

Layer charge and heavy metals structures in hydrated 2 : 1 silicates: state of the art and new advances on cadmium

Daniele Malferrari^I, Maria Franca Brigatti^{*,I}, Chiara Elmi^I, Angela Laurora^I and Giovanni Valdrè^{II}

^I Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, L.go S. Eufemia 19, 41100 Modena, Italy

^{II} Dipartimento di Scienze della Terra e Geologico-Ambientali, Università di Bologna, Piazza di Porta San Donato, 40126 Bologna, Italy

Received October 17, 2008; accepted January 14, 2009

*Montmorillonite / Vermiculite / Layer charge /
Heavy metals / Cadmium /
Powder diffraction structure analysis / X-ray diffraction*

Abstract. This study will discuss how layer charge can affect chemical speciation and topology of heavy metals adsorbed to 2 : 1 layer silicates, by providing: i) an overview of literature data; ii) experimental data on Cd complexes adsorbed by 2 : 1 layer silicates with different layer charge (montmorillonite and vermiculite); iii) a comparison between our results and literature data. This study will also be supported by several different experimental techniques such as chemical and thermal analyses, X-ray powder diffraction and X-ray absorption spectroscopy.

Based on our data Cd atoms were found to complex water molecules in both clay minerals and to show four-fold coordination in montmorillonite (Cd–O distances of 2.24 Å) and six-fold coordination in vermiculite (Cd–O distances of 2.16 and 2.28 Å). Furthermore our models clearly suggest that Cd mainly bonds to interlayer water, without neglecting the more limited, but still significant, Cd multinuclear surface complexes at the octahedral broken edges. Both clay minerals show H₂O/Cd ratio, as evidenced by thermal analyses, drastically higher than expected from X-ray absorption spectroscopy data, thus implying that most of the water molecules are only loosely coordinated to interlayer cations.

Introduction

Layer silicates 2 : 1, such as clay minerals, are widely used also because of their surface properties, which significantly affect the interaction of the layer with waste materials, including heavy metals, organic molecules, and organo-metallic complexes. Surface properties are significantly influenced by layer charge. In swelling 2 : 1 clays, such as montmorillonite- and vermiculite-like structure, the 2 : 1 layers are constituted by two tetrahedral sheets sandwiching an octahedral one, thus finally imparting a negative charge to the layer, which is, by definition, the layer charge [1]. The overall structure neutrality is assured by

interlayer cations, which are placed between two adjacent 2 : 1 layers (*i.e.*, in the interlayer region) and are surrounded by water molecules. Layer silicates can present different values and location of layer charge, which can be generated by tetrahedral or octahedral substitutions. In montmorillonite-like layers, the negative layer charge, resulting from R²⁺-for-R³⁺ substitutions in the octahedral sheet, is distributed among basal oxygen atoms that are thus weakly under-saturated. Otherwise, when Al³⁺-for-Si⁴⁺ substitution occurs in tetrahedral sheet, such as in vermiculite, the charge deficit is distributed among the nearest three neighbour basal oxygen atoms. These oxygen atoms are strongly under-saturated, thus giving strong attractive interactions with interlayer cations, which may result in a lower layer hydration [2, 3]. A further effect is on adsorption processes. According to the HSAB theory of Pearson [4, 5], the hydrated interlayer cations and the layer of smectites can be considered Lewis acids and bases, respectively [6]. The location of the layer charge determines the strength of the Lewis base: the 2 : 1 layer behaves like a soft base when the layer charge is located in the octahedral sheet, whereas it behaves like a hard base when the charge is located in the tetrahedral sites. Hard bases bond preferentially to hard acids and soft bases to soft acids, thus also confirming the fundamental role of layer charge location on exchange processes, since different heavy metal cations can be classified as hard or soft Lewis acids. Furthermore heavy metals do not only form complexes with water molecules in the interlayer (C-like structures, Fig. 1), but also occur in different sorption sites into clay structure, depending from layer charge. These latter structures, as detailed in Fig. 1, can be classified as multinuclear complexes (A- and B-like structures) and as inner-sphere complexes (D-like structures) [7, 8]. Formation of inner sphere complexes occurs when ions bind directly to the surface without involving any water molecule. It is limited to ions, like heavy metals cations, with high affinity for surface sites, also showing covalent bonds. This is, according to recent studies, the case for Cu in vermiculite, which is hosted mainly at vermiculite edges, rather than in the interlayer, without forming any multinuclear surface precipitates. In particular, the presence of a second-shell for Al, Si, or Mg atoms at 3.02 Å and the angle between Cu atom and the mineral sorption

* Correspondence author (e-mail: brigatti@unimore.it)

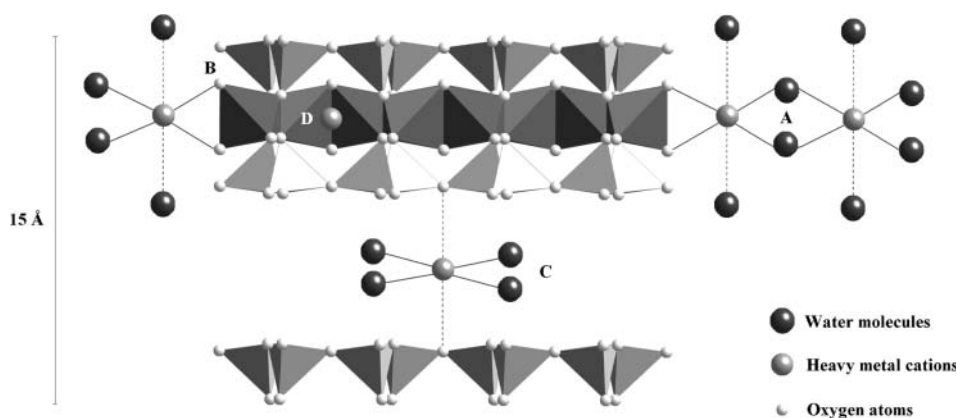


Fig. 1. Sketch of a 2:1 layer silicate with cations forming both multinuclear complexes such as dimers (A), monomer (B) or adsorbed in the interlayer (C, here in four-fold coordination) and inner-sphere complexes (D) bonded to octahedral broken edges.

sites (*i.e.* 68° with respect to [001]) suggest that the bonding environment of Cu in vermiculite edge is corner-sharing, rather than edge sharing, with tetrahedral Si and Al, or with Mg ligands in the octahedron [9]. Finally, at high temperatures, some heavy metal cations can also enter vacant sites in the octahedral sheet [10, 11].

In montmorillonite and in beidellite (a dioctahedral smectite with layer charge mostly located in the tetrahedral sites but with a net negative tetrahedral charge lower than in vermiculite) EXAFS data suggest that Cu is surrounded by four oxygen atoms at Cu–O distances less than 2.0 Å. The Cu–Cu distances of two neighbouring Cu atoms are 3.0 and 6.0 Å, approximately. The first distance agrees with the formation both of inner sphere complexes and multinuclear surface complexes on the mineral edge sites, whereas the latter agrees with hydrated Cu cations in the interlayer [12, 13]. Furthermore, when temperature increases up to 350°C, a proportion of Cu(II) cations diffuses into the octahedral vacancies, which further increase when increasing the heating time [10, 14].

Studies on mercury hosted in 2:1 silicate layers [15, 16] show that the metal binds to the 2:1 layer as interlayer Hg–OH₂ complexes (C-like structure) both in montmorillonite and vermiculite and forms A- and B-like structures at the edge sites only in vermiculite (Fig. 1). In fact, the most relevant contribution to the EXAFS region of montmorillonite can be ascribed to Hg surrounded by six oxygen atoms, three closer to Hg, at a distance of 1.99 Å and the remaining at 2.40 Å. Like in montmorillonite, Hg in vermiculite is surrounded by six oxygen atoms with two triads of atoms at 1.95 and 2.32 Å from the central Hg, respectively. Furthermore, longer Hg–O distances at 2.77 and 2.93 Å and Hg–Hg distances at 3.31 and 3.37 Å confirm the presence of inner sphere and multinuclear surface complexes bonded to the corners of vermiculite broken edges [15]. Thermal behaviour of the two Hg-treated 2:1 layer silicates is different, mostly because of the different layer charge [16]. In montmorillonite Hg ascribed to Hg–H₂O interlayer complexes is removed at temperature below 250 °C, without affecting HgO inner-sphere and multinuclear complexes, at least up to $T = 450^\circ\text{C}$. Afterwards, XANES spectra show that the Hg–L_{III} edge signal gradually decreases and completely disappears at $T = 700^\circ\text{C}$, indicating that the layer is completely Hg free. The thermal behaviour of Hg treated vermiculite suggests the prevalence of HgO inner-sphere and

multinuclear complexes. Both reactions associated to Hg release occur in conjunction with dehydroxylation reactions at $T \cong 500^\circ\text{C}$ and at $T \cong 800^\circ\text{C}$. This behaviour is probably not associated to Hg occupying the octahedral sites, but rather to crystal chemical features of this layer silicate. Mercury oxide, if hosted in the ditrigonal cavity, can strongly bind the silicate layer; the dehydroxylation reaction of the octahedral sheet could, in this way, catalyze the thermal decomposition of the adsorbed Hg.

Clays and related layered minerals are usually fine grained and poorly crystalline materials, lacking long-range order, especially for what concerns the stacking behaviour of the layers. The structure characterization of the crystallographic surrounding of sorbed species is thus mostly based on powder data. This study will include X-ray powder diffraction, thermal analysis and X-ray absorption spectroscopy results, to demonstrate the relevance of layer charge location in controlling the topology of Cd complexes. The structural environment of Cd in the soft base montmorillonite and in the hard base vermiculite will be thus investigated and results compared to previously referenced literature data.

Experimental

Samples and treatments

Samples used here are montmorillonite and vermiculite. The soft base montmorillonite is the Clay Minerals Society standard STx-1 from Gonzales County (Texas), chemical formula $^{[iv]}\text{Si}_{4.0}^{[vii]}(\text{Al}_{1.59}\text{Fe}^{3+}_{0.035}\text{Fe}^{2+}_{0.01}\text{Mg}^{2+}_{0.14}\text{Ti}_{0.01})^{[xiii]}(\text{Ca}_{0.12}\text{Na}_{0.035}\text{K}_{0.005})\text{O}_{10}(\text{OH})_{22}$ and cation exchange capacity (CEC) = 84.4 meq/100 g. The hard base vermiculite is from Bikita (Zimbabwe), with chemical formula $^{[iv]}(\text{Si}_{3.041}\text{Al}_{0.959})^{[vii]}(\text{Ti}_{0.023}\text{Al}_{0.049}\text{Fe}^{3+}_{0.403}\text{Mg}_{2.518}\text{Mn}_{0.007})^{[xiii]}(\text{Mg}_{0.228}\text{Na}_{0.005})\text{O}_{10}(\text{F}_{0.152}\text{OH}_{1.848})$ and CEC = 116 meq/100 g. Additional mineralogical data on studied samples are reported in [17, 18].

The procedure used to obtain Cd-complexed minerals is discussed in detail in Ref. [18] and here briefly summarised. The size fraction $<1\ \mu\text{m}$ of each sample is saturated with 1 M solution of sodium acetate. Cd complexed minerals are then obtained by dipping and continuously shaking each sample in 10^{-3} M Cd solution at pH = 6.5 and $T = 25^\circ\text{C}$. Chosen solution concentration and pH

value are consistent with theoretical calculations performed via the MINTEQA2 program [19]. As described in [18], several washing steps are applied to samples after each treatment.

X-ray powder diffraction (XRPD)

XRPD patterns were recorded from oriented mounts of the air-dried samples in the temperature range $25 \leq T (^{\circ}\text{C}) \leq 400$ (heating rate $2^{\circ}\text{C}/\text{min}$) using a Philips X'Pert PRO diffractometer equipped with X'Celerator detector ($\text{CuK}\alpha$ radiation 40 kV and 40 mA; two theta range: $4\text{--}75^{\circ}$; quartz as standard) and HTK16 Anton Paar *in situ* heating apparatus.

Thermal analysis (TGA)

Thermo-gravimetric behaviour is investigated by a Seiko SSC 5200 thermal analyzer. The instrument is coupled with a quadrupole mass spectrometer (ESS, GeneSys Quadstar 422) to analyze gases evolved during thermal reactions.

X-ray absorption spectroscopy (XAS)

Cd *K*-edge X-ray absorption spectra are collected at the European Synchrotron Radiation Facility (ESRF), GILDA beam-line, in transmission mode on powder-pressed disks constituted from an appropriate mixture of sample (clay mineral) and cellulose. Energy calibration is performed using a Cd metal foil with the first inflection point of the *K*-absorption edge at 26711 eV. Samples are analyzed at liquid nitrogen temperature using an evacuated cryostat.

The experimental Fourier filtered EXAFS spectrum is compared to theoretical EXAFS spectra, calculated via FEFF-8 program [20] using $\text{Cd}(\text{OH})_2$ and CdO as reference compounds. A Fourier transform of the experimental spectrum provides the approximate radial distribution function around the central absorbing atom; the peaks represent shells of atoms surrounding the central one.

Results

After treatment, according to the different CEC values and despite the greater amount of H_2O in montmorillonite, the Cd content is with 9.47 meq/100 g lower than in vermiculite (10.90 meq/100 g) (Fig. 2a). The weight loss related to H_2O molecules in the temperature range $25\text{--}250^{\circ}\text{C}$ is 12.4% for montmorillonite and 9.4% for vermiculite. Similarly, d_{001} values at room temperature are 15.42 and 14.80 Å for montmorillonite and vermiculite, respectively (Table 1). The variation of these distances, as a function of temperature, can be ascribed to the different value and location of layer charge. The position of the (001) reflection decreases continuously in the temperature range $25 \leq T (^{\circ}\text{C}) \leq 300$, suggesting that the closest 2:1 packing configuration is reached at 275°C for soft base montmorillonite ($d_{001} = 9.90$ Å), unlike the hard base vermiculite that maintains a greater periodicity ($d_{001} = 10.30$ Å) up to 300°C . Montmorillonite, despite its higher H_2O

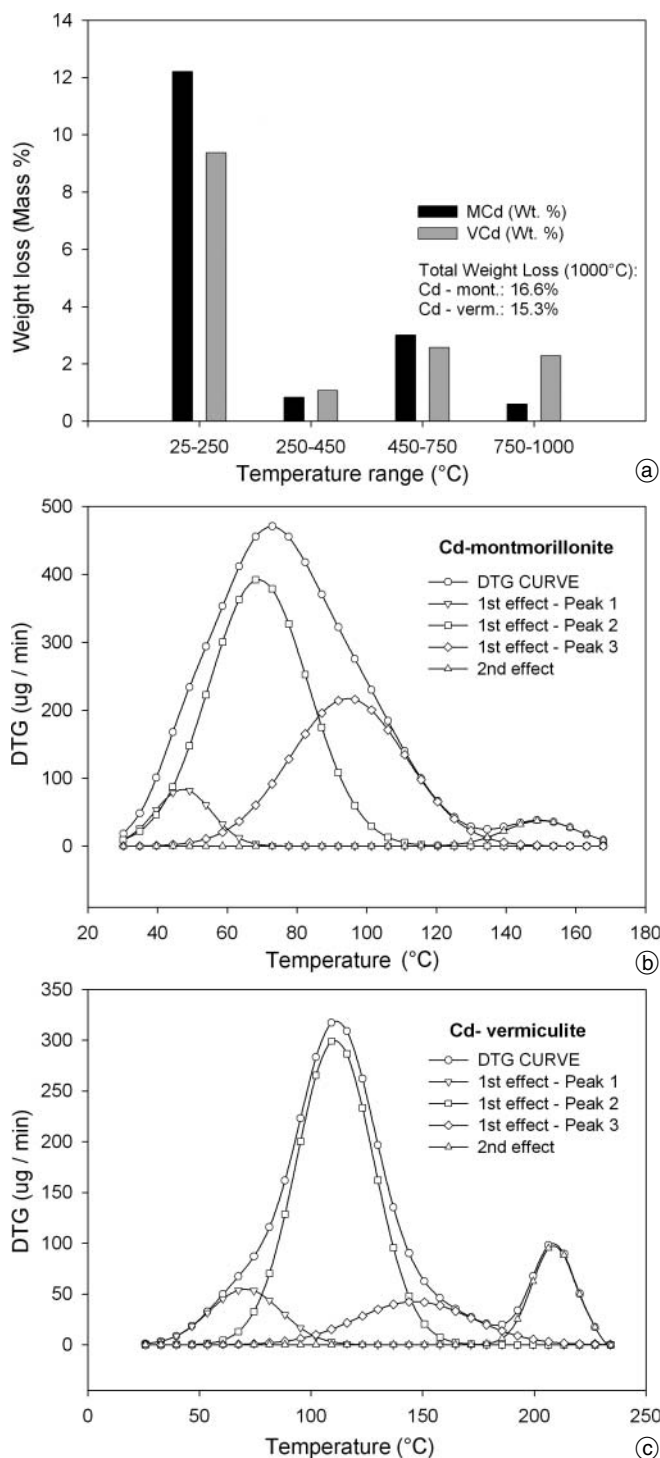


Fig. 2. Thermal analyses of Cd treated montmorillonite and vermiculite. (a) Distribution of the weight loss in various thermal ranges as a function of the main reaction occurring during heating and calculation of the deconvoluted curves for montmorillonite (b) and vermiculite (c).

content, thus requires a lower energy to reach its closest packing configuration, because of the lower bond strength of basal tetrahedral oxygen atoms toward interlayer species. This result is finally consistent with a more disordered H_2O -rich configuration for montmorillonite, where H_2O molecules are weakly bonded to the layer structure.

The different water to heavy metal ratio may also suggest either that the interlayer cation (Cd) is less hydrated

Table 1. Variation of d_{001} (Å) spacing as function of temperature.

Temp. (°C)	Cd(II)-mont.	Cd(II)-verm.
25.0	15.42	14.80
50.0	12.78	12.00
75.0	11.94	11.90
100	11.75	11.80
125	11.28	11.70
150	10.44	11.00
175	10.15	10.50
200	10.07	10.40
225	9.95	10.40
250	9.91	10.40
275	9.90	10.30
300	9.90	10.30

in vermiculite than in montmorillonite or the presence, in this latter, of a greater number of water molecules, not bonded to the cation, also according to what reported in [21].

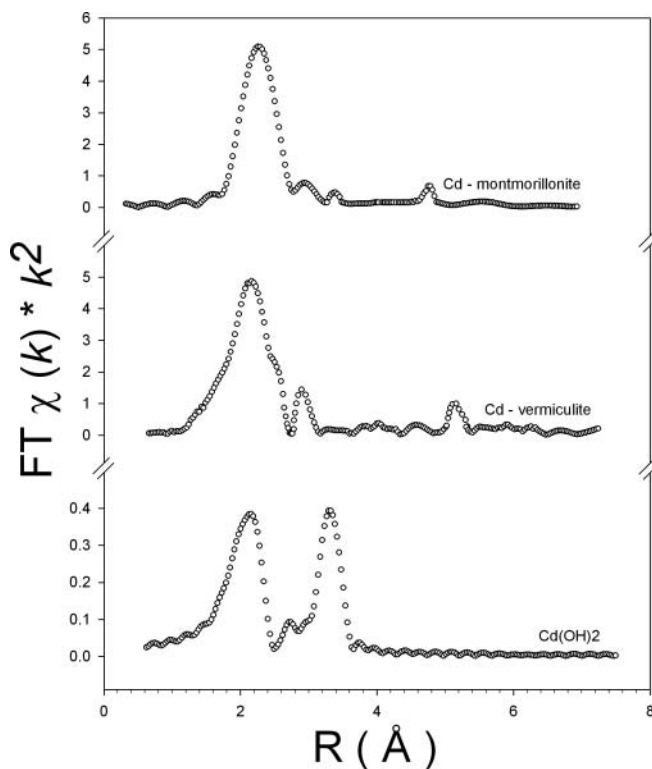
Further information, on the role of the interlayer cation, may be derived from the dehydration dynamics at increasing temperature, since different bond energy and layer topology correspond to different values of reaction temperature. It should however be considered that the hydration heterogeneity may render extremely difficult the characterization of dehydration dynamics.

Reported d_{001} values at room temperature are consistent for both minerals with bihydrated interlayer structures. When increasing temperature, the shape of the peaks (not reported) and d_{001} values (Table 1) suggest that the structures gradually evolve from one hydration state to another, probably via the formation of mixed-layer structures, as also observed for untreated montmorillonite [21]. Dehydration reactions show two main effects for both the clay minerals in $25 \leq T$ (°C) ≤ 250 range (Fig. 2b and 2c), probably contributed by various reactions as suggested by deconvoluted curves. The best fit for the first effect (at $T \cong 75$ °C in montmorillonite and $T \cong 115$ °C in vermiculite) is obtained with the contribution of three Gaussian fitting curves. The temperature values given by the maximum point of the second and third Gaussian curve could represent the transition from two hydrated layer to one hydrated layer structure and from one hydrated layer to dehydrated layer structure, respectively. The maximum of the first Gaussian curve ($T = 45$ and 75 °C in montmorillonite and vermiculite, respectively) and the second effect, revealed at temperatures lower than 250 °C, well evidence that the water to Cd ratio in both clay minerals is drastically higher (35.2 and 23.8 in montmorillonite and vermiculite, respectively) than suggested by X-ray Absorption Spectroscopy (four-fold coordination for montmorillonite and six-fold coordination for vermiculite), thus probably indicating that in both layer silicates most of the water molecules are not coordinated, or only weakly coordinated, to the interlayer cation. The removal of these water molecules strongly depends on their location and could take part both at very low temperature (surface water, first Gaussian curve fitting the first effect) or at higher tem-

perature (micro- and/or macro-pore water, effects at 155 and 210 °C for montmorillonite and vermiculite, respectively).

The higher reaction temperature observed in vermiculite with respect to montmorillonite well agrees with the higher layer charge of the hard base. Besides, the higher Cd content in vermiculite can additionally explain the different dehydration kinetics of the two clay minerals: in vermiculite, the Cd attraction toward water molecules in interlayer is greater than in montmorillonite, thus allowing a better organization of the interlayer complexes.

The experimental EXAFS spectrum ($\chi(k)$) of montmorillonite shows four main coordination shells at 2.24 , 2.98 , 3.30 and 4.76 Å (Fig. 3). The comparison with Cd(OH)₂ model compound suggests that distances at 2.24 Å (four-fold coordination) are consistent with Cd–O bond in Cd–OH₂ complexes (*i.e.*, C-like structures, Fig. 1). A single Cd–Cd distances at 3.30 Å and two-fold coordinated Cd–Cd at 4.76 Å are also present. The first distance is consistent with the formation of multinuclear surface complexes (A-like structures, Fig. 1), the second distance suggests Cd–OH₂ complexes in the interlayer. The shell at 2.98 Å could be attributed to bonds between A- or B-like structures with tetrahedral or octahedral broken-edge corners (*i.e.*, Cd–^[VI]Al or Cd–^[IV](Si, Al) bonds). To clarify previous assumptions a structural model was simulated starting from pyrophyllite atomic positions. Main differences between montmorillonite and pyrophyllite are related to layer thickness, which can be measured for both minerals. Pyrophyllite structural coordinates [22] in *P1* symmetry, were thus converted and suited to montmorillonite unit cell. Different scenarios, either with Cd located only at the interlayer or also bonded to oxygen atoms lo-

**Fig. 3.** Fourier Transform of Cd *K*-edge EXAFS experimental data for Cd-exchanged montmorillonite and vermiculite and for Cd(OH)₂.

cated at the octahedron and/or at the tetrahedron broken edges, were thus formulated. The model clearly suggests that Cd mainly bonds to interlayer water and that multinuclear surface complexes bond to octahedral broken edges.

As in montmorillonite, vermiculite experimental spectra are well fitted by Cd(OH)₂ model compound. In vermiculite, Cd is coordinated to six water molecules, four with Cd–O distances at 2.16 Å and two with Cd–O distances at 2.28 Å. The structural model obtained from parameters reported in [23], suggests that the formation of inner sphere complexes (D-like structure, Fig. 1) and multinuclear surface complexes at the octahedral edges (A-, B-like structure, Fig. 1) cannot be excluded. In fact, the Cd–Cd distances of 2.90 Å indicate that Cd is adsorbed as a multinuclear surface complex. The shell at 5.05 Å is representative of Cd adsorbed in the interlayer. Thus, the interlayer cations appear to be more separated in vermiculite than in montmorillonite, also consistently with its six-fold coordination with water molecules.

Concluding remarks

This contribution addresses the structural surrounding and coordination of Cd in both high and low charge layer silicates. A comparison with literature data is also introduced for Cu and Hg.

All considered heavy metals are demonstrated either to form multinuclear surface complexes at the layer broken edges or to complex interlayer H₂O. However, different structures can be identified depending on layer silicate charge and on the complexing heavy metal. Layer charge location mostly affects the interlayer hydration: in montmorillonite showing low layer charge, water molecules, also not bonded to the interlayer cation, are present in greater amount. Cd and Hg show a distorted six-fold coordination with two longer distances and four shorter ones, where bond lengths depend on layer charge. Cu is an exception because of its predominant four-fold coordination in montmorillonite and does not form interlayer complexes in vermiculite but rather multinuclear complexes at layer broken edges, unlike Cd and Hg, which give both interlayer and multinuclear complexes at layer broken edges. This different behaviour can be possibly ascribed to the heavy metal ionic radius, which is shorter in Cu.

Acknowledgments. Comments from two anonymous reviewers are kindly acknowledged. We would like to acknowledge the financial support from PRIN “Micas: cation ordering, anionic composition as petrogenetic control factors” and the beam-time availability at ESRF (European Synchrotron Radiation Facility, BM08 – Gilda Beam Line). An appreciated support was also provided by Centro Interdipartimentale Grandi Strumenti (CIGS) of Modena and Reggio Emilia University and by its staff.

References

- [1] Brindley, G.W.; Brown, G.: Crystal Structures of Clay Minerals and their X-ray identification. Mineralogical Society, London 1980.
- [2] Laird, D.A.: Model for crystalline swelling of 2:1 phyllosilicates. *Clays Clay Miner.* **44** (1996) 553–559.
- [3] Laird, D.A.: Layer charge influences on the hydration of expandable 2:1 phyllosilicates. *Clays Clay Miner.* **47** (1999) 630–636.
- [4] Pearson, R.G.: Hard and soft acids and bases. *J. Am. Chem. Soc.* **85** (1963) 3533–3539.
- [5] Pearson, R.G.: Hard and soft acids and bases HSAB, part 1: Fundamental principles. *J. Chem. Educ.* **45** (1968) 581–587.
- [6] Xu, S.; Harsh, J.B.: Alkali cation selectivity and surface charge of 2:1 clay minerals. *Clays Clay Miner.* **40** (1992) 567–574.
- [7] Cheah, S.F.; Brown, G.E.; Parks, G.A.: XAFS study of Cu model compounds and Cu sorption products on amorphous SiO₂, Al₂O₃ and anatase. *Am. Mineral.* **55** (2000) 118–132.
- [8] Strawn, D.G.; Palmer, N.P.; Furnare, L.; Goodell, C.; Amonette, J.; Ukkadapu, R.: Mechanisms of copper sorption on smectites. *Clays Clay Miner.* **52** (2004) 321–333.
- [9] Furnare, L.J.; Vailionis, A.; Strawn, D.G.: Polarized XANES and EXAFS spectroscopic investigation into copper(II) complexes on vermiculite. *Geochim. Cosmochim. Ac.* **69** (2005) 5219–5231.
- [10] McBride, M.; Mortland, M.: Copper (II) interactions with montmorillonite: Evidence from physical methods. *Proc. Soil Sci. Soc. Am.* **38** (1974) 408–415.
- [11] Mosser, C.; Michot, L.J.; Villeras, F.; Romeo, M.: Migration of cations in copper(II)-exchanged montmorillonite and laponite upon heating. *Clays Clay Miner.* **45** (1997) 789–802.
- [12] Morton, J.D.; Semrau, J.D.; Hayes, K.F.: An X-ray absorption spectroscopy study of the structure and reversibility of copper adsorbed to montmorillonite clay. *Geochim. Cosmochim. Ac.* **65** (2001) 2709–2722.
- [13] Brigatti, M.F.; Colonna, S.; Malferrari, D.; Medici, L.: Characterization of Cu-complexes in smectite with different layer charge location: chemical, thermal and EXAFS studies. *Geochim. Cosmochim. Ac.* **68** (2004) 781–788.
- [14] Karmous, M.S.; Ben Rhaïem, H.; Naamen, S.; Oueslati, W.; Ben Haj Amara A.: The interlayer structure and thermal behavior of Cu and Ni montmorillonites. *Z. Kristallogr. Suppl.* **23** (2006) 431–436.
- [15] Brigatti, M.F.; Colonna, S.; Malferrari, D.; Medici, L.; Poppi, L.: Mercury adsorption by montmorillonite and vermiculite: a combined XRD, TG-MS, and EXAFS study. *Appl. Clay Sci.* **28** (2005) 1–8.
- [16] Malferrari, D.; Brigatti, M.F.; Marcelli, A.; Chu, W.; Wu, Z.: Modification of Hg complexes in layered silicates with temperature: an in situ XAS study. *Micropor. Mesopor. Mat.* **107** (2008) 128–133.
- [17] Costanzo, P.M.; Guggenheim, S.: Clay Minerals Society Source. *Clays Clay Miner.* **49** (2001) 371–453.
- [18] Malferrari, D.; Brigatti, M.F.; Laurora, A.; Pini, S.; Medici, L.: Sorption kinetics and chemical forms of Cd(II) sorbed by thiol-functionalized 2:1 clay minerals. *J. Hazard. Mater.* **143** (2007) 73–81.
- [19] Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J.: MINTEQA2/PRODEFA2, A geochemical assessment model for environmental system: version 3.0, 1991. United States Environmental Protection Agency, Athens, Georgia 30613.
- [20] Ankudinov, A.L.; Ravel, B.; Rehr, J.J.; Conradson, S.D.: Real space multiple scattering calculation and interpretation of X-ray Absorption Near Edge Structure. *Phys. Rev. B* **58** (1998) 7565–7574.
- [21] Ferrage, E.; Lanson, B.; Sakharov, B.A.; Geoffroy, N.; Jacquot, E.; Drits, V.A.: Investigation of dioctahedral smectite hydration properties by modeling of X-ray diffraction profiles: influence of layer charge and charge location. *Am. Mineral.* **92** (2007) 1731–1743.
- [22] Lee, H.-L.; Guggenheim, S.: Single crystal refinement of pyrophyllite-17c. *Am. Mineral.* **66** (1981) 350–357.
- [23] Shirozu, H.; Bailey, S.W.: Crystal structure of a two-layer Mg-vermiculite. *Am. Mineral.* **51** (1966) 1124–1143.