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Contact pressure effects on vibrational bands of kaolinite during infrared spectroscopic measurements in a diamond ATR cell

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INTRODUCTION

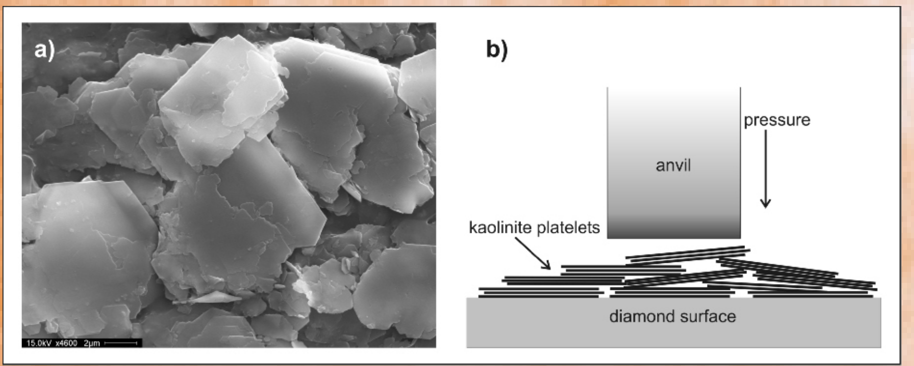
Since decades Fourier transform infrared (FTIR) spectroscopy has been widely used for the investigation of the structures and bonding properties of clay minerals, especially of kaolinites. Various transmission and reflection techniques have been developed over the years. Besides the classic transmission method using KBr pressed disks, recently the diffuse reflectance (DRIFT) technique has become increasingly more important for the investigation of clay minerals. In contrast to these methods, the attenuated total reflection (ATR) technique requires no dilution in KBr, making the sample preparation even easier. With this technique it is possible to study both wet clay suspensions and dry powders. ATR accessories with various crystals like ZnSe, germanium or silicon and with different numbers of internal reflections are available. A special accessory is the Golden Gate single reflection diamond cell. Here small amounts of sample powders are pressed on a diamond crystal by a sapphire tipped anvil.

In this study we compared Golden Gate ATR spectra of kaolinite with transmission spectra. Distinct differences especially in the spectral region between 1240 and 440 cm^{-1} to spectra obtained by the other spectroscopic methods (transmission, DRIFT, ATR without contact pressure) are reported.

In contrast to the effects on the tetrahedral sheet applied by the low uniaxial pressures (< 105 MPa) of the ATR anvil, a number of publications reported complex deformation processes especially in the octahedral sheet and phase transitions in kaolinite group minerals, when exposed to high hydrostatic pressures above 1 GPa. Therefore we suggest, that the spectral changes in our ATR spectra occur due to rotations and shifts within the tetrahedral sheets exerted by shear stress applied by the Golden Gate anvil.

Measurement conditions: A Bruker IFS 66/s spectrometer, equipped with a DTGS detector was employed to obtain the IR-spectra. 64 scans in the 4000 - 400 cm^{-1} spectral range were recorded with a scanner velocity of 1.6 kHz and a resolution of 2 cm^{-1}. For the DRIFT measurements a diffuse reflectance accessory from Spectra-Tech Inc. was used with a polished aluminium-mirror for the background

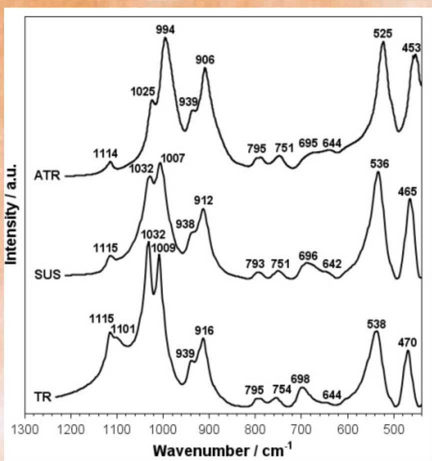
RESULTS



Kaolinite

Kaolinite has a platy pseudohexagonal morphology with particle sizes of normally around 2-5 µm and a varying thickness between 0.2 and 1 µm.

Pouring kaolinite powders on a flat surface result in:
(a) strong orientation of the platelets.
(b) This means, the anvil of an ATR-accessory presses the platelets along their c-axes, thus perpendicular to the tetrahedral sheets (ab-planes).



Spectra comparison

Transmission-, DRIFT-, and ATR-spectra of dried suspensions on a ZnSe crystal showed analogue band positions.

Only measurements with a Golden Gate ATR accessory revealed remarkable changes depending on the applied pressure.

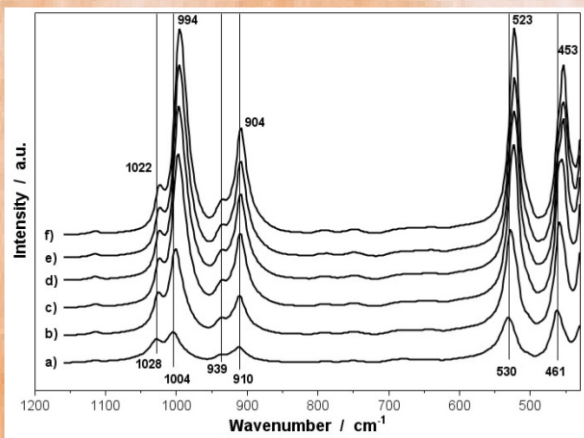
Observations

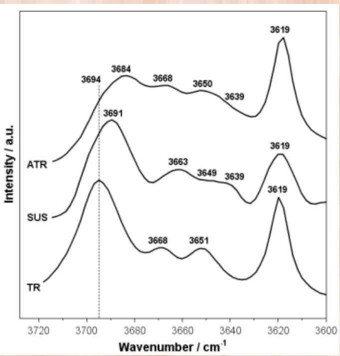
(1) Five Band positions between 1240 cm^{-1} and 440 cm^{-1} are affected by the applied contact pressure

(2) Most of these vibrations can be assigned to basal Si-O bonds.

(3) All of them shift to lower wavenumbers.

(4) Sensitive OH-stretching vibrations are not affected by the applied pressure! This does not concern a simple compression of the mineral!





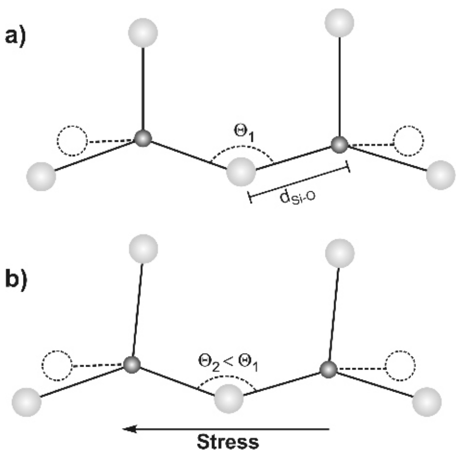
OH-stretching bands

With increasing contact pressure:

(a) increased intensity of very weak TO-mode of the inner surface hydroxyls (3684 cm^{-1})

(b) strongly decreased intensity of LO mode at 3694 cm^{-1}.

In the Golden Gate ATR spectra both bands are visible, due to strong alignment of the platy kaolinite particles along their ab-planes during the applied pressure.



The results of the comparative study suggest that the applied pressure of a Golden Gate diamond cell affects the tetrahedral vibrations of kaolinite. This occurs due to applied shear forces, which lead to a rotation and distortion of the SiO_4 tetrahedra.

[1] J.T. Klopproge (ed.), CMS Workshop Lectures, 13 (2005) 285 pp. **[2]** J. Madejova, Vibrational Spectroscopy, 31 (2003) 1. **[3]** D. Bougeard, K.S. Smirnov, E. Geidel. Journal of Physical Chemistry, Part B 104 (2000) 9210. **[4]** M. Holtz, S.A. Solin, T.J. Pinnavaia, Physical Review B, 48 (1993) 13312.

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