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Different level of fluorescence in Raman spectra of montmorillonites

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ABSTRACT

The paper presents the study of selected montmorillonite standards by Raman spectroscopy and microscopy supported by elemental analysis, X-ray powder diffraction analysis and thermal analysis. Dispersive Raman spectroscopy with excitation lasers of 532 nm and 780 nm, dispersive Raman microscopy with excitation laser of 532 nm and 100× magnifying lens, and Fourier Transform-Raman spectroscopy with excitation laser of 1064 nm were used for the analysis of four montmorillonites (Kunipia-F, SWy-2, STx-1b and SAz-2). These mineral standards differed mainly in the type of interlayer cation and substitution of octahedral aluminium by magnesium or iron. A comparison of measured Raman spectra of montmorillonite with regard to their level of fluorescence and the presence of characteristic spectral bands was carried out. Almost all measured spectra of montmorillonites were significantly affected by fluorescence and only one sample was influenced by fluorescence slightly or not at all. In the spectra of tested montmorillonites, several characteristic Raman bands were found. The most intensive band at 96 cm^{-1} belongs to deformation vibrations of interlayer cations. The band at 200 cm^{-1} corresponds to deformation vibrations of the AlO_6 octahedron and at 710 cm^{-1} can be assigned to deformation vibrations of the SiO_4 tetrahedron. The band at 3620 cm^{-1} corresponds to the stretching vibration of structural OH groups in montmorillonites.

1. Introduction

Montmorillonite is a common clay mineral with a unique layered structure belonging to the smectite group. The crystal structure of montmorillonite is composed of tetrahedral sheets of SiO_4 (with occasional aluminium substitution for silicon) and octahedrally coordinated sheets of aluminium, magnesium or iron, sandwiched between other tetrahedral sheets of SiO_4. The theoretical formula is $(OH)_4\,Si_8Al_4O_{20}\cdot nH_2O$ (interlayer) and the theoretical composition without the interlayer material is SiO_2, 66.7%; Al_2O_3, 28.3%; and H_2O, 5%. Owing to the isomorphous substitution of Al, Mg or Fe atoms in the octahedral sheet, a negative charge imbalance is created, and a cation-exchange site is produced so that the imbalance may be offset. The most prominent cations in that site are calcium, sodium, magnesium and potassium. Calcium montmorillonite (Ca^{2+} MMT) and sodium montmorillonite (Na^{+} MMT) are the most important clay minerals in the smectite group. The main structural difference between calcium and sodium montmorillonite is in the water layer. Calcium montmorillonite possesses two water layers in the interlayer position while sodium montmorillonite has only one water layer. The sodium montmorillonites have a higher swelling capacity and viscosity than calcium montmorillonites [1–3].

The small particle size of clay grains (less than 2 or 4 μm) and specific crystallographic habit of these clay minerals (a layer structure with one dimension in the nanometer range) give clays a very high surface area, which can be modified (by adsorption, ion exchange, or grafting), and plasticity [1,2,4]. Owing to the extraordinary properties and common availability of clays (like no other group of inorganic materials), these clay minerals find many practical applications [5–7].

Raman spectroscopy is considered as a suitable method for the analysis of clay minerals. The method is based on the inelastic scattering of photons and was predicted by Smekal [8] and subsequently described by Raman and Krisnan [9] and Landsberg

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and Mandelstam [10]. Raman spectroscopy is a useful method for mineralogical and petrografical analyses. Studies of clay minerals by Raman spectroscopy have been published since the seventies of the last century, e.g. [12–23]. Currently, Raman spectroscopy is increasingly applied in the analysis of geological materials. Not only for research of minerals and rocks on earth [24–31], but also on other planets—e.g. from Mars [32,33]. Raman spectroscopy plays also a significant role in the analysis of intercalated clay minerals, e.g. [34–38].

Generally, a large impediment of Raman spectroscopy is fluorescence interference. Because of the low cross-sections of Raman scattering, small fluorescence can already overlap the Raman bands. Either the sample or impurities may absorb the laser radiation and reemit it as fluorescence. If this occurs, Raman spectra can be obscured by a broad, strong fluorescence band, which intensity could be as much as 10^4 larger than the Raman signal [11,39]. The probability of exciting fluorescence falls off substantially at long wavelength of the laser [40].

The occurrence of fluorescence in Raman spectroscopy of clay minerals is quite frequent. However, in the case of some clay minerals the fluorescence appears only in a weak form or not at all. The same behavior has been observed in Raman spectra of tested montmorillonites. Most of the montmorillonite representatives exhibit a very high fluorescence level, but in a small part of them the fluorescence is almost absent. The origin of fluorescence excitation at measuring Raman spectra of clay minerals is rarely discussed in the literature. In addition, the authors do not have a unified opinion what causes the fluorescence. For example according to Ref. [21], the main explanation for the excitation of fluorescence is the presence of iron(III) hydroxide or the presence of organic matter in samples of clay minerals. Košařová and co-workers [39] noticed a high fluorescence in Raman spectra of clay minerals measured by a 1064 nm laser which is probably caused by the presence of iron directly in the structure of clay minerals. Another study [37] suggested that the reason of fluorescence excitation is the absence of polymeric structures in intercalated clay minerals.

The aim of this paper is to describe the limits of Raman spectroscopy and to point out the differences among the levels of fluorescence in Raman spectra of different montmorillonites standards. Apart from Raman spectra, results of XRD, thermal and elemental analysis (by wavelength dispersive XRF fluorescence) are also presented.

2. Samples and methods

2.1. Samples

Four montmorillonites samples (Kunipia-F, SWy-2, STx-1b, and SAz-2) were selected for this experimental study. These mineral standards were obtained from the Source Clays Repository of the Clay Minerals Society, USA and from the collection of minerals available at the Institute of Geonics of the AS CR. The Kunipia-F sample contains only sodium in its interlayer, whereas the SWy-2 sample contains both sodium and calcium cations in the interlayer. The interlayer cation of samples STx-1b and SAz-2 is calcium. All standards were heated the same way in a furnace overnight at 150 °C to minimize the absorbed water content according to the study of Madejova and co-workers [41]. A list of all samples of mineral standards is given in Table 1.

Table 1
List of samples.

Sample	Locality	Description	Impurities
Kunipia-F	Kunimine Co., Japan	Na-montmorillonite	mica, quartz
SWy-2	Wyoming, USA	Ca, Na-montmorillonite	mica, quartz
STx-1b	Texas, USA	Ca-montmorillonite	opal
SAz-2	Arizona, USA	Ca-montmorillonite	quartz

2.2. Raman spectroscopy and microscopy

Raman spectra of powder montmorillonite samples were obtained using two instruments: a dispersive Raman spectrometer DXR SmartRaman (Thermo Scientific, USA) with CCD detector and a Nicolet 6700 FT-IR spectrometer equipped with a Nicolet NXR FT-Raman module (Thermo Scientific, USA) including an InGaAs detector. A 180° reflective sampling configuration was used for the Raman measurements; their parameters were as follows:

(a) excitation laser wavelength of 780 nm (20 mW), aperture 50 μm, exposure time 1 s, number of exposures 2500, spectral region 1800–50 cm^{-1} (dispersive Raman spectrometer)
(b) excitation laser wavelength of 532 nm (8 mW), aperture 25 μm, exposure time 1 s, number of exposures 2500, spectral region 4000–50 cm^{-1} (dispersive Raman spectrometer)
(c) excitation laser wavelength of 1064 nm (112–300 mW), aperture 150 μm, number of scans 1000, spectral region 4000–50 cm^{-1} (FT-Raman spectrometer).

A 100× magnification lens was used for Raman microscopy measurement by the dispersive Raman microscope DXR Raman Microscope (Thermo Scientific, USA). The measurement parameters were as follows: excitation laser wavelength of 532 nm (8 mW), aperture 50 μm, exposure time 1 s, number of exposures 2500, and spectral region 4000–50 cm^{-1}.

2.3. X-ray powder diffraction analysis

The X-ray powder diffraction (XRD) analysis was performed using the X-ray diffractometer Ultima IV RIGAKU (Japan), which operated at 40 kV and 40 mA with CuKα line as source of radiation (reflection mode, Bragg-Brentano arrangement, scintillation counter). The XRD patterns were recorded in the two theta range of 2–60°, 2θ with a step size of 0.05 and a scanning rate of 2.3°/min. The phase identification was achieved by means of the PDF-2 database.

2.4. Elemental analysis

The determination of major elements has been performed by means of a wavelength-dispersive sequential X-ray fluorescence spectrometer ARL PERFORM'X 4200 W (Thermo Scientific, USA). The fusion bead method has been preferred for the preparation of pressed pellets in order to eliminate the heterogeneity due to grain size and a mineralogical effect and to reduce inter-element effects by dilution of the sample. Fused beads (40 mm) have been prepared by fusion of the samples with lithium tetraborate on a VULCAN 4 M fusion machine in Pt/Au crucibles.

2.5. Thermal analysis

Thermal analysis was performed by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) using the thermal analyzer Setsys 12 (Setaram, France) with a thermal measurement head TG ATD Rod. TG and DTA curves were recorded in a static air atmosphere at a heating rate 10 °C min^{-1} up to the final temperature of 1000 °C. The sample mass was about 50 mg, a thermocouple Pt-Pt_{90}/Rh_{10} and inert material Al_2O_3 was used with no pressing in a crucible, i.e. loosepacked. The kinetics of the dehydroxylation process was studied using the Arrhenius equation applied to solid state reactions. The activation energy was