

Mg K-edge XANES of sepiolite and palygorskite

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Abstract

We present a study of the Mg K-edge on sepiolite and palygorskite performed at the INFM BEAR beamline at Elettra Synchrotron Light Source (Trieste). These two clays, although having very similar structures, show some different features in their near-edge. Mg is in octahedral coordination with oxygens, hydroxyl groups or water, for both palygorskite and sepiolite. The differences found in the near-edge seem to reflect the fact that, on average, an Mg atom in palygorskite “sees” less Mg in higher coordination shells than sepiolite.

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Introduction

Sepiolite and palygorskite are fibrous clay minerals which differ from laminar clays by having channels in their structure. This is the result of the inversion of the tetrahedra layers every 8 octahedral positions in sepiolite (giving channels of 5.7×11 Å) or 5 positions in palygorskite (channel dimension 3.7×6 Å). These channels can hold zeolitic water and other molecules. Sepiolite is a trioctahedral phyllosilicate (all octahedral positions are occupied, in this case by Mg in the “ideal” sepiolite) and palygorskite is more dioctahedra than sepiolite (1/5 of the octahedral positions are vacant, in theory) with Mg and Al in the center of the octahedra. The theoretical formulas are $\text{Si}_6\text{Mg}_4\text{O}_{15}(\text{OH})_2 \cdot 6 \text{H}_2\text{O}$ (sepiolite) and $\text{Si}_8(\text{Mg}_2\text{Al}_2)\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$ (palygorskite). Theoretical models of the crystallographic structure for sepiolite and palygorskite have been proposed. However, real palygorskites and sepiolites vary depending on the origin, formation conditions, chemical environment, etc., therefore they separate from the theoretical model.

These clays have been known and exploited since ancient times. Sepiolite has been used for making pipes. Ancient Maya created the "Maya blue" pigment, by combining natural indigo with palygorskite. In Spain it was used between 1735 and 1808 for making the paste used in the Spanish “Buen Retiro” porcelain. The characteristic fibrous structure of these clays control their physico-chemical properties that make these materials very suitable for a large number of applications. In particular, they present a great specific surface area. Their great absorptive power and the good rheologic properties make them ideal for industrial applications, like litter and bedding for poultry and pets, for refining oil, and for soil conditioners for greenhouses and golf courses. They can also be used as a carrier for organic molecules (insecticides, fungicides, etc.) and as a catalyst support. The world production is

estimated to be $0.4 \cdot 10^6$ tons/year for sepiolite (95% produced by Spain) and 10^6 tons/year for palygorskite (75% of the production comes from USA).

Mg K-edge X-ray Absorption studies on materials and minerals are not very frequent in the literature for several reasons. One of them is the technical difficulty of obtaining intense synchrotron beams in the 1-2 keV energy range, where the Mg K-edge is found (1303 eV). This is a transition zone not covered by usual crystal monochromators, like silicon, that work well from 3 keV, nor by grating monochromators that are efficient at much lower energies. Some particular monochromators using “exotic” crystals have been developed for covering this zone, like YB_{66} [1, 2] or KTP [3], but the number of beamlines equipped with these crystals is scarce. Moreover, most phyllosilicates containing Mg, although presenting complex structures, show similar XANES spectra [4]. A thorough analysis of the XANES requires the use of sophisticated computer tools for performing ab-initio calculations. This explains the restricted bibliography, in spite of the fact that magnesium is the eighth most abundant element in the Earth, and the number of minerals containing Mg as a main component, or where Mg substitutes other cations is very high. Additionally, there are many artificial compounds using Mg, which are very important for applications not only in Mineralogy and Chemistry, but also in Metallurgy, Agriculture, Environmental Science and also Biotechnology. A good review of the Mg K-edge XANES of tens of samples (minerals and model compounds) can be found in [4].

In this paper we report for the first time the Mg K-edge XANES of the fibrous clays sepiolite and palygorskite.

Experimental

Mg K-edge XANES spectra were recorded at room temperature at the ELETTRA synchrotron on the bending magnet beamline BEAR [5]. The synchrotron was operating in multibunch mode at 2.0 GeV. The photon flux reaching the sample was not very intense (of the order of 10^4 photons/s), because the working energy (around the K-edge energy of Mg: 1303 eV) is at the upper limit of the spectral range achievable at BEAR. A grating monochromator with 1200 lines/mm was used, with the exit slits open to 100 μm (vertical) \times 900 μm (horizontal), providing an energy resolution of about 1 eV at the Mg K-edge. The spot size on the sample is defined by the exit slits settings. XANES data were recorded with a typical energy step of 0.5 eV in the range 1280 eV - 1360 eV and counting 1 sec per point. The spectra were acquired in total electron yield mode using a Keithley 6517 picoammeter to measure the drain current of the sample. Each scan took about 6 minutes. In order to increase the quality of the spectra and to check for beam damage effects, several scans were sequentially recorded and added (30 for sepiolite, 24 for palygorskite). The I_0 was measured by recording the total electron yield of a tungsten mesh placed just before the beamline end station. All the measurements were performed with the beam impinging at normal incidence on the sample.

The palygorskite sample comes from Ticul, Yucatan (Mexico). Transmission Electron Microscopy analysis gave an structural formula of $(\text{Si}_{7.85}\text{Al}_{0.15}) \text{O}_{20} (\text{Al}_{1.57}\text{Fe}^{3+}_{0.24}\text{Mg}_{2.21}\text{Ti}_{0.01}) (\text{OH})_2 (\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$. X-ray diffraction analysis did not detect any impurity. The sepiolite sample is from Yuncuillos, Toledo (Spain) and has a purity of 90-95%, with small impurities of quartz, calcite and feldspars (minerals that do not contain Mg in their composition). Samples were crushed in a mortar. A small quantity of powder was deposited on a carbon tape, which was placed in the experimental chamber under ultra-high vacuum. The samples were aligned by moving the sample until being

illuminated by the beam from the zero-th order of the grating monochromator, which reflects photons in the energy range of visible light. For all experimental spectra, we subtracted a linear pre-edge background and then normalized the edge-jump to one. XANES Mg K-edge spectra of palygorskite and sepiolite are shown in Fig. 1. The zero of energy has been set to the edge's inflexion point for both spectra.

Discussion

The spectrum of sepiolite presents a triplet structure in the white line (labeled A, B and C in Fig 1), corresponding to the Full Multiple Scattering zone. It also presents two oscillations (D and E) in the Intermediate Multiple Scattering zone. Palygorskite presents a XANES spectrum similar to sepiolite but with some differences. The most important one comes from the C peak in sepiolite, which is only a shoulder in palygorskite. Moreover, there is a clear shoulder, labeled A', which is present in palygorskite and absent in sepiolite. Other differences are perhaps hidden by the high noise of the spectrum.

Sepiolite's spectrum is very similar to the XANES spectra of many other minerals with Mg in octahedral coordination, as discussed later. However, the absence of a clear peak C in palygorskite is a significant feature that characterizes the XANES of this clay. We will discuss the reasons for this difference between the XANES spectra of sepiolite and palygorskite.

When comparing the recorded spectra with reference compounds reported in literature, we find that the XANES spectra of MgO (periclase) [6, 7], or its equivalent near-edge structure in electron-energy loss spectrum [8], is very different to those of sepiolite and palygorskite. The fact is that MgO has a cubic structure (NaCl structure),

and although its first coordination shell has 6 oxygens (an octahedron), similar to palygorskite and sepiolite, the arrangement of successive coordination shells is different for MgO, therefore presenting completely different multiple scattering paths, producing significantly different features in the Full multiple scattering zone. This is compatible with the fact that *ab-initio* calculations of one octahedral shell of oxygen give a XANES [9, 10] consisting of a single sharp peak or white line (without a triplet structure as we see) and two oscillations that appear close to our D and E structures. The next compound to analyze is Mg(OH)₂ (brucite), in which Mg²⁺ is octahedrally coordinated by hydroxyl groups. These octahedra share adjacent edges to form sheets of layers. All Mg atoms in brucite are equivalent, in the sense that they have the same atomic environment. The XANES spectrum of brucite [4, 6, 7] is very similar to that of sepiolite, showing the triplet A, B and C plus the two oscillations D and E and a small peak D'. The most intense peak is B, then C and then A for brucite. We also find that B is the most intense peak for sepiolite, but then A and then C, therefore inverted with respect to brucite. The XANES spectrum for synthetic brucite [4], has a shoulder on the edge, similar to the A' structure we find in palygorskite. In data from [6, 7], this shoulder is not detected, as in our data, perhaps because these XANES spectra are recorded with lower resolution. Sepiolite and palygorskite have layers of octahedra similar to brucite, with the difference that in brucite the layer is continuous with hydroxyl groups at the vertex of the octahedra, whereas in fibrous clays, the layer is discontinuous, due to the fact that the tetrahedral sheets of Si that sit on top and bottom of the octahedral layer invert their tetrahedra every 8 octahedral positions in sepiolite (5 for palygorskite). Moreover, sepiolite and palygorskite may have O, OH and H₂O at the vertices of the octahedra. Therefore, the similarity of the XANES for brucite and sepiolite might be due to the existence of a large sheet of octahedra all

containing Mg in the center (this sheet is continuous in brucite and has a significant large width (along the b axis of the unit cell) of 4 octahedra) (Fig. 2). By contrast, the sheet of octahedra in palygorskite is narrower (2-3 filled octahedra) which are not occupied by Mg, but can also be vacant or contain Al^{3+} , and there are not two contiguous position occupied by Mg. The Mg in palygorskite occupies the most external positions in the ribbon and it has one hole and two Al as neighbors, whereas in sepiolite may have four different Mg: one *trans* surrounded by six Mg, one *cis* surrounded by six Mg, one placed in the external position with three Mg as neighbors and two water molecules, and the last one in another external position but surrounded by five Mg.

Our sepiolite Mg K-edge spectrum is not only similar to brucite, but also to many minerals where Mg is in octahedral coordination with O viz. OH, like spectra of other trioctahedral layered silicates, like phlogopite, biotite, talc, or clintonite, among others reported in [4].

Ab-initio calculations of XANES spectra based on Multiple Scattering theory [11, 12], or band-structure calculations, as in [8], help to explain unambiguously the origin of the different features found in the experimental spectra. These calculations need the definition of the cluster of atoms around a photoabsorber, and the exact position of each atom. This is a problem for the case of sepiolite and palygorskite, for which the crystallographic structure is only known for the “theoretical” formula. Real minerals often differ from the theoretical formula, as they may show vacancies, ion substitution, etc. with a local deformation of the atomic environment. Moreover, the fact that each octahedron may have different O groups in the vertices (O, OH or H_2O) will certainly distort the octahedral geometry, and affect the XANES. A further problem is the number of independent octahedral sites present in the structure. The

experimental spectra should then be compared with the weighted sums of the independent partial spectra generated by the photoabsorber when located in each different environment. Several papers with *ab-initio* calculations for the K-edge of Mg in octahedral oxygen environment have been published. Cabaret et al. [10] present an experimental and simulation work on two pyroxenes (diopside, with Mg in a single site and enstatite, with Mg in two different sites). Their experimental spectra resembles our sepiolite spectrum in the main structures A, B, C, D and E. They found that peaks A, B, and C are clearly related to the medium range ordering, whereas E is a signature of the local atom arrangement around the absorbing Mg, that can mainly be assigned to multiple scattering in the first coordination sphere. The C feature, that differentiates sepiolite and palygorskite spectra only appears in diopside for calculated clusters with more than 6 Å of radius. For enstatite, one site (a regular octahedron) gives similar results, whereas the second Mg site (a distorted octahedron) produces more structured XANES for the same coordination radii. Mg K-edge of other pyroxenes [13] display similar results concerning the structures found in the spectra and the necessity of including many atoms in the cluster used for the XANES calculation (89 atoms in synthetic diopside) for reproducing the C structure of the experimental data. The fact that the medium order arrangement affects peak C is also evidenced experimentally by the XANES of diopside glass and diopside crystal reported in [14]. The XANES of diopside crystal is almost equivalent to our sepiolite spectrum, whereas for the glass, the peak C is converted into an appreciable shoulder, as we have found for palygorskite. Thus, in our case, it is reasonable to assign peak C in sepiolite to the existence of octahedral sheets of relatively large dimensions (must be larger than 6 Å [10]). In fact, the width of the channel (or in other words, the width of the octahedral sheet) is 11 Å in sepiolite and only 5.7 Å in palygorskite. Moreover,

in palygorskite the octahedra may be occupied also by Al or be vacant (dioctahedral), altering considerably the environment of an “average” Mg with respect to sepiolite (trioctahedral). The different intensities of the peaks might be related to the distortion of the octahedra, which is expected to be greater in the case of palygorskite than in sepiolite. We have not found any published XANES data on the Mg K-edge on dioctahedral layered silicates, which might help to address the question of how the presence of vacancies and the presence of Mg and Al in alternate positions may affect the XANES spectrum.

Summary and Perspectives

We presented, for the first time, the experimental Mg K-edge XANES for sepiolite and palygorskite. The features found in sepiolite are related to the existence of quite large octahedral sheets with Mg occupying the octahedra, as in brucite and other trioctahedral layered silicates. The XANES of palygorskite resembles that of sepiolite, but it has a shoulder where a peak was found for sepiolite (labeled C in Fig. 1). We relate this difference to the medium-range ordering (6 Å or more) around an average magnesium atom. In sepiolite, this medium-range ordering is more important than in palygorskite, because of the trioctahedral nature of sepiolite, and the larger width of the channels (11 Å for sepiolite and 5.7 Å for palygorskite). *Ab-initio* calculations and XANES measurement at the Si and Al edges, in addition to Mg, will help to improve our knowledge of the structure of these clays. It might also be very useful to compare these results with other reference compounds, in particular dioctahedral phyllosilicates.

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Figure Captions

Fig. 1. Magnesium K-edge XANES spectra of palygorskite (top) and sepiolite (bottom).

Fig 2 Schematic view of a $1 \times 1 \times 2$ supercell of palygorskite (top) and a single cell of sepiolite (bottom). Left graphs represent perspective views and right graphs show projections onto the (b,c) plane. Octahedra in palygorskite may have in the center a vacancy (open white circle), Mg atom (grey dashed circle) or Al (grey solid circle). All octahedral are filled by Mg in sepiolite. Tetrahedra always have a Si in the center. Tetrahedra have been omitted in the (b,c) projections for clarity.

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