

Vanadium in ancient carbonaceous sedimentary rocks of marine origin: Zvonce black shale

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The vanadium in Zvonce black shale was determined by emission spectrography (100 ppm) and atomic absorption spectrometry (100 ppm). To obtain an indication of the chemical nature of the vanadium present in this shale, a sample was analysed for vanadium at various stages of demineralization. It was found that 70% of the vanadium was soluble in 4M hydrochloric acid, a further 11% was soluble in 0.25M hydrochloric acid: 22 M hydrofluoric acid, and the remaining 19% was retained in the extractable organic and kerogen fractions. It is suggested that a likely source of vanadium in Zvonce black shale was normal sea water and that most of the vanadium was adsorbed in the shale iron oxides.

The East Serbian Silurian sequence, which is wholly marine, includes well-dated strata of the early Llandovery through Ludlow-Pridoli age to early Devonian.¹ Silurian black shales are important because they can be the host for Kupferschiefer-type ore deposits of the source of metals for metamorphic-type ore deposits—higher grade mineralization. These rocks were deposited in reef-controlled, warm-water regions. The Zvonce (Middle and Upper) Silurian sedimentary deposits belong to the E. Serbia Silurian units. They are calcareous and carbonaceous black shales with graptolitic faunal associations.

The Zvonce graptolitic shale is believed to have been deposited under reducing conditions in sheltered areas of a shallow epicontinental sea, during a period of widespread marine transgression.¹ This shale was probably laid down at moderate depths below the influence of wave action. This accounts for the observed accumulation of well-preserved graptolite remains and much of the associated organic matter.

Although Silurian graptolitic black shale occurs throughout E. Serbia, our investigations have centered on an outcrop area near the village of Zvonce (Fig. 1). Petrographic studies²⁻⁴ indicate that the black shale from near Zvonce is well laminated with carbonate interbeds and consists of a mixed assemblage of organic matter within a matrix of silicate and clay minerals.

Extensive work has been done on the geology and paleobiology of Zvonce black shale and related geological materials; the reader is referred to Petković,⁵ Petković and Milojević,² Veselinović,⁶ Veselinović and Krstić,⁷ Pantić *et al.*⁸ Despite

this interest in Zvonce no modern detailed chemical analysis of this rock is available in the literature. Premović⁹ investigated the occurrence of vanadyl (VO^{2+}) ions in Zvonce shale and other ancient sedimentary rocks of marine origin. It was concluded that these ions are located in the clay/silicate fraction (probably associated with interstratified mica-montmorillonite clay).

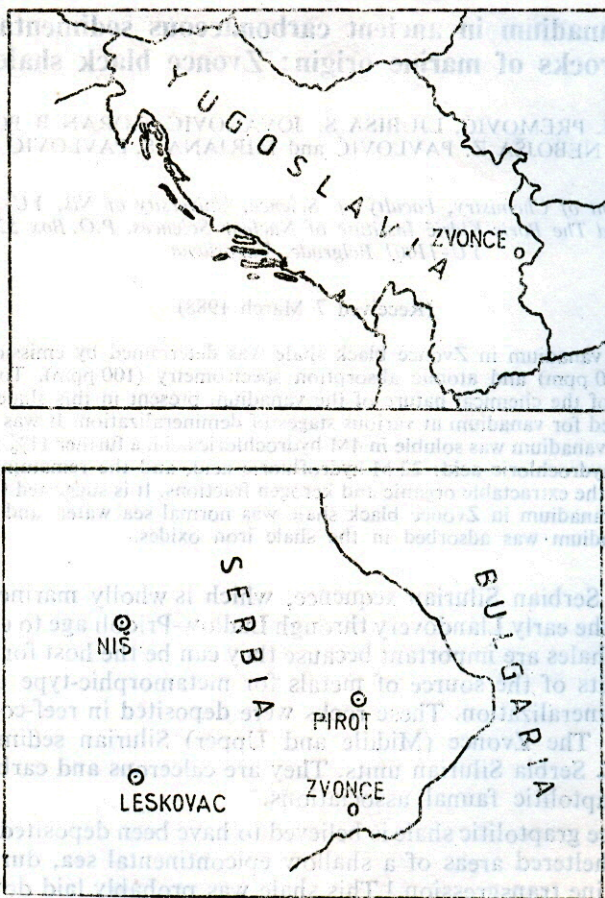


Fig. 1. Location of the sample and the outcrop of Zvonce black shale (according to Petković and Milojević²)

Recently, Premović *et al.*¹⁰ determined the distribution of vanadium (V) (and VO^{2+} porphyrins) in fractions of Serpiano marl (Middle Triassic, Switzerland) and La Luna shaly limestone (Upper Cretaceous, Venezuela) by employing a variety of geochemical and spectroscopic techniques. It was concluded that most of the V (ca. 50% of the total V) in these rocks is associated with kerogen fractions.

A Sample of Zvonce shale was investigated in order to establish the chemical distribution of V.

EXPERIMENTAL

Sample. A sample of the shale material was obtained from an outcrop on the left bank of Blatnica River in Zvonačka Banja, near Zvonice. The location of the sample site is shown in Fig. 1.

Emission spectrography. Semiquantitative spectrochemical analysis was performed using a Schoentag vessel with an atmosphere of 20% oxygen in argon. The method is similar to that described by Marinković.¹¹ The spectrographic analyses were carried out in the laboratories of the Research and Development Center (RDC) of the Đuro Salaj Non-Ferrous Industry, Niš, using a Carl Zeiss (Jena) Model PGS-2 spectrograph. Emission spectra were recorded on ORWO UV 1-photoplates.

Atomic absorption spectrometry (AAS). AAS was carried out on a Perkin-Elmer model 360 AA spectrophotometer with a UDR-3 digital read-out unit. A nitrogen (I) oxide (N_2O)-ethyne (C_2H_2) flame was used. Further details of the analytical procedure and associated controls for precision and accuracy are given in Ref.¹²

Infrared (IR) spectrophotometry. Rock samples were finely powdered and evenly dispersed in potassium bromide pellets. The pellets were then dried for at least one hour at 373 K, before spectra were taken using a Perkin-Elmer 457 IR spectrophotometer set to give undeformed spectra.

Analysis and fractionation. The extraction and fractionation procedure was similar to that used by Saxby^{13,14} and Premović *et al.*¹⁰ The flow chart in Fig. 2 outlines the major steps in preparing the four fractions. They were as follows:

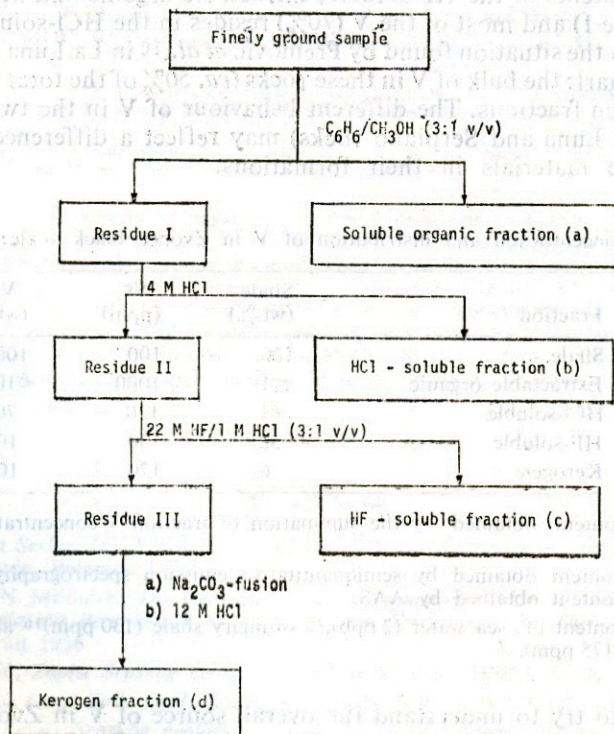


Fig. 2. Flow chart of the extraction and fractionation procedure

a) Powdered rock (10 g) was extracted with benzene/methanol (3:1 v/v) for 90 h in a Soxhlet apparatus.

b) The residue remaining in the Soxhlet thimble was treated with boiling hydrochloric acid (HCl, 4M) to remove most of the carbonates. Carbonate removal was checked by IR analysis. The HCl-soluble materials constitute the second fraction.

c) The insoluble residue from (b) was demineralized further by repeated treatment with boiling hydrofluoric acid/HCl (HF/HCl, 22 M and 0.25 M, respectively). This acid mixture removes silicates and the removal was checked by IR analysis.

d) The final residue from (c) is kerogen. It contained only small traces of inorganic minerals, including pyrite, as confirmed by AAS, electron microscopy and microprobe analysis. It was fused with excess anhydrous sodium carbonate and the fused material was then dissolved in HCl (12 M).

All fractions were examined for V (in all chemical forms) by AAS. Fraction (a), unfractionated (original) rock sample, (1 g) was examined by AAS for total V after a fusing procedure similar to that employed for the kerogen fraction.

RESULTS AND DISCUSSION

The distribution of V in the various fractions of shaly rock is shown in Table I. This table reveals that the levels of total V in the rock sample, determined by emission spectrography (superscript b), by AAS (superscript c) and the sum of V in the various rock fractions (superscript a), are in good agreement with one another within experimental error.

The V contents of the HF-soluble, extractable organic and kerogen fractions are small (Table I) and most of the V (70%) resides in the HCl-soluble phase. This is in contrast to the situation found by Premović *et al.*,¹⁰ in La Luna shaly limestone and Serpiano marl: the bulk of V in these rocks (*ca.* 50% of the total V) is associated with the kerogen fractions. The different behaviour of V in the two sets of rocks (Zvonce *vs.* La Luna and Serpiano rocks) may reflect a difference in the nature of the organic materials in their formations.

TABLE I. Concentration and distribution of V in Zvonce black shale: 100^a, 100^b

Fraction	Shale (wt.%)	V ^c (ppm)	V (wt.%)
Shale	100	100	100
Extractable organic	≤1	≥1000	≤10
HCl-soluble	61	120	70
HF-soluble	32	30	10
Kerogen	6	170	10

^a The V content obtained by the summation of fraction V concentrations, determined by AAS.

^b The V content obtained by semiquantitative emission spectrography.

^c The V content obtained by AAS.

^d The V content of: sea water (2 ppb),¹⁵ ordinary shale (130 ppm)¹⁶ and Black Sea sediments (175 ppm).¹⁷

In order to try to understand the overall source of V in Zvonce graptolitic shale, the metal content of sea water, ordinary shale and Black Sea sediments were compared to Zvonce shale, Table I. Relative to sea water Zvonce black shale is enriched (*ca.* 10⁵ times) in V but similar to ordinary shale and recent Black Sea sediments in V abundance. Holland¹⁸ showed by calculation for several black shales of marine origin that 10⁵ metal enrichments including V could be obtained by removing these metals from normal sea water. Thus, we suggest that V in Zvonce black shale is syngenetic and extracted from sea water.

HCl-soluble V may represent: V associated with shale iron oxides, V adsorbed on clay minerals of V precipitated in limestone.¹⁹ However, Krauskopf²⁰ has shown that hydrated Fe₂O₃ is the most effective adsorbent for V in solution and the association of V with sedimentary iron oxides is well known. Thus, the content of HCl-soluble V may reasonably be explained in terms of adsorption on shale iron oxides. Our analysis indicates that Zvonce shale contains a relatively high content of iron oxides: 2.43%. However, in the absence of an adequate technique for separating pure fractions of the HCl-soluble shale components for analysis, the location of V cannot be more precisely defined.

Finally, it can be seen from Table I that the extractable organic fraction of Zvonce black shale contains a relatively high concentration of V (≤ 1000 ppm). This indicates that the organic matter was also the control for the V abundance in the shale. The organic matter usually has functional groups that are able to ion-exchange or to chelate V, probably before it reaches the sediment.

ИЗВОД

ВАНАДИЈУМ У ДРЕВНИМ УГЉЕНИЧНИМ СЕДИМЕНТНИМ СТЕНАМА
МОРСКОГ ПОРЕКЛА: ЗВОНЦЕ ЦРНИ ШКРИЉАЦ

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Ванадијум у Звонце црном шкриљцу одређен је емисионом спектрографијом (100 ppm) и атомском апсорпционом спектрометријом (100 ppm). Да би се указало на хемијску природу ванадијума у овом шкриљцу, узорак је анализиран на ванадијум у различитим фазама дe-минерализације. Нађено је да 70% ванадијума је растворено у 4 М хлороводоничној киселини, а даљих 11% било је растворено у 0,25 М хлороводоничној киселини: 22 М флуороводоничној киселини, а остатак од 19% заостало је у органски растворној и керогенској фракцији. Предложено је да је вероватни извор ванадијума у Звонце Шкриљцу била нормална морска вода а да је већи део ванадијума адсорбован на оксидима гвожђа шкриљца.

(Примљено 7. марта 1988)

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РЕЗОМЕ

ИЗВЕШТАЈ О РАДИЈОХИМИЈИ СЕДИМЕНТАРНОГ ПЕРИОДА У ВОЈВОДИНИ

АУТОРИ: М. ПЕРМОВИЋ, М. ПЕРМОВИЋ, М. ПЕРМОВИЋ, М. ПЕРМОВИЋ, М. ПЕРМОВИЋ

У раду се износи резултати радиохијмијске анализе седиментарног периода у Војводини. Истраживања су обављена на примерцима из различитих делова Војводине, укључујући и области са значајним налазиштима угљеничног шиста. Радијоактивност је измерена помоћу рачунарске анализе спектра. Резултати показују да је у овим седиментима присутан природни радиоактивни материјал, нарочито радон и његови кћерци. Концентрације су изражене у Бк/г и Бк/л. Уочено је да се концентрације разликују од места до места, али уопште говорећи, налазишта угљеничног шиста имају веће концентрације радиоактивности. Циљ истраживања је био да се утврди да ли се у овим седиментима налазе материје које могу бити извор опасности за животну средину и њену заштиту.

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