

NOTE

Vanadyl ions in ancient marine carbonaceous sediments

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(Received September 8, 1982; accepted in revised form January 4, 1984)

Abstract—Vanadyl ions in ancient shaly-type sedimentary rocks of marine origin from a variety of world sources and geological periods have been investigated using electron spin resonance. These and other results provide evidence that there are two types of vanadyl ions. The first is inorganically bound in the clay/silicate fraction of these rocks and the second type is associated with vanadyl porphyrin compounds.

INTRODUCTION

THERE ARE A number of organometallic compounds in carbonaceous shales, the most common being porphyrins. Much spectrophotometric work has been performed to detect the presence of vanadyl (VO^{2+}) porphyrins in carbonaceous shales since they are readily separated by extraction. However, very little is known concerning the nature of vanadyl compounds other than porphyrins, due principally to the poor sensitivity of the more common techniques for characterization of metal compounds. Electron spin resonance (ESR), a sensitive and non-destructive method for investigation of transition metal ions, has been used for trace metal characterization in petroleum by several workers (SARACENO *et al.*, 1961; BOUCHER *et al.*, 1969; DICKSON *et al.*, 1972; PREMOVIĆ, 1978). ESR allows detection of many transition metal ions *in situ* at ppm level in small samples (0.1 g or less). One great advantage of *in situ* study is that it allows characterization of transition metal ions in their unmodified rock matrix, and thus allows their association with inorganic and organic constituents to be determined.

Vanadyl compounds have been studied by ESR in a wide range of geological materials including soils (CHESHIRE *et al.*, 1977; ABDUL-HALIM *et al.*, 1981); coals (CHINENOV, 1975); and clays and clay minerals (HALL *et al.*, 1974; MEADS and MALDEN, 1975; and ANGEL and VINCENT, 1978). Recently, HOCKING and PREMOVIĆ (1978) have successfully employed this method for the detailed study of vanadyl porphyrins in the coal inclusions of the Athabasca tar sands, without prior extraction.

The results reported here are part of an investigation of the nature and abundance of trace metal species in ancient sedimentary rocks. The purpose of the present paper was to carry out an ESR study of vanadyl compounds in several ancient marine carbonaceous sediments, which might contribute to a general understanding of the origin of vanadium in geoporphyryns.

EXPERIMENTAL

ESR measurements were performed on the finely-ground powder of rock samples which were transferred to an ESR quartz tube. Spectra were recorded on a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz. The g -value and hyperfine coupling constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for which $g = 2.0055 \pm 0.0001$ and the nitrogen hyperfine splitting, $a_N = 1.309 \pm 0.001$ mT (FABER and FRAENKEL, 1967). Spin concentration of vanadyl ions in the carbonaceous sediments was determined by the sample interchange method (ALGER, 1968) using powdered ammonium sulfate doped with a 0.1% copper(II) standard.

RESULTS AND DISCUSSION

Analysis of the spectra of selected sediments, Table 1, to yield spin-Hamiltonian parameters for the vanadyl compounds present, is hindered by the overlapping resonance structures of the vanadyl and manganese(II) ions. However, after removal of carbonate fractions of these sediments by washing with 0.2 M hydrochloric acid (HCl), the manganese(II) lines diminish. The removal of carbonates was checked by infrared (IR) analysis. ESR spectra of carbonaceous shales in Table 1 were similar to the spectrum of the Zvonca shale, shown in Fig. 1a. In general, these spectra gave a 16-line anisotropic pattern, due to interaction of the ^{51}V nucleus ($I = 7/2$) with its unpaired electron, and displayed parallel and perpendicular features characteristic of polycrystalline samples. No ligand superhyperfine interactions were observed in the above spectra.

All the spin-Hamiltonian parameters derived from the spectra are given in Table 1 assuming the axially symmetric spin-Hamiltonian,

$$\mathcal{H} = g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)$$

where g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} , are the parallel (z) and perpen-

Table 1. ESR parameters for vanadyl ions in ancient shaly-type sediments of marine origin.

Lithology and rock unit	Region	Geologic period	Age ca. 10 ⁶ y	$g_{\parallel} \pm$	$A_{\parallel} \pm$	VO ²⁺ (ppm)	Geological reference
				0.003 $g_{\perp} \pm$ 0.010	0.2 mT $A_{\perp} \pm$ 0.4 mT		
Zvonce black shale	Serbia	Silurian	430	1.946	18.6	40	Petković
Antrim black shale	USA	Devonian	390	1.980	5.9	70	Milojević (1956)
Kupferschiefer	W. Germany	Permian	280	"	"	3	Belsky et al., (1965)
Posidonienschiefer	W. Germany	Jurassic	190	"	"	10	Gregory (1930)
Atlantic Ocean DSDP-41: 368-63-1 (68 cm - 76 cm)	S.W. Africa	Cretaceous	130	"	"	70	Baker et al., (1978)
368-60-4 (55 cm - 63 cm)						15	
Serpiano marl	Switzerland	Triassic	220	1.951	17.6	900**	Treibs (1934)
La Luna Mara limestone	Venezuela	Cretaceous	130	1.985	5.7	400**	Hedberg (1931)
Georgia kaolin (Mine 24)	USA	-	-	1.946	18.7	7	
				1.980	6.0		

*Vanadyl content in carbonate-free sample. **As vanadyl in vanadyl porphyrins.

dicular (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.

Data from carbonaceous shales differ significantly from that of the shaly limestone of the La Luna Mara Formation (Venezuela) and the Serpiano marl (Switzerland). One of the remarkable characteristics of the latter two units is the high content of vanadyl compounds of deoxyphylloerythroetioporphyrin (DPEP), as much as 3% (or even higher) (GRANSCH and EISMA, 1966) and 0.45% (BLUMER, 1950). Experimental ESR spin-Hamiltonian parameters for the vanadyl compounds in the La Luna Mara limestone (and the Serpiano marl) sample, derived from its ESR spectrum (Fig. 1b), also listed in Table 1, are in good agreement with previously published values for vanadyl porphyrins in petroleum (O'REILLY, 1958, 1959), coals (HOCKING and PREMOVIĆ, 1978) as well as for synthetically prepared vanadyl porphyrin complexes (ASSOUR, 1965). Therefore, one may conclude that the ESR parameters found for vanadyl compounds in these sediment samples are representative of vanadyl porphyrins. This interpretation is further supported by our visible spectral study (PAVLOVIĆ and PREMOVIĆ, unpublished). Finely ground La Luna Mara limestone (and the Serpiano marl) sample, after removal of carbonates, was extracted in a Soxhlet extractor with a benzene:methanol mixture (3:1 v/v or 7:1 v/v) for 72–90 h. This treatment removed almost all extractable vanadyl compounds (99.9%) in these samples. The vanadyl ions removal was checked by ESR analysis. The extracts showed the visible spectra (HODGSON *et al.*, 1967) and the ESR spectra (O'REILLY 1958, 1959; HOCKING and PREMOVIĆ, 1978) characteristic of natural-occurring vanadyl porphyrins found in petroleum and carbonaceous shales.

It has been recently shown that ESR parameters are particularly sensitive to direct ligand substitution in vanadyl complexes (HOLYK, 1979; CHASTEEN, 1980). Thus, the differences in ESR parameters, especially A_{11} (which is the most sensitive parameter to the bond-

ing), can represent the differences in the bonding ligands around the vanadyl in a vanadium complex. Model compound studies have shown this to be valid (HOLYK, 1979). For this reason, a comparison of the spin-Hamiltonian parameters for vanadyl ions of the shales examined and in the La Luna Mara shaly limestone (or the Serpiano marl), given in Table 1, suggests that the vanadyl compounds in the shales are of a non-porphyrin type. To substantiate this claim, the samples of finely ground shales, after removal of carbonates, were extracted in a Soxhlet extractor with benzene:methanol mixture (3:1 v/v or 7:1 v/v) for 72–90 h. This extraction did not affect the concentration of vanadyl ions found in the carbonate-free shale samples. Further support for this conclusion comes from the geochemical study of the Cretaceous black shales of the Cape Verde Rise and Basin (S. W. Africa in the Deep Sea Drilling Project (DSDP BAKER *et al.*, 1978). The exhaustive solvent extraction technique employed in this report to remove any strongly-adsorbed pigments in the black shale DSDP 368-60-4 (55 cm–63 cm) failed to show the presence of any metalloporphyrin pigment. The limit of detection in that case was about 0.01 ppm for porphyrin material. However, our ESR signal intensity measurements indicate that the concentration of vanadyl ions in this rock is in the range of 15 ppm. Assuming that all these ions are in the vanadyl porphyrin form and if 465 is taken as the mean molecular of the vanadyl ion-complexed porphyrins (BAKER, 1969), then the concentration of vanadyl porphyrins in this shale as found by ESR should be approximately 100 ppm.

To obtain a further indication of the chemical nature of VO²⁺ present in the ancient shales studied, their carbonate-free samples were treated for several hours with boiling HCl, hydrofluoric (HF), sulfuric (H₂SO₄), and nitric (HNO₃) acids (LANGMYHR and SVEEN, 1965; SAXBY, 1969, 1970, 1976) and boiling sodium hydroxide (NaOH). These samples were then analyzed at various stages of demineralization by ESR for VO²⁺. It was found that VO²⁺ is completely dissolved in 12 M HCl (for ca. 4 h), 6 M HF (ca. 2 h), 28 M H₂SO₄

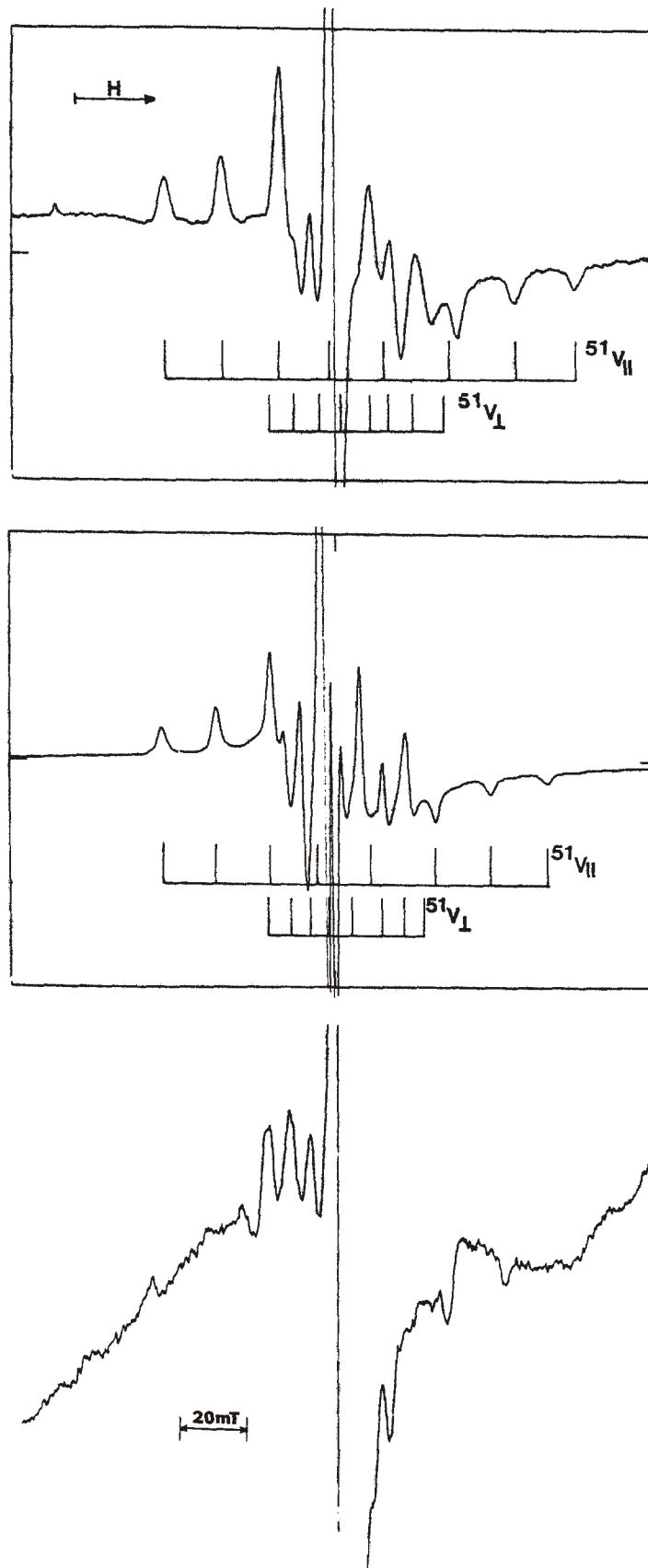


FIG. 1. First derivative, room temperature, X-band ESR spectrum of: (a) Zvonce black shale; (b) La Luna Mara shaly limestone. After removal of carbonate fraction; and (c) Georgia kaolin (Mine 24).

(ca. 2 h), 14 M HNO₃ (ca. 6 h), 5 M NaOH (ca. 2 h) and 0.1 M NaOH (ca. 24 h). Carbonate-free samples of these shales were also treated with 29 M HF and 1 M HCl (3:1 v/v) to remove silicates (SAXBY, 1970). The removal of silicates was checked by IR analysis. This treatment also resulted in a complete disappearance of the ESR signal attributed to the vanadyl ions in the carbonaceous shales examined. Similar acid/base treatments had no effect on vanadyl-DPEP ESR signals of the La Luna Mara limestone and Serpiano marl carbonate-free samples. It is obvious from these results that VO²⁺ in the shales investigated may occur only in those chemical forms in which this ion is part of the structure of clays or micas but not relatively labile adsorbed (on clays, oxides or hydrous oxides) or precipitated species (SAXBY, 1976). Furthermore, many oxides (of iron and manganese), which strongly adsorb vanadium, are readily soluble in hot acids such as HCl (REMY, 1956).

A number of natural kaolinites from a variety of world sources have been investigated using ESR by MEADS and MALDEN (1975). They observed in Georgia kaolins (Georgia, USA) and in the Eureka halloysite (Utah, USA) a spectrum characteristic of the vanadyl single d-electron in a ligand field of strong axial symmetry. But no further details are given in this report. Recently, ANGEL and VINCENT (1978) also identified vanadyl ions in kaolins from various locations in Georgia using ESR. They suggested that vanadyl ions are located on the surface or within the structure of kaolinite but not associated with micas or other impurities present. For this reason, we studied the ESR spectrum of vanadyl ions in the Georgia kaolin (Mine 24) sample (Fig. 1c) and compared it with spectra of vanadyl ions in the carbonaceous shales in question. These results, in particular the similarity of the overall pattern of ESR spectra (Fig. 1a and 1c) and the agreement between the spin-Hamiltonian parameters (Table 1) support our hypothesis that VO²⁺ ions in these shales are probably incorporated in their clay/silicate fraction. Moreover, the acid/base treatments described above produced results similar to those obtained previously for ancient carbonaceous shales.

Finally, agreement between anisotropic parameters for vanadyl compounds of the carbonaceous shales studied is found to be satisfactory though there are small differences (within experimental error) between the shales. This suggests that the same or similar structural types of vanadyl compounds are present in these shales and the Georgia kaolin. The fact that it was not possible to resolve well the ⁵¹V structures in the spectra indicates either relatively weak magnetic interactions between neighboring paramagnetic species take place or the presence of variety of vanadyl compounds in the sediment studied. We may expect much stronger magnetic interactions if VO²⁺ ions are adsorbed on iron or manganese oxides. In that case, these interactions would cause a more pronounced effect on the ESR signals of VO²⁺ species, in particular on their linewidths.

Acknowledgments—Reliable samples for this study were provided through a variety of sources and the author expresses his deep thanks to the following scientists who collected specimens for analysis: the late Professor C. W. Correns (Posidonienschiefer and Kupferschiefer); Professor M. Calvin (Antrim shale); Professor H. Rieber (Serpiano marl); Professor E. W. Baker (DSDP shales); Professor G. Eglinton (La Luna Mara limestone); Professor B. R. Angel (Georgia kaolin) and Dr. L. Pešić (Zvonce shale). The author expresses his sincere thanks to Dr. Laurence Castle for his constructive and patient review. The author's research noted in this report was supported by the Republic Science Association of Serbia and Faculty of Science, University of Niš.

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