (Badajoz)	40	52	5		5		tr	
2	Hinojosa del Duque (Córdoba)	12	78	5		5		tr	
3	Almuradiel (Ciudad Real)	5	20	5	70		tr		
4	Cabeza del Buey (Badajoz)	31	47	16					6
5	Hillsboro, North Carolina	90	5	5					

tr = trace; Pyroph. = pyrophyllite; Kaol. = kaolinite; Qtz. = quartz; Feld. = feldspars; Smec. = smectite; I/S = illite/smectite; Goe. = goethite.

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Table 2. Chemical analysis of pyrophyllite-rich samples (wt. %).

	Sample (see Table 1)			
	1	2	3	4
SiO_2	54.79	51.03	90.22	49.02
Al_2O_3	33.13	33.35	4.73	30.09
Fe_2O_3	0.23	0.85	0.86	8.23
TiO_2	1.25	1.23	0.69	1.88
MnO	0.00	0.00	Tr	0.06
CaO	0.26	0.20	0.93	0.40
MgO	0.25	0.24	0.07	0.47
Na_2O	0.78	0.69	0.10	0.31
K_2O	2.76	3.49	0.27	2.78
P_2O_5	0.15	—	0.02	0.16
L.O.I.	5.93	8.18	1.95	7.31
Total	99.53	99.26	99.84	100.71

L.O.I. = loss on ignition; Tr = trace; — = not determined.

because the strongest XRD reflection of calcite (3.03 Å) is close to a major peak of pyrophyllite at 3.06 Å. After the hydrofluoric-perchloric-nitric acid treatment, the residues amounted to 45, 16, 8, and 36% of the original samples 1, 2, 3, and 4, respectively.

The XRD diagrams and data of the residues are shown in Figure 2 and Table 3, respectively. The results are similar for all samples. XRD peaks corresponding to illite, kaolinite, feldspars, quartz, smectite, and illite/smectite were not present; however, the pattern of pyrophyllite 1*Tc* is present and is similar to that obtained by Brindley and Wardle (1970).

Pyrophyllite 1*Tc* is less widespread in nature than the 2*M* type (Nemecz, 1981). The XRD patterns showed reflections at 3.24 and 2.48 Å which are characteristic of rutile; other reflections of rutile at 2.18, 1.68, 1.62, and 1.36 Å were masked by pyrophyllite reflections. Rutile is a minor constituent of some clays and is difficult to identify because its reflections are masked by the accompanying minerals. The acid treatment demonstrated that much of the titanium in these samples was present as a pure mineral and not as a constituent of the silicates.

Chemical analysis shows that the residue consists of Si, Al, and Ti only, with the following percentages: 63.06% SiO_2, 27.34% Al_2O_3, 5.08% TiO_2, and 4.83% loss on ignition. The chemical formula, after assigning TiO_2 to rutile, is:

$$Al_2(Si_{3.97}Al_{0.03})O_{10}(OH)_2,$$

which agrees well with pure pyrophyllite.

The treatment of samples with hydrofluoric-sulfuric-nitric acid mixture gave similar results to those obtained with the hydrofluoric-perchloric-nitric acid mixture. The residues contained pyrophyllite and rutile, with a small quantity of calcium sulphate in sample 1, probably formed by the reaction of calcium carbonate in the sample with sulphuric acid.

To determine the influence of the acid attack on

Table 3. X-ray powder diffraction data of an acid-leached and untreated pyrophyllite.

	Pyrophyllite[1]		Residues[2]	
hkl	d(Å)	I/I_o	d(Å)	I/I_o
001	9.20	80	9.20	85
002	4.60	30	4.60	38
110	4.42	100	4.41	90
11$\bar{1}$	4.26	80	4.26	75
021	4.06	60	4.06	40
1$\bar{1}$1	3.76	5	3.76	5
111				
112	3.45	5	3.48	5
11$\bar{2}$	3.45	5	3.45	5
			3.24	20 R
022	3.18	20	3.16	8
003	3.06	100	3.06	100
112	2.95	20	2.95	10
11$\bar{3}$	2.74	3	2.74	5
1$\bar{1}$3	2.71	4	2.71	2
20$\bar{1}$	2.56	30	2.56	35
130				
13$\bar{1}$	2.54	30	2.54	40
200				
1$\bar{3}$1	2.53	40	2.53	35
			2.48	5 R
20$\bar{2}$	2.41	80	2.41	74
131				
201	2.34	10	2.33	5
113				
004	2.30	5	2.30	5
2$\bar{2}$0	2.21	4	2.21	2
220				
1$\bar{1}$4	2.17	15	2.17	16
041				
20$\bar{3}$	2.15	15	2.15	11
132				
22$\bar{1}$	2.08	20	2.08	16
13$\bar{3}$				
02$\bar{4}$	2.06	25	2.06	15
1$\bar{3}$3				
22$\bar{2}$	1.88	12	1.88	5
204				
005	1.84	10	1.83	11
04$\bar{3}$	1.82	2	1.82	2
24$\bar{1}$				
025				
150				
24$\bar{1}$	1.69	12	1.69	20
22$\bar{3}$				
24$\bar{0}$				
151				
1$\bar{3}$4	1.65	30	1.65	10
15$\bar{1}$				
242				
151				
24$\bar{2}$				
20$\bar{5}$	1.63	20	1.62	15
134				
24$\bar{1}$				
15$\bar{2}$				
060				
33$\bar{1}$	1.49	30	1.49	35
3$\bar{3}$1				
22$\bar{4}$	1.48	10	1.48	10
31$\bar{2}$				

[1] Brindley and Wardle (1970).
[2] R = rutile.

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pyrophyllite in mineral mixtures, artificial mixtures of several minerals with different amounts of the Hillsboro pyrophyllite were prepared. This pyrophyllite contains about 10% of kaolinite and illite. The artificial mixture contained 30% illite, 20% kaolinite, 20% montmorillonite, 10% plagioclase feldspar, 10% alkali feldspar, and 10% quartz. To this mixture, pyrophyllite was added in the following proportions: 18%, 27%, 36%, 45%, 54%, 63%, and 72%, respectively. The percentages have been corrected for the 10% impurities in the raw pyrophyllite. The samples were treated in triplicate by the selective method. The percentage of pyrophyllite recovered was 97% with a standard deviation of 0.62. These data show that the pyrophyllite was not dissolved and that the precision of the method was high and independent of the amount of this mineral in the mixture.

The method has also been checked using 20 samples from pelitic rocks located in the southern and southwestern part of the Iberian massif of Spain. The pyrophyllite content, determined in the insoluble residue following acid treatment of these samples ranged from 7% to 45%.

The dissolution of silicates by strong acids involves preferential removal of Al, Mg, and Fe from the structure, leaving a silica framework saturated with protons. On the other hand, the dissolution of silicate minerals by hydrofluoric acid is entirely stoichiometric. For the samples studied in this investigation, the dissolution depended essentially on HF.

The observed characteristics of the dissolution of silicates in HF are best explained by a mechanism in which the rate-determining step is the adsorption of HF "molecules" on the surface of the structure (Kline and Folger, 1981). The degree of this adsorption is a function of the structure and composition of the silicate structure. It is possible that the structural characteristics of pyrophyllite prevent the adsorption of HF molecules on the surface of the mineral, and consequently, the acid dissolution.

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