ELECTRON SPIN RESONANCE OF VANADYL IONS IN THE CRETACEOUS/TERTIARY BOUNDARY LAYER FROM THE STARKVILLE-SOUTH SITE, THE RATON BASIN, USA

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ABSTRACT: Vanadyl (VO^{2+}) ions in the Cretaceous/Tertiary (KT) boundary layer: the Starkville-South Site (SVS), the Raton Basin, USA – have been investigated by electron spin resonance (ESR). It was found that VO^{2+} ions are associated with the kaolinite structure of this sedimentary rock. The VO^{2+} content in this clay mineral is 75 ppm as determined by ESR. Axial symmetry (seen from the ESR spectrum) and the g_{II} principal component of the g-tensor indicate the C_{4v} symmetry from the ligand field around the incorporated VO^{2+} ion: a compressed octahedron with the principal (fourfold) symmetry axis colinear with the V=O bond. It is suggested that the VO^{2+} ion is coordinated with the oxygen atoms and located either on the surface or within the kaolinite structure.

INTRODUCTION

Since the discovery by Alvarez *et al.* (1980) of an iridium (Ir) anomaly at the planktonic KT boundary in marine sedimentary rocks at Gubbio (Italy), over 50 more sites world wide with unusually high concentrations of Ir have been found in marine sediments exactly at the KT boundary (Alvarez *et al.* 1983). Alvarez *et al.* (1980) explained the high Ir concentration in terms of the impact of an asteroid depositing a worldwide layer of Ir. Most of these anomalies were discovered in marine sedimentary rocks, but in the Raton Basin the palynological KT boundary interval occurs in a rock sequence deposited in fresh water swamps and flood plains (Pillmore and Flores 1987). At SVS a thin shaly bed, between the base of the coal and the kaolinitic-clay layer, contains the highest concentration in the Basin (56 ppm). In addition to Ir the KT boundary layers in the Raton Basin are also enriched in other trace metals, such as vanadium (V) (Gilmore *et al.*, 1984). According to these authors the content of V in these rocks ranges

from 110 ppm to 187 ppm and is thus of the same order of magnitude as in other ancient shaly-type sedimentary rocks (Turekian and Wedepohl 1961).

The oxicity and anoxicity of the environment of sedimentation exerts a marked influence, not only on the amount of V preserved in the sediment, but also on its composition at the molecular level (Meinecke 1973). For instance, chemical conversion of V compounds on the sediment-water interface into VO^{2+} compounds is strictly conditioned by the depositional environment: both the redox potential and acidity are key factors in the preservation of VO^{2+} compounds in this environment (Meinecke 1973). Thus, VO^{2+} compounds are excellent geochemical indicators of paleoenvironmental conditions of sedimentation. This fact led us to search for VO^{2+} ions in the SVS KT layer which might contribute to a general understanding of the origin and nature of the KT boundary layers and their mineral components.

VO^{2+} compounds have been studied by electron spin resonance (ESR) in a wide range of geological materials including clay and clay minerals (Meads and Malden 1975, Angel and Vincent 1978). Recently Premovič (1984) successfully employed this method for a detailed study of VO^{2+} compounds in a variety of sedimentary rocks.

EXPERIMENTAL

Fourier transform (FT), Infrared (IR) spectrometry

Rock samples were powdered finely and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). The pellets were then dried for at least one hour at 373 K before the spectra were recorded at room temperature using Perkin-Elmer 1600 FTIR spectrophotometer set to give undeformed spectra.

ESR

ESR measurements were performed on the finely-ground powders of rock samples which were transferred to an ESR quartz tube (4 mm o.d., 3 mm i.d.). The spectra were recorded on a Bruker ER 200 ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz. The g-values and hyperfine coupling constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for which g = 2.0055 ± 0.0001 and the nitrogen hyperfine splitting a_N = 1.309 ± 0001 mT (Faber and Fraenkel 1967). A quartz tube (approximately 2 mm o.d., 0.8 mm i.d.) was used for Fremy's solution (ca. 10^{-3} M) and was taped to the exterior of the rock sample tube. Spin concentrations of VO^{2+} ions in the KT rock samples were determined by the sample interchange method

using powdered potassium tartarate dopped with 0.01 % VO^{2+} standard. Further details of the ESR concentration measurements and associated control procedures for precision and accuracy are given in Nikolić (1993).

X-ray analysis

X-ray analysis of the whole sediment sample, the carbonate-free and silicate fractions were performed by Philips diffractometer (PW 1050/25) equipped with a proportional counter and discriminator, using Ni-filtered Cu radiation at 40 kV and 20 mA.

Analysis and fractionation

The fractionation procedure was similar to that used by Saxby (1976), Premovič (1984) and Schmitz *et al.* (1988). The major steps are: (a) the powdered rock sample (10 g) was treated with cold hydrochloric acid (HCl, 6M) to remove most of the carbonates. Carbonate removal was checked by FTIR analysis. The soluble materials constitute the carbonate-free fraction. (b) The insoluble residue from (a) was demineralized further by repeated treatment with boiling HCl (6M). (c) The insoluble residue from (b) was demineralized with boiling hydrofluoric acid HF/HCl (22M and 0.25 M), respectively. This acid mixture removes silica (SiO_2) and this removal was checked by FTIR and X-ray analyses. (d) The final residue from (c) is the organic fraction.

RESULTS AND DISCUSSION

Mineralogical analysis

Mineralogical analysis of the SVS sample shows that this rock contains major authigenic mineral: kaolinite and minor detrial mineral: anatase, Fig. 1. The distribution of VO^{2+} in the various fractions of SVS is shown in Tab. 1.

ESR and VO^{2+} ion

The investigation of the untreated SVS sample yielded a partly multiline ESR spectrum similar to the spectrum od $CaCO_3$ doped with Mn^{2+} as reported by Hurd (1954). The spectrum of the untreated SVS sample is given in Fig. 2a.

After removal of the carbonate fraction of the rock sample (by treating with cold 6M HCl) the Mn^{2+} lines diminished. Carbonate removal was checked following the disappearance of the CO_3^{2-} IR bands at 885 cm^{-1} and 706 cm^{-1} (Nakamoto 1978), Fig. 3b.
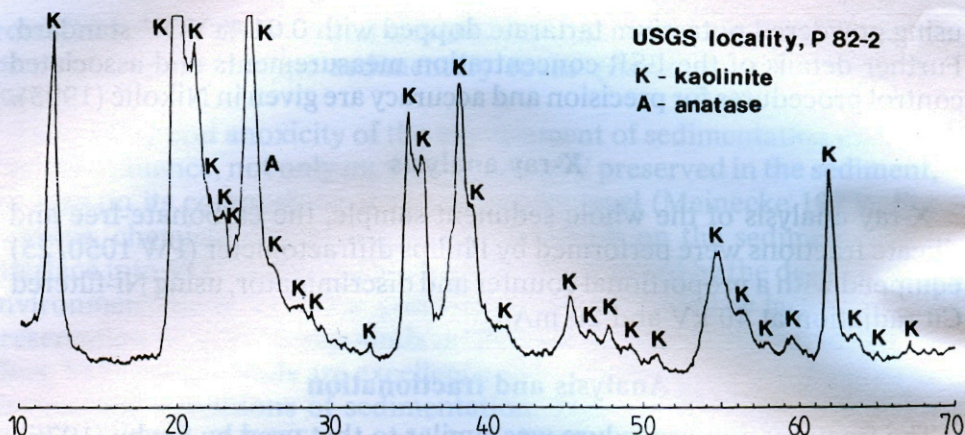
Fig. 1. X-ray diffractogram of the SVS sample.

The ESR spectrum of the SVS sample (after removal of the carbonates), Fig. 2b, was identical to the ESR spectrum recorded by Premović (1984) for VO^{2+} ions associated with the clay fractions of ancient shaly-type sedimentary rocks of marine origin. These ESR signals can be described by the spin-Hamiltonian valid for d^1 metal ions in axial symmetry:

$H = \beta_o \left[g_{II} H_z S_z + g_\perp (H_x S_x + H_y S_y) + A_{II} S_z I_z + A_\perp (S_x I_x + S_y I_y) \right]$, where g_{II}, $g_\perp$ are the parallel (z) and perpendicular (x, y) components of the g-and ^{51}V-hyperfine coupling tensors, respectively. H_i, S_i and I_i represent the vector components of the magnetic field, electron spin, and ^{51}V nuclear spin along the $i = (x, y, z)$ axes, respectively. These parameters for VO^{2+} ion in SVS are given in Tab. 1.

The HCl demineralizing step removes 50 % of the sediment. This is a result of the total dissolution of calcite (cold HCl, 3 %) and the destruction of clay minerals, i. e. mainly kaolinite (boiling HCl, 46 %). The kaolinite destruction was checked following the disappearance of the 3695 and 3622 cm^{-1} IR bands (van der Marel and Beutelspacher, 1976), Fig. 3c.

Tab. 1. Demineralization of the SVS sample and ESR data for VO^{2+} ions[x] associated with the kaolinite mineral fraction.

Fraction	Clay (wt. %)	VO^{2+} (ppm)[xx]
Sediment	100	75
Cold HCl	3	–
Boiling HCl	46	160
HF	50	–
Organic	1	–

[x] The ESR parameters:
$g_{II} = 1.942 \pm 0.003$; $g_\perp = 1.979 \pm 0.010$;
$A_{II} = 18.6 \pm 0.02$ mT; $A_\perp = 6.2 \pm 0.4$ mT
[xx] The VO^{2+} content in the carbonate-free sample, determined by ESR.

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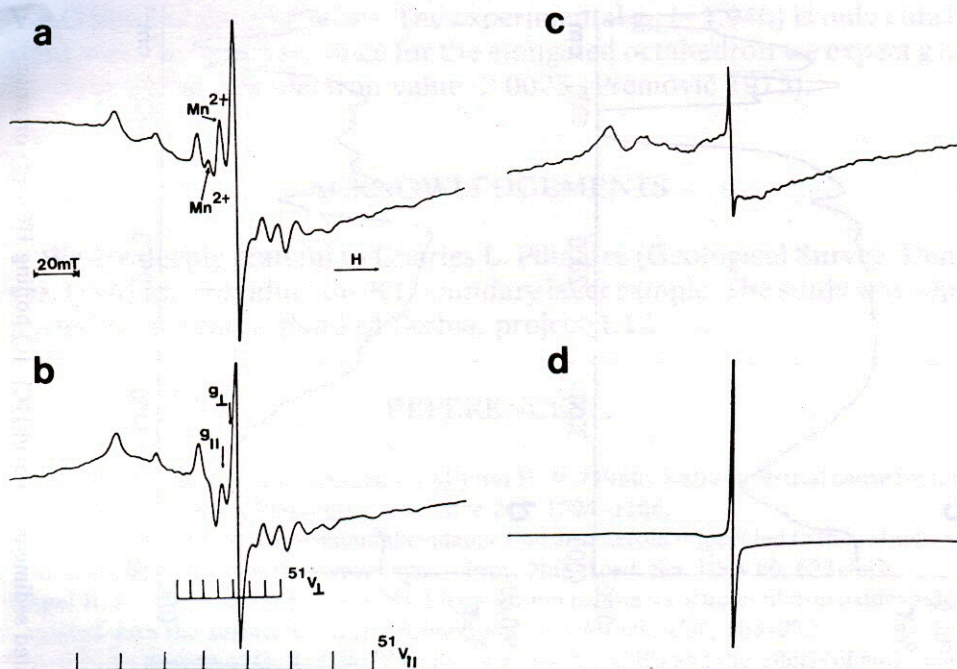*Fig. 2.* ESR spectrum of the SVS sample residue: (a) untreated sediment; (b) cold HCl; (c) boiling HCl; (d) organic.

SiO_2, which is an important constituent of the clay mineral lattices, seems relatively unaffected (ca. 40 %) by the boiling HCl demineralization. This indicates that protons (H^+) replace Al at its sites in the kaolinite lattice. Much of the SiO_2, however, also exists as HCl-insoluble quartz. VO^{2+} ions disappear completely during the boiling HCl treatment, Fig. 2c, suggesting an association with the kaolinite fraction. It is obvious, then, from these results that the VO^{2+} ions of SVS may occur only in those chemical forms in which these ions are part of the kaolinite structures. Therefore, it may be reasonable to assume that VO^{2+} ions either lie on the surface or are located inside the kaolinite lattice and at the same time coordinated to the clay oxygen atoms. In general, the VO^{2+} ion is known to coordinate ligands with oxygen atoms (Holyk 1979).

The HF step removes almost all the remaining SiO_2 (of all the SiO_2 in the sample > 99 % is lost), Fig. 3d. The dominant phase of the HCl/HF demineralization residue is organic matter (> 70 %) (Nikolič 1990).

On the basis of axial symmetry for the ligand field around the VO^{2+} ion determined by ESR, we suggest C_{4v} as the local point symmetry for this species in SVS. There are two types of C_{4v} symmetry, namely: compression or elongation along principal (fourfold) symmetry axis (colinear with the
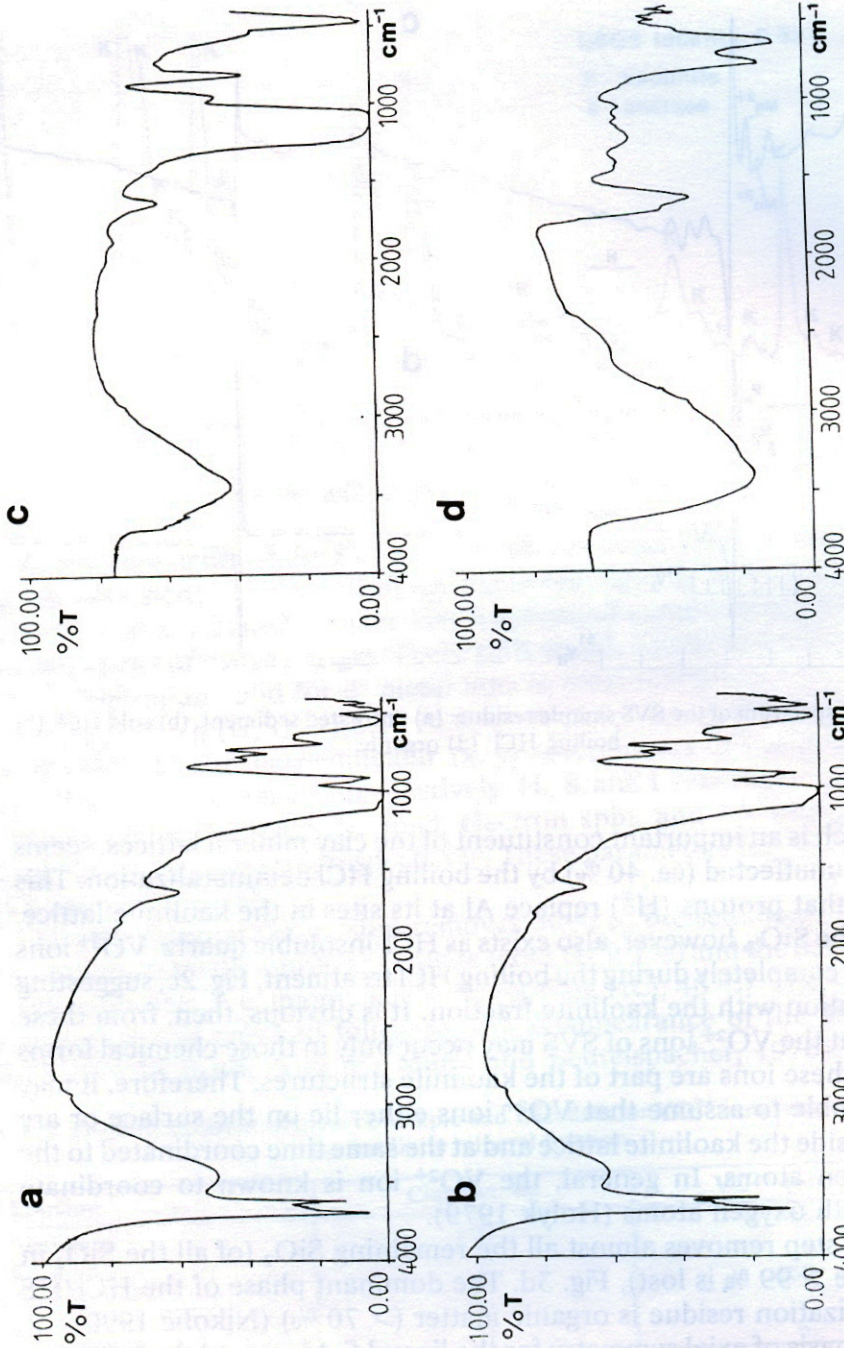
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Fig. 3. FTIR spectrum of the SVS sample residue: (a) untreated sediment; (b) cold HCl; (c) boiling HCl; (d) organic.

V = O bond of the VO^{2+} ion). The experimental g_{II} (= 1.946) is only consistent with the first case, since for the elongated octahedron we expect g to be close to the free electron value: 2.0023 (Premović 1975).

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