

THE CHEMICAL FORM OF VANADIUM (IV) IN KAOLINITE

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Abstract—A combined application of electron paramagnetic resonance (EPR) and Fourier-transform infrared (FTIR) spectroscopies with thermal methods was used to determine the chemical form of V(IV) in a Georgia kaolinite (KGa-1). Precise values of the EPR spectroscopic g -values and hyperfine coupling constants were obtained for an untreated sample ($g_{\parallel} = 1.940$, $A_{\parallel} = 18.71$ mT; $g_{\perp} = 1.966$, $A_{\perp} = 7.63$ mT). Heating the sample to 1000°C in steps while monitoring phase changes with EPR and FTIR spectra led to the following structural interpretations: 1) Vanadium (IV) occurs almost entirely as an isomorphically substituted species in the octahedral sheet of KGa-1 kaolinite; 2) during the dehydroxylation of kaolinite at about 500°C and the subsequent formation of metakaolinite, V(IV)-substituted octahedral sites are readily converted into truncated octahedra exhibiting fourfold coordination; and 3) in these highly distorted four-coordinated sites, V(IV) is metastable, being completely oxidized at about 800°C.

Key Words—Electron paramagnetic resonance, Isomorphous substitution, Kaolinite, Vanadium.

INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy has revealed the common presence of V(IV), most probably as the species VO^{2+} , in natural kaolinites (Angel and Hall, 1973; Meads and Malden, 1975; Angel and Vincent, 1978; Watanabe *et al.*, 1987). The EPR spectrum of V(IV) is produced by a $3d^1$ ($S = 1/2$) electronic configuration, with hyperfine splitting arising from the interaction between the electron spin and the ^{51}V nucleus (99.8% abundance, $I = 7/2$) to create generally overlapping octets from each of the g_{\parallel} and g_{\perp} resonances (Hall, 1980; McBride, 1990). The hyperfine coupling constants, A_{\parallel} and A_{\perp} , are sensitive indicators of the local bonding environment of V(IV) coordinated to oxygen ligands, with more intense ligand fields corresponding to smaller values of the hyperfine coupling constants (McBride, 1990).

Both Hall (1980) and McBride (1990), in their reviews of EPR studies of clay minerals, cite unpublished data which they interpret to support the hypothesis of Angel and Vincent (1978), that V(IV) occurs in kaolinite principally as a species substituting for either Al^{3+} or Si^{4+} in the structure. The approximate hyperfine coupling constants they quote ($A_{\parallel} \approx 16.5$ mT, $A_{\perp} \approx 5.5$ mT, from Hall, 1980; $A_{\parallel} \approx 17.0$ mT, $A_{\perp} \approx 6.0$ mT, from McBride, 1990) are significantly smaller than those for $\text{VO}^{2+}(\text{aq})$ ($A_{\parallel} = 20.3$ mT, $A_{\perp} = 7.8$ mT; McBride, 1990). Thus, a much stronger ligand field should be associated with V(IV) in kaolinite, consistent with isomorphous substitutions at octahedral or tetrahedral sites. Ambiguity remains, however, because precise values of the hyperfine coupling constants are not

available and, even if they were, neither adsorbed species of V(IV) nor inclusions of V(IV) as VO_2 microclusters is likely to be ruled out by consideration of these constants alone.

Resolution of this issue may be possible by adopting the methodology developed recently by Gehring and his coworkers (1990, 1992) to determine the speciation of paramagnetic ions in multiminerological samples without chemical pretreatment. Gehring and Karthein (1990) showed that samples from a sedimentary iron deposit could be analyzed non-invasively by EPR spectroscopy in conjunction with calorimetric and magnetic methods. The differing thermal stability of the ferrous minerals in the samples between room temperature (RT) and 800°C permitted the assignment of paramagnetic ions [Fe(III) and Mn(II)] to specific mineralogical phases and the monitoring of thermal conversion processes by EPR. Calorimetric and spectroscopic methods—Fourier-transform infrared (FTIR) and EPR—were used by Gehring *et al.* (1992) to demonstrate the presence of defect free radicals, as well as Fe(III) and V(IV) (as the species VO^{2+}) in substituted sites in the structures of mica and kaolinite occurring in saprolite samples collected from a pallid zone of a lateritic soil profile. The persistence of the hyperfine splitting in the V(IV) EPR signal up to 900°C showed that VO^{2+} was located at octahedral sites in the mica structure. These prototypical studies indicate that correlation of the thermal stability of the EPR signal arising from paramagnetic centers [Fe(III), Mn(II), V(IV)] with the thermal stability of different mineralogical phases makes it possible to assign isomorphous substitutions involving the paramagnetic ions to specific

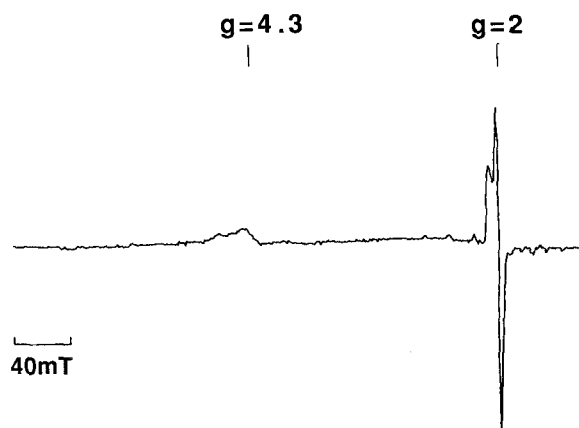


Figure 1. Wide-range EPR spectrum of untreated kaolinite.

minerals. The purpose of the present study is to apply this approach to determine the speciation of V(IV) associated with a well-crystallized, natural kaolinite.

MATERIALS AND METHODS

The kaolinite sample (KGa-1) used was obtained from the Source Clay Repository of The Clay Minerals Society. Summaries of the chemical and mineralogical properties of this well-crystallized kaolinite from a Cretaceous deposit in Georgia have been published by van Olphen and Fripat (1979) and Lombardi *et al.* (1987). The total V concentration in the kaolinite sample, as determined by ICP-AES analysis (see below) of a hydrofluoric acid digest (Bernas, 1968), was 203 ± 21 mg kg^{-1} , which is relatively low among Georgia kaolinites (Meads and Malden, 1975).

Spectroscopic analyses were performed on untreated samples and on samples that had been heated progressively from 200° to 1050°C for 5 hr at each step. Fourier-transform infrared spectra in the wavenumber range 400–4000 cm^{-1} were recorded on a Mattson Cygnus 100 spectrometer for both untreated and heated samples. The FTIR spectra were obtained in the absorbance mode on pellets containing 0.5 mg sample in 50 mg KBr. The EPR spectra were recorded on a Bruker 200ER spectrometer equipped with an Oxford Instruments EPR-900 cryostat and operating at X-band frequency with 100 kHz magnetic field modulation. The spectrometer settings with 2 mW microwave power, 0.1 mT modulation amplitude, and 9.38 GHz frequency. The EPR spectra, recorded at both room temperature (RT) and at 10 K, were analyzed to calculate g -values (N,N-diphenylpicrylhydrazyl (DPPH) as g -reference) and hyperfine coupling constants using computerscope programs from R. C. Electronics of Santa Barbara, California. Power-saturation experiments were performed in the range between 2 and 100 mW at 10 K on samples heated previously to 450 and 500°C, in order to distinguish isolated substituents and

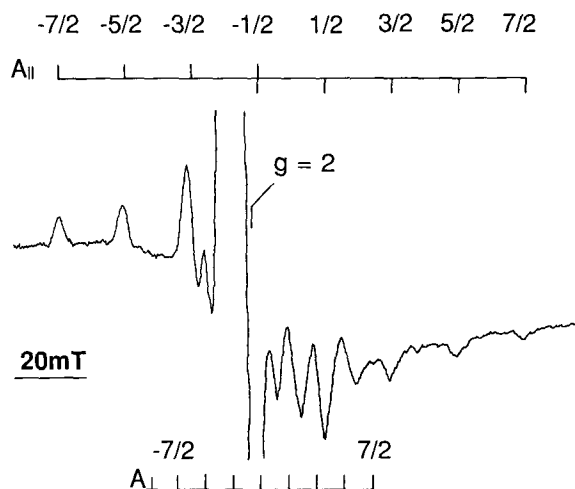


Figure 2. Narrow-range EPR spectrum of untreated kaolinite.

clusters with dipolar interactions. For evaluation of the power saturation data, a log-log plot of $[S/\sqrt{P}]$ against P was used (Beinert, 1972), where S is the signal intensity in arbitrary units and P is the microwave power in mW. If there is no saturation, $[S/\sqrt{P}]$ is independent of P , whereas increasing saturation of the signal is indicated by a decrease in $[S/\sqrt{P}]$ with increasing P .

To study the extractability of V, 0.5 g of an untreated kaolinite sample was equilibrated at pH 5 with 20 g of a solution containing 0.01 mol kg^{-1} EDTA and 1 mol kg^{-1} KNO_3 . The suspension was stirred for 16 hr at RT, then filtered through a Whatman No. 2 filter. The filter residue was washed with double-deionized water and air-dried for EPR analysis. The undiluted filtrate was analyzed for total V using inductively coupled plasma-atomic emission spectrometry (ICP-AES; Perkin Elmer Plasma 40).

RESULTS

The EPR spectrum of kaolinite at RT exhibited two principal resonances around $g = 4.3$ and $g = 2$ (Figure 1). The feature at $g = 4.3$ is observed typically in natural kaolinites and has been attributed to Fe(III) in a strongly distorted orthorhombic crystal field (Jones *et al.*, 1974; Meads and Malden, 1975; Hall, 1980). The resonances around $g = 2$ consist of an overlay of a sharp, isotropic signal and a broader signal with an eight-line hyperfine splitting (HFS). Upon heating, the intensity of the isotropic signal decreased and ultimately disappeared near 500°C. This signal has been attributed to free radicals caused by defects in the kaolinite structure (Cutler, 1980).

The HFS feature contained both parallel and perpendicular components (Figure 2). For the parallel component, $g_{\parallel} = 1.940 \pm 0.001$ and $A_{\parallel} = 18.71 \pm 0.04$ mT, while for the perpendicular component, $g_{\perp} = 1.966 \pm 0.003$ and $A_{\perp} = 7.63 \pm 0.04$ mT. These

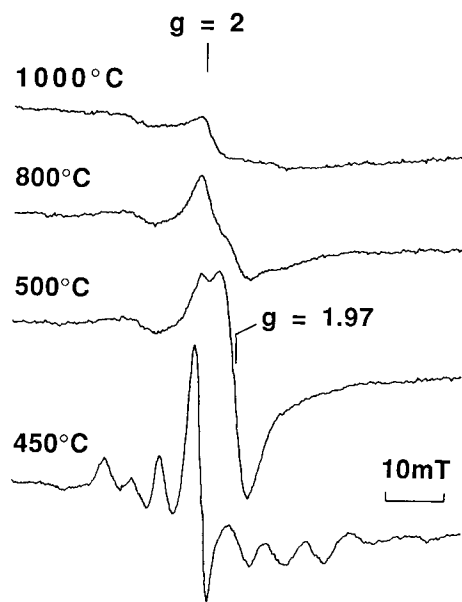


Figure 3. Narrow-range EPR spectra at RT after heating the sample to 450°, 500°, 800°, and 1000°C.

values are characteristic of V(IV) (Goodman and Raynor, 1970; McBride, 1990). Upon heating, the intensity of the HFS signal began to decrease at about 350°C and disappeared at 500°C, after which a new resonance appeared, with $g = 1.973 \pm 0.004$ and a linewidth of 5.12 ± 0.07 mT. This signal was thermally unstable and vanished at about 800°C (Figure 3). A second resonance with a slightly higher g -value was stable up to 1000°C. It was not possible to determine whether this signal was the result of transformations caused by heating or was simply masked at lower temperatures by the V(IV) HFS signal. The V(IV) HFS signal and the $g = 1.973$ signal formed by heating exhibited similar power-saturation behavior (Figure 4).

The EDTA extraction led to the dissolution of 7.8% of the total V in the kaolinite; the EPR spectra were identical before and after EDTA treatment.

The FTIR spectrum in the wavenumber range 3500–3800 cm^{-1} (Figure 5a) for the untreated kaolinite sample showed the stretching vibrational bands of structural OH groups (3697, 3670, 3656, and 3621 cm^{-1}) typical for kaolinite (Farmer, 1974). In the mid-infrared region, the untreated sample showed a characteristic Si–O stretching band near 1000 cm^{-1} ; OH deformations at 936 and 913 cm^{-1} ; and mixed Si–O deformations and octahedral sheet vibrations in the lower wavenumber range (Figure 5b). Upon heating the sample to 500°C, a drastic change in the IR spectrum was observed (Figure 5a): The absorption bands assigned to the vibration of OH groups (3697, 3670, 3656, 3621, 936, and 913 cm^{-1}) disappeared. Three major broad absorption bands around 1077, 813, and 460 cm^{-1} appeared, indicating a newly formed phase.

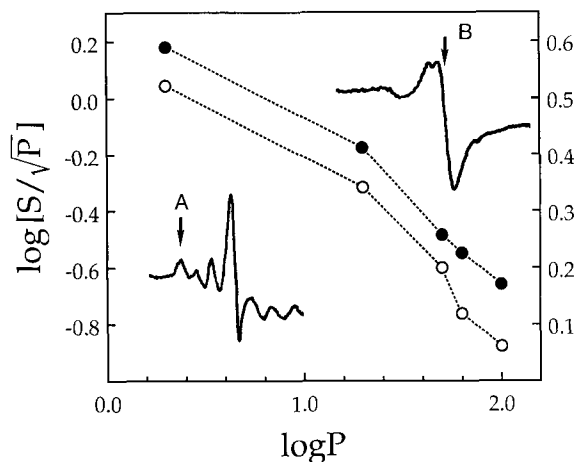


Figure 4. Log-log plot (see Materials and Methods) to evaluate the effects of power saturation on the V-3/2 EPR feature (arrow A in the lower spectrum) of a sample heated at 450°C (closed circles) and on the $g = 1.973$ resonance (arrow B in the upper spectrum) of a sample heated at 500°C (open circles). Spectra recorded at 10 K with signal intensity S , microwave power P .

They did not change significantly upon heating to 800°C (Figure 5b). These broad bands are typical of metakaolinite (Percival *et al.*, 1974).

DISCUSSION

The small amount of V extracted by EDTA from the Georgia kaolinite (0.31 mmol kg^{-1}) indicated that adsorbed species of V(IV) are of minor importance. McBride (1979) reported that the EPR spectrum of V(IV) in a kaolinite sample whose exchange sites were saturated with VO^{2+} (5 mmol kg^{-1}) was similar to the spectrum of $\text{VO}^{2+}(\text{aq})$ and, therefore, quite unlike the spectra in Figures 1–3. The well-resolved EPR resonances in these figures indicate also that V(IV) is magnetically dilute, which is inconsistent with the presence of VO_2 microclusters. This leaves isomorphic substitution as the principal mode of occurrence of V(IV) in the KGa-1 kaolinite.

The HFS constants determined in the present study are significantly larger than the (admittedly approximate) values of A_{\parallel} and A_{\perp} quoted by Hall (1980) or McBride (1990) for V(IV) in kaolinite. They are, however, close to the values compiled by McBride (1990) for V(IV) substituted in $\text{Al}(\text{OH})_3$ and in vermiculite (cf. Figures 8–11a in McBride, 1990). Gehring *et al.* (1992) found $A_{\parallel} = 18.6$ mT for V(IV) substituted in the octahedral sheet of a saprolitic mica. As shown in Figures 3 and 5, the HFS signal disappears in the same temperature range as that for the dehydroxylation of kaolinite and its conversion to metakaolinite. Since metakaolinite formation leads to structural rearrangement mainly within the octahedral sheet (Brindley and Nakahira, 1959; MacKenzie *et al.*, 1985; Watanabe *et*

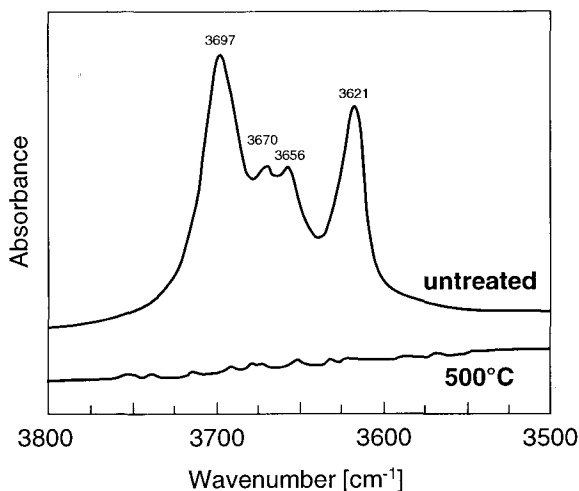


Figure 5a. Near-infrared spectra of untreated kaolinite and after heating to 500°C.

al., 1987), it is likely that V(IV) is located at octahedral sites in the KGa-1 kaolinite.

Given this conclusion, V(IV) can be assumed to be in coordination with six oxygen ligands (2 O and 4 OH), as in an AlO_6 -octahedron, with an average bond length of 0.192 nm (Leonard, 1977). One V–O bond should be a vanadyl triple bond (Ballhausen and Gray, 1962) with an average length of 0.159 nm (Clark, 1968). The V^{4+} ion is then positioned above the equatorial plane of the octahedral complex, such that the angle between the vanadyl and the equatorial V–O bonds is larger than 90° . Such distortion is often observed for vanadyl compounds (Cotton and Wilkinson, 1989). The length of the equatorial V–O bonds then becomes 0.195 nm, which agrees well with values of 0.195–0.205 nm observed typically for vanadyl complexes with O ligands (Clark, 1968). The V–O bond *trans* to the vanadyl bond has a length of 0.225 nm that compares favorably with bond-length measurements for vanadyl compounds (0.22–0.28 nm). Thus, stereochemically speaking, V(IV) can substitute comfortably for Al(III) in the octahedral sheet of kaolinite.

The HFS signal for V(IV) was not stable during the dehydroxylation of kaolinite (Figure 3). The appearance of a new, isotropic signal ($g = 1.973$) simultaneously with the disappearance of the hyperfine splitting suggests that V(IV) changed its coordination during thermal conversion at about 500°C. Non-resolved HFS has been reported for VO_2 because of linewidth broadening from dipole-dipole interactions (Arija *et al.*, 1967). The narrow linewidth of 5.12 mT, the low total V concentration (203 ppm), and the power saturation behavior of the $g = 1.973$ signal at 10 K (Figure 4) argue against the dipole-dipole interactions expected for newly formed VO_2 clusters. Therefore, it appears that V(IV) is substituted within the structure of metakaolinite.

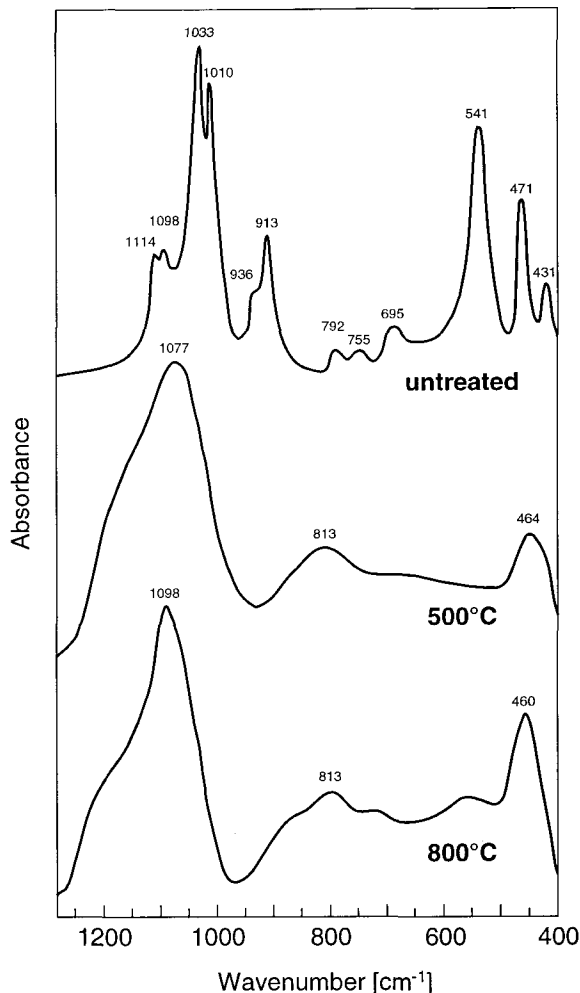


Figure 5b. Mid-infrared spectra of untreated kaolinite and after heating at 500° or 800°C.

Metakaolinite, an intermediate phase in the kaolinite-mullite reaction sequence, occurs in the temperature range between 550° and 1000°C (Lombardi *et al.*, 1987). In the metakaolinite structure, which exhibits a high concentration of lattice defects and no well-defined long-range order, Al(III) is in octahedral as well as tetrahedral coordination (Percival *et al.*, 1974; Leonard, 1977). Computer simulations by MacKenzie *et al.* (1985) show that the formation of metakaolinite leads to an additional, distorted, fourfold coordination for Al(III). This coordination can be considered schematically as a truncated former octahedron with two ligands missing (Figure 6). In principle, the V(IV) sites in kaolinite can be transformed similarly to those of Al(III) during thermal conversion. Indeed, the drastic EPR signal change at about 500°C indicates that V(IV) is no longer located in octahedral sites.

Two different sites with fourfold coordination are apparent in Figure 6: a regular tetrahedral site (*b*) and

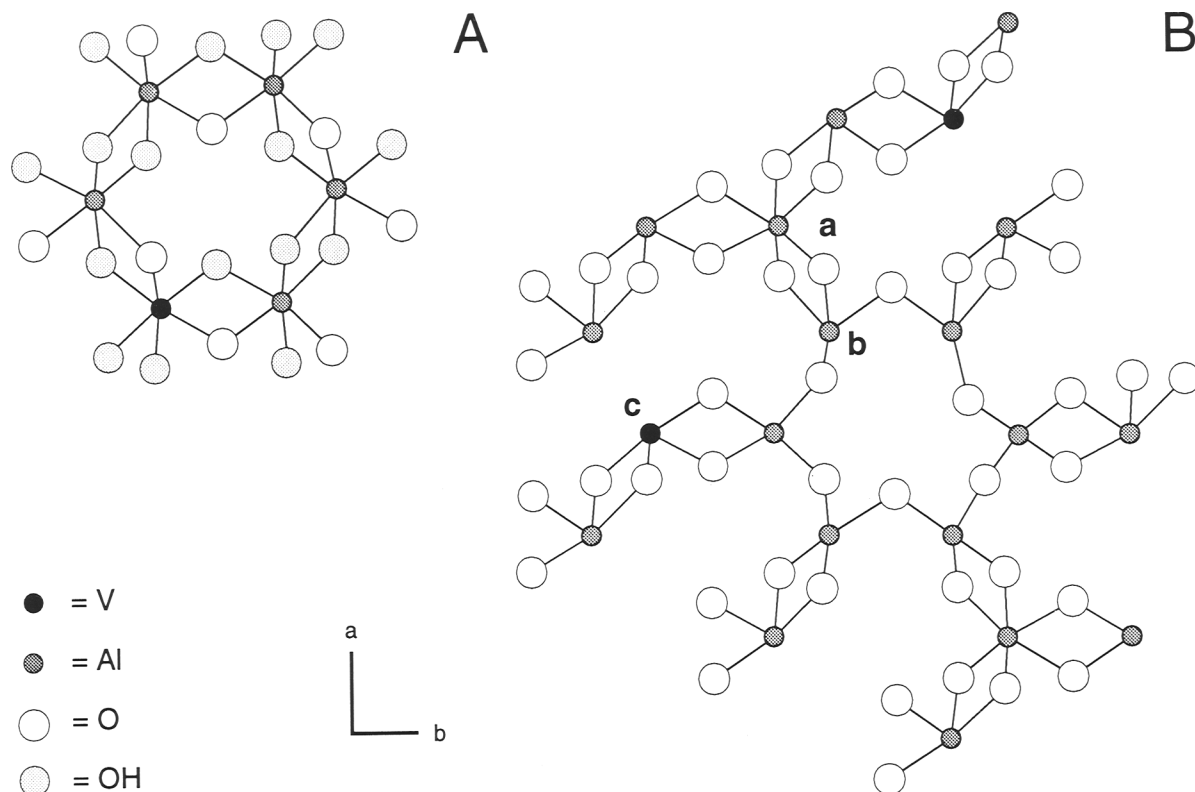


Figure 6. Structural elements of A) an octahedral sheet in a kaolinite and B) a dehydroxylated metakaolinite, after MacKenzie *et al.* (1985): a) regular octahedral sites, b) regular tetrahedral sites, and c) distorted, four-coordinated (truncated octahedral) sites.

a strongly distorted one (c). The EPR spectra of V(IV) in regular tetrahedral coordination nearly always show HFS (Goodman and Raynor, 1969). Since the $g = 1.973$ resonance showed no HFS, it is very unlikely that V(IV) is located at undistorted tetrahedral sites in the metakaolinite structure. However, as mentioned in the Introduction, the HFS of the V(IV) signal (i.e., the distance of the free electron from the V nucleus) is very sensitive to the ligand field (Goodman and Raynor, 1969; McBride, 1990; Gehring *et al.*, 1992). Thus, a loss of HFS can be explained as the result of a strong delocalization of the free electron away from the paramagnetic center. The shift in the g -value of the signal that appears between 450° and 500°C toward that of the free electron is in agreement with this interpretation. In the metakaolinite structure (Figure 6), a delocalized system would occur most likely within strongly distorted tetrahedral sites. These truncated sites have no ligands on one side of the coordination center to force the free electron to approach closely enough to the center for a detectable interaction. Therefore, V(IV)-substituted octahedra in kaolinite would be easily converted into truncated octahedral sites during the transformation into metakaolinite. The disappearance of the $g = 1.973$ signal upon heating to 800°C shows also

that V(IV) in these truncated sites is not stable within the metakaolinite range of the kaolinite-mullite thermal sequence.

CONCLUSIONS

The non-invasive, thermal-spectroscopic approach of Gehring and coworkers (1990, 1992) was applied successfully to determine the chemical form of V(IV) in a well-crystallized Georgia kaolinite (KGa-1). Analysis of the data led to the following structural interpretation:

- 1) Vanadium (IV) occurs almost entirely as an isomorphically substituted species in the octahedral sheet.
- 2) During the dehydroxylation of kaolinite (at about 500°C) and the subsequent formation of metakaolinite, V(IV)-substituted octahedral sites are very likely converted into truncated octahedra with fourfold coordination.
- 3) In the highly distorted four-coordinated sites, V(IV) is metastable and is completely oxidized at about 800°C.

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