Vanadyl ions in ancient marine carbonaceous sediments

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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; Mead 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 geoporphyrins.

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 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 Zvonce shale, shown in Fig. 1a. In general, these spectra gave a 16-line anisotropic pattern, due to interaction of the $^3$Na 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,

$$
\mathcal{H} = g_S I_S + g_L (I_L S_S + H_S S_L) + A_S S_L I_L + A_L (S_L I_S + S_S I_L)
$$

where $g_S$, $g_L$, $A_S$, $A_L$, are the parallel ($z$) and perpen-
Table 1. ESR parameters for vanadyl ions in ancient shaly-type sediments of marine origin.

<table>
<thead>
<tr>
<th>Lithology and rock unit</th>
<th>Region</th>
<th>Geologic period</th>
<th>Age $t$</th>
<th>$g_z \pm 0.003$</th>
<th>$g_{\pi} \pm 0.2 \text{MT}$</th>
<th>$g_{\perp} \pm 0.4 \text{MT}$</th>
<th>VO$^{2+}$ (ppm)</th>
<th>Geological reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zvonec black shale</td>
<td>Serbia</td>
<td>Silurian</td>
<td>430</td>
<td>1.946</td>
<td>18.6</td>
<td>40</td>
<td>Petković (1956)</td>
<td></td>
</tr>
<tr>
<td>Antrim black shale</td>
<td>USA</td>
<td>Devonian</td>
<td>390</td>
<td>1.980</td>
<td>5.9</td>
<td>70</td>
<td>Belsky et al. (1965)</td>
<td></td>
</tr>
<tr>
<td>Kupferschiefer</td>
<td>W. Germany</td>
<td>Permian</td>
<td>380</td>
<td>1.980</td>
<td>5.9</td>
<td>3</td>
<td>Gregory (1930)</td>
<td></td>
</tr>
<tr>
<td>Posidonionspiefer</td>
<td>W. Germany</td>
<td>Jurassic</td>
<td>190</td>
<td>1.980</td>
<td>5.9</td>
<td>10</td>
<td>von Gaertring (1966)</td>
<td></td>
</tr>
<tr>
<td>Atlantic Ocean (DSUP-41)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>368-63 (60 cm - 76 cm)</td>
<td>S.W. Africa</td>
<td>Cretaceous</td>
<td>130</td>
<td>1.951</td>
<td>17.6</td>
<td>70</td>
<td>Baker et al. (1978)</td>
<td></td>
</tr>
<tr>
<td>368-60 (65 cm - 63 cm)</td>
<td>Serpiano marl</td>
<td>Switzerland</td>
<td>220</td>
<td>1.985</td>
<td>5.7</td>
<td>900**</td>
<td>Treibs (1934)</td>
<td></td>
</tr>
<tr>
<td>La Luna Mara limestone</td>
<td>Venezuela</td>
<td>Triassic</td>
<td>130</td>
<td>1.946</td>
<td>18.7</td>
<td>400**</td>
<td>Hubbard (1931)</td>
<td></td>
</tr>
<tr>
<td>(Mine 24)</td>
<td>USA</td>
<td></td>
<td></td>
<td>1.980</td>
<td>6.0</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

diccular ($x, y$) components of the $g$- and $^{51}V$ hyperfine coupling tensors, respectively. $H_z, S_z$, and $I_z$ represent the vector components of the magnetic field, electron spin, and $^{51}V$ nuclear spin along the $z = (x, y, z)$ 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 deoxyphylloerythroteoporphyrin (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 petroleums (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 Soxlet 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 petroleums and carbonaceous shales.

It has been recently shown that ESR parameters are particularly sensitive to direct ligand substitution in vanadyl complexes (Holyk, 1979; Chasteyn, 1980). Thus, the differences in ESR parameters, especially $A_{11}$ (which is the most sensitive parameter to the bonding), can represent the differences in the bonding ligands around the vanadyl in a vanadum 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 Soxlet 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 VO$^{2+}$ present in the ancient shales studied, their carbonate-free samples were treated for several hours with boiling HCl, hydrofluoric (HF), sulfuric ($H_2SO_4$), and nitric ($HNO_3$) 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 VO$^{2+}$. It was found that VO$^{2+}$ is completely dissolved in 12 M HCl (for ca. 4 h), 6 M HF (ca. 2 h), 28 M H$_2$SO$_4$.
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 disappear-
ance 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
mari carbonate-free samples. It is obvious from these results that VO⁴⁺ ion 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 absorb 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 sym-
metry. 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 impuri-
ties 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. a c and d) and the agree-
ment between the spin-Hamiltonian parameters (Table 1) support our hypothesis that VO⁴⁺ 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 ¹⁸¹⁴V 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 VO⁴⁺ ions are absorbed on iron or manganese oxides. In that case, these inter-
actions would cause a more pronounced effect on the ESR signal of VO⁴⁺ species, in particular on their
linewidths.

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