Determination of the Ti speciation in commercial kaolins by Raman spectroscopy

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ABSTRACT: Raman spectra of a selection of kaolins with widely varying TiO₂ contents revealed the presence of anatase in 17 of 18 samples. A significant positive correlation was observed between the intensity of the main anatase Raman band at ~145 cm⁻¹ and the total TiO₂ contents of the kaolins as determined by chemical analysis. No TiO₂ modification other than anatase was detected in any of the samples.

The determination of the anatase contents in kaolins by XRD becomes increasingly difficult as the concentration of this mineral decreases below ~0.5%. In contrast, anatase and brookite concentrations an order of magnitude lower can still be readily identified by Raman spectroscopy. The specificity and sensitivity of Raman spectroscopy for these TiO₂ polymorphs, coupled with the simplicity and rapidity of measurement, therefore make this a viable technique for the routine study of these accessory minerals in kaolins.

The Ti contents of commercial kaolins can amount to several percent. Part of the Ti may be incorporated in the kaolinite structure, but significant proportions are often bound in accessory titaniferous minerals. Ancillary minerals whose association with kaolinites has been frequently reported are the TiO₂ polymorphs anatase, rutile and brookite. Leucoxene, a greyish white alteration product of ilmenite that usually consists of aggregates of fine grained anatase and/or rutile, often associated with Fe-bearing phases such as pseudorutile (Fe³⁺TiO₅) and Fe oxides, is another common accessory. Many of these minerals contain Fe — either as an essential or a minor constituent — and may therefore reduce kaolin whiteness. Titanium and Fe furthermore affect the colour of porcelain, so that the named minerals can have a notable effect on the economic value of commercial kaolins.

As a result of the possible presence of titaniferous minerals, the Ti contents of kaolins that have been determined by chemical analyses cannot be attributed to any phase a priori, and the determination of the Ti speciation of kaolins requires the application of specific mineralogical procedures.

The use of optical microscopy for the identification of ancillary minerals associated with kaolinites is confined by the fact that some of these minerals — in particular anatase, which is often of secondary origin (Salger, 1958) — may occur in particles significantly below the micrometer size range. Thus, although ancillary minerals down to ~2 μm in particle size can be identified using phase contrast microscopy (Köster, 1964a), optical microscopic techniques will usually not allow a comprehensive assessment of the Ti mineralogy of kaolins to be made.

Of the fore-named minerals, anatase is a particularly common accessory of commercial kaolins and related materials (Jepson, 1988; Milnes & Fitzpatrick, 1989). Basically the identification and quantification of anatase in kaolins should be possible by X-ray diffraction (XRD).
The total proportion of anatase in commercial kaolins, however, rarely exceeds 1–2 wt%, so that this mineral will usually produce only weak XRD peaks. In the presence of an excess of kaolinite, the determination of anatase by XRD is further complicated by the fact that the strongest anatase peak, 101 with a d-spacing 3.52 Å, is usually overshadowed by the nearby 002 peak of kaolinite with a d-spacing of 3.573 Å (Fig. 1), the intensity of which is often further enhanced as a result of sample texture. These adverse effects combine to complicate the determination of the anatase content of kaolins by XRD, and render this impossible as concentrations fall significantly below 0.5 wt%.

Selective dissolution of kaolinite, e.g. by NaOH or hexafluorotitanic acid (Sayin & Jackson, 1975), has been suggested as a means of determining the titaniferous constituents of commercial kaolins. The isolates, however, may contain a variety of minerals that are not removed by this procedure, and a mineralogical characterization of samples that have been treated in this manner (e.g. by XRD) will still be necessary.

In a study of ten kaolins of widely varying provenance and Ti contents, Murad (1987) showed that the Raman spectra in the structural region (~100–1000 cm⁻¹) of most of the samples were dominated by bands that can be attributed to anatase. Of these, a band at ~145 cm⁻¹, assigned by Ohsaka et al. (1978) to an $E_g$ ($v_6$) mode in anatase, is particularly intense. Although the other TiO₂ polymorphs – in particular brookite – also have intense and specific Raman bands, no evidence for the presence of these was found in any of the samples. Other arguments that advocate the use of Raman spectroscopy for the study of ancillary TiO₂ phases in kaolins are the simplicity of preparation and rapidity of measurement using modern (Fourier-transform) instrumentation.

Raman spectroscopy could, therefore, be useful for the detection of TiO₂ minerals in kaolins, in particular when samples contain small amounts of...
these minerals that make an analysis by XRD difficult or impossible. To test this possibility we studied a selection of 18 commercial kaolins, of widely varying Ti contents (0.02–2.08% TiO₂) and one halloysite by Raman spectroscopy. The Ti-rich samples were also studied by XRD and selected samples by IR and Mössbauer spectroscopy.

**MATERIALS AND METHODS**

A list of the studied kaolins and their TiO₂ contents is given in Table 1. Some samples were particle-size fractionated and/or treated with Na dithionite (Mehra & Jackson, 1960) prior to measurement. Finely ground natural anatase, brookite and rutile diluted with KBr served as standards for the pure TiO₂ phases.

The XRD was performed using Co-Kα radiation on a Philips PW1820 instrument equipped with a sample spinner and a diffracted-beam graphite monochromator. Powder specimens of the samples were step-scanned in 2θ steps of 0.02° between 20 and 60 s per step. Random mounts of selected samples were furthermore scanned in steps of 0.02°2θ for 30 to 100 s per step using Co-Kα radiation on a Huber System 600 Guinier diffractometer. This system has an inherently higher resolution than the (standard) Bragg-Brentano set-up, thus allowing a better separation of the neighbouring anatase and kaolinite peaks. Peak profiles were determined by fitting the XRD data with a Voigt profile using a program described by Stanjek & Friedrich (1986).

Fourier-transform infrared (FTIR) and Raman spectra were taken on a Nicolet Magna 550 instrument equipped with a Raman accessory. The resolution for both IR and Raman spectra was 4 cm⁻¹ (data spacing 1.928 cm⁻¹). Infrared spectra were taken in the transmission mode in the mid-IR region using pellets generally comprising a 1 mg sample diluted with 300 mg KBr.

Excitation of Raman spectra was achieved by irradiating the samples with a Nd:YVO₄ laser (wavelength 1064 nm = 9394 cm⁻¹) producing 0.18 W at the sample. The TiO₂ minerals were diluted with KBr to minimize broadband thermal fluorescence. Samples were packed into NMR glass tubes and 4 to 8 runs of at least 2000 scans each were taken at different positions of the tube. Instrumental settings included a 180° reflective sampling configuration, a CaF₂ beamsplitter and an InGaAs detector operated at room temperature.

**Table 1. Samples studied and their Ti contents.**

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>Fraction, pretreatment</th>
<th>TiO₂ (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Burela 201, Spain</td>
<td>&lt;2 μm, DCB*</td>
<td>0.02</td>
<td>Köster (1964b)</td>
</tr>
<tr>
<td>2</td>
<td>China Clay 10, Cornwall</td>
<td>&lt;2 μm</td>
<td>0.022</td>
<td>Köster (unpublished)</td>
</tr>
<tr>
<td>3</td>
<td>Kolloid-Kaolin, Zettlitz</td>
<td>&lt;2 μm</td>
<td>0.14</td>
<td>Köster (1964b)</td>
</tr>
<tr>
<td>4</td>
<td>Thiele 281-132, Georgia</td>
<td>&lt;2 μm</td>
<td>0.16</td>
<td>Shi (pers. comm.)</td>
</tr>
<tr>
<td>5</td>
<td>Premier-Kaolin, Zettlitz</td>
<td>&lt;2 μm, DCB*</td>
<td>0.20</td>
<td>Köster (1964b)</td>
</tr>
<tr>
<td>6</td>
<td>‘Wolfka’, Kemmlitz</td>
<td>&lt;2 μm</td>
<td>0.24</td>
<td>Köster (1964b)</td>
</tr>
<tr>
<td>7</td>
<td>Dorfner K160, Hirschau</td>
<td>&lt;2 μm, DCB*</td>
<td>0.28</td>
<td>Köster (1964b)</td>
</tr>
<tr>
<td>8</td>
<td>AKW K I, Hirschau</td>
<td></td>
<td>0.42</td>
<td>Köster (unpublished)</td>
</tr>
<tr>
<td>9</td>
<td>Mesa Alta, New Mexico, 9a</td>
<td></td>
<td>0.50</td>
<td>Kodama (pers. comm.)</td>
</tr>
<tr>
<td>10</td>
<td>Tirschneuth A, Bavaria</td>
<td></td>
<td>0.62</td>
<td>Köster (unpublished)</td>
</tr>
<tr>
<td>11</td>
<td>Mufreesboro, Arkansas, 1a</td>
<td></td>
<td>0.86</td>
<td>Kodama (pers. comm.)</td>
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<tr>
<td>12</td>
<td>Euroclay Amazon 88 (Rio Jari)</td>
<td>&lt;2 μm</td>
<td>1.07</td>
<td>Murray &amp; Partridge (1982)</td>
</tr>
<tr>
<td>13</td>
<td>Kamig-Kaolin, Schwertberg</td>
<td>&lt;2 μm</td>
<td>1.11</td>
<td>Köster (1964b)</td>
</tr>
<tr>
<td>14</td>
<td>CMS KGa-1</td>
<td></td>
<td>1.39</td>
<td>van Olphen &amp; Fripiat (1979)</td>
</tr>
<tr>
<td>15</td>
<td>Lamar pit #5, Bath, S.C.</td>
<td></td>
<td>1.39</td>
<td>Köster (unpublished)</td>
</tr>
<tr>
<td>16</td>
<td>Georgia kaolin #3, Birch pit</td>
<td></td>
<td>1.49</td>
<td>Köster (unpublished)</td>
</tr>
<tr>
<td>17</td>
<td>Georgia kaolin #4, Oueal pit</td>
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<td>Köster (unpublished)</td>
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<td>18</td>
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<td>2.08</td>
<td>Van Olphen &amp; Fripiat (1979)</td>
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<tr>
<td></td>
<td>Hallyosite, Bedford, Indiana, 12b</td>
<td></td>
<td>0.15</td>
<td>Kodama (pers. comm.)</td>
</tr>
</tbody>
</table>

* Treated with dithionite-citrate-bicarbonate (Mehra & Jackson, 1960)
Fig. 2. Raman spectra of 2.5% anatase ('a', solid line), 2.0% brookite ('b', broken line) and 2.5% rutile ('c', thin, dotted line) in a matrix of KBr. All samples are of natural origin and were finely ground before mixing with KBr.

RESULTS AND DISCUSSION

X-ray diffraction revealed the presence of anatase in some of the samples with total TiO₂ contents in excess of 0.4 wt% by a minor 101 hump bordering the kaolinite 002 peak. In the samples containing ≤0.25 wt% TiO₂, however, no anatase 101 peak could be detected (Fig. 1). Guinier diffractograms showed the anatase 101 peak, where present, more clearly, but the Guinier measurements (which are carried out in the transmission mode) did not enable an estimate of mineral proportions to be made because sample thicknesses could not be standardized. The other anatase peaks are significantly weaker than 101, and many of these are overlain by kaolinite peaks, so that even computer-fitting did not allow them to be reliably quantified. No evidence for the presence of any of the other TiO₂ polymorphs was obtained from XRD.

In spite of the relatively long counting periods, the precision of the anatase 101 peak (where observed) area determination was rather poor, with repeated scans of a single sample differing by as much as 50%. There may be several reasons for this low precision: poor counting statistics because of low anatase contents; interference from the neighbouring kaolinite peak, the degree of which varies as a function of kaolinite texture; and possibly, sample heterogeneities.

Infrared spectroscopy allowed characterization of the kaolinites, e.g. with respect to their crystallographic nature (Parker, 1969) but, because of the poor sensitivity of this technique for minor components,
did not reveal the presence of ancillary TiO$_2$ phases in any of the samples.

Raman bands of anatase and brookite in the structural region (Fig. 2a,b) are about three orders of magnitude more intense, and those of rutile (Fig. 2c) about two orders of magnitude more intense than those of kaolinite. It is therefore not surprising that the Raman spectra of most of the kaolins show several distinct anatase bands in this region, besides those of kaolinite and an occasional quartz band at 464 cm$^{-1}$. The intense anatase v$_6$ band at $\sim$145 cm$^{-1}$ was particularly distinctive (Fig. 3). This band was, for example, still clearly manifest in the Kolloid-Kaolin from Zettlitz (Czech Republic), which has a total TiO$_2$ content of 0.14% and could be fitted to the spectrum of China Clay 10, the TiO$_2$ content of which amounts to a little over 0.2%. Other, weaker, anatase bands at 198, 397, 514 and 638 cm$^{-1}$ were also observed in the more anatase-rich kaolins. Raman spectra of the halloysite did not show any anatase bands.

No bands that can be unequivocally attributed to brookite or rutile were detected in any of the kaolins or the halloysite. This indicates that brookite, which has an intense Raman band at 154 cm$^{-1}$ (Fig. 2b), is absent from the samples. The most intense Raman bands of rutile at 448 and 610 cm$^{-1}$ are an order of magnitude weaker than those of the other TiO$_2$ polymorphs. The fact that these bands were not observed, therefore, cannot be taken as proof of the absence of rutile, especially since optical microscopy has indicated the presence of minor amounts of this mineral in some of the studied kaolins (Köster, 1964a).

Raman band intensities are known to be susceptible to numerous influences, making a direct estimate of mineral contents on the basis of individual band intensities difficult. Although carrying out measurements under identical conditions may significantly reduce the influence of extraneous factors, individual mineral properties such as particle size and morphology, colour,

![Image](image_url)

**Fig. 3.** Raman spectra of anatase-free kaolin Burela 201 $<2$ μm (dotted line), anatase-poor kaolin ‘Wolfka’ Kemmlitz $<2$ μm (broken line) and anatase-rich kaolin CMS KGa-1 (solid line).
transparency, etc. still play a role. An exacting quantification of the constituents of an assemblage of complex mineralogy therefore requires specific techniques, e.g. point-counting (Haskin et al., 1997). Nevertheless, a highly significant positive correlation was observed between the total TiO\(_2\) contents determined by chemical analysis and the area of the anatase \(v_6\) band (Fig. 4), with \(r = 0.80\) for the 18 studied samples.

It is conceivable that a significant proportion of the Fe contents of many Fe-poor kaolins, rather than being incorporated in the kaolinite structure, may be bound in an associated TiO\(_2\) phase, generally anatase. As an example the CMS KGa-1 kaolin, that consists essentially of kaolinite with \(\sim 0.5\%\) mica and some ancillary anatase, has a total Fe content of only 0.15%. The anatase content of this kaolin, as determined by XRD, amounts to \(\sim 1.0\%\). If this anatase should contain \(5\%\) Fe — a proportion that studies by Sayin and Jackson (1975) and Schwertmann et al. (1995) have shown to be realistic — then this mineral could contribute \(\sim 0.05\%\) Fe to KGa-1, corresponding to roughly one third of the total Fe content of the sample. A \(^{57}\)Fe Mössbauer spectrum of KGa-1 showed an unusually high Fe\(^{2+}/\)Fe\(^{3+}\) ratio of \(\sim 0.51\) (Murad & Wagner, 1991), which was attributed to the presence of a high proportion of Fe\(^{2+}\) in the kaolinite structure. The present study indicates that this interpretation might have to be reassessed, since an unequivocal interpretation of the spectrum could have to take a possible contribution from Fe in anatase to the Mössbauer spectrum into consideration.

**CONCLUSIONS**

The presence of anatase in 17 of 18 studied commercial kaolins was established on the basis of the Raman \(E_g\) band at \(\sim 145\) cm\(^{-1}\). The variation of the relative area of this band as a function of total TiO\(_2\) contents indicates a detection limit for anatase of \(\leq 0.03\) wt\%. The high intensity of this band and the simplicity of sample preparation combine to make Raman spectroscopy an exceedingly useful method for the observation of minor amounts of this mineral in kaolins that may elude detection by other methods.

Knowledge of the anatase content of kaolins is important not only because this mineral controls the Ti speciation in most kaolins, but also because it may have a major bearing upon the Fe speciation in Fe-poor samples and thereby have an effect on possible commercial uses of these.

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**REFERENCES**


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