

## XRD OF WET SPECIMEN – SOURCE OF INTERESTING INFORMATION

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## ABSTRACT

Some minerals, particularly clay minerals, are humidity sensitive. Expansion and shrinkage of clays is caused by interaction with water. Changes of volume of clay masses endanger engineering structures of any kinds, buildings, road and waterworks. Besides threatening actions, expanding clays find numerous applications for instance as sealing material, packing material and as drilling fluids. In laboratories, expandability of clays is frequently studied by means of X-ray powder diffraction (XRD) of hydrated or glycolated specimens. Although hydration is a natural process a majority of researchers prefers glycolation rather than hydration. Generally, the examination of wet clay brings more information and improves understanding of clay behaviour. If the impact of humidity on smectite is disregarded, misinterpretation of XRD patterns can happen. That concerns mainly the detection of mixed layer clay minerals. Comparison of hydration and glycolation of smectite is discussed. Examples of hydration of a few smectites, a halloysite and an illite are given.

**KEYWORDS:** X-ray powder diffraction, clay minerals, smectite, humidity, hydration, glycolation, swelling

## 1. INTRODUCTION

Humidity sensitive minerals change when exposed to humid or dry atmospheres. They change their appearance and their physical and chemical properties. Some minerals change their structure or even decay. (Kühnel and Van der Gaast, 1996). Clay minerals, due to their fineness and large surface area are strongly humidity sensitive. Commonly they change appearance, getting darker hue when wet and paler when dried as consequence of changed reflectance and selective light absorption.

In addition to surface adsorption, smectite, halloysite, and illite exhibit adsorption of water molecules in the interlayer space. In the case of smectite water molecules are associated in hydrous complexes around exchangeable cations that

compensate charge imbalances. During uptake of water in the interlayer the thickness will change. Water uptake and water loss at varying temperatures and varying relative humidity (RH) of smectite is often associated with structural changes. Their lattice expands or shrinks instantly when ambient conditions change. In laboratories without air conditioning, RH fluctuates with seasons and/or outdoor climate. Their lattice expands or shrinks instantly when ambient conditions change. The prevailing cation in the assembly of exchangeable cations in smectite interlayers attracts spontaneously different amounts of water and subsequently  $d_{001}$  value change. In Table 1 ranges are listed according to  $d_{001}$  values of montmorillonite exchanged for mono- and di-valent cations between 20 and 80 % RH.

**Table 1** Variations of basal reflections (Å) of smectite (exchanged for different cations) in the range of 20 to 80% RH.

Cation	20 % RH	80 % RH	Cation	20 % RH	80 % RH
Li <sup>+</sup>	12.49	15.79	Mg <sup>2+</sup>	14.32	16,04
Na <sup>+</sup>	12.41	15.50	Ca <sup>2+*</sup>	<b>14.50</b>	<b>15.69</b>
K <sup>+</sup>	11.60	12.69	Sr <sup>2+</sup>	12.71	16.14
Rb <sup>+</sup>	12.02	15.09	Ba <sup>2+</sup>	13.63	16.34
Cs <sup>+</sup>	12.38	12.52	Data of montmorillonite, Wyoming, from Kühnel and Van der Gaast (1993)		
H <sup>+</sup>	12.95	19.43			

Note: \*Ca-exchange of smectite and smectitic clays is recommended for all hydration studies of clays because of the least variation

Each smectite expands differently. Some smectites exhibit only limited expansion. For instance hydrated beidellite expands only to 15.1 Å (Brindley 1972) and vermiculite to 15.3 Å. Glycolated vermiculite does not expand and glycolated beidellite expands as other smectites.

## 2. DEVELOPMENT OF HUMIDITY CONTROLLED BY X-RAY POWDER DIFFRACTION

The recognition of expandability of some clay minerals led instantly to development of procedures for detection and quantification of that phenomenon. MacEwan (1944) introduced glycolation (using ethylene glycol  $C_2H_6O_2$  or glycerol  $C_3H_8(OH)_3$ ). The first trials with XRD of wet samples followed instantly (O'Brian, 1948). Glycolation (with ethylene glycol) became more popular because of its simplicity. Nevertheless, from the early applications it became clear that the procedure is more complex than first realized. Over the years numerous glycolation procedures were developed as shown by a list of references in Thorez (1975), section II, Methods of Preparation.

Because expandability of some phyllosilicates is an extremely anisotropic property, XRD is a suitable technique for measurement in defined crystallographic directions. The maximum expansion and shrinkage of smectites proceed in the direction 001 (along the *c*-axis).

Trials of XRD analysis under controlled humidity started with measuring wet clay specimens in capillaries (and fibres). Later on methods were developed for analysis of oriented clay specimens on glass plate, ceramic tile and Si-wafers. These specimens were then conditioned in flow of wetted air produced by mixing of wet and dry gases from a humidity generator or air conditioned above saturated salts (O'Brian, 1948; Kühnel and Van der Gaast, 1993). All results achieved "at room conditions", however, are not reliable because the surfaces of clay specimens that are exposed to varying laboratory conditions undergo uncontrolled desiccation or will take up water from the atmosphere. A comparable impact can be obtained if for a short time a specimen is removed from a measuring chamber with controlled humidity. This is a matter of seconds, especially with the milligram-sized specimens that are often used in XRD analysis. That lowers the reliability of measurements.

## 3. COMPARISON OF HYDRATION AND GLYCOLATION

There are substantial differences between hydration and glycolation of smectite. In the first place hydration is a natural process while glycolation is artificial. Hydration simulates better the natural process associated with volume changes. Moreover, it enables estimation and/or measurement of swelling forces in solving geotechnical problems in which, under natural conditions, only water is involved.

Hydration and dehydration allows studies of both expansion and shrinkage in progress while glycolation gives data only on a final expanded state. Also hysteresis of expansion and contraction can be studied with hydration. Regarding the size of water molecules and that of ethylene glycol, the rate of expansion and/or shrinkage differs; penetration of water molecules in the interlayer is faster than that of ethylene glycol.

Another (major) difference is the interaction of water and ethylene glycol with exchangeable cations. These cations are responsible for differences of clay behaviour. The Interlayer Cations (IC) are different in size, charge and hydration energy. They compensate charge imbalances of clay minerals. The IC generate attractive forces that constrain the mobility of water molecules. Generally,  $d_{001}$  values of smectites after glycolation exceed rarely 18 Å while hydration commonly leads to values higher than 20 Å.

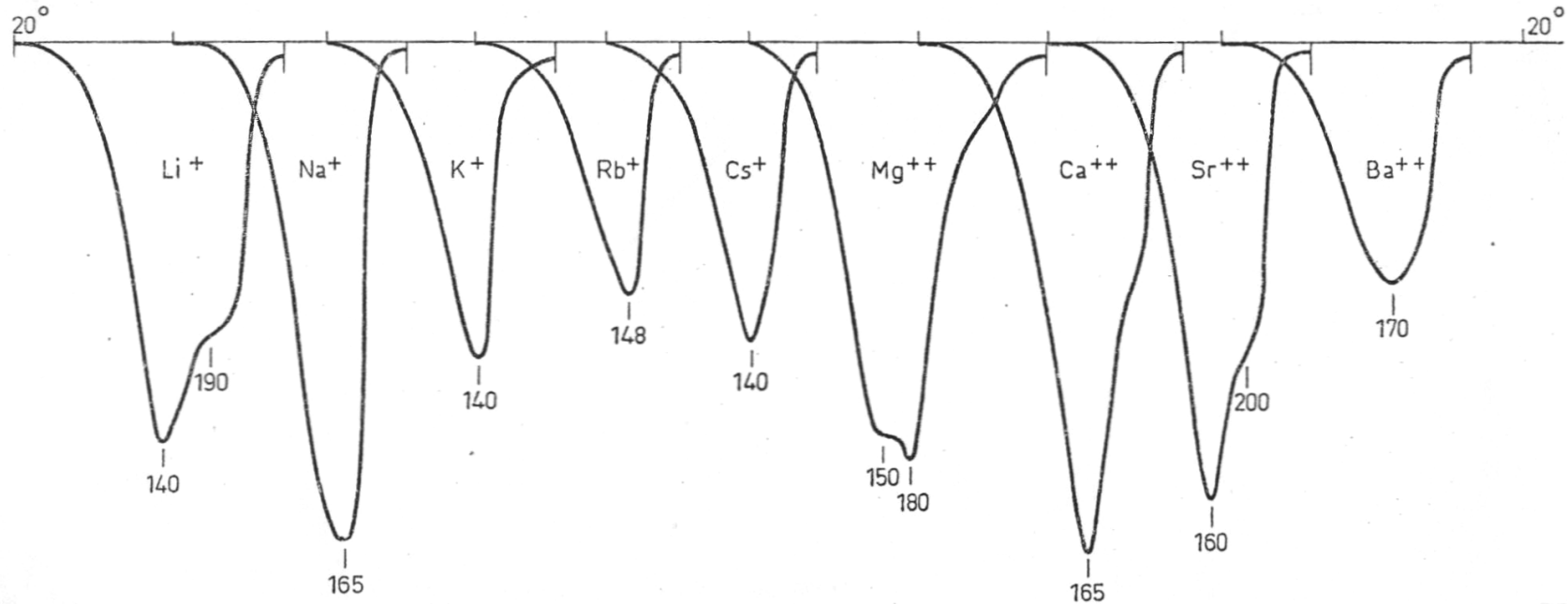
The hydration energy  $-\Delta H_h$  of the exchanged cation is responsible for generation of hydrous complexes ( $Me^{+,++}.n H_2O$ ) around IC located in the interlayer. This additional water in the interlayer forms different configurations as described by Güven (1991), Prost (1998) and Van der Gaast et al. (1999). Water molecules form shells that are situated around cations. Ethylene glycol forms multi-layers in the interlayer space. For every type of cation this hydrous complex holds different amounts of water molecules. Moreover, besides this interlayer water there is also water adsorbed at the surfaces of the clay mineral particles.

In Fig. 1 the thermal analyses of 0.2-2 µm size fraction of Wyoming montmorillonite exchanged for some mono- and di-valent cations are shown. A sample of 1 gram was conditioned at 50 % RH at 20 °C before measurement in the M.O.M. derivatograph. It can be seen that depending on the type of exchanged cation different amounts of interlayer water, chemically bound water, and total amount of water are released on the heating path. Interlayer water includes also water released below 100 °C. Dehydration of smectites exchanged for different cations is completed generally below 300 °C in one or two steps. Such a two step water release is exhibited by smectites exchanged for cations that have high hydration energy, such as lithium, magnesium, calcium and strontium. Fig. 1 also includes data on ionic radii and hydration energies after Zeman (1966) and Greenwood (1970).

Some residual water is always presented in the examined clays. It is captured in the interlayers around the exchangeable cations. The amount of water in interlayers is controlled by the charge and size of present cations and the prevailing RH. Some water remains in interlayers even after evacuation or drying. When glycolation is applied, water is assimilated by the ethylene glycol and both act as one solution. The major differences between hydration and glycolation are summarized in Table 2.

**DEHYDRATION OF WYOMING MONTMORILLONITE (0.2-2 $\mu$ m) EXCHANGED WITH DIFFERENT CATIONS**

(Derivatograph M.O.M., Differential thermogravimetric curves DTG, 1 g sample, laboratory temperature 20°C, relative humidity 50%, heating rate 10°C/min in air)



H <sub>2</sub> O <100°C (%)	3.5	3.25	3.0	3.5	3.5	3.25	2.35	2.25	1.75
Interlayer H <sub>2</sub> O (%)	18	16.5	8.70	7.0	8.7	20	19.5	14.25	8.35
End dehydration (°C)	270	230	220	200	205	330	270	270	260
Chem. bound H <sub>2</sub> O (%)	5.2	5.0	4.4	4.4	4.4	5.0	4.6	4.5	4.8
Total loss of wt. (%)	23.2	21.5	13.7	11.4	13.1	25.0	24.1	21.0	14.9
- $\Delta H_h$ (kcal/mol) <sup>a</sup>	127	101	81	75	67	468	386	353	320
Cation radius (Å) <sup>b</sup>	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43
Cation	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Mg <sup>++</sup>	Ca <sup>++</sup>	Sr <sup>++</sup>	Ba <sup>++</sup>

**Fig. 1** Differential thermogravimetric curves of Wyoming montmorillonite exchanged for mono- and divalent cations. Hydration energies of cations -  $\Delta H_h$ , according to Greenwood (1970) and ionic radii after Zeman (1966). Dehydration culminates at different temperatures, sometimes in two steps and water release varies from 4.5 to 16.5 %.

**Table 2** Comparison of hydration and glycolation processes

HYDRATION	GLYCOLATION
- natural process	- artificial process
- fast equilibration of clay-water system	- slower equilibration of clay-glycol-(water) system
- higher expansion	- limited expansion
- continuous (stepwise) observation	- initial and final state
- only H <sub>2</sub> O is involved	- interference of water present
- response of exchangeable cations	- no response of exchangeable cations
- dehydration studies	- n.a.
- hysteresis study	- n.a.
- simple specimen preparation	- complex specimen preparation
- closed cell required	- handling in open space
- lower stability of hydrated state	- higher stability of glycolated state
- <i>in situ</i> measurement	- necessary specimen replacements
- high reproducibility	- reproducible
- direct indication of beidellite	- n.a.
- direct indication of vermiculites	- n.a.
- studies of clays with electrolytes	- n.a.

#### 4. CONSTRAINTS OF SWELLING

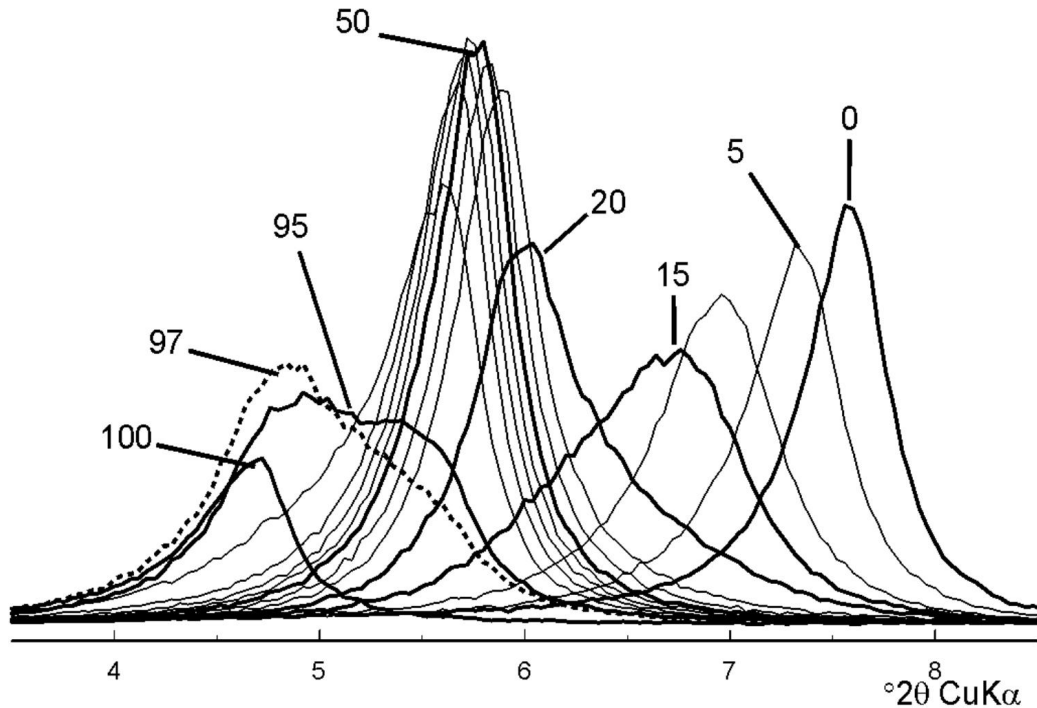
Sometimes, swelling of (smectitic clay) smectite is constrained. The main reason is the presence of mixed-layered clay minerals. In such cases the expansion does not reach the expected d-values. If, there is no evidence of mixed layer structures, additional reason could be presumed. (1) Presence of amorphous phases (e.g. opal). These may form a thin film at the surface of smectite particles. This phenomenon was observed on weathered rocks when liberated silica from altered alumino-silicates was not removed. A short treatment with diluted NaOH could help to dissolve the silica film. Generally, all amorphous and X-ray amorphous substances can contribute to such "blocking" of expansion. (2) Small particle sizes and particle deformation (e.g. Jonas and Roberson, 1960). Desiccation of clay generates a slight underpressure in some micropores. This gives to clay higher "green" strength. It also obstructs a return of water or ethylene glycol molecules in the interlayer of desiccated, collapsed crystallites. This happens often on very fine particles getting curved if collapsed. Subsequently the hysteresis of rehydration increases accordingly. (3) Partial pillaring in smectite interlayers. This may happen when precipitation of some compounds from the solutions (e.g. oxides, oxide-hydroxides of Al, Fe or Mg) takes locally place in smectite interlayers. (4) Besides inorganic compounds also organic molecules might have constraining effect on swelling. This leads to a partial collapse at low humidities. In such cases, line broadening increases as consequence of sheet deformation.

#### 5. PROCEDURE

If a humidity generator is not available, a simplified procedure can be applied. There are two prerequisites for the preparation of a wet specimen: (1) Separation of the fraction < 2 μm, (2) Ca<sup>++</sup> exchange. A few droplets of a thick clay suspension are placed either on glass plate, ceramic plate or any other support. Most suitable is a porous ceramic plate that keeps water in its pores and thus gives water to the clay film during the measurement. Thickness and smoothness of the clay layer is crucial. No cracks, neither deformation may occur. The specimen loses slowly its fluidity. This must be done under laboratory conditions, without additional heating! Temperature and RH in the laboratory should be noted. The suspension loses slowly excess of water. The thin paste-like coating (film) on the support is formed and the specimen should not show desiccation of the rims. After completing the measurement it is recommended to check the position of the recorded basal reflection.

#### 6. EXAMPLES

Fig. 2 shows a steady dehydration of a Ca-exchanged montmorillonite of the size fraction < 2μm (derived from bentonite, Jelšovský Potok, Slovakia) from an oriented specimen on a ceramic tile. The first measurement was carried out on a wet specimen. After that the specimen was slowly dried in the measuring chamber at 97 % RH and measured at that condition. Then the specimen was equilibrated at 95 % RH for 10 minutes and measured again. This procedure was followed at 90, 80, 70, 60, 50, 40, 30, 20, 15, 10, 5 and 0 % RH. The d-value of the basal reflection decreased from 18.9 Å at 100 % RH to



**Fig. 2** Stepwise dehydration of montmorillonite. Locality: Jelšovský Potok, Slovakia. The basal reflection of montmorillonite shifts irregularly towards higher  $2\theta$  angles. On dehydration the position, the intensity and the line width change.

11.65 Å at 0 % RH. Between each step the specimen was conditioned for 10 minutes for the following RH. During the whole procedure the oriented specimen remained fixed in the specimen holder in the measuring chamber of the XRD apparatus. Upon dehydration, the basal reflection of montmorillonite shows a steady shift towards higher  $2\theta$  angles. Note that also the intensity and the line width change. Some line profiles exhibit a double peak that is caused by temporary coexistence of two different hydrous complexes in the montmorillonite interlayers. Rate of dehydration/hydration can be estimated from the shift per interval of the RH change. If montmorillonite would be exchanged with another cation, the positions of the peaks, the intensity, and the line widths will be different.

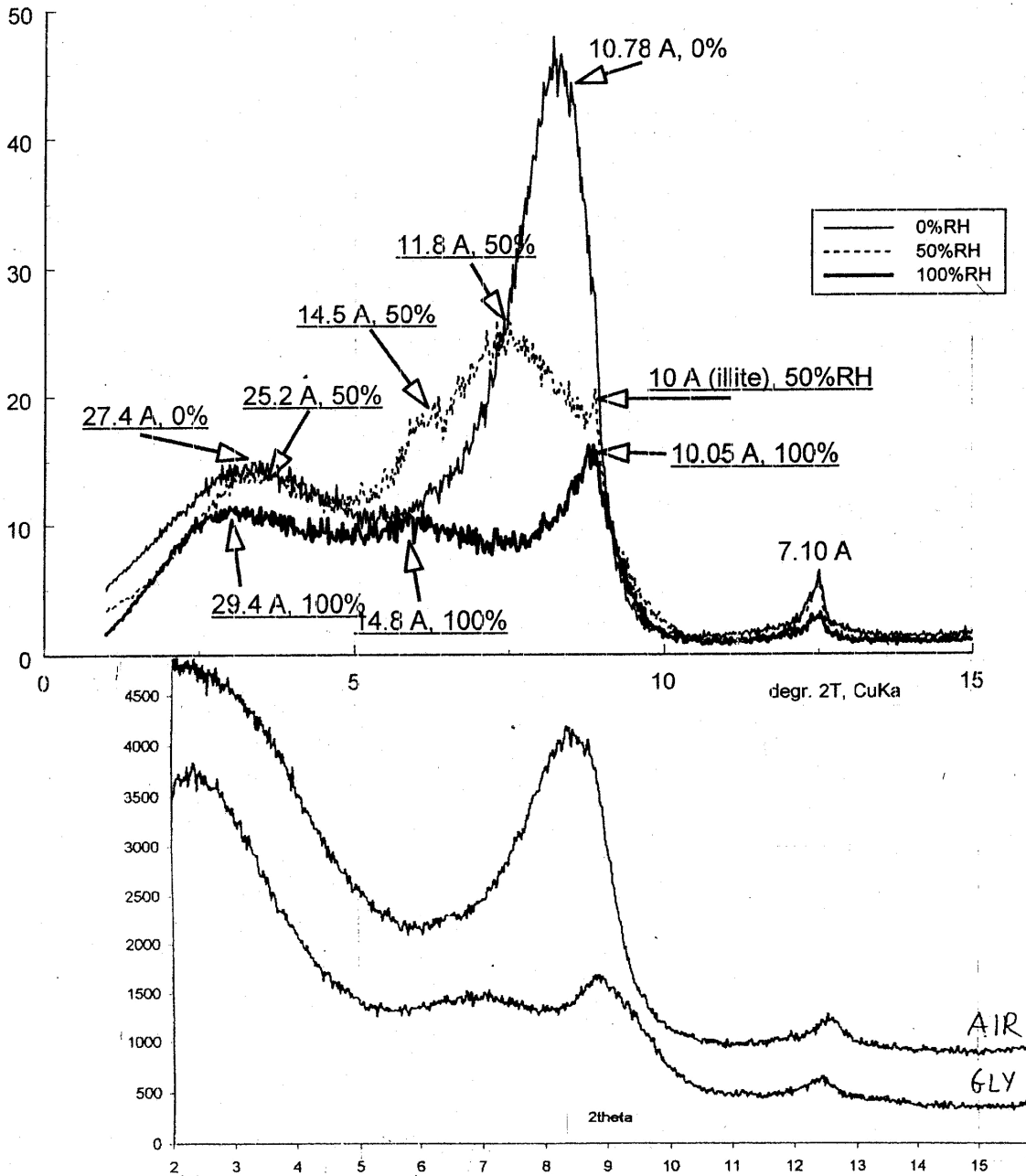
Fig. 3 shows a comparison of patterns of one sample hydrated and a glycolated  $< 0.2 \mu\text{m}$  clay fraction derived from a rock (locality Jodłówka, Poland, received through courtesy T. Dudek and J. Środoń) containing illite/smectite (I/S) mixed layer clay mineral with a minor amount of 7.10 Å mineral. The pattern of the air dried sample in the lower figure and the pattern at 0 % RH in the upper figure look similar. The pattern of the glycolated specimen (lower figure) is close to the pattern measured at 100 % RH (upper figure). New information is supplied by measurement at 50 % RH. The line profile is now

modulated, showing several additional peaks at 10.0 Å, 11.8 Å and 14.5 Å. It looks that in addition to the I/S mineral there are present other phases, probably pure illite (10 Å peak), partially expanded I/S (broad 11.8 Å peak), and a chloritized smectite (14.5 Å). The broad band at low angles is due to the extremely fine particles (Van der Gaast et al., 1986).

Fig. 4a shows a SEM photomicrograph and XRD patterns of the basal reflections of tubular halloysite (El Negredo, Central Spain) at 100, 50 and 0 % RH. At 100, 50 % RH both the 7.6 Å and 10 Å halloysite phases coexist. At 0 % RH the 10 Å phase apparently disappears.

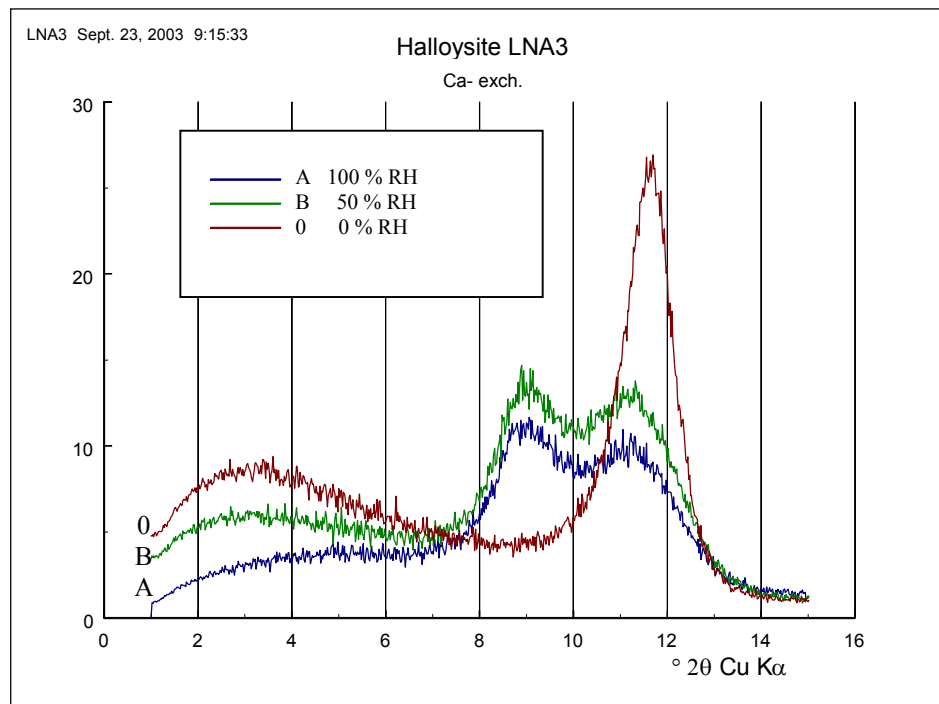
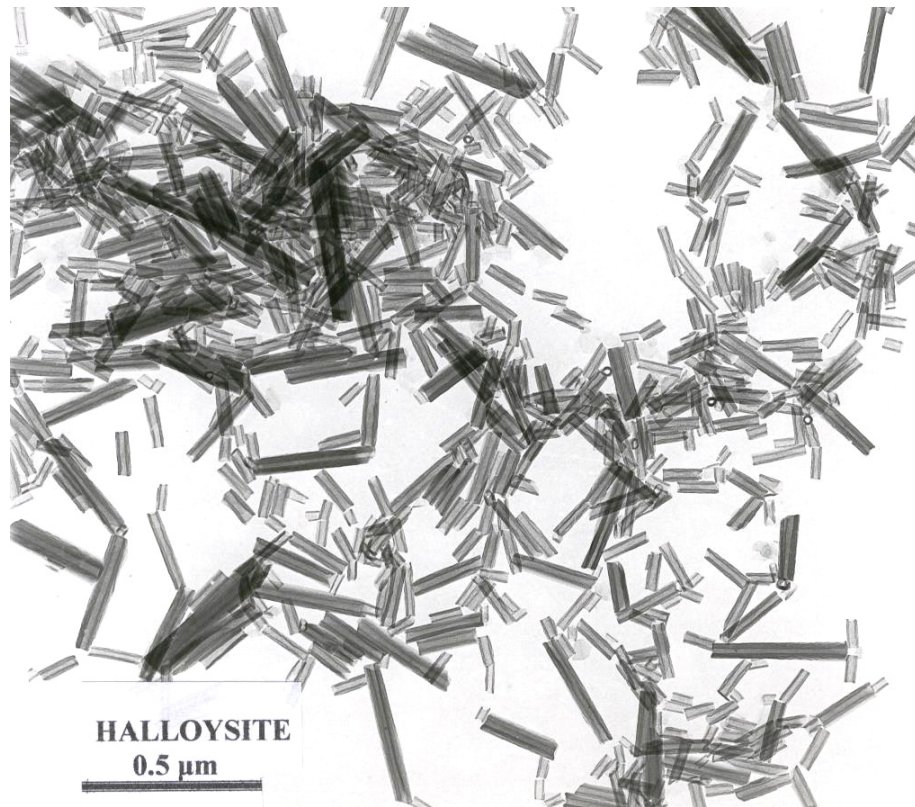
Fig. 4b shows the fit results (Peak Fit, Jandell©) of the three halloysite patterns. At 100 and 50 % RH the peaks of 7.6 and 10 Å are found, however, now in combination with two additional peaks, one at 8 and one at 8.9 Å. At 0 % RH the intensities of the 10 Å phase and of two intermediate phases decrease strongly. In contrast the peak of the 7.6 Å phase increases in intensity. These new intermediate phases are not yet completely understood.

Fig. 5 shows a recently discovered contraction of celadonite upon wetting. Kühnel and Van der Gaast (2001) reported such a contraction of maximally 0.2 Å for a number of micaceous 10 Å minerals (illite, celadonite, glauconite, including phengite and sericite). This effect is attributed to protonation of

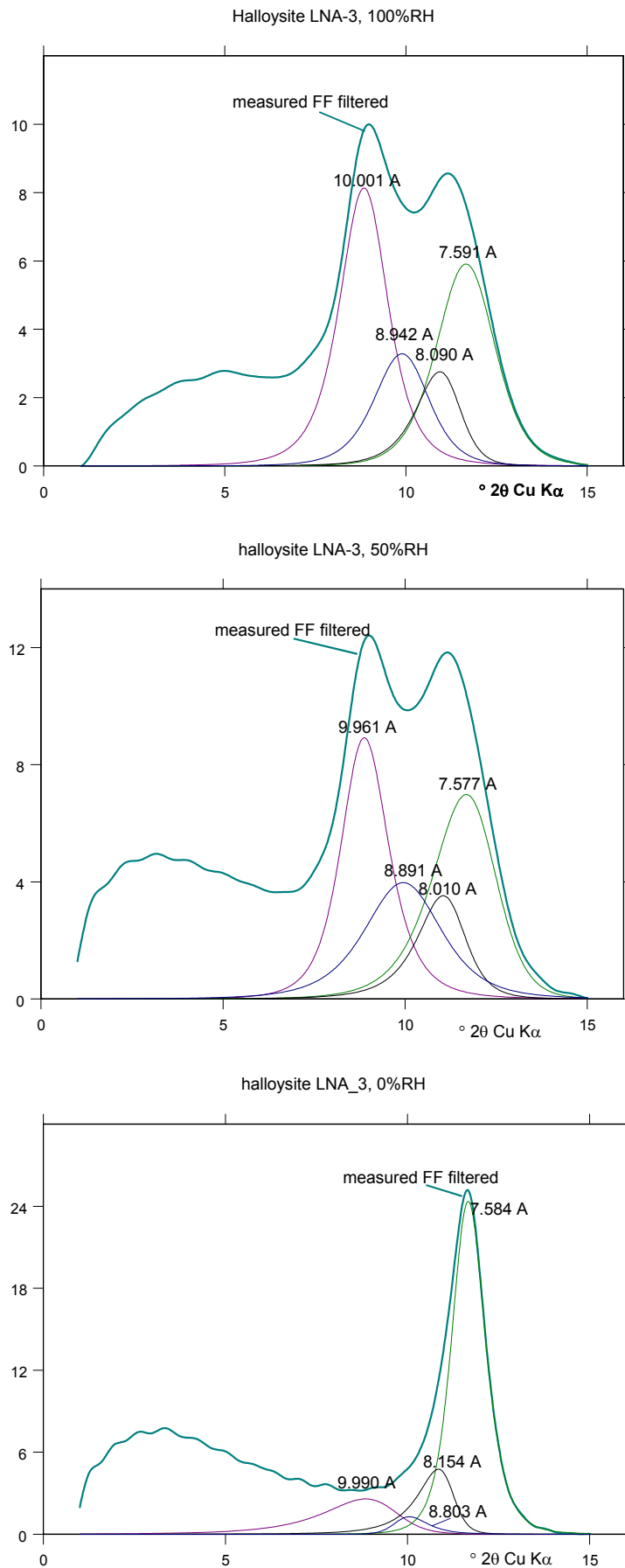


\*) kindly supplied by J.Środon and T.Dudek

**Fig. 3** Comparison of basal reflections from patterns of hydrated and glycolated specimens from a illite/smectite bearing clay fraction ( $< 0.2 \mu\text{m}$ ). Air dry and glycolated scans, courtesy T. Dudek, Poland.

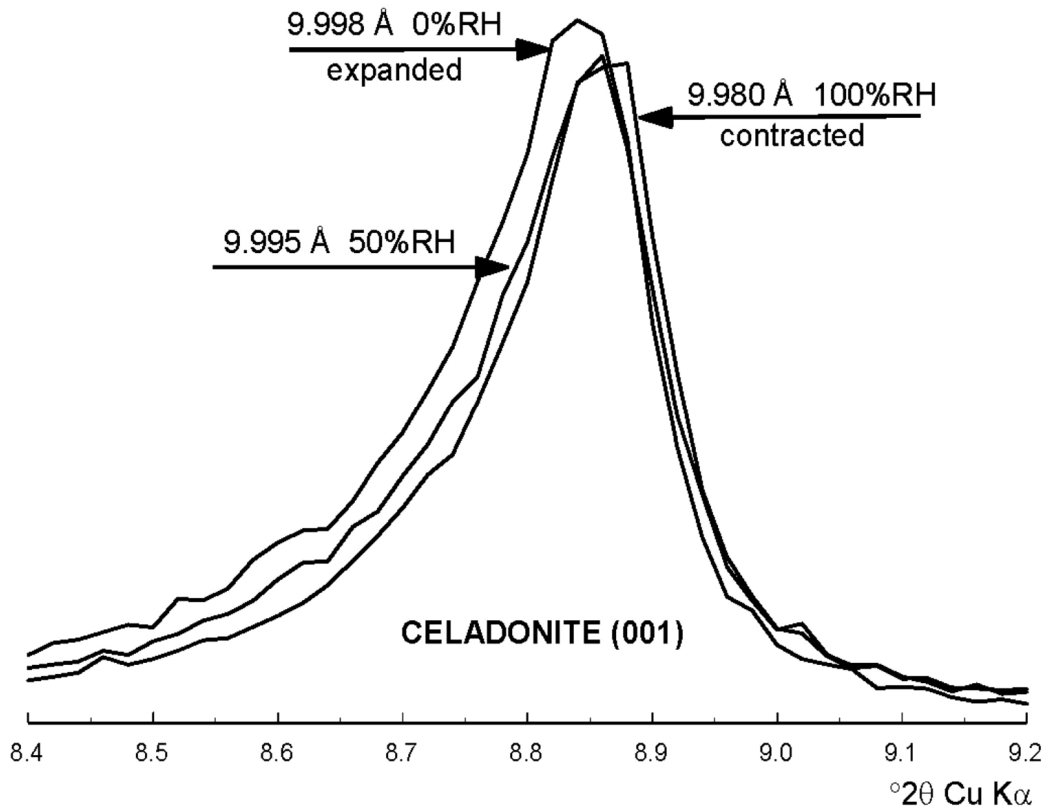


**Fig. 4a** SEM photomicrograph and basal reflections of 7.6 and 10  $\text{\AA}$  halloysite at 0, 50 and 100 % RH.



**Fig. 4b** Fitted line profiles using Peak Fit, Jandell©. The deconvolution proves the coexistence of 7.6 and 10Å halloysite and the presence of two intermediate phases, 8.1 and 8.8Å respectively.





**Fig. 5** An example of contraction of celadonite in wet state. (Celadonite from vesicles in a basaltoid, Gran Canaria, Spain)

water molecules that are located at deficient  $K^+$  positions in the interlayer upon drying the clay minerals. The protonation leads to expansion. In the wet state the protons are partially released from these water molecules. Contraction of the lattice follows instantly. With the celadonite a contraction of  $0.018 \text{ \AA}$  is detected.

## 7. CLOSING REMARKS

- Examination of wet samples is a tool for clay research. It supplies more information on expansion and shrinkage of clay minerals. It allows following hydration/dehydration process in progress. It enables estimation of reaction rate and hysteresis in considering effects of different exchangeable cations.
- In wet specimens the contraction of illite and other micaceous minerals can be also observed. Limited expansion in wet state helps also in detection of beidellite and vermiculite.
- Due to the humidity, XRD analyses of clay minerals carried out in different laboratories are often not comparable. Causes of that are in a different laboratory temperature and humidity during the measurement through the year. Therefore, reporting these data for all XRD analyses is a necessity.

- The exchangeable cations with different hydration energy affect significantly clay hydration/dehydration/rehydration. Consequently, XRD clay analyses show differences in d-values of basal reflections. Exchange of cations in interlayer of smectite by  $Ca^{++}$  improves the comparability of XRD results.

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