Applied Clay Science 135 (2017) 226–233

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Wetting-induced layer contraction in illite and mica-family relatives

Radko A. Kühnel [a,1], Sjierk J. Van der Gaast [b,2], Maarten A.T.M Broekmans [c,*], Benny K.G. Theng [d]

[a] Technical University Delft, The Netherlands
[b] Royal Netherlands Institute for Sea Research (NIOZ), Den Burg, The Netherlands
[c] Geological Survey of Norway (NGU), Trondheim, Norway
[d] Landcare Research, Palmerston North, New Zealand

ARTICLE INFO

Article history:
Received 15 March 2016
Received in revised form 20 September 2016
Accepted 23 September 2016
Available online 19 October 2016

Keywords:
Contraction/expansion
Humidity-controlled XRD
Hydronium
Illite
Mica
Protonation/deprotonation

ABSTRACT

When dry illite is wetted, its layer structure contracts along the c-axis by up to 0.2 Å. This behavior contrasts with that of smectite which shows interlayer swelling on wetting. Layer contraction has also been found to occur in glauconite and celadonite that are structurally more disordered than illite, as well as with phengite and artificially degraded hydromuscovite. In contrast, muscovite proper does not show contraction. The contraction is ascribed to the deprotonation of hydronium ions ($H_3O^+ \rightarrow H_2O + H^+$) occupying interlayer K^+ positions. The hydronium ion is approximately 5% larger than the neutral water molecule. This difference in size is proportional to the magnitude of contraction. The change in molecular volume and interlayer separation of illite particles may explain the anomalous decrease in density after dehydration under pressure. This paper reports on wetting-induced contraction in illite and related layer silicates, using humidity-controlled X-ray diffraction.

1. Introduction

Illite is a common constituent of the clay fraction of soils and sediments, and has been the subject of many investigations (Bailey, 1984a, 1984b; Środoń and Eberl, 1984; Meunier and Velde, 2004). Nevertheless, the physical and colloid chemical properties of illite are still incompletely understood. Compared to kaolinite-rich clays, illitic clays are more plastic in dispersion, and show a large increase in green-body strength after drying. On heating, illite-rich clays tend to sinter owing to the presence of potassium and mineralizers (e.g. H_3O^+ and F). Illites also show large variations in chemical composition, structure, and particle shape as well as in dehydration and rheological properties.

The term 'illite' was originally proposed by Grim et al. (1937) to denote a micaceous clay mineral with a 10 Å basal reflection, from the state of Illinois. This value has since been shown to vary from 9.8 to 10.2 Å (10.447 Å for tobelite, an ammonium mica). The thickness of the tetrahedral (T) and octahedral (O) sheet stack is related to the size and packing of the constituent ions (Radoslovich, 1960). Differences in the size of structural ions also lie behind the variation in layer thickness and reflection broadening when illite layers are deformed. Illite particles often contain smectite layers that expand on glycolation (MacEwan et al., 1961; Środoń and Eberl, 1984; Wilson, 1987). However, the presence of expandable material below 10% is difficult to detect, due to limits defined by instrumentation and analytical protocol. This has led Stixrude and Peacor (2002) to state that "…despite the importance of illite-smectite interstratified clay minerals, their structure is still controversial", while Bleam (1993) has advocated the use of atomic theories, quantum chemistry, electrostatic theory and crystal chemistry to characterize illites and mixed illite-smectites. Since the publication by Grim et al. (1937), hundreds of papers describing the structure and crystal chemistry of illite have been published. For details on origin, occurrence, application, structure, and properties of illite, the reader is kindly referred to the elaborate reviews by Bailey (1984a, 1984b), Środoń and Eberl (1984), and Meunier and Velde (2004).

The crystal structure of the true mica mineral illite can be described as a stack of tetrahedral-octahedral-tetrahedral (TOT) composite layers, held together by a range of possible interlayer species compensating the net negative charge of the TOT composites. Chemical bonding within the TOT-composite layer is predominantly covalent, lending rigidity against mechanical comminution and abrasion, as well as chemical stability against alteration. The composite layer consists of two tetrahedral layers with a single octahedral layer, hence micas are commonly referred to as '2:1 layer minerals'. Different stacking orders of the TOT composite layer gives rise to polytypism.

Details on crystalline structure and chemistry of micas are elaborated in Rieder et al. (1998), who group illite together with glauconite under the dioctahedral interlayer-deficient micas. Both illite and glauconite are recognized as series names, indicating the variable composition of the octahedral layer in the TOT-composite layer, as well as composition and degree of occupation of the interlayer. In contrast, muscovite is a

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[*] Corresponding author.
E-mail address: maarten.atm.broekmans@gmail.com (M.A.T.M. Broekmans).
[1] Deceased 05 December 2009.
[2] Retired.

http://dx.doi.org/10.1016/j.clay.2016.09.027
0169-1317/

potassic dioctahedral true mica with a nominally fully occupied interlayer, forming a series with its near siblings celadonite and aluminoceladonite, differing in the amounts of Mg and minor Fe^{2+} (but always subordinate to Al) in the octahedral layer in the TOT-composite layer. Similarly, phengite is a series name referring to potassic dioctahedral true micas close to the joins muscovite-celadonite or muscovite-aluminoceladonite.

Hydromuscovite has been referred to as 'hydrous mica' since the 4th International Congress of Soil Science in Amsterdam/NL in 1950 (see e.g. Heystek, 1954), and is considered distinct from illite; some varieties may represent mixed-layer silicates. Hydromuscovite contains less potassium, and hence more silica, alumina and structural water (released upon heating $\gg$100 °C) than 'muscovite sensu stricto' (also see 'ideal mica' of Brown and Norrish, 1952). Whereas Rieder et al. (1998) recommend use of 'interlayer-(cation-) deficient mica', the existence of 'hydromica' (or 'hydrous mica') is not formally discredited.

In contrast, chlorite is not a mica but defines its own hydrous-phyllosilicate group (e.g. Bailey, 1988). The structure of the commonest chlorite-group minerals clinochlore, sudoite and chamosite can be described as having a dioctahedral TOT-composite layer as in mica, but with the interlayer instead occupied by a layer of octahedrally coordinated (Al, Mg, Fe)-hydroxide, colloquially dubbed 'gibbsite-brucite layer'. Other chlorite-group members may contain other or additional element species. Consequently, opportunities for interlayer exchange in chlorite-group minerals are rather limited compared to micas.

In commenting on some discrepancies in Hower and Mowatt's (1966) mineralogical survey of illites, Loucks (1991) pointed out the lack of analytical precision and the presence of impurities in sample materials. He further proposed that the interlayer space of illite might be occupied by (1) neutral water molecules and cations, (2) hydronium ions and cations, or (3) cations, hydronium ions and neutral water molecules. Loucks (1991) then calculated the number of hydronium (H_3O^+) ions in the structure formulae of seventy-two illite samples.

As the name suggests, humidity controlled X-ray diffraction (XRD) analysis allows the specimen to be examined in an atmosphere at a strictly controlled relative humidity (RH). Using this technique, Kühnel and Van der Gaast (1993, 1996, 2001, 2005) have shown that wetting and drying induce instant, minor, and reversible changes in the illite structure. This study applies humidity-controlled XRD analysis to measure the wetting-induced layer contraction along the c-axis in illite and structurally related phyllosilicates of different origin, as well as to assess changes in the bonding of interlayer water molecules on wetting and drying.

2. Materials and methods

From the more than one hundred pure illites and smectite-bearing illites in the authors' clay samples collections, many show interlayer contraction on wetting, yet do not appear to contain any expansible smectite layers. For the present investigation, ten different pure illite samples (including celadonite and glauconite) were selected, together with one sample of muscovite and phengite. A sample of sericitic hydromuscovite separated from white phyllite collected at Jutulhogget along county road Rv3 through Rendalen, central Norway was also examined, in order to verify whether the applied sample preparation protocol would attribute chemical and structural degradation, leading to analytical artifacts.

Sample numbers, main constituent mineral, location, origin, impurity minerals, and the Munsell color codes of the selected samples are tabulated in Table 1.

The clay fraction, comprising particles <2 μm in 'equivalent spherical diameter', was separated by dispersing sample materials in water and subsequent gravity sedimentation. The charge-balancing cations in the thus obtained clay fractions were replaced with Ca^{2+} through exchange with 0.5 M $mol \cdot L^{-1}$ solution of $CaCl_2$, and subsequent removal of excess $CaCl_2$ by rinsing with a 0.001 M $mol \cdot L^{-1}$ solution of $CaCl_2$. This pretreatment enables reliable identification of illite-smectite mixed-layer structures by XRD upon glycolation (e.g. Fiore et al., 2011).

Oriented specimens for humidity controlled XRD analysis were mounted by placing an aqueous dispersion containing ~10 mg of solid sample material on a porous ceramic tile, and finished with an object carrier glass for microscopy, achieving a final specimen layer thickness on the order of 30 μm.

The thus prepared specimen was then firmly affixed in a closed specimen chamber. Relative humidity of the chamber atmosphere was precisely controlled by flushing with a mixture of dry and wet N_2 gas from a RH generator, for 0% RH with dry N_2 only. The experimental and instrumental setup are elaborated in detail in Kühnel and Van der Gaast (1993). X-ray diffractograms for wet specimens (labeled "100% RH" in Figs. 1–7) were acquired immediately after introduction into the chamber. The specimens were then allowed to dry at ambient room conditions (within 22 ± 2 °C, 50–60% RH over the course of the measurements) for 12 h prior to re-analysis at 50% RH, and finally at 0% RH. Specimens resided in the controlled-humidity sample chamber until all analyses at 100%, 50%, and 0% RH were completed, so as to eliminate possible specimen displacement and peak-position shifts. With 1% specimen expansion, initial specimen layer thickness of 30 μm theoretically increases to 30.3 μm, and at 5% expansion to 31.5 μm.

Mounted specimens were measured on a custom-built θ-θ goniometer, consisting of two one-circle Huber 420 goniometers with 200 mm radius. The precision of the combined θ-θ goniometer is ±0.001°2θ (about ~3.5 μm, i.e., 2.3× larger than 5% specimen expansion, and over 11× larger than 1% expansion), equivalent to a resolution of ±0.001 Å at typical angles where the basal (001) reflection of illite is measured. At low diffraction angles, first-order reflections can be considered as single peaks in fitting procedures.

Table 1
Characteristics of samples analyzed in this paper.

Sample	Mineral name	Location	Origin[a]	Impurity constituents	Munsell[b]
BB-0	muscovite	Georgia, USA	P	chlorite	n/a
BB-1	illite, cambrian shale	Montana, USA	S/M	quartz, chlorite	n/a
BB-2	illite, ordovician shale	Spain	S/M	quartz, kaolinite, organic matter	n/a
BB-3	hydro muscovite	Norway	M	quartz	N9[c]
BB-4	illite, precambrian	Argentina	S/M	goethite	10YR 6/6
BB-5	phengite	Brazil	H	quartz, feldspar	5Y 7/2
BB-6	synthetic NH_4-illite	Šucha et al. (1998)	H	illite/smectite mixed-layer	n/a
BB-7	glauconite	Netherlands	S	quartz, feldspar, kaolinite	n/a
BB-8	celadonite from basalt	Spain	H	chlorite/smectite, quartz	n/a
BB-9	illite, permian shale	Czech Republic	S	quartz, chlorite	5Y 8/1
BB-10	celadonite	Brazil	H	quartz	10G 6/2
BB-11	celadonite	Cyprus	H	feldspar, quartz	10GY 6/4

[a] P = pegmatitic, S = sedimentary, M = metamorphic, H = hydrothermal.
[b] Color code cf. Munsell Rock Color Book (2009).
[c] Identical for subsamples BB-3 A and BB-3B in Table 3.