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Study of the occurrence of titanium in kaolinites by micro-Raman spectroscopy

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Abstract

Variations in the far infrared region of the Raman spectra of kaolinites are related to the incorporation of titanium in the kaolinite lattice and to the presence of accessory anatase. The spectra of titanium-free kaolinites exhibit weak kaolinite bands. An exceptional intensity of a kaolinite band at 130 cm^{-1} in anatase-free kaolinites is characteristic of titanium-bearing kaolinites. The incorporation of titanium in the octahedral sheet increases the intensity of the $(Al,Ti)O_6$ vibration due to the easily polarizable character of the titanium atoms in the kaolinite lattice.

The spectra of anatase-rich kaolinites are dominated by strong bands of anatase. The extreme Raman sensitivity of the main anatase band at 144 cm^{-1} is explained by the easily polarizable character of titanium atoms in the anatase lattice and the high symmetry of the O–Ti–O vibration. In anatase-poor kaolinites the band at 144 is accompanied by the band at 130 cm^{-1}, whereas in anatase-rich kaolinites the former band overlays the latter band.

Keywords: Anatase; Band; Far infrared; Kaolinite; Polarizability; Raman; Spectra; Spectroscopy; TiO_2; Titanium; Vibration

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1. Introduction

Kaolinite $[Al_2Si_2O_5(OH)_4]$ is a layer silicate appearing in micro-crystals, commonly around 2 micrometers in size. Their crystal structure consists of a single silica tetrahedral sheet and a single alumina octahedral sheet. Titanium occurs in kaolinites both as substituted form in the kaolinite lattice and as free oxide [1–3]. Accessory anatase (TiO_2) is frequently encountered associated with kaolinite [4–8]. Its amounts may range from zero to several percentages. In kaolinites rich in titanium, an average of 86% of the total titanium is found to be in the TiO_2 form, primarily anatase, and the rest appears in the kaolinite structure [2]. Similarly, in Georgia kaolins, comparison of total TiO_2 with anatase content reveals that there is a significant non-anatase titanium component present [9]. The nature and content of titanium in kaolinite has technological implications on the quality of the raw material for the ceramic, paper, plastic, filler and paint industries.

Raman spectroscopy has been used for the study of the lattice vibration region of kaolinite-group minerals [4,5,10–17] and for identification of accessory anatase [4,6–9]. In 1995 we reported firstly that the Raman spectra of anatase-containing kaolinites are dominated by strong Raman bands of anatase and only weak kaolinite bands [4]. We drew attention to the extreme Raman intensity of the main anatase band at 144 cm^{-1} and related the variations in its intensity to the amount of the anatase in individual kaolinite. Moreover, we reported that the spectra of KGa-1 and KGa-2 kaolinites are dominated also by strong bands of accessory anatase, located at about 144, 198, 396–398 and 514–516 cm^{-1} [4]. Frost [18] also detected an intense

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band at 143 cm^{-1} in Raman spectra of KGa-1 and KGa-2 kaolinites and related its very large intensity to a vibrational mode which induces a very large change in polarizability. He noted that the titania mineral anatase may have a very intense band in this spectral region. In later works, Murad [6,7] and Murad and Koster [8] suggested Raman spectroscopy as a viable method for determining the amounts of anatase in kaolins.

In the present study, the variations in the far infrared region of the Raman spectra of kaolinites are determined by using a curve-fitting technique. We demonstrate two spectral variations for anatase-free kaolinites: spectra of titanium-free and titanium-bearing kaolinites. In addition, we demonstrate two spectral variations for anatase-containing kaolinites: spectra of anatase-poor and anatase-rich kaolinites. By using Raman spectroscopy, we confirm that titanium is incorporated in the octahedral sheet of the kaolinite.

2. Experimental

2.1. Kaolinite samples

Reference and local kaolinites with widely different titanium content were investigated. A list of the kaolinite samples and their sources is given in Table 1. The reference kaolinites were supplied by the Wards Scientific Establishment, by the Source of Clays Repository of The Clay Minerals Society and by colleagues. The characteristics of the investigated kaolinites are described in previous works [4,5,17,19–25].

2.2. Methods

2.2.1. Raman spectroscopy

Micro-Raman spectra were recorded with a Dilor XY multichannel micro-Raman spectrometer equipped with an Olympus optical microscope, a triple monochromator and an EG&G CCD multichannel detector. Spectra were obtained with a 50× objective; their accumulation, at a resolution of 3 cm^{-1}, required 360 s. A Spectra Physics 2016 Argon ion laser and 514.5 nm line were used for excitation. Spectra were recorded at a laser power of 250 mW. Frequencies were calibrated with external (521 cm^{-1} silicon line) and internal (argon plasma line) standards. Measurements were performed on freshly fractured surfaces of the natural kaolinites so as to prevent possible damage to the kaolinite domains during sample preparation.

Table 1
A list of the reference and local kaolinites investigated and their sources

Samples	Sources	References
Keokuk	Keokuk Iowa, USA	[19]
DVC (DEC)	Decaseville Bassin, France	[20]
MR-11P, MR-12P	Makhtesh Ramon, Israel (P = from phenocrysts)	[4]
MS-1, MS-6, MS-205	Makhtesh Ramon, Israel, (from pisolites)	[5]
Nopal 1, C-14	Nopal uranium deposit, Chihuhua, Mexico.	[21]
Lal-lal	Lal-lal, Victoria, Australia	[17]
Bath	Lamar Pit, Bath, South Carolina, USA	[22]
KGa-1; KGa-2	Washington County, Georgia, USA	[23]
Macon	Oneal Pit, Macon, Georgia, USA	[22]
SMA-5	Makhtesh Ramon, Israel	[24]
MR-11G, MR-12G, MR-3, MR-33,	Makhtesh Ramon, Israel (G = from groundmass)	[4]
UB-1	Um Bugma, Sinai	[25]

2.2.2. Curve fitting

The micro-Raman spectra were analyzed using the peak fitting function in "Galactic" ("Grams") software. Lorentzian components and linear baseline were used for the fitting (except anatase-rich kaolinites for which Mix Gaussian–Lorentzian components were used). Multiple points were selected for baseline correction. The positions, heights and widths of the band components were determined without fixation.

2.2.3. Chemical analyses

The amounts of the titanium in the samples were determined by chemical analyses. The analyses were carried out using a JEOL (JSM-840) instrument with an attached LINK EDS (Oxford ISIS). Calculations were made using the ZAF4/FLS program.

3. Results

Curve-fitted micro-Raman spectra in the range of 300–50 cm^{-1} are demonstrated in Figs. 1–3. In addition to kaolinite and/or anatase bands the spectra exhibit argon plasma lines at 66, 77 and 115–116 cm^{-1}. The latter bands were used for calibration of the frequencies of the Raman spectra.

3.1. Anatase-free kaolinites

Two spectral variations for anatase-free kaolinites are demonstrated in Fig. 1. The spectrum in Fig. 1a of titanium-free kaolinite exhibits a weak kaolinite band at about 130 cm^{-1} and the spectrum in Fig. 1b of titanium-bearing kaolinite displays an exceptional intensity of this band.

3.2. Anatase-containing kaolinites

Two spectral variations for anatase-containing kaolinites: spectra of anatase-poor and anatase-rich kaolinites are demonstrated in Figs. 2 and 3. In Fig. 2 two spectral types of anatase-poor kaolinites are represented. The spectrum in Fig. 2a exhibits a weak anatase band at about 144 cm^{-1} and a distinct band at about 130 cm^{-1} and the spectrum in Fig. 2b displays higher intensity of the former band accompanied by a distinct intensity of the latter band. In Fig. 3 two spectral types of anatase-rich kaolinites are