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Compositional variations of the Unterrupsroth beidellite

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Abstract

The Unterrupsroth beidellite is shown to be composed of separable materials of varying montmorillonitic and beidellitic character. After Na-saturation, the beidellitic portion is concentrated in the >3 μm fraction whereas a more montmorillonitic portion is concentrated in the <1.4 μm fraction. This fractionation is indicated by infrared spectroscopy (IR) and supported by X-ray fluorescence (XRF) chemical analysis and ^{27}Al and ^{29}Si solid-state nuclear magnetic resonance spectroscopy (NMR). Differences in the morphology of the two materials are also established by electron microscopy. The beidellitic portion is composed of large complex aggregate grains whose surfaces exhibit a delicate rosette habit, whereas the montmorillonitic fraction is composed of very thin, well defined, curled sheets and plates, in addition to irregular masses. X-ray diffraction (XRD) confirms the smectite nature of the various size fractions but is unable to distinguish any structural differences between them. The results demonstrate the utility of IR, XRF and NMR in the identification of beidellite in smectite clay materials. As the montmorillonitic and beidellitic fractions have similar layer charge, the difference in their dispersibility when Na-saturated is related to the site of the layer charge and/or morphological differences of the mineral aggregates. The beidellitic fraction disperses when Li-saturated.

Introduction

Although the status of beidellite has been the subject of some controversy, (Ross and Hendricks, 1945; Weir and Greene-Kelly, 1962) it is now accepted that the mineral represents the Al-for-Si tetrahedrally substituted end member of the dioctahedral smectite series whereas montmorillonite represents the Mg-for-Al octahedrally substituted end member (Brindley, 1980). Complete characterization of beidellitic clays is not always possible because the bulk clay material is often heterogeneous in composition, being found primarily in veins of hydrothermally altered igneous rocks, often in association with zeolites. Moreover, because of the nature of their geological occurrence, beidellitic clay deposits are limited in extent and most of the classic localities are now, unfortunately, depleted.

The present investigation concerns a white clay sample of the Unterrupsroth Beidellite, number B2 collected in 1959 by A. Weiss (courtesy of G. Lagaly), and is analogous to sample R studied by Glaeser and Mering, (1975). The Unterrupsroth clay (Fig. 1) occurs either in veins between pillars of phonolite (where the clay is relatively pure with a reddish color) or in almond-shaped cavities in association with zeolites (Heide, 1928). Because initial work indicated that the beidellite portion of sample B2 is concentrated in the coarse size fractions of the Na-dispersed material, a more detailed investigation was undertaken to characterize fully the various size fractions of the clay. Indirect techniques to detect beidellite by X-ray diffraction (XRD) involving Li-saturation, and heat treatment (Hoffman and Klemen, 1950; Greene-Kelly, 1952) have been used extensively, but are unfortunately, subject to some uncertainties (Byström Brusewitz, 1975). Because of this, more direct analytical methods were employed here to determine the beidellitic nature of the Unterrupsroth material.

Experimental procedure

Sample B2 from Unterrupsroth, Germany, was characterized by XRD (Fe filtered CO$K\alpha$ radiation on a Philips 2 kW diffractometer) and infrared spectroscopy (IR). The sample was then Na-saturated and separated into >3.0 μm, 3.0–1.4 μm and <1.4 μm fractions by centrifugation. The size fractions were again characterized by XRD using the sedimented aggregate and powder camera techniques, (Brown and Brindley, 1980). IR absorption spectra were recorded on a Perkin-Elmer 580-B spectrometer over a range of 4000-200 cm^{-1} using 13-mm-diameter KBr pressed disks containing 2 mg of sample. Weakly adsorbed water was removed by heating the disks for 16 h at 150°C. Certain samples were also examined by scanning and transmission electron microscopy (SEM and TEM) and ^{29}Si and ^{27}Al solid state nuclear magnetic resonance spectrometery (NMR). Portions of the various clay fractions were also Ca-saturated and analyzed by X-ray fluorescence spectrometery (XRF) using the method of Norrish and Hutton (1969) for sample fusion and corrections for background and interelement effects. The $K\alpha$ lines were measured on a Philips PW 1540 spectrometer equipped with a 2 kW Cr tube and a flow proportional counter fitted with a 1 μm polypropylene window, using pulse-height discriminator settings approrpriate to each element.

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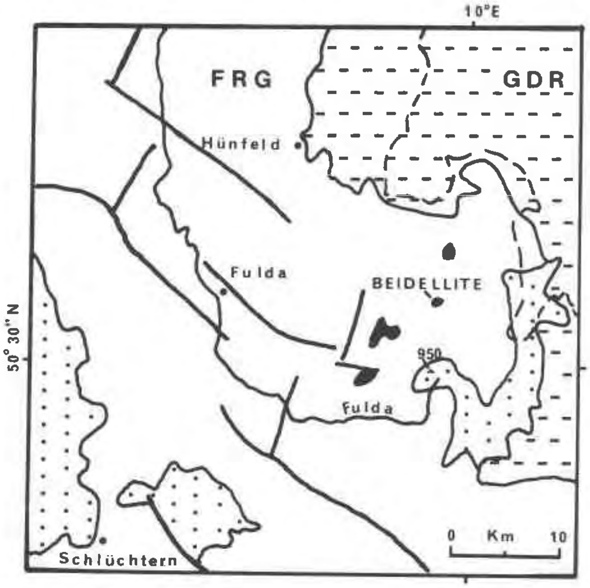

Fig. 1. Generalized geologic map modified from Walther and Zitzmann (1969) showing Unterrupsroth beidellite sample locality. Solid areas represent phonolite, dotted areas Tertiary basalt, dashed areas Triassic limestone, and unshaded areas Triassic (New Red) sandstone. Faults are indicated by heavy lines.

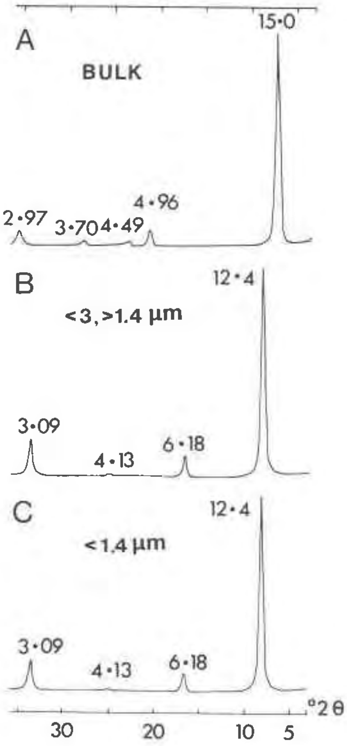

Fig. 2. X-ray diffraction patterns (maxima in Å) of air-dried sedimented aggregates of Unterrupsroth clay, Co$K\alpha$ radiation; A = bulk sample, B = Na-saturated <3 µm >1.4 µm, C = Na-saturated <1.4 µm. Higher basal spacing of bulk sample (15.0Å) indicates that the clay in the natural state is saturated with divalent exchangeable cations.

Results

The X-ray diffraction trace of the air-dried sedimented aggregates of the bulk material shows that it is a smectite (Fig. 2A). Notable features are the 15Å basal spacing, which indicates that the clay is saturated with a divalent

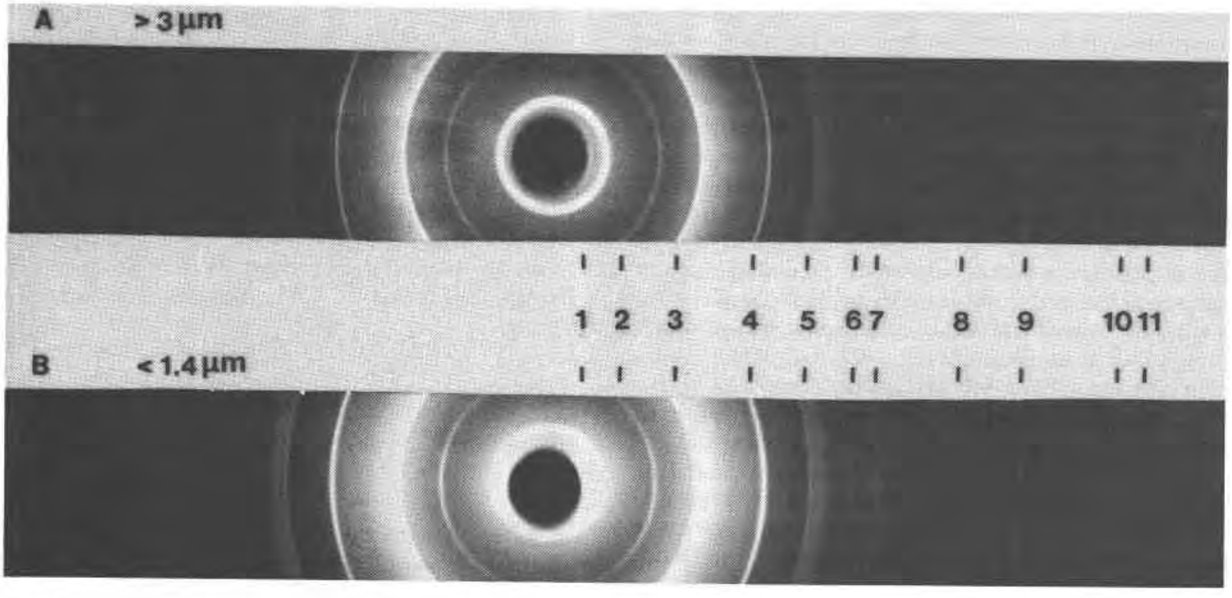

Fig. 3. X-ray powder camera photographs of the >3.0 µm (A) and <1.4 µm (B) fractions of the Na-saturated Unterrupsroth clay. Line numbers refer to Table 1. Note the similarity of the two powder photographs.

Table 1. X-ray powder film data

Line (Fig. 4)	d (Å) A >3.0 μm	I*	d (Å) B <1.4 μm	I*	001, hk indices after Brindley, 1980
1	12.4	100	12.4	100	001
2	6.19	40	6.2	50	002
3	4.47	70	4.48	80	02, 11
4	3.1	50	3.1	60	004
5	2.57	20	2.57	25	20, 13
6	2.231	2	2.238	5	04, 22
7	2.060	5	2.064	10	006
8	1.691	5	1.693	10	24, 31, 15
9	1.494	10	1.496	10	06, 33
10	1.293	2	1.293	2	26, 40
11	1.241	2	1.240	2	0010, 17, 35, 42

* I - approximate intensity

cation, probably Ca^{2+} or Mg^{2+} (MacEwan and Wilson, 1980), and the presence of the *hk* diffraction band at 4.49Å which shows that some of the material is randomly oriented. The XRD traces of the sedimented aggregates of the Na-dispersed finer materials (Fig. 2B–C) are those of Na-saturated smectites and do not show the *hk* band present in the bulk material. The >3.0 μm and <1.4 μm fractions were examined as random powders using X-ray film methods. The results (Fig. 3, Table 1) confirm that both fractions are Na-saturated smectites, the relationship between the silicate layers being turbostratic (Brindley, 1980). The size fractions are indistinguishable based on XRD data alone. Minor amounts of NaCl present are responsible for the weak lines at 2.82 and 2.0Å.

The IR spectra of the three size fractions (Fig. 4) demonstrate some concentration of the beidellitic portion (Si–O–Al bands at 818 cm^{-1} and 770 cm^{-1}) in the >3.0 μm coarse fraction and concentration of the montmorillonitic portion ($MgAl(OH)_2$ band 845 cm^{-1}) in the <1.4 μm fine fraction (Farmer and Russell, 1967).

The >3.0 μm material, when examined by SEM, is composed of large grains of complex clay aggregates (Fig. 5a–d). The surface of the aggregates exhibits a delicate "rosette" pattern of platy clay layers, showing a lack of preferrd orientation. The finer grained portions when examined by TEM (Fig. 5e–f) are primarily composed of well-defined, often very thin flakes which commonly show a tendency to fold or "scroll" (c.f. Mering and Oberlin, 1971; Guven and Pease, 1975) and other irregular masses which are typical of montmorillonites.

The ^{27}Al and ^{29}Si NMR spectra for the <1.4 μm and >3.0 μm fractions are shown on Figure 6. The ^{27}Al spectra show a higher proportion of tetrahedral Al (69.1 ppm) in the >3.0 μm fraction than in the <1.4 μm material. This observation is supported by the ^{29}Si spectra where the effect of Al for Si tetrahedral substitution is indicated by the three silicons, one aluminum nearest neighbor maximum at -87.3 (-87.7) ppm compared with four silicons nearest neighbor maximum at -92.3 (-92.6) ppm.

The XRF chemical analyses of the three size fractions indicate that the samples are primarily composed of SiO_2, Al_2O_3, and MgO (Table 2). The coarse fraction is enriched in Al and deficient in Si and Mg relative to the finer fractions. In order to establish that the Ca content of the Ca-saturated clay was totally exchangeable, determinations for Ca as well as for S and Cl were performed on Sr-saturated samples. The results revealed that there was <0.05 weight percent of these elements present.

The structural formulae based on the chemical analyses (Table 2) confirm the IR and NMR data showing increased Al for Si tetrahedral substitution in the >3.0 μm fraction. Interestingly the Mg for Al octahedral substitution decreases proportionally with increasing Al for Si tetrahedral substitution and thus the overall layer charge, although quite high for a smectite, is approximately constant for the three size fractions at about 1.2 per formula unit. This information is in good agreement with the interlayer Ca contents of the Ca-saturated clays. Ammonium cation exchange capacities (CEC) on Li-saturated samples show uniform CEC's of the size fractions of about 160 mEq/100 g on an ignited basis, which is also in good agreement with the interlayer Ca and total layer charge (Table 2).

Discussion

The analytical results demonstrate the differences in Al-for-Si tetrahedral and Mg-for-Al octahedral isomorphous substitution of the various size fractions of the Unterrupsroth beidellite. The XRD data establish the isostructural nature of the clay. IR is useful in determining the beidellitic vs. montmorillonitic content. The intensity of the 818 and 770 cm^{-1} bands are not, however, a sensitive indicator of

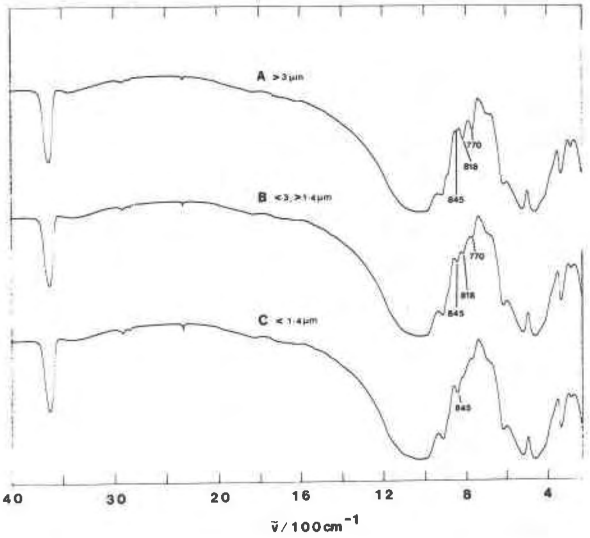

Fig. 4. Infrared spectra of the Na-saturated >3.0 μm (A), <3.0 μm >1.4 μm (B) and <1.4 μm (C) size fractions of the Unterrupsroth clay. Note increase in intensity of absorption bands at 818 and 770 and decrease in intensity at 845 with increasing particle size.

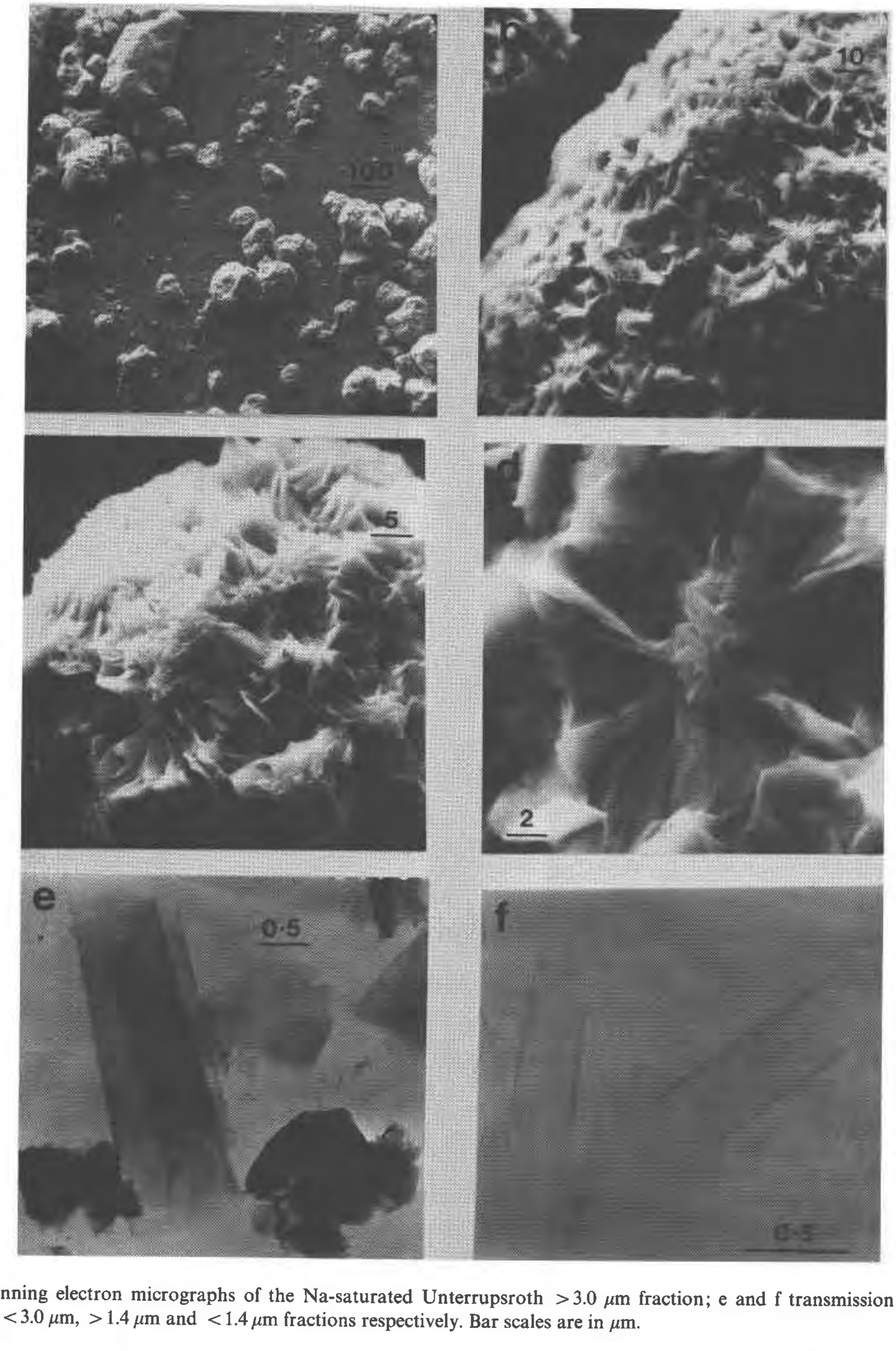

Fig. 5. Scanning electron micrographs of the Na-saturated Unterrupsroth >3.0 μm fraction; e and f transmission electron micrographs of the <3.0 μm, >1.4 μm and <1.4 μm fractions respectively. Bar scales are in μm.

tetrahedral Al. They may reflect the presence of long-ranged Si–O–Al–O–S structures, whose concentrations will depend on the nature and amount of the Al substitution in the tetrahedral layer. In contrast, the band at 845 cm^{-1}, which arises from AlMgOH groupings, is more nearly proportional to octahedral Mg content, and indicates the presence of Mg in the >3 μm fraction, where it contributes only 19% of the total layer charge.

Although the Unterrupsroth beidellite is heterogeneous in composition, the calculated structural formulae, which necessarily assume homogeneity, are useful in assessing the extent of isomorphous substitution within the various size

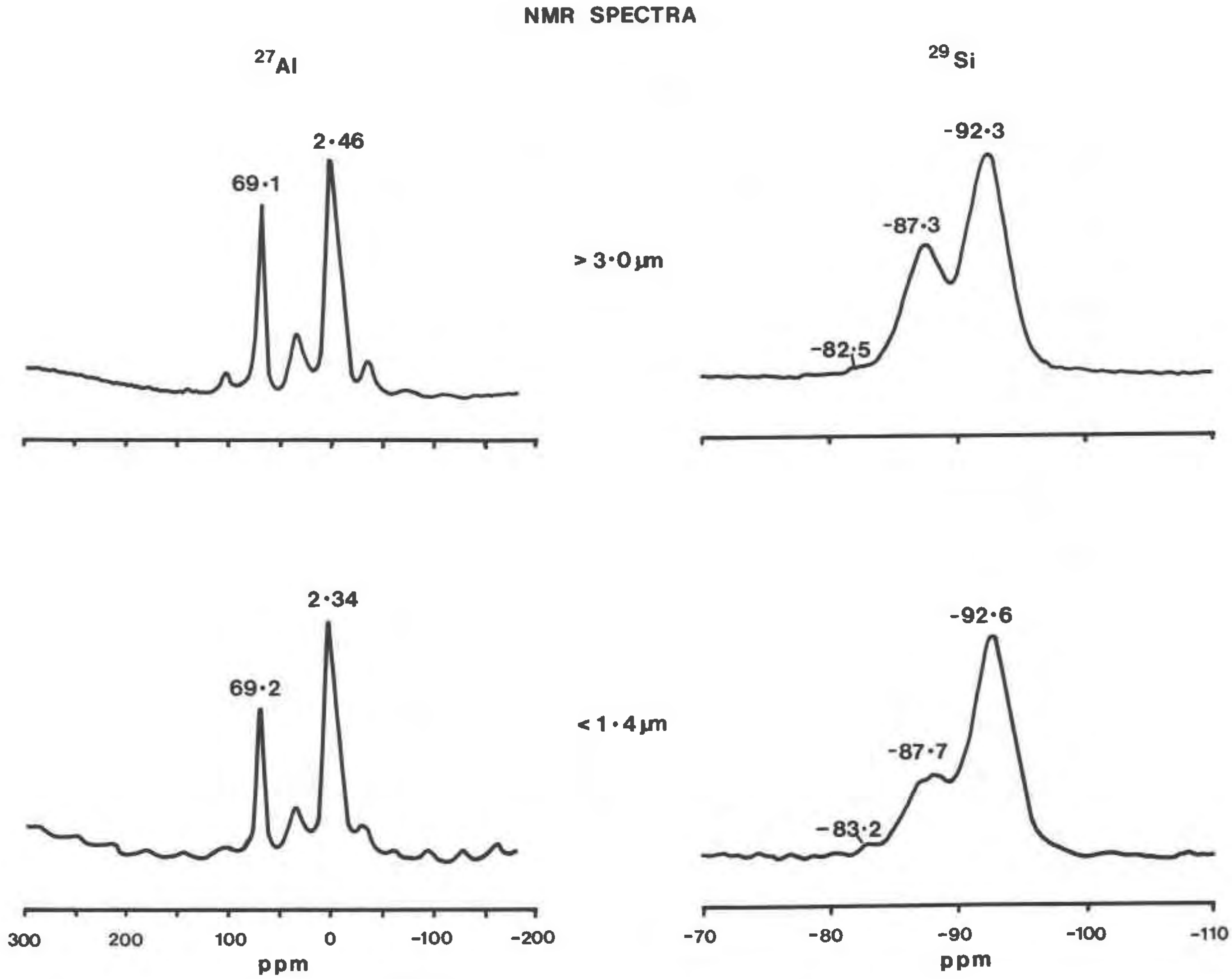

Fig. 6. ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) analysis in 9.395 T of the >3.0 and <1.4 μm fractions of the Na-saturated Unterrupsroth clay.

fractions. The >3.0 μm fraction whose chemical formula on a half cell basis is, $R_{0.61}(Al_{1.87}Fe^{3+}_{0.02}Mg_{0.12})(Si_{3.50}Al_{0.50})O_{10}(OH)_2$, has an almost identical composition to that of the beidellite from Black Jack Mine, Idaho (Weir and Greene-Kelly, 1962). In addition, however, the coarse fraction has some Mg:Al octahedral substitution which gives it a higher overall charge. The <1.4 μm fraction, although having lower Al-for-Si tetrahedral and higher Mg-for-Al octahedral isomorphous substitution, still derives more than half of its total layer charge from tetrahedral substitution.

The work of Lippmaa et al. (1980), Klinoski et al. (1981), Smith et al. (1983) and de Jong et al. (1983) has established criteria whereby the degree of silica polymerisation, the amount of Al for Si substitution, and the proportion of Al in tetrahedral as opposed to octahedral sites can be derived from ^{29}Si and ^{27}Al NMR spectra. The NMR data presented here clearly show that there is more tetrahedral Al in the >3.0 μm fraction and less, but still some, in the <1.4 μm fraction. Due to differences in peak widths and possibly also in side band structure it is not possible to make a quantitative assessment of the proportion of Al^{IV} by simply comparing the peak height of the Al^{IV} signal (69.1 ppm) with that of the Al^{VI} (2.4 ppm). However these problems do not arise for the ^{29}Si NMR signals and the ratio of Al^{IV}/Si can be calculated from the formula

$$\frac{2Si^2 + (Si^1 - 4Si^2)/3}{Si^0 + Si^1 + Si^2}$$

where Si^0, Si^1 and Si^2 represent the intensity of the NMR peaks for Si atoms with zero (~ -92 ppm), one (~ -87 ppm), and two (~ -82 ppm) first neighbor tetrahedral sites occupied by Al. The ratio of $Si^0:Si^1:Si^2$ is around 42:25:2 for the >3.0 μm fraction, and 43:14:1 for the <1.4 μm fraction. These ratios predict an Al substitution per unit cell of 0.98 for the >3.0 μm fraction, and 0.67 for the <1.4 μm fraction. The nearly exact agreement with the analytical data may be somewhat fortuitous, in that the

Table 2. Chemical analyses (by X-ray fluorescence) and structural formulae of Ca-saturated sample

	<1.4 μm	$>1.4<3$ μm	>3 μm		<1.4 μm	$>1.4<3$ μm	>3 μm
SiO_2	48.03	48.97	45.08	Tetrahedral			
TiO_2	0.01	0.01	0.04	Si	7.33	7.25	7.00
Al_2O_3	23.23	24.76	25.83	Al	0.67	0.75	1.00
Fe_2O_3*	0.03	0.05	0.34	Octahedral			
				Al	3.51	3.57	3.73
MgO	2.24	1.93	1.00	Fe^{3+}	0.00	0.01	0.04
CaO	3.48	3.62	3.67	Mg	0.51	0.42	0.23
Na_2O	N.D.	N.D.	N.D.	Σ	4.02	4.00	4.00
K_2O	<0.01	<0.01	0.02	Interlayer			
L.O.I	22.10	18.74	22.89	Ca	0.57	0.57	0.61
Total	99.12	98.08	98.87	Total layer charge	1.12	1.17	1.23
				NH_4 C.E.C.† (mEq/100 g)	157	157	162

* Total iron as Fe_2O_3

N.D. - not determined

† Determined on Li-saturated material

calculation is sensitive to the value for Si^2, which cannot be measured with any accuracy. Nevertheless, it does appear that ^{29}Si NMR can give a good estimate of the degree of substitution of Al for Si in clays.

The results also demonstrate that the Unterrupsroth sample B2 can be readily fractionated into beidellitic fractions and montmorillonitic fractions by Na-saturation and centrifugation into the coarse (>3.0 μm) and fine (<1.4 μm) fractions respectively. The dispersibility of the material is not related to the total layer charge of the clay as shown in Table 2. Although the beidellitic fraction did not disperse in the Na-form, it was almost completely dispersible in the Li-form. It appears therefore, that this property is a function of tetrahedral subsitution (rather than of total charge) and/or the morphological character of the mineral aggregates. Other workers have also found variations in the nature of various size fractions of smectite clays (Grim and Kulbicki, 1961).

The compositional variation described here suggests a complex genetic history of the material, which is most probably related to its geological occurrence. An early investigation of the clay concluded that it is a crystallization product from hydrothermal aqueous solution after solidification of the igneous host rock (Heide, 1928). The morphology exhibited by the aggregate grains of the coarse size fraction (Fig. 5, a–d) supports this view. Hydrothermal argillization commonly produces a wide variety of clay and other mineral products, a consequence of their complex thermal and chemical histories (cf. Schoen et al., 1974). Because the beidellitic portion occurs in coarse aggregate grains it probably formed prior to fine grained montmorillonitic material, suggesting a paragenetic sequence beidellite → montmorillonite. Further research of these clay materials is required, however, and should consider in greater detail the geological parameters related to their occurrence.

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