

## Identification of minor amounts of anatase in kaolins by Raman spectroscopy

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### ABSTRACT

The Raman spectra of anatase, rutile, and brookite consist of several intense bands, whereas kaolinite has only a weak Raman spectrum. Raman spectra of ten relatively pure kaolin and two halloysite samples that varied significantly in Ti content revealed the presence of anatase but neither rutile nor brookite in all samples. Comparison with chemical data indicates that Raman spectroscopy allows the detection of anatase in kaolin down to a concentration of 0.02%. The strongest Raman bands of many kaolins thus do not result from kaolinite but from ancillary anatase. Raman spectroscopy can therefore be recommended as a technique for the identification of anatase, rutile, and brookite in a variety of natural and synthetic materials over a wide range of concentrations.

### INTRODUCTION

Anatase and rutile are common constituents of many soils, sediments, and clays. Knowledge of the content of these minerals in industrial clays, especially kaolins, is particularly desirable because anatase and rutile may contain Fe (Sayin and Jackson 1975; Schwertmann et al. 1995) and thus have a strong influence on whiteness (Jepson 1988). Pure anatase and rutile are diamagnetic and can only be removed from kaolins by magnetic separation if they contain Fe. In the absence of information on the presence of anatase and related minerals in kaolins, any Ti detected by chemical analysis would be, possibly erroneously, assigned to the kaolinite structure. Identification of anatase in kaolins and related clays is thus important because the presence of this mineral has mineralogic, crystal-chemical, and technological implications.

X-ray diffraction is undoubtedly the most useful instrumental technique for the characterization of clays and clay minerals. However, because the strongest anatase peak (101) at 0.352 nm is very near the 002 peak of kaolinite at 0.357 nm, minor amounts of anatase in kaolins may escape detection during routine X-ray diffraction. Other techniques that have been used for the characterization of titaniferous minerals in clays and soils, such as electron microscopy and chemical dissolution, also suffer from various disadvantages, such as involving considerable effort and lack of specificity (Milnes and Fitzpatrick 1989).

In Raman spectroscopy absorption occurs because of changes in polarizability, whereas infrared spectroscopy results from changes in the dipole moment. Because of the ionic character of bonding, silicates usually yield only weak Raman spectra. Substances with transition-metal–O bonds, in contrast, have a more covalent character and therefore give more intense Raman bands (Griffith 1974). Although Raman scattering has a low efficiency, only about  $10^{-6}$  of the exciting radiation contributing to a Ra-

man spectrum, modern instruments enable spectra to be recorded within a few minutes. Raman spectroscopy requires minimal preparation and is largely insensitive to the presence of H<sub>2</sub>O. Fourier-transform Raman spectroscopy has further advantages over the conventional method, foremost among which are the reduction of thermal emission (fluorescence) and decomposition for most samples in spite of high light throughput and accurate and reproducible wavenumber calibration.

A thorough review of Raman spectroscopy and its applications to mineralogy was given by McMillan and Hofmeister (1988), who noted that molecules with easily polarizable atoms such as Ti have much stronger Raman spectra than molecules with less polarizable atoms such as Si and O.

Raman data on kaolinite-group minerals were published by Wiewióra et al. (1979) and Johnston et al. (1985). Both papers showed Raman spectra and listed band positions in the wavenumber ranges 100–1000 cm<sup>-1</sup> and the OH-stretching region (3600–3700 cm<sup>-1</sup>). The 141 cm<sup>-1</sup> band in the CMS KGa-1 and Mesa Alta kaolins that Johnston et al. (1985) observed as the most intense was absent in spectra of the Keokuk kaolinite and a nacrite from Nowa Ruda, Poland (Wiewióra et al. 1979). Raman spectra of rutile were described by Porto et al. (1967), and Raman spectra of anatase by Ohsaka et al. (1978). In a Raman study of kaoline-group clays, Frost (1995) described bands at 142.7, 395.4, and 636.5 cm<sup>-1</sup> in two samples of Georgia kaolin. Strong bands at 143 cm<sup>-1</sup> and weaker bands at 636.5 cm<sup>-1</sup> were also observed in one each of two dickites and halloysites. The bands at 143 cm<sup>-1</sup> were attributed to O–Al–O symmetric bending and those at 636.5 cm<sup>-1</sup> to Si–O–Si stretching vibrations. Although mention was made of a very intense band in anatase in the 143–154 cm<sup>-1</sup> range, the variations in band intensities were attributed to structural differences between the individual clay minerals.

**TABLE 1.** Data on kaolinite samples studied by Raman spectroscopy

Sample (Fraction; treatment)*	Composition	Hinckley Index	TiO <sub>2</sub> (%)	RA (147)**
CMS KGa-1 (B; U, D)	<i>Kt, At, Q</i>	1.07	1.39	1.37
Euroclay Amazon (C; U, D)	<i>Kt, At</i>	0.30	1.07	0.34
Dorfner K160 (C; D)	<i>Kt, Ms, Gb, Q</i>	1.55	0.28	0.08
Burela 201 (C; D)	<i>Kt, Ms, HI, Gb, Q</i>	0.94	0.02	<0.01
Sedlec Premier (C; U, D)	<i>Kt, Ms, II, Gb, Q</i>	1.08	0.20	0.02
Bath S.C. no. 5 (B; U, D)	<i>Kt, II, Gb, At</i>	0.67	1.39	0.61
ST026 Paranam (C; D)	<i>Kt, Q</i>	0.92	n.d.	0.25
ST027 Onverdacht (C; D)	<i>Kt, Q</i>	0.42	n.d.	0.45
Mesa Alta N.M. 9a (B; U)	<i>Kt, Q</i>	1.31	0.50	0.11
Murfreesboro AR 1a (B; U)	<i>Kt, Q</i>	1.55	0.86	0.09
Bedford IN 12b (B; U)	<i>HI†</i>	†	0.15	<0.01
Waldhäuser BW208 (C; D)	<i>HI, II, Gb, Q</i>	‡	n.d.	<0.01

Note: Mineralogic compositions and Hinckley indices from Murad and Wagner (1981) and Murad (unpublished data). *Kt* = kaolinite, *HI* = halloysite, *At* = anatase, *Q* = quartz, *Ms* = muscovite, *Gb* = gibbsite, *II* = illite; major constituents shown in italic letters. TiO<sub>2</sub> values from Murray and Partridge (1982; Amazon), van Olphen and Fripiat (1979; KGa-1), Köster (1964; Dorfner, Burela, Premier), Kodama (personal communication 1990; Bath, Mesa Alta, Murfreesboro, Bedford) n.d. = not determined.

\* B = bulk sample, C = clay fraction, U = untreated, D = dithionite treated.

\*\* Area of the anatase band at 147 cm<sup>-1</sup> relative to that of pure natural anatase (in percent).

† Sample consists of 92% halloysite (Kodama, personal communication 1990). No further data on sample composition are available.

‡ Determination inhibited because of interference from other minerals.

In the present paper Raman spectroscopic data on a selection of kaolin and halloysite samples and on anatase and rutile are presented, and Raman spectroscopy is suggested as a promising technique for the identification of minor amounts of anatase and rutile in the presence of layer silicates.

## MATERIALS AND METHODS

The mineral assemblages of the majority of kaolin and halloysite samples used in this study were described by Murad and Wagner (1991). The samples show considerable variation in crystalline order and minor element composition. Several samples were studied before and after removal of iron oxides with sodium dithionite (Mehra and Jackson 1960), and one sample after firing to 500 °C. Selected mineralogic and chemical data on the samples are given in Table 1.

Anatase spectra were obtained from commercial TiO<sub>2</sub> (Merck no. 808) and a natural sample. X-ray diffraction showed both samples to consist essentially of well-crystallized anatase. Rutile spectra were taken from a com-

**TABLE 2.** Raman band positions and areas (in parentheses) of selected samples

KGa-1*	Amazon*	Burela 201	Natural anatase
135**	133**	132 (0.88)	
147 (20.9)	147 (5.2)	148 (0.01)	146 (1580)
—	—	172 (0.04)	
183**	180**	183**	
200 (0.53)	200 (0.20)	201 (0.14)	199 (35)
247 (0.66)	245 (0.27)	246 (0.32)	
277 (0.87)	276 (0.22)	277 (0.44)	
339 (1.18)	338 (0.38)	338 (0.54)	
400 (0.58)	398 (0.20)	—	397 (100)
422**	421**	422**	
433 (0.85)	431 (0.30)	432 (0.56)	
469**	—	—	
475 (1.58)	473 (0.67)	474 (1.19)	
—	507**	506 (0.03)	
514 (1.04)	513 (0.35)	—	514 (80)
639 (3.17)	638 (0.84)	—	638 (220)
709 (0.31)	709 (0.08)	710 (0.21)	
754 (0.61)	754 (0.23)	754 (0.34)	
792 (0.67)	789 (0.20)	791 (0.35)	
915 (0.83)	914 (0.35)	914 (0.50)	

\* Values given are averages for untreated and dithionite-treated samples.

\*\* Position of band was determined using the first or second derivative; area of band could not be reliably determined.

mercial sample (W. Franke, Frankfurt) and a pure natural sample described by Murad et al. (1995).

X-ray diffraction data were obtained using a Philips PW1050/70 diffractometer with CoK $\alpha$  radiation and a graphite monochromator. Oriented powder samples were scanned in steps of 0.02° 2 $\theta$  for 10–60 s per step. An additional assessment of the structural order of the kaolinite was performed using the crystallinity index defined by Hinckley (1963) by counting random mounts of selected samples in steps of 0.02° 2 $\theta$  for 30–100 s per step using CoK $\alpha$  radiation on a Huber System 600 Guinier diffractometer.

Fourier-transform infrared and Raman spectra were obtained using a Nicolet Magna 550 instrument equipped with a Raman accessory. Resolution for both infrared and Raman spectra was 1.9 cm<sup>-1</sup>. Infrared spectra were obtained in the transmission mode in the midinfrared region using pellets generally comprising 1 mg of sample diluted with 300 mg of KBr.

Excitation of Raman spectra was achieved by irradiating the samples with an Nd:YVO<sub>4</sub> laser generally operated at 1.0 W. Colored samples, e.g., the natural anatase and rutile, were diluted with KBr or irradiated with reduced laser power to avoid broadband thermal emission. Instrumental settings included a 180° reflective sampling configuration, a CaF<sub>2</sub> beamsplitter, and an InGaAs detector at room temperature. Samples were packed into NMR glass tubes, and two to five measurements, generally consisting of 200 scans each, were obtained at different positions of the tube. Band maxima and areas were determined using the Nicolet OMNIC software. All Raman band positions are given as shifts relative to the wavelength of the exciting radiation (1064 nm = 9394 cm<sup>-1</sup>).

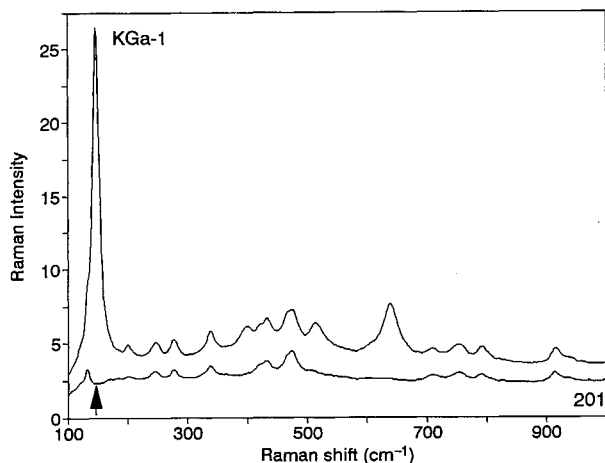


FIGURE 1. Raman spectra of the KGa-1 (top) and Burela 201 (bottom) kaolins. Note the strong anatase band at  $147\text{ cm}^{-1}$  in KGa-1. The arrow points to the position of this band, which is not perceptible at the scale of this figure, in the Burela 201 kaolin.

### RESULTS AND DISCUSSION

Raman spectra of the kaolins and the Bedford halloysite were relatively complex, consisting of 14–16 bands in the wavenumber region  $100\text{--}1000\text{ cm}^{-1}$ . Band positions and relative intensities for selected samples are given in Table 2. The band positions agree relatively well with those listed by Wiewióra et al. (1979) and Johnston et al. (1985). A striking feature of the spectra is that the intensities of several bands, in particular the most intense band of the KGa-1 and Amazon kaolins at  $147\text{ cm}^{-1}$ , vary by several orders of magnitude between samples (Fig. 1 and Table 2).

Raman spectra of the anatase samples were considerably simpler than those of the kaolins, consisting of five well-developed and some weaker bands (Fig. 2 and Table 2). The strongest bands were located at  $146$  and  $638\text{ cm}^{-1}$ , thus corresponding to the bands that varied most in intensity between the kaolins. The rutile spectra consisted, in agreement with Porto et al. (1967), of two major bands at  $447$  and  $611\text{ cm}^{-1}$  (which were significantly weaker than the main anatase band at  $146\text{ cm}^{-1}$ ; see Fig. 2) and subordinate bands at  $145$  and  $244\text{ cm}^{-1}$ . None of the main rutile bands was observed in any of the studied kaolins. A Raman spectrum of a natural brookite sample consisted of 15 well-developed bands in the wavenumber range  $100\text{--}700\text{ cm}^{-1}$ . The strongest band was located at  $155\text{ cm}^{-1}$  and had an intensity of 1800, which is comparable to that of the main anatase band at  $146\text{ cm}^{-1}$ . The fact that none of the kaolins showed a band at  $155\text{ cm}^{-1}$  indicates brookite to be absent in these, too. The above-mentioned differences among the Raman spectra of the individual kaolins can therefore be unequivocally attributed to the presence of anatase in different proportions.

The sensitivity of Raman spectroscopy to the presence of anatase in kaolins is best documented by the obser-

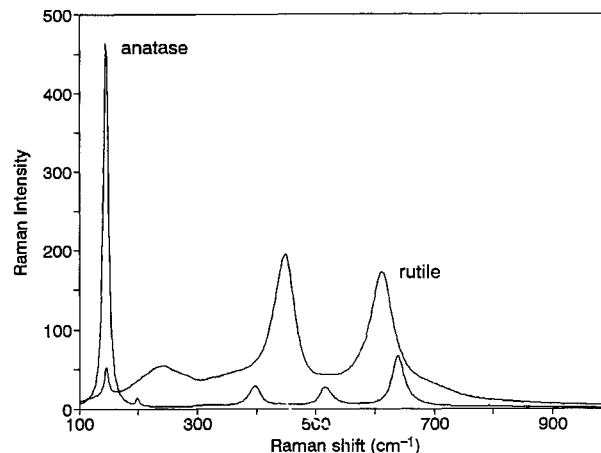


FIGURE 2. Raman spectra of the commercial anatase and rutile samples. Note that although both samples display a band near  $146\text{ cm}^{-1}$ , this band is more intense in anatase by more than one order of magnitude.

vation of a weak but still distinct band at  $146\text{ cm}^{-1}$  in the Burela 201 sample, which chemical analysis showed to have a  $\text{TiO}_2$  content, and thus a maximum possible anatase content, of 0.02% (Köster 1964). In contrast, the Raman spectra of the anatase-poor kaolins (e.g., the Burela 201 sample) displayed several bands that were partly (e.g., at  $132$ ,  $186$ , and  $202\text{ cm}^{-1}$ ) or completely (e.g., at  $171\text{ cm}^{-1}$ ) masked by intensive anatase bands in other samples.

Comparison of the Raman spectra of the untreated kaolins with those of their counterparts that had been treated with sodium dithionite to remove the iron oxides revealed no shifts in band positions. Insignificant reductions, if any, of band intensities showed that the dithionite treatment did not have a major effect on the anatase content of the kaolins.

The KGa-1 kaolin was also studied after heating to  $500\text{ }^\circ\text{C}$  for 30 h. The Raman spectrum of the dehydroxylated sample was different from that of the original kaolin, most of the original bands having disappeared. The most distinct remaining bands were still located at  $148$  and  $638\text{ cm}^{-1}$ , showing that anatase had not transformed to rutile.

The Raman spectrum of the Bedford halloysite did not differ noticeably from those of the anatase-poor kaolins. The BW208 halloysitic clay had a relatively poorly developed spectrum with weak bands at positions similar to those of the other samples, plus an additional band at  $464\text{ cm}^{-1}$  that can be assigned to quartz. This band was also observed in Raman spectra of some of the kaolins, usually as a shoulder bordering the band at  $474\text{ cm}^{-1}$ .

In an attempt to quantify anatase contents, the Amazon kaolin was mixed with different proportions of commercial and natural anatase. The areas of the  $146\text{ cm}^{-1}$  band in the commercial anatase-kaolin mixtures showed an excellent linear increase in Raman intensity with increasing anatase ( $R^2 = 0.997$  for four samples with increases up to 3% and an essentially linear extension of this trend to

pure anatase). The correlation of this trend with the natural anatase-kaolin mixture, however, was only poor, the relative intensities of the  $146\text{ cm}^{-1}$  band in the natural anatase being stronger by a factor of 3 than those of the commercial sample. Because X-ray diffraction indicated that the commercial anatase was essentially pure, the cause for the relatively low radiation yield of this material must be sought elsewhere. The observation that transmission infrared spectra of the two samples were quite different indicates that particle size or morphology (Tarte 1963) or other properties such as sample color may play a role in this respect.

Accurate determinations of the anatase contents require either spiking of the kaolins with anatase and rutile or the admixture of a suitable internal standard. Problems may possibly result in both cases owing to particle-size and texture effects and different degrees of fluorescence. Spectra obtained under identical experimental conditions nevertheless provide an approximate indication of the relative anatase contents of the kaolins. Comparison of the intensities of the  $147\text{ cm}^{-1}$  band of the kaolins to that of the natural anatase shows the anatase contents of the kaolins to vary from a maximum for KGa-1 [indicating that much if not all of the Ti content of this sample (1.39%  $\text{TiO}_2$ ) is incorporated in an ancillary anatase] to at most 0.02% in Burela 201 (Table 1).

### CONCLUSIONS

The differences in sensitivities to the various mineral phases, the simplicity of preparation, and the short measurement times make Raman spectroscopy an ideal method for the detection of anatase, rutile, and brookite in kaolinitic clays over a wide range of concentrations. Furthermore, it is possible to estimate the abundance of these minerals in kaolins and probably also in a variety of other geologic materials and technical products by Raman spectroscopy.

Wang et al. (1995) recently proposed the application of Raman spectroscopy as a technique for the remote mineralogical analysis of lunar materials. The present paper shows that, because of its high sensitivity for  $\text{TiO}_2$  phases, Raman spectroscopy would be particularly suitable for the possible identification of such minerals in the course of lunar and planetary missions.

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