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Identification of halloysite (7 Å) by ethylene glycol solvation: the 'MacEwan effect'

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ABSTRACT: X-ray powder diffraction patterns of halloysite (7 Å) are characteristically altered following solvation with ethylene glycol. Some effect was first noted in the classic work of MacEwan but its value in the unequivocal identification of halloysite (7 Å) seems to have been overlooked subsequently. The response to ethylene glycol solvation involves a decrease in the intensity (peak height) of the peak at ~7.2 Å and an increase in the intensity (peak height) of the peak at ~3.58 Å thus narrowing the 7.2 Å/3.58 Å peak height intensity ratio. For pure samples of halloysite, this ratio is narrowed by an average of ~50%. This distinctive change is related to the interstratitified nature of halloysite (7 Å), specifically the presence of 'residual' interlayer water, i.e. halloysite (10 Å), which can be replaced with ethylene glycol so forming 10.9 Å layers, a spacing that is almost exactly one and a half times the thickness of dehydrated (7.2 Å) layers which do not imbibe ethylene glycol. Thus the separation between the 001 peaks in the 7.2 Å/10.9 Å interstratification is increased and the $002_{7.2}$ (3.58 Å) and $003_{10.9}$ (3.63 Å) peaks become more or less coincident, compared to the 7.2 Å/10 Å interstratification, i.e. the partially hydrated state. The widespread use of ethylene glycol solvation in clay mineral studies makes it a particularly useful and simple test to determine the presence of halloysite. Pure halloysites should be readily identifiable and experiments indicate a 'routine' sensitivity of ~20% halloysite in mixtures with kaolinite, although this will depend on factors such as 'crystallinity' and could be improved with careful attention to intensity measurements. It is proposed to call this phenomenon the 'MacEwan effect' in honour of its discoverer Douglas Maclean Clark MacEwan.

KEYWORDS: halloysite, kaolinite, kaolin, ethylene glycol, X-ray powder diffraction, MacEwan.

The fundamental feature that distinguishes halloysite from other members of the kaolin subgroup is the presence of interlayer water (Churchman & Carr, 1975). In a completely hydrated state, samples of halloysite exhibit X-ray powder diffraction (XRPD) patterns with an intense peak at 10 Å. This corresponds to a single sheet of water molecules ~2.8 Å thick between the 7.2 Å layers. In this state the identification of halloysite is straightforward. For example, analysis by XRPD before and after heating should be definitive (Brindley & Brown, 1984). The interlayer water is, however, very labile so that halloysite is most commonly observed in a more dehydrated form. Furthermore, changes in the state of hydration have substantial affects on XRPD patterns of halloysite, and were largely the source of much early debate over nomenclature (summarized by Churchman & Carr, 1975). This has been resolved by the general acceptance of the recommendation that the '*d*-spacing' of the 001 peak, which reflects the state of hydration, is appended to the name halloysite, and other names such as

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'metahalloysite' have been dropped (Churchman & Carr, 1975; Bailey, 1980; Giese, 1988). Halloysite (7 Å), i.e. the largely dehydrated form, poses some problems of identification since its XRPD pattern resembles that of many kaolinites, with which it is commonly admixed. Indeed, Brindley *et al.* (1963), using prepared mixtures of halloysite (7 Å) and kaolinite, suggested that up to 60% halloysite (7 Å) could be easily overlooked when examined by XRPD. In detail, features in XRPD patterns such as broader peaks (FWHM >0.3°2θ) and larger basal spacings (>7.15 Å) than those normally observed for kaolinite, as well as relatively intense non-basal peaks in oriented sample mounts, point strongly to the presence of halloysite (7 Å). A variety of other techniques including electron microscopy, thermal analysis and IR spectroscopy may also indicate the presence of halloysite in a sample. The merits and perspectives of each of these techniques were summarized by Churchman & Carr (1975). Nonetheless, confirmation of the presence of halloysite is generally based on empirical tests that rely on differences in the chemical reactivity of halloysite with various organic compounds when compared to other kaolins (Wada, 1961; Miller & Keller, 1963; Range *et al.*, 1969; Churchman *et al.*, 1984; Theng *et al.*, 1984). The most recent test of this kind proposed by Churchman *et al.* (1984) relies on the much more rapid formation of a 10 Å complex by halloysite compared to kaolinite (and dickite and nacrite) when treated with formamide. This test has been widely adopted (e.g. Singer, 1993; Merriman & Kemp, 1995; Kretzschamer *et al.*, 1997), no doubt in part because it consists of a single step and is therefore relatively quick and easy to apply, but also because it appears to provide an accurate indication of the amount of halloysite present (Churchman, 1990) in comparison to other techniques.

In his classical investigations into the formation of halloysite-organic intercalates, MacEwan (1946, 1948, 1949) demonstrated that a one-layer ethylene glycol halloysite complex could be formed from the fully-hydrated 10 Å form of halloysite. Later work has also shown that the one-layer ethylene glycol intercalate can be prepared from less hydrous halloysite (7 Å), via prior steps involving the displacement of other intercalates (e.g. Miller & Keller, 1963). Previously, MacEwan (1946, 1948) had also noted the direct, but partial, reaction of 'metahalloysite' (halloysite 7 Å) with ethylene glycol and the exceptional nature of this reaction amongst the other organic compounds that he studied. He also noted that the reaction was not observed after heating his samples (75°C, 12 h) prior to exposure to ethylene glycol. The purpose of the current paper is to reaffirm MacEwan's observations regarding halloysite (7 Å). This is done by illustrating, using modern approaches, that the intensity and the shape of the basal peaks on XRPD patterns of halloysite (7 Å) that we have examined, are invariably, and often dramatically, affected by ethylene glycol solvation, depending upon heating history. The changes observed are explained by comparison with simulated XRPD patterns. Additionally, the results suggest that the effect of ethylene glycol on halloysite (7 Å) is sufficiently distinct to form the basis of a routine and reliable test for its presence in a sample without recourse to other treatments. The utility of such a test lies in the widespread use of ethylene glycol solvation as an aid to the characterization of other common clay minerals. Experiments with prepared mixtures indicate that comparison of the changes between XRPD patterns recorded for the air-dried and subsequently the glycolated state is routinely capable of detecting as little as 20% halloysite mixed with kaolinite.

MATERIALS AND METHODS

Five kaolins known to contain halloysite were selected from the Macaulay Institute mineral collection, namely; Hal-9, Hal-12, Hal-14, Hal-26 and Hal-27. Hal-9 is also labelled 'Heddle's Halloysite' and comes from Hospital Quarry, Elgin, Scotland (Heddle, 1882). Hal-12 and Hal-14, are from an unknown locality in Surinam (possibly 'Brokopondo', Sjerry Van de Gaast pers. comm., 2001), whilst Hal-26 is from Hong Kong (Merriman & Kemp, 1995), and Hal-27 is sold by Wards Natural Science as 'Allophane' (catalogue number 49-0616). All samples had been stored at room temperature and humidity prior to analysis, some for many years. Additionally, numerous samples of kaolinite were also selected. Clay fractions (<2 μm) were separated from all samples by timed sedimentation and prepared as oriented specimens on 3 cm^2 glass slides by a filter peel transfer method, similar to that described by Drever (1973). The XRPD patterns were recorded routinely from 2–45°2θ using Co-*K*α radiation successively on the same samples, after drying in air, after solvation by ethylene glycol vapour at 60°C overnight, and after heating to 300°C for 1 h. Subsequently, all samples were re-exposed to ethylene glycol vapour overnight following heating to 300°C. Additionally, four 100 mg mixtures of Hal-9 with a reference kaolinite (KGa-2, available from the Clay Minerals Society, Source Clay Minerals Repository) were prepared by weighing out freeze-dried <2 μm size fractions. Note that freeze drying was verified to have no noticeable affect on the response of Hal-9 to solvation with ethylene glycol. Mixtures were prepared with concentrations of 5, 10, 20, and 40% Hal-9, dispersed in de-ionized water using an ultrasonic probe and oriented mounts prepared and examined as described previously. All XRPD patterns were obtained by step scanning in 0.02°2θ steps, counting for 2 s per step, using fixed 1° divergence and anti-scatter slits, 0.6 mm receiving slits, and tube settings of 40 kV and 40 mA. Peak height intensity measurements were made using Bruker Diffrac Plus software by first automatically subtracting the background using parameters of 0 and 1 for curvature and threshold, and then using the peak search algorithm to locate peaks and automatically determine intensities (peak height).

RESULTS

The XRPD patterns obtained from the air-dried halloysite samples indicated that all were, by and large, dehydrated 7 Å forms, although some (notably Hal-27) showed clear evidence of a minor 10 Å component (Fig. 1). Nevertheless, comparison of the various patterns recorded for each and all specimens revealed clear and consistent responses of the 7 Å peaks to glycolation and to heating. Thus, without exception, the peak height intensity of the peak near 7.2 Å decreased and the peak height intensity of the peak near 3.58 Å increased in the glycolated patterns (Fig. 2), relative to their values in the air-dried patterns (Fig. 1). Furthermore, in all but one sample, glycolation resulted in the peak near 3.58 Å becoming the most intense peak (height) in the patterns. Thus the 7.2 Å/3.58 Å peak height intensity ratio was reversed from that observed in the air-dried state. This results in a rather odd looking diffraction pattern for a kaolin mineral since the 3.58 Å peak becomes the strongest peak in the pattern, whereas normally the 7.2 Å is the more intense peak (assuming a diffractometer with fixed divergence slits). Additionally, changes in peak shape were apparent. In this respect, the 7.2 Å peak tends to sharpen up, sometimes associated with the development of a small peak at ~10.9 Å, other times with a more diffuse increase in intensity in this region of the pattern, best described as a low-angle tail. Similarly, the increase in the intensity of the 3.58 Å peak upon glycolation is associated with a noticeably narrower intensity spread of its peak tails to both low and high

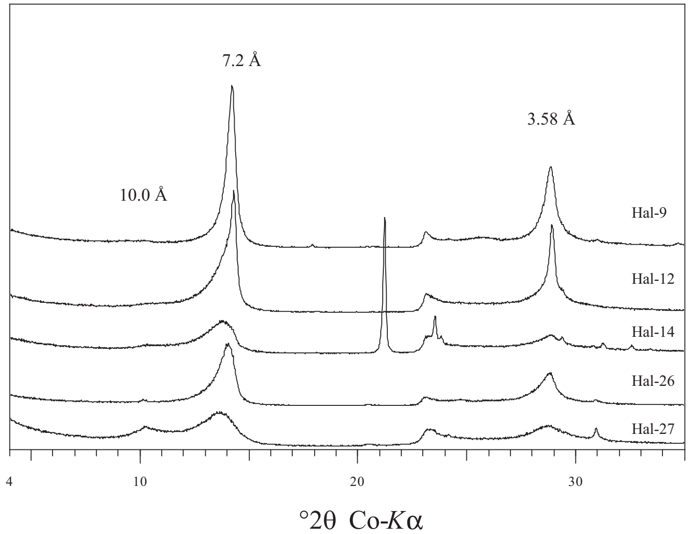

FIG. 1. XRPD patterns of <2 μm oriented samples of halloysite after drying in air. Note Hal-14 contains a notable amount of gibbsite. Patterns are displaced along the vertical axis for clarity.

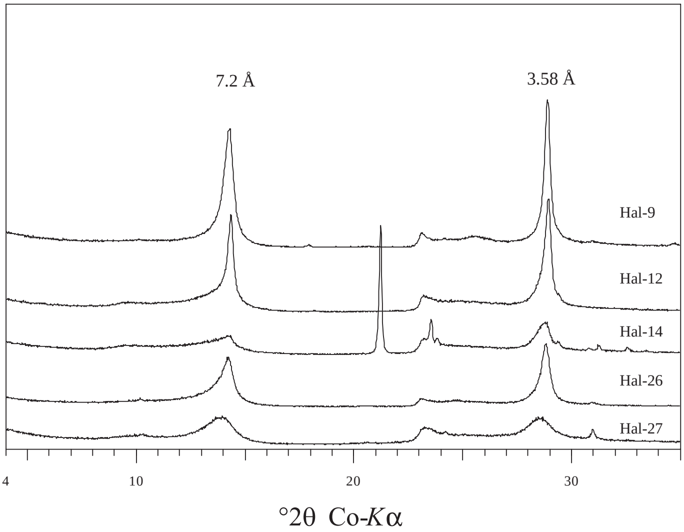

FIG. 2. XRPD pattern of <2 μm oriented samples of halloysite after exposure to ethylene glycol. Note the reversal of the 001/002 peak height ratio compared to that in the air-dried samples (Figure 1). Patterns are displaced along the vertical axis for clarity.

angles. Patterns recorded after heating to 300°C for 1 h also demonstrated a noticeable increase in peak height intensity compared to both air-dried and glycolated traces, a narrowing of peak widths, and the restoration of a more 'normal' 7.2 Å/3.58 Å peak intensity ratio (Fig. 3). These changes are apparent for all the patterns illustrated in Figures 1, 2 and 3 but are most fully appreciated by directly overlaying the various diffraction patterns as illustrated for one sample in Fig. 4. Attempts to effect changes in the XRPD patterns after heating to 300°C by a second exposure to ethylene glycol vapour showed only negative or slight responses. A slight response was characterized by a small

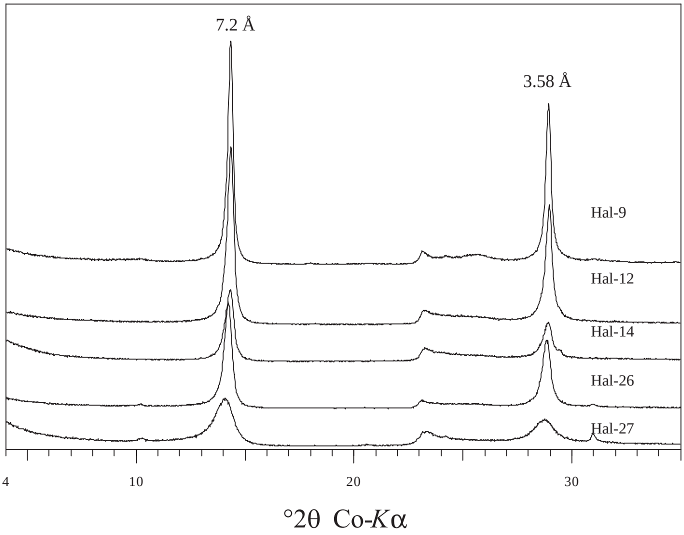

FIG. 3. XRPD patterns of <2 μm oriented samples of halloysite after heating to 300°C for 1 h. Patterns are displaced along the vertical axis for clarity.

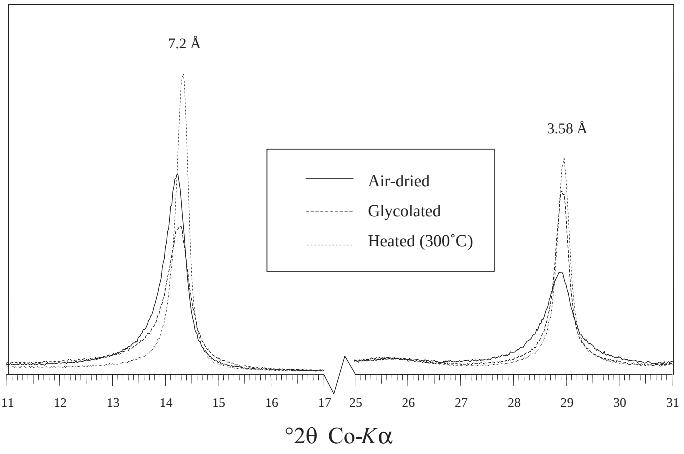

FIG. 4. Detailed comparison of air-dried, glycolated and heated XRPD patterns for sample Hal-9.

decrease in the peak height of the 7.2 Å peak and a small increase in the peak height of the 3.58 Å peak, relative to the heated trace. In contrast to these observations for halloysite, examination of numerous samples of kaolinite showed no obvious changes in peak intensities, widths or shapes, regardless of treatment. Measured peak height intensities and ratios for all samples of halloysite, along with those for the prepared mixtures of Hal-9 and the pure reference kaolinite KGa-2 are listed in Table 1. The percentage change of the ratio between air-dried and glycolated states is also listed since this parameter is independent of experimental factors such as fixed *vs*. variable slit systems and is therefore a most useful measure of the change. As mentioned previously, MacEwan noted the exceptional nature of the reaction of ethylene glycol with halloysite (7 Å) amongst the organic compounds that he studied. This included glycerol which was stated to have 'proved less effective' than ethylene glycol, and we have confirmed this by exposure of some samples to glycerol vapour for periods up to several days at 110°C.

DISCUSSION

Ever since the pioneering work of MacEwan (1946, 1948, 1949) it has been known that the fully hydrated 10 Å form of halloysite can form a one-layer complex with ethylene glycol with a resultant spacing of ~10.9 Å. Furthermore, MacEwan (1946,

TABLE 1. Intensity data (peak height, counts per second) for air-dried and glycolated states, peak height ratios, and percentage change of peak height intensity ratios, for samples of halloysite, reference kaolinite (KGa-2), and prepared mixtures of halloysite (Hal-9) and kaolinite (KGa-2).

Sample	Halloysite	Air-dried		Glycolated	Air-dried	Glycolated	Change	
	%	7.2	3.58	7.2	3.58	7.2/3.58	7.2/3.58	%
Hal-9	100	3966	2003	2888	3657	1.98	0.79	60
Hal-12	100	2977	2166	2378	2795	1.37	0.85	38
Hal-14	100	766	453	411	793	1.69	0.52	69
Hal-26	100	1510	819	1187	1573	1.84	0.75	59
Hal-27	100	730	491	654	663	1.49	0.99	34
KGa-2	0	20342	12923	21159	13436	1.57	1.57	0
5% Hal-9	5	24244	16998	25102	17971	1.43	1.40	2
10% Hal-9	10	21708	17997	22280	18920	1.21	1.18	2
20% Hal9	20	15099	10969	15715	12050	1.38	1.30	5
40% Hal-9	40	9276	6659	9486	7676	1.39	1.24	11

1948) also recorded some susceptibility of more dehydrated forms of halloysite to treatment with ethylene glycol. In the first edition (Brindley, 1951) of the Mineralogical Society Monograph on the X-ray identification and crystal structures of clay minerals, Brindley commented on the work of MacEwan and noted, in accordance with earlier comments by MacEwan (1948), that it ..seems probable that the entry of glycol into the structure depends on the silicate layers being already kept partly open by residual water layers. In later editions of the monograph (Brindley & Brown, 1984), however, these observations were not recorded in the text or remarked upon in tables. Thus Table 5.8 in Brindley & Brown (1984) for example, although concerned mainly with changes in *d*-spacings, contains no remarks on the response of halloysite (7 Å) to solvation with ethylene glycol, or to heating at 300–350°C. This conveys the impression that halloysite (7 Å) is unaffected by such treatments. Our results, however, reaffirm the observations made by MacEwan and demonstrate that changes in the XRPD patterns before and after treatment are substantial.

Although changes in peak shape and intensity are more subtle than changes in position, the question arises as to why the affect of ethylene glycol on halloysite appears to have been largely forgotten. Certainly, examination of a number of excellent monographs and books with chapters on kaolin (Gieseking, 1975; Brindley & Brown, 1984; Dixon & Weed, 1989; Moore & Reynolds 1997) suggests that MacEwan's observations have somehow missed gaining widespread recognition. In part this may be due to the fact that although such observations are easily made with modern computerized collection of XRPD data, the direct comparison of patterns recorded on older XRPD diffraction equipment required more effort and attention to detail. Furthermore, it was, and still is, not uncommon to record one pattern over a large angular range but restrict the recording of other patterns to much shorter ranges, in order to save time. Procedures such as this may have caused many workers to miss the changes that occur to halloysite (7 Å) following ethylene glycol solvation. Others may have dismissed any differences as due to small misalignments of sample positioning between one recording and the next, perhaps because their consistency from one basal peak to another may not have been apparent.

A comparison of the response of halloysite (7 Å) to ethylene glycol, and to heating, and most importantly to ethylene glycol solvation after heating suggests little reason to doubt MacEwan's and Brindley's explanation that the entry of ethylene glycol into halloysite depends on the presence of 'residual' water layers. Although water is very easily and irreversibly lost or removed from halloysite in the laboratory, according to the work of Brindley & Goodyear (1948) complete removal of interlayer water requires heating to temperatures of ~400°C, at which the layers themselves are on the point of decomposition. Samples of halloysite (7 Å) invariably contain some amount of residual interlayer water, indeed its presence is implied by definition (Churchman & Carr, 1975). Furthermore, the presence of this water is probably the key to the use of the wide variety of empirical tests for halloysite based on chemical reactivity (Churchman & Theng, 1984), especially since many are affected by the heating history of the sample prior to their application. Whilst compounds which form strong hydrogen bonds are capable of re-expanding dehydrated layers, polar organic compounds cannot. Presumably then, the XRPD response of halloysite (7 Å) to ethylene glycol solvation is a result simply of the replacement of the 'residual' water layers with layers of ethylene glycol. It follows that if interlayer water were to be lost completely, there should be no response to ethylene glycol solvation, as effectively shown by samples heated prior to glycolation (MacEwan, 1948).

Perhaps the most peculiar feature of the diffraction patterns from the glycolated halloysites is the reversal of the 7.2 Å/3.58 Å intensity ratio compared to their air-dried counterparts. Peculiar though it appears, a simple explanation for this behaviour is suggested from a consideration of the layer spacings that result following glycolation compared to those present prior to it. As discussed previously, it seems reasonably certain that ethylene glycol only replaces the layers, or partial layers, of water present in halloysite (7 Å), presumably more or less completely. Furthermore, it does not result in the opening up or levering open of those layers, or parts of layers, where water is not present, at least not to any noticeable extent since the result would be the end-member halloysite-ethylene glycol complex. Instead, some form of interstratification results between a one-layer glycol halloysite complex with a spacing of ~10.9 Å and other layers or parts of layers with no glycol, and a spacing of 7.2 Å. The key to the behaviour of the relative intensities upon glycolation is that the 003 peak from a halloysite glycol complex is almost exactly coincident with the 002 from the 7.2 Å component, whereas this is not the case for the hydrate. Additionally, the 001 peaks are correspondingly less coincident. Simply applying Mering's principle (e.g. see Moore & Reynolds, 1997) to this scenario would predict diminished intensity for the 7.2 Å peak and increased intensity for the 3.58 Å peak. In other words the effect is due to the ethylene glycol halloysite complex being almost exactly one and a half times the thickness of the uncomplexed, i.e 7.2 Å layers. That this change in the layer spacings will indeed produce the observed effects can be illustrated by calculated XRPD patterns. Fig. 5 illustrates a pattern calculated for a random interstratification of 7.15 Å layers with hydrated 10.1 Å layers in the proportion 9:1 compared to the same structure with the hydrated layers replaced by glycolated layers with a spacing of 10.9 Å. The patterns were calculated using the program developed by Plançon & Drits (1999) with experimental parameters appropriate for comparison to the real patterns, and assuming a log normal crystallite size distribution with a mean of 10 layers. Trial and error modelling of several different patterns for different layer proportions all showed that the reversal of the intensity ratio was a consistent effect, but the details were also found to be sensitive to different particle size distributions. Modelling of some patterns with a discrete diffraction maximum in the region of 10 Å also clearly requires an element of R1 (Reichweite = 1, i.e. nearest neighbour) segregation of layer types to be introduced in accordance with the work of Churchman *et al.* (1972). Thus, segregation may need to be considered in order to model the experimental patterns precisely. Nonetheless, both random and partially segregated structures indicate a reversal of the intensity ratio from the hydrated to the glycolated state. The other point that the modelling brings home is that the basal peaks of partially dehydrated halloysite samples are really mixed-layer peaks, i.e. the '001' at ~7.2 Å and '002' at ~3.58 Å are more precisely combinations of 001/001 and 002/003 peaks. That is, of course, assuming only two components/spacings are involved whereas it may be necessary to consider three, at least where the hydrate interstratification is concerned (Costanzo & Giese, 1985).

The value of using ethylene glycol solvation to identify halloysite lies mainly in its routine use for other purposes. If the changes in the XRPD patterns that we have described are observed, they provide an unequivocal identification of the presence of halloysite. Certainly, they are sufficiently distinct from the response of minerals such as mixed-layer kaolinite-smectite to glycolation and heating. It is perhaps conceivable that some mixtures may be too complex for its application, but we have found it to be a valuable test in studies of reasonably complex mixtures from tropical soils containing both 10 Å

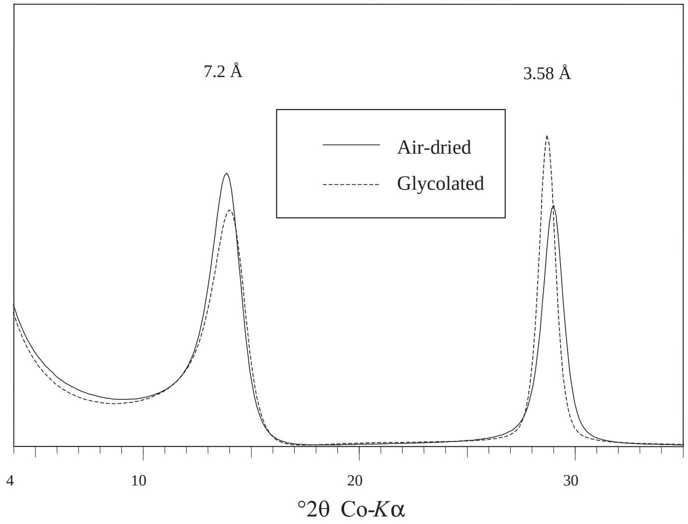

FIG. 5. Computer-simulated XRPD patterns of air-dried and glycolated halloysite with 10% of layers containing water (air-dried) or ethylene glycol (glycolated).

and 7 Å halloysite (Kautz & Ryan, 2000; Ryan & Kautz, 2001). For samples in which the kaolin present is pure halloysite the change in the peak height intensity ratio between air-dried and glycolated states should be obvious. The simplicity of the method, however, precludes a precise and/or universal analysis of its sensitivity because of a variety of factors that may affect the measured peak height ratios. Firstly, the percentage change in the intensity ratio of different halloysite samples varies between 34 and 69% (Table 1). The lowest value was obtained for Hal-27. This sample has the broadest peak widths, suggesting that factors such as 'crystallinity' and/or the initial proportion of hydrated *vs*. dehydrated layers may have important effects on the simple peak height ratio. Indeed, the amount of residual water layers in halloysite (7 Å) is unlikely to be the same in different specimens, although many will probably lie within a restricted range. Secondly, all five halloysites examined are only assumed to be pure with respect to the kind of kaolin present, i.e. halloysite, so that it is difficult to exclude the possibility that some of the variation is due to the presence of other kaolin minerals in some samples. Examination of data for the percentage change in the basal peak height ratio from many more samples will be needed to address this point. Finally, comparison of the intensity data for the halloysites with those for the kaolinite KGa-2, as given in Table 1, illustrates the very common observation that the intensity of diffraction from halloysite in oriented specimens measured as peak height is invariably very much weaker compared to kaolinite. Given the similarity of composition and structure, these differences in intensity can be confidently assigned to both lower 'crystallinity' and less 001 preferred orientation of halloysite. In a mixture in which kaolinite and halloysite have exactly the same degree of 'crystallinity' and of preferred orientation with respect to the 00l series of planes then the relationship between the proportion of halloysite and the percentage change in the measured intensity ratio should be linear. However, because halloysite is generally more poorly 'crystalline' than kaolinite and if, as is likely, halloysite mixed with kaolinite adopts a different degree of preferred orientation, then the percentage change in the intensity ratio between air-dried and glycolated patterns will also depend on these differences. Such factors will make the relationship of the percent change in the intensity ratio *vs*. halloysite concentration non-linear, as found for the mixtures of Hal-9 with the kaolinite KGa-2 (Fig. 6). The importance of these effects is that differences in 'crystallinity' and preferred orientation will undoubtedly vary for samples of

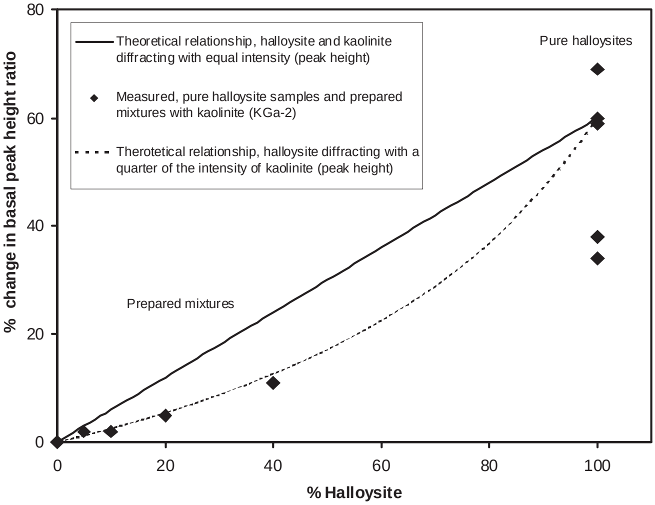

FIG. 6. Plot of % halloysite *vs*. % change in the basal peak height ratio. The solid line represents a theoretical relationship if both halloysite and kaolinite diffracted with equal intensity (peak height). The dashed line represents a theoretical relationship for a peak height intensity of halloysite which is a quarter of that of kaolinite, for example due to factors such as a lower degree of preferred orientation and poorer 'crystallinity' of halloysite. Both theoretical lines assume that the percentage change in the peak height ratio for pure halloysite is 60%.

different origins, so that the sensitivity of detecting and/or quantifying halloysite will likewise vary.

Measurements of changes in peak ratios for the prepared mixtures of Hal-9 with KGa-2 indicated that 20% halloysite produced a 5% change in the intensity ratio, and 40% halloysite an 11% change (Table 1, Fig. 6.) For smaller amounts of Hal-9, only a 2% change was observed. A 2% change is probably too close to the overall precision of 'routine' intensity measurements to be certain that a small amount of halloysite is present. However, employing strategies to increase the number of counts accumulated and/or directing special attention to ensure the reproducibility of intensity measurements between runs could no doubt provide better sensitivity if needed.

CONCLUSIONS

A suite of XRPD patterns for air-dried, ethylene glycol-solvated, and heated samples, such as is normally recorded routinely for many studies, is sufficient to determine whether or not halloysite (7 Å) is present in a sample. An effect of ethylene glycol solvation on halloysite (7 Å) was originally discovered by MacEwan (1946). Our experience with the rediscovery of this fact is that MacEwan's observations deserve to be more widely publicized. It is proposed to call the phenomenon the 'MacEwan effect' in honour of Douglas Maclean Clark MacEwan (1917-2000) who first observed and recorded it whilst working at the Macaulay Institute in the late 1940's. The presence of interlayer water is central to the definition of halloysite and appears to be a prerequisite for the intercalation of ethylene glycol. There can, therefore, be no ambiguity concerning the identification of halloysite following the use of the ethylene glycol test; such as may remain if identification is based on morphology alone. Although a problem, perhaps semantic, that we do not believe to have been completely addressed, is the nature of, and thus what to call, material that was formerly halloysite, if no interlayer water whatsoever remains?

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