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SPECTROSCOPIC APPROACH FOR INVESTIGATING THE STATUS AND MOBILITY OF Ti IN KAOLINITIC MATERIALS

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Abstract—The form under which Ti occurs in kaolinitic materials from various environments has been investigated using second derivative diffuse reflectance spectroscopy. The position of the absorption edge may be used as a diagnostic band to determine Ti-phases (anatase, rutile, Ti-gels). Ti-oxides may be detected in kaolins, down to 0.1 wt. % TiO_2. Diffuse reflectance spectra show the presence of Ti-gel-like phases occluded in sedimentary kaolinite particles. These phases, which record conditions at the time of kaolinite growth, constitute the first direct evidence of Ti mobility at the scale of mineral assemblages and question the substitution of Ti for Al in kaolinite. The nature of the Ti-oxides associated with kaolinite particles gives some constraints on the temperature conditions of hydrothermal kaolins, the evolution of sedimentary kaolin during basin diagenesis and the source of parental material in soil kaolins.

Key Words—Diffuse reflectance spectroscopy, Kaolins, Ti-mobility, Ti-status.

INTRODUCTION

Kaolinitic materials are ubiquitous materials having major geological and industrial importance. They have developed under a wide range of conditions: surficial weathering, such as the lateritic weathering that affects one-third of the emerged continents (Nahon 1986), sediment deposition and diagenesis and low temperature hydrothermal alteration (Murray 1988). Regardless of parent materials, all kaolins contain impurities such as iron and titanium (Jepson 1988). Several examples have shown that Ti behaves as an immobile or low-mobility element in soils (Hutton 1977, Brimhall and Dietrich 1987). However, there is good evidence for the mobility of Ti under intense weathering over long periods of time, as during laterite formation (Beauvais and Colin 1993). The form under which Ti occurs in altered rocks may influence the geochemical behavior of Ti during alteration. Titanium impurities have been suggested to occur either substituted in the kaolinite structure (Dolcater *et al* 1970, Weaver 1976, Rengasamy 1976) or as associated phases in kaolinitic materials (Jepson 1988). Because all kaolins contain significant amounts of titanium, the location of this element may be used as an indicator of the geochemical conditions during alteration and sedimentation processes. Such results may also lead to a better understanding of industrial kaolins in which titanium oxides have undesirable effects on physical properties (Jepson 1988).

The location of Ti in kaolins is difficult to determine because of the finely divided nature of Ti-phases (less than 0.1–0.2 micrometer, Sayin and Jackson 1975) which frequently form pellets tightly bound to each other and to kaolinite plates (Weaver 1976). A major difficulty in determining these phases in kaolins arises from the fact that the X-ray peaks of minority Ti-oxides (e.g., anatase 101 and rutile 110 reflections) are hidden by the most intense X-ray peaks of kaolinite and other associated silicates (Hutton 1977, Maynard *et al* 1969). An alternative method (Malengreau *et al* 1994), may be the second derivative diffuse reflectance spectroscopy which has been used for studying Fe-speciation in natural kaolins. However, with the noticeable exception of rutile (Bevan *et al* 1958, Hunt *et al* 1971), diffuse reflectance spectra of Ti-oxides are not well known.

We show in this paper that rutile, anatase and Ti-gel, which are the major Ti-phases suspected in kaolins, may be distinguished by their second derivative diffuse reflectance spectra. This spectroscopy allows the analysis of the status of titanium in kaolinitic materials down to 0.1 wt. % Ti. Ti-gel-like phases exist in kaolinite and may be considered as indicators of the growth conditions. This investigation demonstrates the mobility of Ti at the scale of mineral assemblages.

MATERIALS AND METHOD

Materials

Natural kaolins. Kaolins from hydrothermally altered rocks, sediments and soils were examined. These samples have already been described in a previous paper (Malengreau *et al* 1994). GB1 comes from the *in situ* china clay deposit located within the Cornubian ore field of southwest England (St Austell, Cornwall;

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Table 1. Sources, analytical Ti and Fe contents of the investigated (deferrated) kaolins.

Samples	Origin/locality	TiO_2 (%)	Fe_2O_3 (%)
GB1	hydrothermal/St Austell (Cornwall)	0.06	0.40
C15	hydrothermal/Nopal (Mexico)	0.10	0.83
KGa-1	sedimentary/Georgia (USA)	1.54	0.21
FBT4	sedimentary/Charentes basin (France)	3.54	1.22
R2	soil/Llanos (Colombia)	2.20	1.20

Jackson *et al* 1989). C15 is a kaolin from the kaolinitic alteration of Tertiary ignimbritic tuffs (Nopal I U-deposit, Chihuahua, Mexico) (Calas 1977, Aniel and Leroy 1985) and is a white sample from the fissural system close to an U-mineralized breccia pipe structure (Muller *et al* 1990). KGa-1 is a well-crystallized reference kaolin from Georgia kaolin deposits (Van Olphen and Fripiat 1978). FBT4 is a poorly crystallized sedimentary kaolin with a high specific surface (Fontbouillant, Charentes, France) (Delineau *et al* 1994). The R2 sample comes from an intermediate, red and clayey zone from a weathering profile formed from sandstones under a tropical climate and a savanna cover (Llanos area, East Colombia) (Faivre *et al* 1983).

The TiO_2 content of these kaolins ranges between about 0.1% and 1.5–3.5% in hydrothermal kaolins and soil and sedimentary kaolins, respectively (Table 1). These values encompass the Ti concentration range encountered in most natural kaolins (e.g., Maynard *et al* 1969). Ancillary Ti-phases were searched by X-ray diffraction using a PW 1740-Philips powder diffractometer (CuK_α radiation) equipped with a post-monochromator. Anatase was detected in KGa-1, FBT4 and R2 samples, though the main peak at 3.51 Å (101 peak) was largely hidden by the 002 peak of kaolinite at 3.57 Å. An additional peak at 3.25 Å (110 peak), which could correspond to the main diffraction peak of rutile, was also observed in R2. Except iron oxides (Malengreau *et al* 1994), the main other impurities detected were gibbsite in R2 and quartz and micas in KGa-1 and FBT4 samples. The dithionite-citrate-bicarbonate (DCB) method of Mehra and Jackson (1960) was used to remove iron oxides (Malengreau *et al* 1994). Acid NH_4-oxalate was also used as a selective extractant for amorphous TiO_2 and microcrystalline anatase (Fitzpatrick *et al* 1978).

Reference samples. Analytical grade micronized anatase (Hombitan FF Pharma pigment) and spectrally pure rutile (Johnson Mattheys Chemicals) were used as references for optical spectra. A freshly precipitated titanium hydrous oxide gel was prepared from hydrolysis of a titanium alkoxide by a butyl alcohol-water solution (Bulent 1986). This gel was dried at 120°C and kept at room temperature up to 11 months. A hk scattering band around 3.50 Å is observed up to five months which confirms the amorphous nature of this gel (Figure 1). Poorly crystallized anatase appears after this

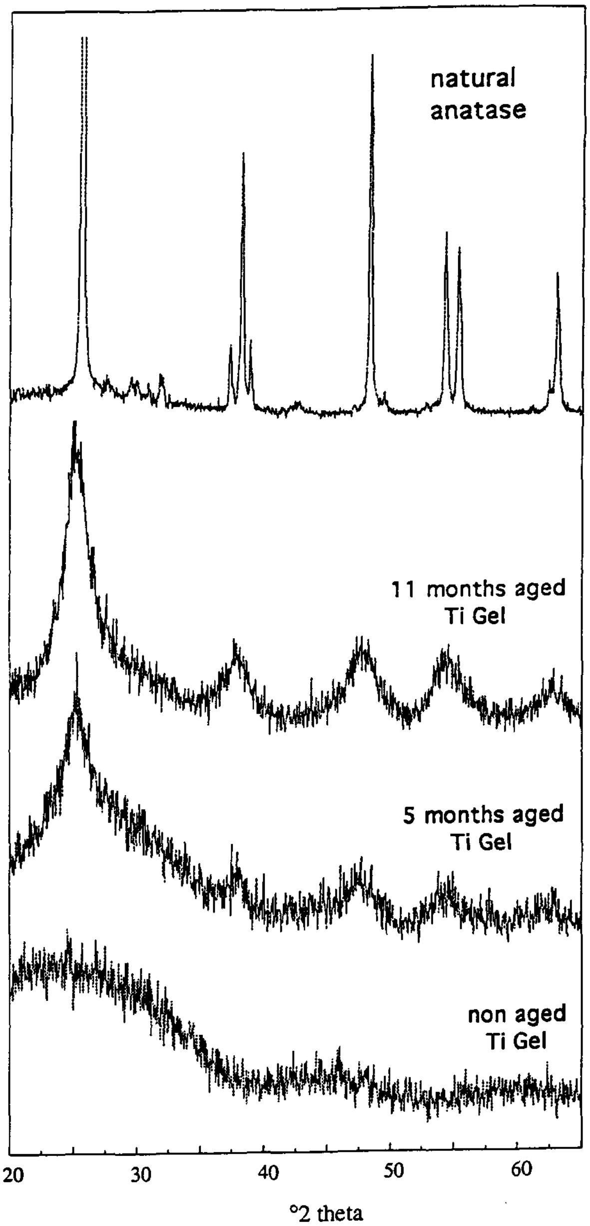

Figure 1. X-ray powder diffraction patterns of fresh and aged Ti-gels, and of anatase.

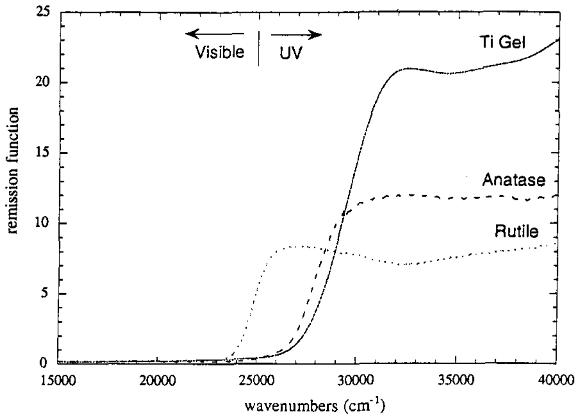

Figure 2. Raw spectra of reference Ti-phases (anatase, rutile, Ti-gel) in the 15,000–40,000 cm^{-1} range.

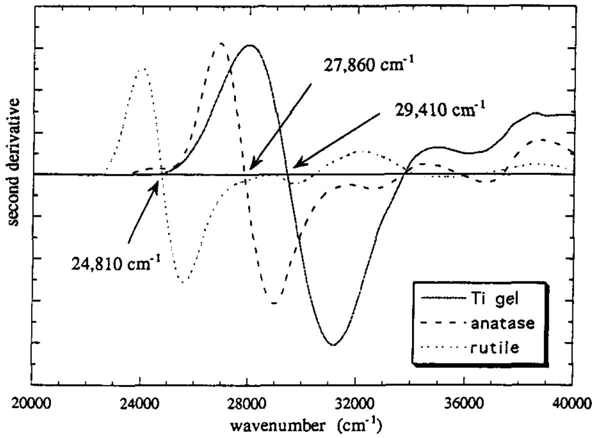

Figure 3. Second derivative curves of Ti-phases (anatase, rutile, Ti-gel) in the 20,000–40,000 cm^{-1} range. The position of the zero of the second derivative curves are indicated by arrows and the corresponding energy values are given.

time. Anatase proportion increases with the ageing time, as observed in previous studies (Fitzpatrick *et al* 1978).

Method

Diffuse reflectance spectra have been studied in the UV-visible range using a CARY 2300 spectrophotometer (Malengreau *et al* 1994). Measurements were made relative to a Halon standard. The Kubelka-Munk (KM) formalism was used to model the absorption of the scattered light under the form of a remission function (e.g., Wendlandt and Hecht 1966). Noise reduction of the experimental spectra was performed using a cubic spline smoothing technique. The absorption edge position due to charge transfer phenomena (see below) was determined by the zero of the second derivative curve, and its width was measured from the separation between the maximum and minimum of the second derivative function. Light scattering was considered to be negligible with respect to charge transfer processes and does not affect the zero of the second derivative. Remission functions were normalized respective to the OH overtone of kaolins at 7160 cm^{-1}. The accuracy in the band position is estimated to be 300 cm^{-1}.

RESULTS AND INTERPRETATIONS

Diffuse reflectance spectroscopy of reference Ti-phases

Because isolated Ti^{4+} ions do not exhibit optical absorption bands arising from internal 3d transitions, diffuse reflectance spectra of Ti-oxides display an intense absorption edge in the UV region. This edge is shifted toward higher wavenumbers from rutile to anatase and non aged Ti-gel (Figure 2) and may be assigned to an oxygen-to-titanium charge transfer by analogy to rutile ($1t_{1g} \rightarrow 2t_{2g}$ transition: Tossell *et al* 1974). Edge position values have been taken at the zero of second derivative of the remission function. They are located at 24,810, 27,860 and 29,410 cm^{-1} for rutile, anatase and Ti-gel, respectively and thus allow a clear separation among the three Ti-oxides (Figure 3). Diffuse reflectance spectra of 50–50 rutile-goethite and anatase-goethite mixtures show an absorption edge located at 25,130 and 27,400 cm^{-1}, respectively. These values are close to those corresponding to pure Ti-oxides and still allow a distinction among the two phases. Fe-oxides have thus a small influence on the optical spectra of anatase and rutile, due to the high intensity of charge transfer processes (Burns 1985).

As ageing proceeds, the absorption edge of Ti-gels (Figure 4) slightly shifts toward lower wavenumbers, from 28,410 to 28,250 cm^{-1} at 5 and 11 months ageing, respectively. This position is intermediate between that of fresh Ti-gels (29,410 cm^{-1}) and anatase (27,860 cm^{-1}). These results confirm the presence of anatase crystallites within aged Ti-gels, as revealed by XRD. The absorption edge is broader in the initial gel than in the final anatase, 3200 and 2200 cm^{-1}. However, edge broadening and second derivative lineshape do not vary much during gel ageing, which shows that the contribution of anatase to the optical spectra remains small.

Diffuse reflectance spectroscopy of kaolins

Two sets of distinct absorption features are superimposed on a rising background (Figure 5). The position and intensity of these features vary among the samples. Except for GB1, a first set of bands is located near 27,000–31,000 cm^{-1}. According to the above mentioned data, it can be related to a Ti-O charge transfer in TiO_2 ancillary phases. A second set of bands appears in the range 37,000–40,000 cm^{-1}. It can be attributed to an O-Fe^{3+} charge transfer (Karickhoff and Bailey 1973, Strens and Wood 1979) in relation with the presence of Fe^{3+} substituted in the kaolinite structure. Indeed, the intensity of this absorption band par-

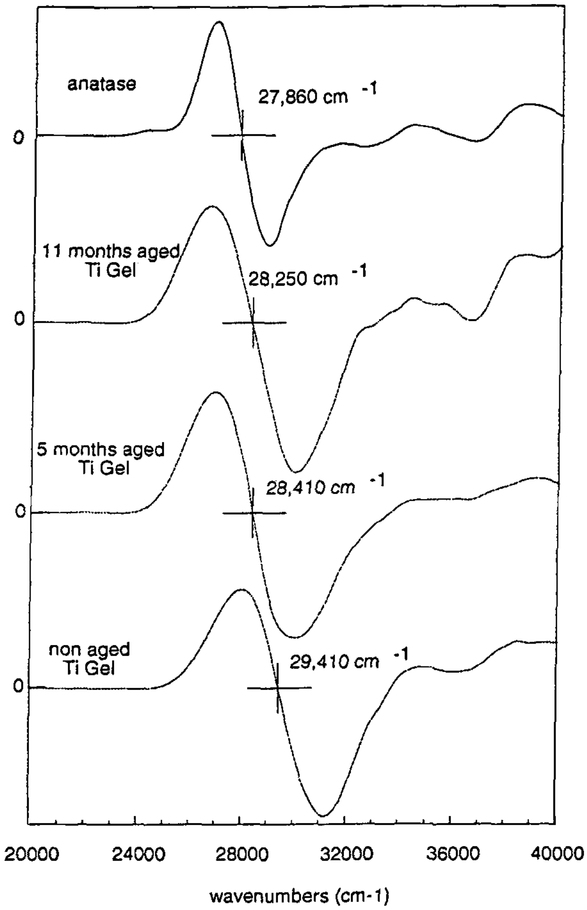

Figure 4. Second derivative curves of fresh and aged Ti-gels, and of anatase in the 20,000–40,000 cm^{-1} range. The position of the zero of the second derivative curves are indicated by crosses and the corresponding energy values are given.

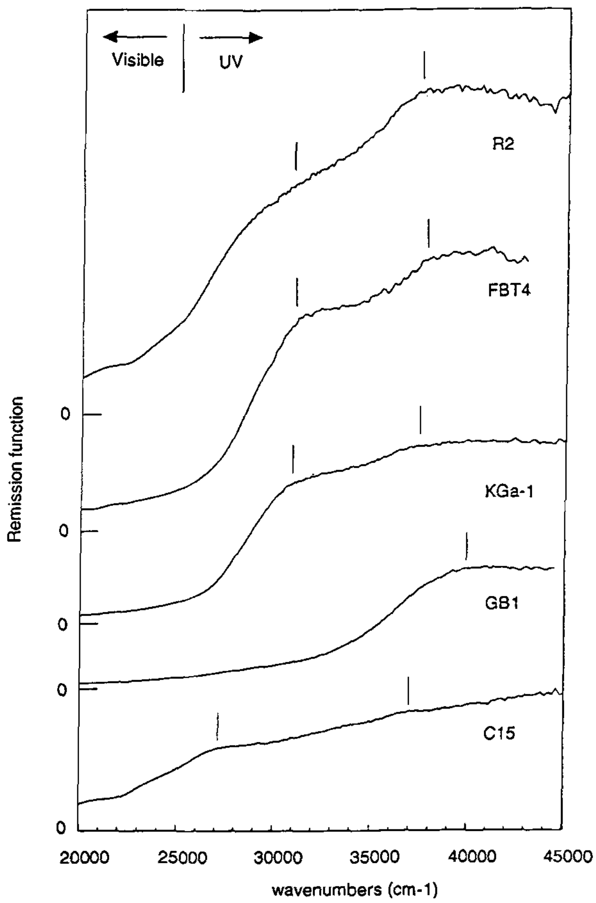

Figure 5. Raw spectra of hydrothermal (C15, GB1), sedimentary (KGa-1, FBT4) and soil (R2) kaolins, in the 20,000–45,000 cm^{-1} range. The vertical bars indicate the positions of bands determined from second derivative curves.

allels the concentration of structural Fe^{3+}, determined by electron paramagnetic resonance in the same samples (Muller and Calas 1993).

Second derivative spectra give a more precise indication of the nature of the Ti-bearing phases associated with kaolins than diffuse reflectance spectra. Sedimentary kaolins, FBT4 and KGa-1, exhibit marked bands with a zero point at 28,900 cm^{-1} and 28,490 cm^{-1}, respectively (Figure 6a). These positions are intermediate between those of anatase and non aged Ti-gel. The minimum points at 31,060 and 30,490 cm^{-1} in FBT4 and KGa-1, respectively, are close to that characteristic of non aged Ti-gel (31,150 cm^{-1}). It can then be inferred that both samples contain an aged Ti-gel like phase with a less ageing in FBT4 than in KGa-1. The TiO_2 content and the optical spectra remain identical before and after treatment of KGa-1 with acid NH_4-oxalate, a selective extractant for Ti-gels. The Ti gel-like phases are thus occluded within kaolin particles.

The second derivative spectra of the C15 hydrothermal kaolinite and of the R2 soil sample, show somewhat different signatures (Figure 6b): besides the marked bands due to Ti-phases, they display two weak minima at about 20,500–21,000 cm^{-1} and 23,300 cm^{-1}, that can be assigned to goethite (Malengreau *et al* 1994). The spectrum of C15 kaolinite shows a well-defined feature with a zero at 25,320 cm^{-1}. This position is shifted toward higher wavenumbers relative to pure rutile, as observed in rutile-goethite mixtures (see above). These observations indicate an intimate association of rutile and goethite in C15, in agreement with the high content of Fe relative to Ti found by chemical analysis (Table 1). The second derivative spectrum of R2 soil sample exhibits a marked band with a zero point at 26,670 cm^{-1}. This position is intermediate between that of anatase (27,860 cm^{-1}) and rutile (24,810 cm^{-1}) which confirms the XRD patterns (see materials). Moreover, the position of the minimum (28,330 cm^{-1}) is also intermediate between that observed for anatase and rutile, but is closer to

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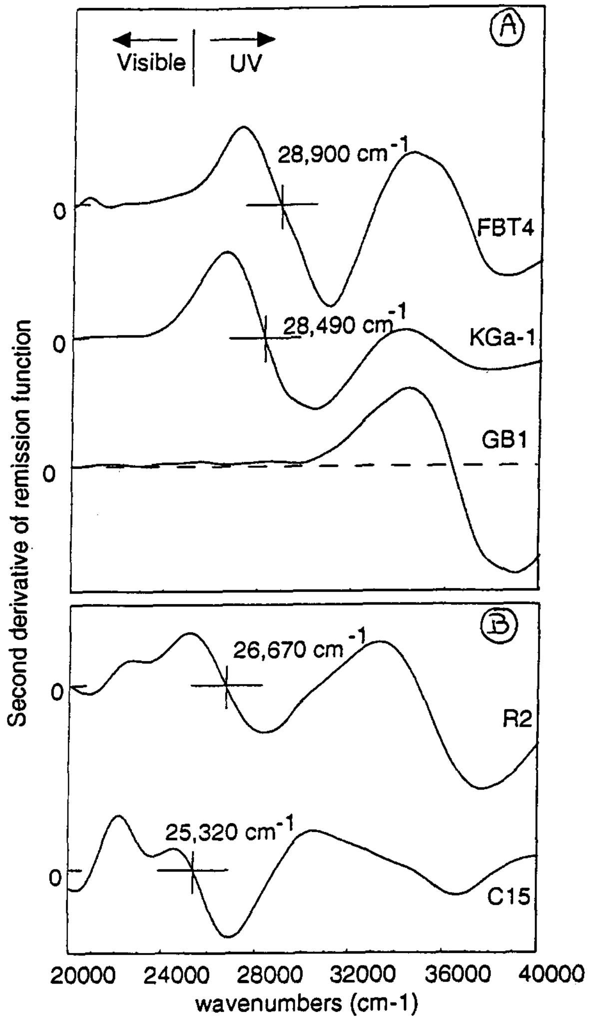

Figure 6. Second derivative curves of (A) hydrothermal (GB1) and sedimentary (KGa-1, FBT4) kaolins, (B) hydrothermal (C15) and soil (R2) kaolins, in the 20,000–40,000 cm^{-1} range. The position of the zero of the second derivative curves are indicated by crosses and the corresponding energy values are given.

that of anatase, showing that anatase is probably the predominant phase.

DISCUSSION

Significance of Ti-phases in hydrothermal and soil kaolins

The presence of rutile in C15 kaolinite could be related to ilmenite alteration (Temple 1966) since ilmenite was identified as a primary mineral source of Ti in the Nopal rhyolotic tuff (George-Aniel *et al* 1991). The hydrothermal origin of C15 kaolinite is still under debate. A temperature of about 60°C has been proposed for the hydrothermal alteration of the Nopal 1 area (Ildefonse *et al* 1990). Alteration of ilmenite and pseudorutile usually leads to the formation of rutile (Wort and Jones 1980). The presence of goethite, evidenced by diffuse reflectance spectroscopy (Malengreau *et al* 1994), confirms low alteration temperature conditions.

As R2 comes from a lateritic profile developed on alluvial materials eroded from sedimentary rocks (Gaviria 1993), the presence of anatase and rutile may represent two distinct processes. These Ti-oxides might be either inherited from the sediment bedrock or formed by subsequent alteration of primary oxides in the detrital sediment or during soil formation and evolution. Indeed, ilmenite in beach and sand deposits is largely altered in pseudorutile and Ti-oxides (Grey *et al* 1983). Since goethite and rutile have modified HCP anion arrangements (Waychunas 1991), they are expected to be intimately associated in the alteration products. This may explain the simultaneous presence of optical absorption features characteristic of these structures on the diffuse reflectance spectra.

Significance of the presence of Ti-gels in sedimentary samples

Rare occurrences of X-ray amorphous TiO_2 have been documented in young, slightly weathered soils (Bain 1976, Berrow *et al* 1978). This indicates a possibility for Ti to be mobilized in natural solutions, possibly as colloidal hydrated titanium oxides which may be ultimately dehydrated to form fine-grained anatase (Bain 1976) or rutile (Walker *et al* 1969). The spectroscopic evidence of aged Ti-gel within sedimentary kaolins is thus of special interest as it is the first direct evidence of Ti mobility on the scale of mineral assemblages. The presence of these gels, not previously mentioned in kaolins, indicates a local mobility of this element, perhaps assisted by organic compounds (Dumon 1976). After the gel is trapped in kaolinite, the hindrance of gel ageing may be due to the presence of impurities, such as Cl (Fitzpatrick *et al* 1978) or organic matter (Schwertmann 1966). Ti-gels are also stabilized during coprecipitation of Fe/Ti hydrous oxides (Fitzpatrick *et al* 1978). As already observed for aged hydrous ferric oxides associated with kaolins (Malengreau *et al* 1994), trapped Ti-gels are syngenetic with kaolinite. This confirms the hypothesis that sedimentary kaolinites partly suffer dissolution-recrystallization processes during steady state basin diagenesis (Muller and Calas 1993).

Substitution of titanium in kaolinite structure

Although C15 and GB1 have a similar Ti-content, only the former shows absorption features due to the presence of Ti-oxides (Figure 6a). This is an indication that Ti is substituted for Al within the kaolinite structure of GB1 and agrees with the absence of identified Ti-phases in Cornwall kaolinite (Dolcater *et al* 1970). In most kaolins, the evidence of Ti-Al substitution relies on indirect analysis. However, the presence of occluded gel-like phases casts doubts on this interpretation. For instance, the selective dissolution of kaolinite using the hydrofluotitanic acid (Rengasamy 1976) is known to dissolve amorphous TiO_2 (Dolcater *et al* 1970). On the other hand, chemical analysis of individual particles (Jepson and Rowse 1975) cannot discriminate between Ti-phases trapped within the kaolinite particles and Ti substituted in the kaolinite structure. Ti-Al substitution may therefore not be a general process acting in kaolins.

CONCLUSIONS

Diffuse reflectance spectroscopy is a powerful tool to determine the form under which Ti occurs in kaolins.

(1) There is doubt on the presence of Ti^{4+} cations substituted in kaolinite, apart from GB1 kaolin.

(2) The use of second derivative spectra improves the sensitivity of diffuse reflectance data. This allows the use of the $1t_{1g} \rightarrow 2t_{2g}$ transition in the UV region as a diagnostic band for deciphering among the various Ti-oxides present in kaolins (anatase, rutile and Ti-gels) down to 0.1 wt. % TiO_2 while they are not observed with other methods.

(3) Ti-gel-like phases evolving into anatase exist in sedimentary kaolins. Comparison of spectra of kaolinitic materials before and after selective extraction of TiO_2 gels shows that these gels are occluded within kaolinite particles. These occluded Ti-phases are the first direct evidence of Ti mobility at the scale of mineral assemblages.

(4) The presence of Ti-gel-like phases within sedimentary kaolinites supports the hypothesis that sedimentary kaolinites suffer dissolution-recrystallization processes during steady state diagenesis. The simultaneous presence of rutile and goethite in C15 confirms the low temperature hydrothermal origin of this sample.

A detailed study of the oxides associated with kaolinite may then lead to original information on the formation and evolution processes of natural kaolins.

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