

Brinrobertsite: a new R1 interstratified pyrophyllite/smectite-like clay mineral: characterization and geological origin

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ABSTRACT

Brinrobertsite, an ordered, mixed-layered, dioctahedral pyrophyllite-smectite (P/S), occurs in a metabentonite in the Ordovician Nant Ffrancon Formation near Bangor, N Wales. It comprises ~30% of the metabentonite, in association with quartz (~50%) and chlorite (clinocllore; 20%) which replaced glass shards and fine-grained glass matrix. Transmission electron microscopy (TEM) images show sequences of dominant ~24 Å 001 lattice fringes inferred to correspond to 2:1 layers with alternate pyrophyllite-like (low-charge) and smectite-like (higher-charge) interlayers (i.e. R1 ordering). The $hk0$ diffraction patterns are mostly hexanets with some spotty circles, implying that layers are largely coherently related, but with some turbostratic stacking. Collective data show that $d_{100} = 5.2$, $b = 9.1$, and $d_{001} = 24\text{--}25$ Å, assuming monoclinic or pseudomonoclinic symmetry. The composition, as determined by energy dispersive spectral analysis, is $(\text{Na}_{0.22}\text{K}_{0.07}\text{Ca}_{0.06})(\text{Al}_{3.81}\text{Mg}_{0.08}\text{Fe}_{0.08})(\text{Si}_{7.84}\text{Al}_{0.16})\text{O}_{20}(\text{OH})_4 \cdot 3.54\text{H}_2\text{O}$, as consistent with the sum of the compositions of pyrophyllite-like and smectite-like units. Water content was determined by DTA/TGA analysis. The powder diffraction patterns have a principal peak with $d_{001} = 24.4$ Å. Patterns of air-dried and glycol-saturated brinrobertsite, including Na- and Ca-saturated and untreated samples, were modelled satisfactorily as R1-ordered P/S by the program NEWMOD-for-Windows[™]. The unique composition of brinrobertsite relative to R1 IS, which is ubiquitous in metabentonites, was caused by leaching of alkalis and alkaline-earth elements by hydrothermal fluids associated perhaps with a nearby intrusion, as demonstrated by bulk-chemical analyses of the metabentonite. The crystal structure is modelled as having Al/Si distributions symmetrical by reflection across interlayers. This causes all 2:1 layers to be equivalent in having one tetrahedral sheet with little or no Al, and the other with significant Al substitution, giving rise to alternate high- and low-charge interlayers. Geological evidence suggests that brinrobertsite is a back-reacted product of hydrothermal alteration in the sequence: glass → pyrophyllite → brinrobertsite.

KEYWORDS: brinrobertsite, mixed-layered pyrophyllite-smectite, transmission electron microscopy, X-ray diffraction, metabentonite, clay mineral.

Introduction

MIXED-LAYER clay minerals are formed at or close to the Earth's surface in a variety of geological settings, ranging from soils and other weathering environments, to diagenetic sedimentary basins, to hydrothermal zones. These minerals are

generally the metastable intermediate products of a sequence of reactions involving end-member clay minerals (Merriman and Peacor, 1999). The most common mixed-layer clays are either dioctahedral, such as illite-smectite, or trioctahedral, such as chlorite-smectite, whereas di/trioctahedral minerals are rare (Srodoń, 1999). Thus, the most common mixed-layer clays are characterized by an expandable smectite end-member and a non-expandable end-member, illite or chlorite. Due to similarity in structure of the

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two end-members, wide ranges in ratios of the component end-members of mixed-layer phases can form which therefore have a range of expandability. Where these appear to form ordered 1:1 interstratifications (designated R1, where R = Reichweite), they have usually been given mineral names, e.g. rectorite for illite-smectite and corrensitite for chlorite-smectite.

Among mixed-layer minerals, the illite-smectite (I/S) series has been most intensely studied and is perhaps the best understood (e.g. Altaner and Ylagan, 1997; Dong *et al.*, 1997, and references therein). The transformation of smectite to illite has been shown to depend on time and temperature and is a potential index to the generation of petroleum and natural gas (Eslinger and Pevear, 1988; Moore and Reynolds, 1997). The smectite-illite series of mixed-layer clay minerals is ubiquitous in pelitic basin sediments, the smectite having been largely derived through alteration of volcanic ash during terrestrial weathering or in shallow basin sediments, with subsequent formation of mixed-layer material. The proportions of illite layers increase with increasing depth of sediment burial. The transition(s) from smectite to mixed-layered phases require(s) the presence of K, that element normally being present in sufficient concentration to accommodate the formation of illite-rich material.

Kodama (1958) made the first observation of naturally-occurring, regularly-interstratified pyrophyllite-smectite, in association with pyrophyllite. He proposed that the smectite component is montmorillonite. During an experimental investigation of the illite-smectite stability field, Eberl (1979) subsequently reported hydrothermal synthesis of 1:1 regularly interstratified pyrophyllite-smectite (P/S). Eberl (1979) synthesized mixed-layer P/S from Wyoming montmorillonite, the interlayer sites of which are dominated by Ca and Na, by treating the clay in a hydrothermal solution. This study reports the occurrence of mixed-layer pyrophyllite-smectite from an Ordovician metabentonite from the Welsh Basin. It has been characterized by X-ray diffraction (XRD) analysis, scanning and transmission electron microscopy (SEM and TEM), X-ray fluorescence (XRF) analysis, wet chemical analysis, and thermogravimetric analysis (TGA). Furthermore, the computer program NEWMOD-for-Windows[®] was used to model its powder diffraction pattern. Such a calculation allows confirmation of structural sub-units.

The mineral has been named brinrobertsite, in honor of Dr Brin Roberts of Birkbeck College, University of London, in recognition of his extensive research on the mineralogy and low-grade metamorphism of pelitic rocks of the United Kingdom. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association. Type material is preserved in the Museum of Natural History, Washington, D.C., the Department of Geological Sciences, the University of Michigan, Ann Arbor, MI, USA, the British Geological Survey, Keyworth, Nottingham, UK, and Department of Geology, Miami University, Oxford, OH, USA.

Geology and samples

Brinrobertsite occurs in a metabentonite (sample BRM 620) within a sequence of dark grey mudstones belonging to the Nant Ffrancon Formation of Caradoc age (Roberts and Merriman, 1990). The pale-cream coloured metabentonite forms a thin (20 cm) bed of soapy mudstone within foreshore exposures, 750 m NE of Penrhyn castle, near Bangor, N. Wales, United Kingdom. (National Grid reference: SH 60907235). Blue-grey flinty mudstones, up to 30 cm thick and overlying the metabentonite, were also sampled (BRM 621). A sample of the more extensive dark-grey mudstones (BRM 622) containing the two lithologies was collected from exposures ~3 m above the metabentonite. Due to the cover of glacial deposits, the foreshore rocks form one of the few extensive exposures of the Nant Ffrancon Formation in this part of the Aber-Dinlle-Dinorwic fault system. A nearby dolerite sheet, up to 100 m thick, is exposed some 700 m to the northwest, and appears to be intruded into the lower part of the mudstone sequence (British Geological Survey, 1985).

Typical samples of the metabentonite (BRM620), which have an appearance similar to that of a pale-grey, silty mudstone, have high contents of quartz (50%), chlorite (20%) and brinrobertsite (30%), as determined by qualitative analysis of XRD patterns. Thin-section, optical petrography shows that the metabentonite has a well-developed vitroclastic texture of glass shards in a matrix of glass dust, but no bedding fabric is present (Fig. 2c of Roberts and Merriman, 1990). The orange-brown shards, up to 0.15 mm across, have been replaced by radiating intergrowths of

chlorite showing anomalous grey interference colours. Brinrobertsite forms anhedral colourless grains, up to 0.02 mm across, and comprises aggregates of small crystals or packets of crystals, as indicated by radial extinction under crossed polars. These grains are intergrown with pale-green chlorite and quartz, and together, these minerals replace the glass-dust matrix of the bentonite. The size of individual crystals (packets) of brinrobertsite is $<1 \mu\text{m}$, and these are only observable at the TEM scale (see below).

The nearby mudstones (BRM 622) also lack a bedding-parallel fabric, and consist of randomly-oriented intergrowths of white mica, chlorite and opaque oxide grains with scattered detrital quartz grains ($<0.03 \text{ mm}$) and muscovite flakes ($<0.05 \text{ mm}$). Analysis, by XRD, of the clay fraction ($<2 \mu\text{m}$) indicates that the matrix consists largely of illite, mixed-layer illite-smectite and chlorite, with minor Na-K mica, paragonite and quartz. A similar mineral assemblage and microtexture is found in the flinty mudrock immediately above the metabentonite, but detrital quartz and mica grains can be seen only rarely.

Due to its small grain size, many of the physical properties of brinrobertsite are not determinable. In hand specimen it appears grey to yellowish grey with a grey streak and translucent lustre. The estimated hardness is close to that of talc on Mohs' scale. The crystals show $\{001\}$ cleavage as observed by TEM only (see below). No parting was observed and density was not determined due to the difficulty of separating pure material.

X-ray diffraction analysis

In order to accurately characterize brinrobertsite, a relatively pure, $<2 \mu\text{m}$ fraction was isolated. The separation was achieved by dispersing a crushed portion of the sample in deionized water using a combination of shaking and ultrasound, followed by gravity settling using Na hexametaphosphate ('Calgon') as a dispersing agent. Unsaturated, Na-saturated and Ca-saturated oriented mounts were prepared by suspending 100 mg of the $<2 \mu\text{m}$ fraction in deionized water, pipetting onto a ceramic tile in a vacuum apparatus and adding a small volume of the relevant cation chloride. Analysis, by XRD, was carried out using a Philips PW1700 series diffractometer fitted with a cobalt-target tube and operated at 45 kV and 40 mA. The oriented mounts were scanned from $2-70^\circ 2\theta$ at

$0.3^\circ 20 \text{ min}^{-1}$, air-dried, after glycol solvation and after heating to 375°C for 2 h and then 550°C for 2 h. Diffraction data were analysed using Philips X'Pert software coupled to an International Center for Diffraction Data (ICDD) database running on a Gateway personal computer system.

All XRD peaks were indexed based on comparisons of observed d -values and d -values calculated using the NEWMOD-for-Windows[®] program (Reynolds and Reynolds, 1996). Portions of the powder diffractometer patterns are shown in Fig. 1 for the Na-saturated mount (air-dried and glycol-solvated) and NEWMOD-for-Windows - calculated profiles (air-dried and glycol-solvated). The d -values for air-dried and glycol-saturated samples are listed in Table 1. NEWMOD-for-Windows[®] modelling was carried out assuming an air-dried value for d_{001} of 9.6 \AA for pyrophyllite, a value for d_{001} of 12.6 \AA for air-dried smectite, and a value for d_{001} of 16.9 \AA for glycol-solvated smectite. The composition and mean defect-free distances were varied in order to find a best match between the observed and calculated patterns. The best-modelled profile-fit for both the air-dried and glycol-saturated material occurred with a 50:50 ratio of pyrophyllite:smectite, Reichweite 1, pyrophyllite (0 Fe, 0.1 Na), Na-smectite (0.2 Fe), a crystallite-size distribution between 1 and 20 layers and a mean defect-free distance of 8 layers. One layer of water (air-dried) and two layers of glycol (glycol-solvated) were found necessary to give the most accurate fit. These fitting parameters are consistent with those measured by TEM, verifying that this phase is indeed R1 mixed-layer pyrophyllite-smectite. The observed d -values fall between the calculated d -values for 40% and 60% smectite-like interlayers in ordered P/S, respectively (Eberl, 1979), further implying that this material is ordered 1:1 mixed-layer P/S. The d_{001} value for air-dried, untreated brinrobertsite varied slightly according to the relative humidity, but is $\sim 24.4 \text{ \AA}$.

Electron microscopy

Prior to electron microscope observations, the metabentonite was treated with L.R. White resin following the procedures of Kim *et al.* (1995), in order to prevent collapse of smectite interlayers in the vacuum systems. Sticky-wax-mounted thin-sections were prepared with surfaces cut normal to bedding. Typical areas that contained brinrobertsite were first imaged by SEM to locate the

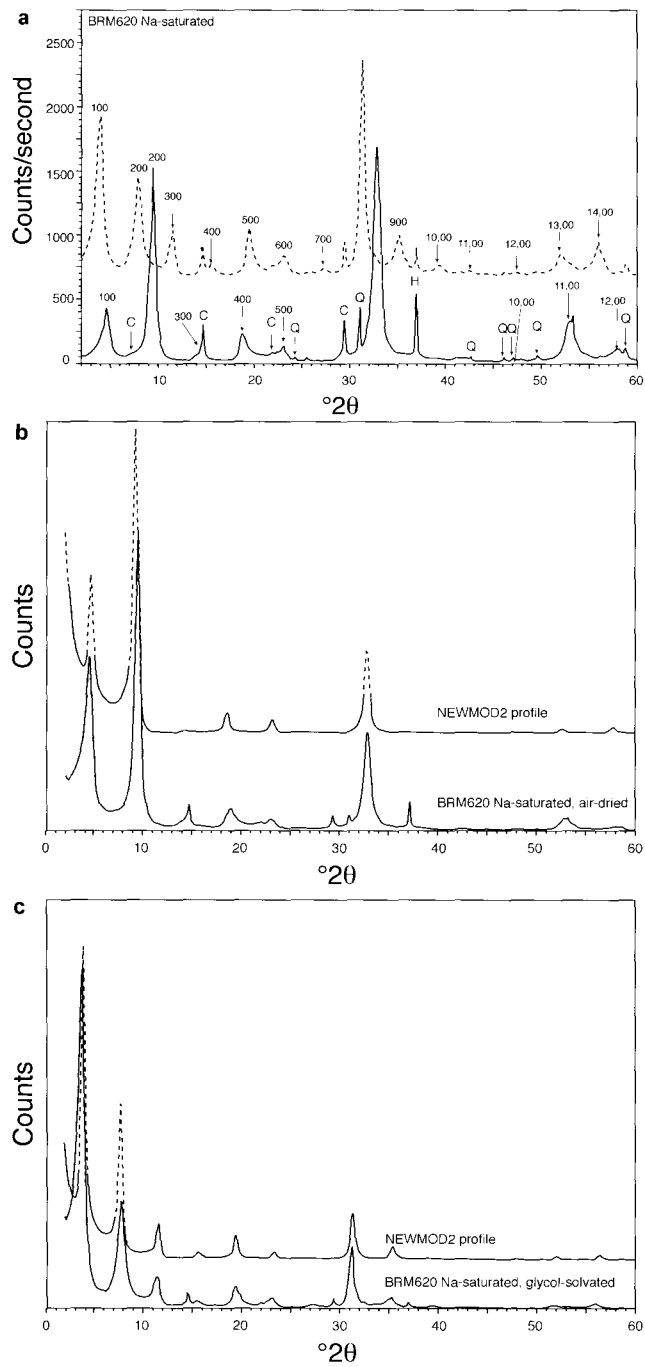


FIG. 1. X-ray powder diffraction patterns of brinrobertsite from sample BRM620. (a) Patterns of Na-saturated brinrobertsite. The lower, solid-lined pattern is of a Na-saturated, air-dried sample; the upper, dashed pattern was glycol-solvated. C = chlorite peak, Q = quartz peak, H = halite peak. (b) Comparison of NEWMOD-for-Windows[®]-calculated pattern and the observed pattern of Na-saturated brinrobertsite. (c) Comparison of NEWMOD-for-Windows[®]-calculated pattern and the observed pattern of Na-saturated, glycol-solvated brinrobertsite.

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TABLE 1. Powder diffractometer data for air-dried and glycol-solvated Na-saturated brinrobertsite from sample BRM620, with corresponding values calculated using NEWMOD-for-Windows[®].

	Air-dried				Glycol-solvated			
	Brinrobertsite		NEWMOD-for-Windows [®]		Brinrobertsite		NEWMOD-for-Windows [®]	
	$d_{\text{obs.}}$	I/I_0	$d_{\text{calc.}}$	I/I_0	$d_{\text{obs.}}$	I/I_0	$d_{\text{calc.}}$	I/I_0
001	22.29	48	22.19	36	26.80	100	26.42	100
002	10.99	100	11.08	100	13.21	33	13.32	53
003	7.32	2	7.32	1	9.02	9	8.93	12
004	5.48	7	5.55	6	6.66	2	6.62	2
005	4.47	3	4.46	4	5.30	7	5.31	8
006	—	—	—	—	4.48	3	4.44	2
007	3.17	33	3.17	28	3.82	1	3.79	<1
008	—	—	—	—	3.33	20	3.31	17
009	—	—	—	—	2.97	3	2.95	4
0010	2.22	<1	2.22	<1	2.66	1	2.65	<1
0011	2.01	4	2.01	1	2.46	<1	2.41	<1
0012	1.84	1	1.85	2	2.22	<1	2.21	<1
0013	—	—	—	—	2.04	1	2.03	1
0014	—	—	—	—	1.91	2	1.90	2

most appropriate areas for TEM observations. These areas, adhering to aluminium washers, were detached from thin-sections, ion-milled and carbon-coated. The TEM observations were made using a Philips CM12 TEM fitted with a scanning system and Kevex Quantum solid-state detector. The TEM was operated at 120 kV and a beam current of 20 μA . All high-resolution lattice-fringe images were obtained at 100,000 \times magnification. An objective aperture 20 μm in diameter was used for imaging. A camera length of 770 mm and a selected-area aperture 10 μm in diameter were used to obtain SAED patterns. Quantitative energy-dispersive spectrum (EDS) chemical analyses were obtained in scanning TEM (STEM) mode using a beam diameter of 5 nm and a scanning area of 30 \times 30 nm. Standards and other conditions for chemical analyses were the same as those given by Jiang *et al.* (1990).

Figure 2 is an SEM back-scattered electron image showing the texture of the metabentonite BRM620. Brinrobertsite (labelled Br) occurs in the matrix, filling interstitial space formed by anhedral to subhedral quartz and chlorite crystals. The approximate estimates of relative weight percent of each mineral are as follows: Brinrobertsite, 30%; quartz, 50%, chlorite, 20%. Crystal morphologies suggest that these minerals crystallized in rocks with a high fluid:rock ratio, e.g. in a hydrothermal system.

Figure 3 is a TEM lattice-fringe image showing the intimate intergrowth of packets of brinrobertsite and chlorite. The brinrobertsite layers occur in thick sequences of layers within which layer

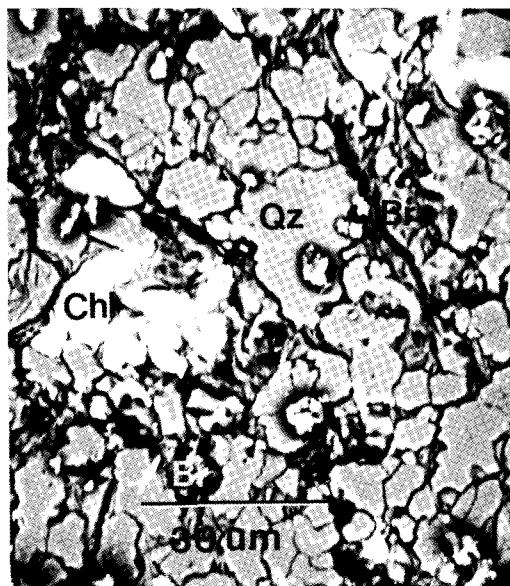


FIG. 2. BSE image showing textural relationships between quartz, chlorite and brinrobertsite. Brinrobertsite occurs as the matrix to the framework of quartz and chlorite crystals. Qz: quartz, Chl: chlorite, Br: brinrobertsite.

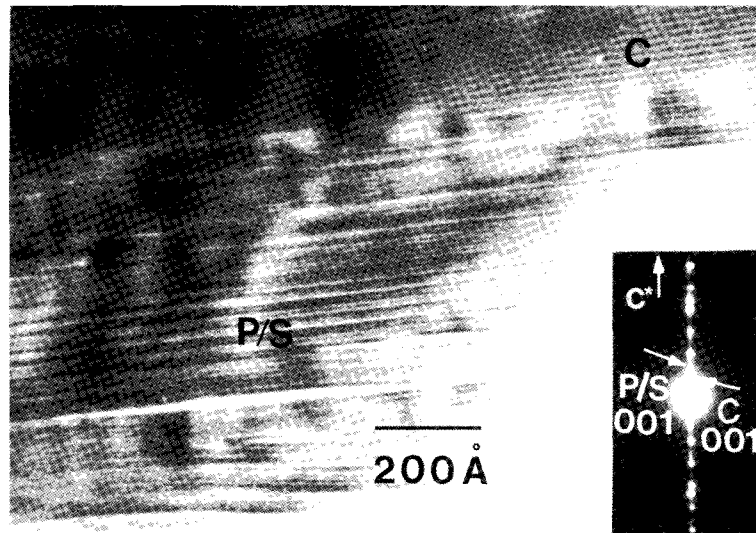


FIG. 3. TEM lattice-fringe image and selected-area electron diffraction (SAED) pattern of brinrobertsite and chlorite. Brinrobertsite layers occur in packets 3–8 layers thick, with a periodicity of 25 Å. Chlorite layers occur in packets 11–12 layers thick, with a layer spacing of 14 Å. The corresponding SAED pattern shows superimposed 00l reflections of brinrobertsite and chlorite. The 00l reflections of brinrobertsite and chlorite have primary spacings of 25 Å and 14 Å, respectively. C: Chlorite; P/S: brinrobertsite.

contrast implies ordered sequences of R1 with a mean thickness of 4 to 5 layers, although longer sequences occur locally, with a layer periodicity of 24 Å. Layers with thicknesses of $\gg 24$ Å occur randomly intercalated within sequences of layers with $d \approx 24$ Å, consistent with local layers of type PPS, PPPS, etc. Such intercalation of additional pyrophyllite-like layers is also the norm for illite-like layers in I/S which is identified by X-ray diffraction as R1 I/S (e.g. Tillick *et al.*, 2001). Chlorite layers occur in packets 11 to 12 layers thick, with a layer spacing of 14 Å. The corresponding SAED pattern shows superimposed 00l reflections corresponding to brinrobertsite and chlorite, respectively. The 00l reflections of brinrobertsite have a primary spacing of 24 Å, consistent with the fringe spacings. The 00l reflections of chlorite have periodicity of 14 Å, consistent with the layer spacing of chlorite. Figure 4 is a lattice-fringe image of brinrobertsite showing alternate fringes with darker and lighter contrast having periodicities of 24 Å. The 24 Å fringes are composed of 2 sub-fringes, one with a spacing of 9.3 to 9.4 Å and the other 14.7 Å, suggesting that brinrobertsite is a mixed-layer phase with two kinds of interlayers having characteristic spacings approximating 9.3 and 14.7 Å. Such interpretations of fringes are

subject to many factors, however, but the correspondence with likely pure phases is nevertheless consistent with other data. The analytical electron microscopy (AEM) data obtained from packets of brinrobertsite, free of contamination from surrounding chlorite (see analytical results), showed strikingly small K, Na and Ca contents relative to commonly observed mixed-layer illite-smectite. The AEM data obtained from chlorite packets showed that Fe and Mg are the dominant cations, and suggesting that it is of clinocllore-like composition.

The observation of 24 Å fringes for L.R. White resin-treated samples is consistent with a R1 I/S-like mineral, because expanded smectite-like interlayers have a spacing of ~ 14 Å, and illite-like interlayers have a spacing of ~ 10 Å. No other stacking sequence (such as R2, R3, etc.) was observed, although local variations in the stacking sequence are common. The unique composition of this mineral, when combined with the observations of sub-fringes, suggests that the illite-like interlayer in illite-smectite has been substituted by another kind of interlayer which is K-deficient and has a smaller spacing than an illite-like interlayer. We infer that this kind of interlayer is pyrophyllite-like. This is confirmed, in part, by the 9.3 to 9.4 Å spacing of the smaller subfringe

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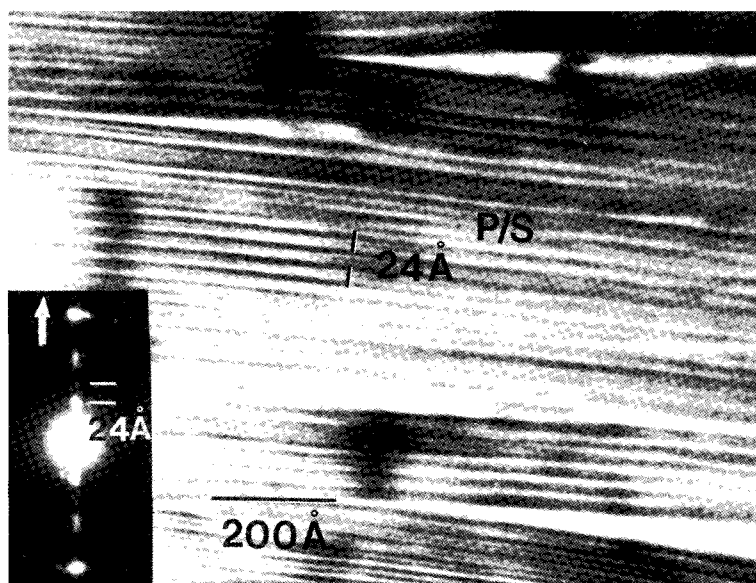


FIG. 4. TEM lattice-fringe image of brinrobertsite showing alternate fringes with darker and lighter contrast having periodicity of 24 Å. The 24 Å fringes are composed of 2 sub-fringes, one with a spacing of 9.3–9.4 Å and the other of 14.7 Å. P/S: brinrobertsite.

which is characteristic of pyrophyllite and much smaller than illite-like or other units.

The chemical composition as determined by EDS analyses is as follows: $(\text{Na}_{0.22}\text{K}_{0.07}\text{Ca}_{0.06})(\text{Al}_{3.81}\text{Mg}_{0.08}\text{Fe}_{0.08})(\text{Si}_{7.84}\text{Al}_{0.16})\text{O}_{20}(\text{OH})_4 \cdot 3.54\text{H}_2\text{O}$. The number of cations was calculated on the basis of 22 oxygen atoms. Infrared spectroscopy did not detect any exchangeable or non-exchangeable NH_4^+ (P. Nadeau, pers. comm.). A simplified formula can be written $(\text{Na}, \text{K}, \text{Ca})_x(\text{Al}, \text{Mg}, \text{Fe})_4(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot 3.54\text{H}_2\text{O}$, $x = 0.35$. Assuming a pyrophyllite formula of $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$, a model composition for smectite was calculated as follows: $(\text{Na}_{0.44}\text{K}_{0.14}\text{Ca}_{0.12})(\text{Al}_{3.62}\text{Mg}_{0.16}\text{Fe}_{0.16})(\text{Si}_{7.68}\text{Al}_{0.32})\text{O}_{20}(\text{OH})_4$. This formula for smectite is consistent with published AEM data for dioctahedral smectite (e.g. Dong *et al.*, 1997), further implying that brinrobertsite has a composition corresponding to equal amounts of pyrophyllite- and smectite-like units, and is dioctahedral.

Brinrobertsite was also studied by TEM using samples in which fine particles were spread over holey C-covered copper grids. The layered clay minerals are preferentially oriented for viewing of 001 layers and $hk0$ diffraction patterns. Individual grains were verified as being brinrobertsite, as

opposed to chlorite, for example, through EDS analyses. Figure 5 shows an $\mathbf{a}^*-\mathbf{b}^*$ electron-diffraction pattern which contains reflections corresponding to a prominent hexanet with symmetry only of a single mirror plane, and with weak, randomly-oriented reflections from other phases which were included in the area analysed. Such patterns confirmed that brinrobertsite is pseudohexagonal but monoclinic in symmetry, C -centred, and with lattice parameters $a \approx d_{100} = 5.2 \text{ \AA}$ and $b = 9.1 \text{ \AA}$. Such parameters are consistent with equivalent parameters for clay minerals in general. The collective diffraction data therefore are consistent with lattice parameters $a \approx d_{100} = 5.2$, $b = 9.1$ and $c \approx d_{001} = 24.4 \text{ \AA}$, the value of d_{001} as obtained from powder X-ray diffraction data. The approximation symbols are a result of our inability to determine a value of β . The $hk0$ diffractions were largely hexanet, but with some spotty cycles also present, implying that layers are largely coherently related, but with some turbostratic stacking.

TGA data

Figure 6 shows TGA data for brinrobertsite ($<2 \mu\text{m}$ fraction separated from the metabentonite). There are two weight-loss events. The first

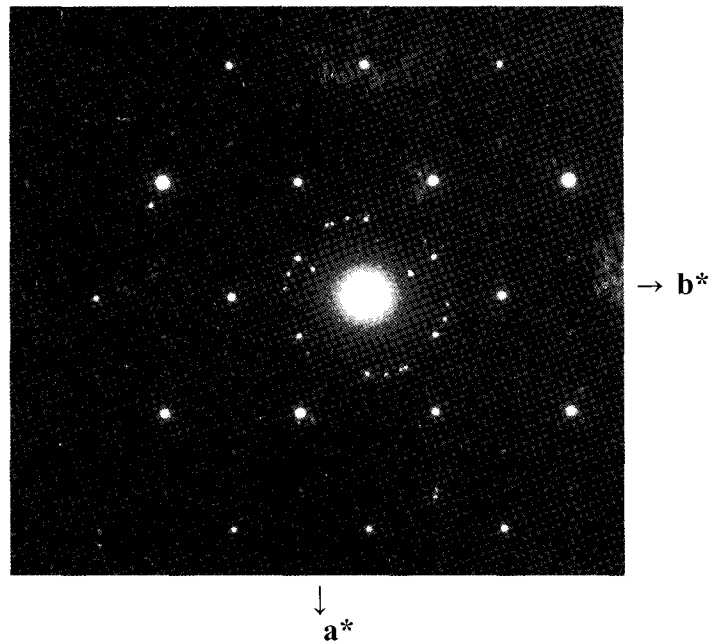


FIG. 5. An a^* – b^* SAED pattern as obtained with grains spread on a holey C-coated Cu grid, showing a pseudo-hexagonal hexanet with weak, randomly-oriented reflections from grains of other minerals. $d_{100} = 5.24 \text{ \AA}$, $b = 9.1 \text{ \AA}$

loss of 4% occurred at $<100^\circ\text{C}$, and the second of 8% occurred at $600\text{--}700^\circ\text{C}$. Chlorite, which is present in the sample, also gives peaks in the observed temperature range. Chlorite, however, is subordinate to the phase even in bulk samples, and the process of separation further favours brinrobertsite relative to the coarser chlorite, as observed by XRD. Although there may be a small contribution of chlorite to the TGA data, that contribution must be very small. The principal weight loss events must therefore be due largely to brinrobertsite, and are inferred to correspond to interlayer water and OH, respectively. The total weight loss is $\sim 50\%$ that of the total water content of smectite (Grim, 1968), as compatible with the proportion of smectite-like interlayers being $\sim 50\%$, as implied by XRD and TEM data.

Rock composition

Major and selected trace element data for the metabentonite and an associated mudstone sample are listed in Tables 2 and 3, with those of three other metabentonites from the Welsh Basin for comparison. Major elements were determined by XRF, and trace elements were determined by both XRF and instrumental neutron activation

analyses). A more comprehensive table of results can be found in Roberts and Merriman (1990, Table 2). In terms of major element abundances, BRM 620 has a significantly higher SiO_2 but lower Al_2O_3 and TiO_2 contents than the

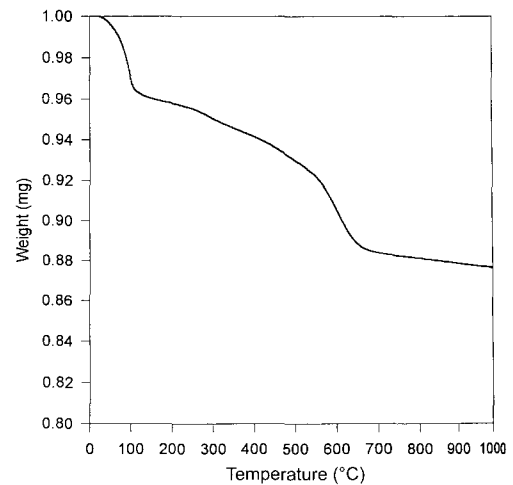


FIG. 6. Thermogravimetric analysis data for brinrobertsite showing two weight losses at temperatures of $<100^\circ\text{C}$ and $600\text{--}700^\circ\text{C}$.

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TABLE 2. Major element analyses (wt.%) of selected metabentonites from the Welsh Basin.

	BRM620	BRM622	BRM210	BRM613	BRM617
SiO ₂	74.82	56.38	66.59	57.58	48.82
Al ₂ O ₃	12.01	23.83	19.86	21.95	30.80
TiO ₂	0.17	1.09	0.34	1.12	0.97
Fe ₂ O ₃	7.66	6.89	1.68	5.68	2.52
MgO	1.03	1.55	1.60	1.67	1.39
CaO	0.17	0.38	0.49	0.44	0.44
Na ₂ O	1.03	0.80	0.77	2.25	0.79
K ₂ O	0.31	3.73	4.22	4.46	8.27
MnO	0.06	0.03	0.24	0.34	0.11
P ₂ O ₅	0.02	0.23	0.09	0.11	0.10
LOI	3.01	5.44	4.15	4.26	5.55
Total	100.30	100.13	100.03	99.87	99.76

LOI: loss on ignition

other metabentonites and the nearby mudstones. The alkali (K), alkaline earth (Mg, Ca) and certain trace (Cs, Rb, and Sr) elements are also depleted relative to those for the three metabentonites and the mudstone, whereas less mobile elements such as Zr and the REE are not significantly depleted. These differences suggest that there has been a significant increase in SiO₂, perhaps balanced by a dilution of Al₂O₃, and depletion in the more mobile elements, such changes in concentration having been accomplished through alteration by hydrothermal solutions.

Discussion

Crystal chemistry and nomenclature

The collective data show that brinrobertsite is composed of approximately equal numbers of alternating pyrophyllite- and smectite-like inter-

layers, and is therefore analogous in structure to R1 I/S (rectorite). Two models have been proposed for the structure of R1 I/S (Dong *et al.*, 1997, and references therein). In one, interstratified I/S is theorized as a mixture of illite and smectite layers (e.g. Nadeau *et al.*, 1984). Illite and smectite layers have equal distributions of ^{IV}Al in the upper and lower tetrahedral sheets of a 2:1 layer, as in mica; i.e. there is symmetry across the octahedral sheet. This results in all interlayers being subject to identical interlayer net-negative charges, and is incompatible with a potential leading to alternation of K-rich and K-poor interlayers. In the second model, upper and lower tetrahedral sheets of all 2:1 layers are modelled as having unequal distributions of ^{IV}Al, with asymmetry in Al/Si distributions occurring across the octahedral sheet (e.g. Brown, 1984). In an R1 sequence, this

TABLE 3. Trace element analysis (ppm) of metabentonites from the Welsh Basin.

	BRM620	BRM622	BRM210	BRM613	BRM617
Cs ⁺	<0.34	8.6	6.94	9.95	12.2
Rb	13	173	142	165	233
Sr	41	92	93	42	41
Zr	208	166	167	395	599
La ⁺	45.9	55.8	45.5	47.4	68.9
Ce ⁺	95.0	115	89.8	108.0	183
Nd ⁺	39.0	44.2	33.8	45.9	112.4
Sm ⁺	5.49	7.32	5.27	7.68	23

distribution results in all 2:1 layers being identical in composition or nearly so, and enantiomorphic with respect to structure. Alternate interlayers of this model are subject to high- and low-net-negative charges, thus providing a potential for ordering of alternate interlayers, which the first model does not. Data in support of the second model for R1 I/S were discussed by Dong *et al.* (1997) and Nadeau (1999). It was recently validated by Stixrude and Peacor (pers. comm.) for R1 I/S through calculations of the structure energies of both models of Al/Si distributions. The model with symmetry in Al/Si distributions across interlayers was shown to have a much smaller structure energy than the other, implying that it is much more stable. That is, ideal R1 I/S is a regular alteration of illite and smectite layers, with a unique structure in which all 2:1 layers are identical, or nearly so.

The crystal-chemical relations for R1 I/S are equally valid for brinrobertsite, i.e. if brinrobertsite comprises pyrophyllite-like and smectite-like layers, it has net-negative charges which are symmetrical across octahedral sheets of 2:1 layers. This is consistent with identical occupancies of all interlayers and is incompatible with a potential for ordering of alternate high- and low-charge interlayers. We therefore infer that, as has been inferred for R1 I/S, the distribution of ^{IV}Al is symmetrical across interlayers, resulting in identical 2:1 layers, but with net-negative charges of interlayers alternating between larger (smectite-like) and smaller (pyrophyllite-like). Such a distribution is compatible with the model inferred e.g. by Brown (1984), in that the interlayer with the largest positive charge (smectite-like in this case) is bordered by tetrahedral sheets which have the greater substitution of Al for Si.

We therefore infer that brinrobertsite does not have a structure consisting of alternating pyrophyllite and smectite layers, *sensu strictu*, but that it is unique in its own right. The 2:1 layers are similar to those of pyrophyllite and smectite only in that they are dioctahedral 2:1 layers, but are as different as are those of smectite relative to pyrophyllite. Indeed, these relations infer that all 2:1 layers are equivalent, unlike those of pyrophyllite as compared with those of smectite, except that contiguous layers are enantiomorphic, i.e. mirror images. The nomenclature 'P/S' would appear to be misleading, therefore, as is the nomenclature for R1 I/S. We use it, but with the above caveats, because it is consistent with

generally accepted nomenclature for ordered mixed-layered structures, and implies that at least the alternate interlayers have net-negative charges similar to those of pyrophyllite and smectite, respectively.

We emphasize that the model proposed here for Al/Si distributions can not be validated through direct crystal structure analysis because of the lack of highly ordered crystals of suitable size, and that it has not been directly verified. Even the equivalent model of R1 I/S may be viewed by some to be problematic, despite the wealth of experimental data supporting it. We propose it however, insofar as it is the only model that gives rise to the necessary potential for ordering of interlayers, and is consistent with the data for analogous I/S.

Geological origin of brinrobertsite

The metabentonite BRM 620 which contains brinrobertsite is geochemically related to silicic volcanic rocks belonging to the Caradocian Llewelyn Volcanic Group which outcrop some 10 km to the southeast in Snowdonia (Roberts and Merriman, 1990). However, these volcanic rocks are largely coarse air-fall and ash-flow tuffs that accumulated close to the centre of eruption, whereas BRM 620 is a distal airborne fine ash which might normally be expected to accumulate several 10s or 100s of km from the volcanic centre. The occurrence of BRM 620 within the Aber-Dinlle-Dinorwic fault system may have been a crucial factor in controlling its depositional setting and also in determining its conditions of secondary alteration. The NE-trending Aber-Dinlle-Dinorwic fault system is part of a major tectonic boundary, the Menai Strait Line, that separates two late Precambrian crustal blocks. Anglesey, to the northwest of the boundary, comprises the Monian-Rosslare terrane, whereas the Avalon terrane southeast of the boundary forms the basement for the Lower Palaeozoic Welsh Basin. Throughout the period of intense Ordovician (Caradoc) volcanism in north Wales, this system of faults appears to have acted as a barrier that permitted only mudrock and rare distal bentonite accumulations within a narrow, graben-like basin. This suggests (e.g. Roberts and Merriman, 1990) that this long-lived system of faults did not evolve solely by normal movement but also involved a considerable element of post-Caradoc strike-slip movement.

Two events are largely responsible for the inferred secondary alteration of the mudrock-dominated sequences within the Aber-Dinlle-Dinorwic fault system. Regional very-low grade metamorphism resulted from burial and a variable but generally weak tectonism within the fault system (Roberts and Merriman, 1985). The dominant microfabric developed during this event is a bedding-parallel alignment of authigenic illite and chlorite (Merriman *et al.*, 1990), much the same as that described from other deeply buried but largely non-tectonized parts of the Welsh Basin (Li *et al.*, 1994; Roberts *et al.*, 1996). The mudstones containing the outcrop of BRM 620 are amongst the lowest grades found within the fault system, with Kübler illite crystallinity indices $>0.41 \pm 2\theta$ indicating late-diagenetic conditions of alteration. Such conditions imply burial under at least 4 km of overburden and temperatures no greater than 200°C, given inferred field gradients in the range 35–50°C/km for the Welsh Basin (Bevins and Merriman, 1988; Roberts *et al.*, 1996). However, detailed TEM studies indicate that, later, a cryptic retrogressive alteration of regionally developed clay minerals also affected some of the mudrocks within the Aber-Dinlle-Dinorwic fault system. Jiang *et al.* (1990) found that ordered illite-smectite (I/S) had replaced authigenic illite in an Llanvirm mudstone sampled close to the Aber-Dinlle Fault, in the southwestern part of the fault system. Authigenic illite, formed in the bedding-parallel microfabric, shows various stages of replacement, from one or two layers of replacement within illite, through thin packets of I/S, to thick packets of locally deformed illite. Regular R1 ordered I/S tends to occur as a replacement of undeformed illite. In addition to major illite and chlorite, Jiang *et al.* (1990) also reported minor amounts of pyrophyllite and K-Na mica in the matrix of the mudstone. Because of its proximity to a major fault, Jiang *et al.* (1990) suggested that fault-controlled fluid-channelling was largely responsible for the retrogressive hydration of illite of regional metamorphic origin.

Elsewhere in north Wales, pyrophyllite-bearing assemblages occur most commonly in mudstones that are in close proximity to the numerous sub-volcanic intrusions of Caradoc age (Merriman and Roberts, 1985). Rectorite, paragonite and Na-K mica are also associated with pyrophyllite. Although the mudstones are indurated and bleached by contact alteration, they are not hornfelses in terms of mineralogy or lithology, suggesting that contact temperatures did not

exceed 300°C. The formation of pyrophyllite by the reaction: 1 kaolinite + 2 quartz = 1 pyrophyllite + 1 H₂O, has been mapped as a regional kaolinite-pyrophyllite isograd, with pressure and temperature conditions estimated at 2.1 kbar and 240–260°C based on vitrinite reflectance and fluid inclusion data (Frey, 1987). Such conditions are also consistent with clay-mineral reactions generated by low-to-medium temperature hydrothermal systems associated with sub-volcanic intrusions. The pyrophyllite-smectite mixed-layer mineral described by Kodama (1958) from Japan was generated in similar conditions. Similar experimental conditions were reproduced by Eberl (1979), who used water-filled autoclaves to simulate hydrothermal conditions and synthesized pyrophyllite-smectite at temperatures in the range 320–400°C.

Previous studies of clay minerals in this region of north Wales suggest that there are three possible origins for brinrobertsite. The merits of the three origins are considered below. The first mode of origin considered is that brinrobertsite formed solely as a prograde product of regional burial diagenesis/very low-grade metamorphism, i.e. as the end-product of the sequence: glass → smectite → I/S → brinrobertsite. This is considered the least likely scenario because; (a) no bedding-parallel microfabric has developed, as would be expected if glass altered to clay minerals during burial; (b) some relict I/S would be expected in the metabentonite but is not present; (c) such an origin overlooks the geochemical evidence of major and trace element depletions, probably related to hydrothermal activity.

The second mode of origin considered is that brinrobertsite formed as prograde product of early diagenesis followed by hydrothermal alteration, i.e. as the end-product of the sequence: glass → smectite → brinrobertsite. This scenario involves early alteration of glassy ash to smectite by reaction with sea water, followed by hydrothermal alteration and the selective stripping of interlayer alkali cations from smectite to produce mixed-layer P/S. Assuming the hydrothermal activity was associated with local volcanism, this brackets the sequence of events to within the Caradoc epoch, 446–455 Ma (Howells *et al.*, 1991). Although the limited time-frame for this sequence of events is consistent with the absence of a burial-related microfabric, some collapse of glass shards during alteration to smectite would be expected but is not evident. Moreover, had smectite been present in abundance, some TEM

evidence of discrete smectite relics would be expected, but is lacking.

The third mode of origin considered is that brinrobertsite is entirely the product of hydrothermal alteration but is a back-reaction product of pyrophyllite in the sequence: glass → pyrophyllite → brinrobertsite. This scenario involves early alteration of glassy ash to pyrophyllite in the aureole of a subvolcanic intrusion, such as the thick sheet of dolerite exposed to the northwest of the metabentonite. Early alteration also caused the replacement of the larger glass shards by chlorite, and generated the random microtexture that characterizes the metabentonite and the associated mudstones. This early phase of alteration occurred soon after emplacement of the nearby subvolcanic intrusion, and was caused by magmatic and connate fluids invading the glassy ash and converting it to a metabentonite, while leaching alkalis, alkaline-earth and certain trace elements from unstable glass, and redistributing other major elements such as SiO₂, Al₂O₃ and TiO₂. A later phase of hydrothermal alteration followed the cooling of the system and probably resulted from seawater circulating through a system of shrinkage cracks and microfractures in the metabentonite, partially rehydrating (retrogressing) clay mineral products from the earlier prograde alteration. During this event pyrophyllite back-reacted to form brinrobertsite.

Given the history of retrogressive alteration within the Aber-Dinlle Fault System, both the second and third modes of origin are possible. On balance however, the third scenario is considered the more likely, i.e. that brinrobertsite is a back-reacted product of hydrothermal alteration in the sequence: glass → pyrophyllite → brinrobertsite.

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