

PRESENCE OF RARE-EARTH ELEMENTS IN BLACK FERROMANGANESE COATINGS FROM VÂNTULUI CAVE (ROMANIA)

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This study examines the rare-earth elements (REEs) found in ferromanganese coatings covering both sandy alluvium and submerged boulders in an underground stream from Vântului Cave, Romania. The black ferromanganese sediments are mainly composed of birnessite and other poorly-crystallized manganese oxide and hydroxides (pyrolusite, romanechite, todorokite, rhodochrosite) as well as goethite and kaolinite. Scanning electron microscope and EDX analyses performed on the black ferromanganese sediments show the material to have concentrated considerable amounts of REEs (La, Ce, Sm, Nd) in iron-rich spheres that build up botryoidal-like aggregates. The correlation of $^{143}\text{Nd}/^{144}\text{Nd}$ ratio for 6 different samples indicates that the REEs were concentrated in the cave environment after being leached from bauxitic and red residual clays from above the cave. Based on our observations, we conclude that an increase in pH resulted in adsorption of REE onto the surface of ferromanganese minerals. This study demonstrates the potential of using Nd isotopes as a tool for paleochemistry studies of the cave environment.

The REEs have been used in several recent studies of oceanic manganese deposits in order to identify possible sources of the elements and, specifically, to assess seawater contributions of metal during their formation. So far, the presence of such elements in the cave environment has not been mentioned. However, REE and Nd isotopes may be useful tools with which to explore the paleochemistry of the waters and to reconstruct the redox chemistry of the waters in which they formed (Graf, 1978).

In this paper, we report the concentrations of Lanthanum (La), Cerium (Ce), Samarium (Sm), and Neodymium (Nd) in the black speleothems that were precipitated on both sandy alluvium, submerged boulders and on the cave walls. In addition, we have also made measurements of the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of black speleothems, and associated bauxitic and red residual clay. Because of the marked fractionation of Sm-Nd between continental and oceanic crust and the alpha decay of ^{147}Sm to ^{143}Nd , the source of the REE in the investigated ferromanganese speleothems from Vântului Cave and the genetic relationship between these elements in the black speleothems can be established using the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Geyh & Schleicher, 1990).

Morphologic, mineralogic and genetic studies on manganese oxides in the cave environment have already been done by Crabtree (1962), Moore (1981), Gascoine (1982), Hill (1982), White et al. (1982), Kashima (1983), Peck (1986), Gradzinski et al. (1995), and Onac (1996).

GEOLOGICAL AND SPELEOLOGICAL SETTING

Karst near Suncuius, in the northwestern part of Padurea Craiului Mountains, Romania (Figure 1), is mostly developed in Lower and Middle Triassic limestones and dolomites. The upper sequence of Middle Triassic rock consists of white limestone of Ladinian age, with a thickness that sporadically reaches 180 m. After the deposition of this unit, an episode of continental evolution (uplift) generated the Ladinian paleokarst (Onac & Popescu, 1991). This paleokarst was subsequently

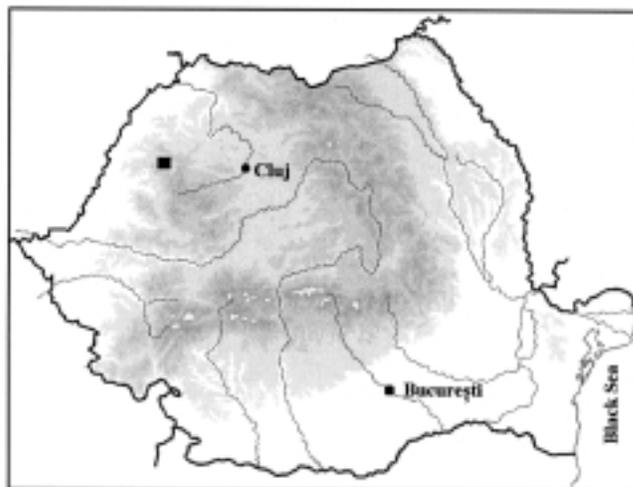


Figure 1. Map of Romania showing the Vântului Cave area (square).

covered by residual red clay and bauxite, sandstone, micro-conglomerate, refractory clay (exploited in mine and quarry in nearby Suncuius), and lenses of siderolithic clay that indicate continental alteration (Corvin-Papiu et al., 1988).

Vântului Cave is located 2.5 km upstream from Suncuius. It has a total length of about 45 km, and is the longest cave system in Romania. The cave is developed on four levels, the lowest having an active stream (Szilagy et al., 1979). Tracer dye labeling has shown that the recharge area of the underground flow to Vântului Cave is linked to diffuse losses in the Recea Mining Brook basin (Oraseanu & Gaspar, 1980-1981). Deciduous forests cover the entire basin, encouraging formation of organic acids derived from abundant decomposing vegetation.

There is also evidence that acid-mine waters (rich in aluminium, iron and silica) drain into the cave flow, having an impact on the cave environment (pollution, corrosion, speleothem deposition).

BLACK SPELEOTHEMS

The underground stream bed in Vântului Cave is covered by black jelly-like sediments. The thickness of these sediments changes as the distance from the sediment-water interface increases (Onac, 1996). The submerged boulders and cobbles can have layers up to 2.5-3 cm thick, while the sandy alluvium is covered with only 2 to 3 mm of this material. The black material will accumulate until a steady-state balance is reached between the deposition of the black speleothem coatings and the physical or chemical processes that remove these coatings. The cave walls alongside the stream are covered with black coatings of the same material, up to the highest level reached by the water. The very same black coatings, partly covered by recent calcite crusts, were observed on the walls in a few passages in the upper level of the cave.

Jet black flowstone and dripstone-like speleothems occur in many places along the active stream gallery.

ANALYTICAL METHODS

X-RAY FLUORESCENCE ANALYSIS

The major elements have been analyzed by X-ray fluorescence (XRF), with a Philips PW 1404 spectrometer, using glass beads prepared according to the method of Norrish and Hutton (1969). Twenty-five international standards were used, refined by least squares procedures, using Philips model PW 1492 software for calibration. Trace elements were determined by XRF, using pressed powder pellets. The standards and software used for the major elements were also used for the calibration of the trace elements.

Twelve samples collected from three different locations have given the following mean values shown in Table 1.

X-RAY DIFFRACTION ANALYSES

X-ray analysis was performed using a Philips powder diffractometer (PW 1710) with CuK α radiation. All specimens were continuously scanned from 10 to 60° 2 θ in increments of 0.5° 2 θ per minute. The digitized scans were then fitted with the PW-1877 curve program (version 3.6).

Diffractometer tracings from the fine-grained black sediments consist of broad diffraction bands with superimposed sharp peaks due primarily to detrital quartz. Minor amounts of birnessite, goethite, kaolinite, and possible romanechite, pyrolusite, todorokite, and hollandite were identified in most of the samples. In all cases, the broad but consistent character of the diffraction maximum indicates a material that is poorly crystallized but certainly not X-ray amorphous.

After heating the samples to 1000°C and performing a new series of X-ray diffraction measurements, the spectra were better resolved. They showed sharp peaks due to Mn-Al-Fe rich spinels, pyrolusite, hausmanite, hematite and quartz. This mineral association revealed that the initial black sediments are composed of amorphous aluminium and silica gel-like material and poorly crystallized oxides and hydroxides of manganese and iron.

SCANNING ELECTRON MICROSCOPE ANALYSIS

Several perfectly rounded spheres with diameters ranging from 4 to 12.5 mm were observed when SEM analyses were carried-out (Figure 2). We also performed several energy dispersive secondary X-ray analyses (EDX) using Tracor NORTON's SQ program, which applies multiple least square analysis and ZAF matrix correction procedure to calculate elemental concentration using a library of references stored on disc. The EDX spectra of the spheres show that they are made

Table 1. Chemical Analyses of the Black Ferromanganese Coatings from Vântului Cave.

Component	Weight Percent	Parts per Million
SiO ₂	28.35	
MnO ₂	27.32	
Al ₂ O ₃	19.80	
Fe ₂ O ₃	4.02	
CaO	3.99	
K ₂ O	1.32	
MgO	0.74	
TiO ₂	0.50	
Ni	0.45	
Ba	0.36	
S	0.29	
Co		860
V		219
La		762
Ce		938
Sm		93
Nd		448

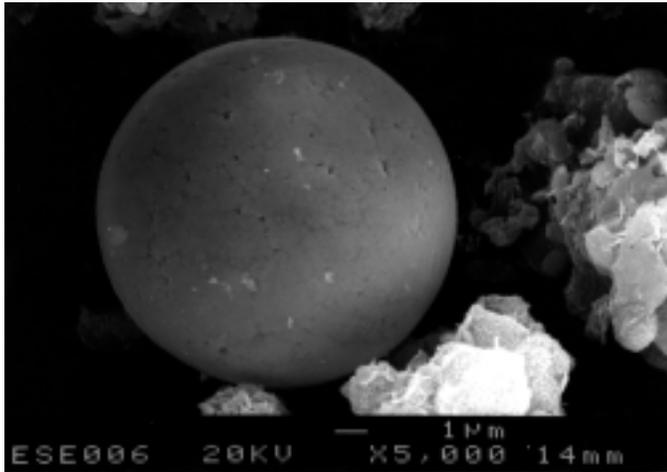


Figure 2. Uncovered sphere made up of iron and rare-earth elements.

up of iron and an association of rare-earth elements (REE), including Ce, La, Sm, and Nd (Figure 3).

SEM indicates the black precipitate is composed of welded botryoidal-like agglomerates covered by clusters of thin platy crystals with pseudo-hexagonal symmetry (kaolinite) (Figure 4).

THERMAL IONIZATION MASS SPECTROMETRY

Nd isotopic composition and Sm and Nd concentrations were measured at the Department of Geology, University of Bergen on a Finnigan 262 instrument. All chemical processing was carried out in a clean-room environment with HEPA filtered air supply and positive pressure. The reagents were either purified in two bottle teflon stills or passed through ion-exchange columns. Sample were dissolved in a mixture of HF and HNO₃.

Rare-earth elements were separated by specific extraction chromatography using the method described by Pin et al. (1994). Sm and Nd were subsequently separated using the method described by Richard et al. (1976). Sm and Nd were loaded on a double filament and analyzed in static mode. Nd isotopic ratios were corrected for mass fractionation using a

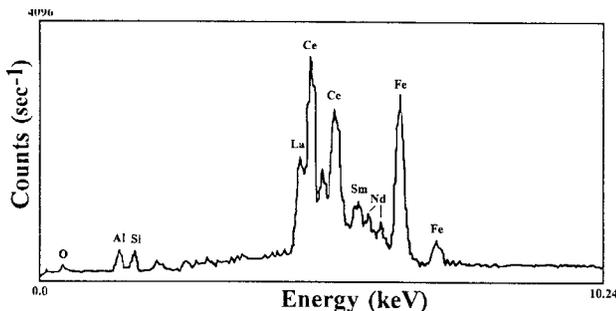


Figure 3. Energy dispersive X-ray spectrum for an uncovered sphere.

¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219. Sm and Nd concentration were determined using a mixed ¹⁵⁰Nd/¹⁴⁹Sm spike. Repeated measurements of the Johnson Matthey Nd standard yielded an average ¹⁴³Nd/¹⁴⁴Nd ratio of 0.511113 ± 15 (2s) (n=62).

The ¹⁴³Nd/¹⁴⁴Nd ratio measured for 3 samples collected in the lower part of the cave stream shows very similar values (Table 2). These values are extremely close or equal to those measured for the bauxitic clay from above the cave and red residual clay accumulated either in the cave environment or at the surface (Table 2).

Table 2. ¹⁴³Nd/¹⁴⁴Nd ratio measured for various samples.

Black Ferromanganese Sediment		
Sample I	Sample II	Sample III
0.512206	0.512209	0.512208
Bauxitic Clay		
0.512206		
Red Residual Clay		
Cave	Surface	
0.512207	0.512209	

DISCUSSION AND CONCLUSIONS

The various analyses to which the black sediments were subjected suggest they are composed of amorphous aluminium and silica gel-like material, birnessite and other poorly crystallized oxides and hydroxides of manganese and iron. Among the minerals ascribed to the later group are: romanechite, todorokite, pyrolusite, rhodochrosite, goethite and possible hollandite. The mechanism suggested for the deposition of the black coatings in Vântului Cave is one controlled by Eh and pH (Onac et al., 1997). The role played by micro-organisms is not exactly known, but the analyses undertaken so far on these black speleothems suggest them as a potential factor in manganese and iron deposition.

In continental systems, percolation of rain water through the rocks will result in low-temperature chemical weathering reactions that will slowly break down the primary minerals, resulting in mobility of the REEs. The chemistry of groundwaters is dependent on the physicochemical environments through which it has passed. A higher content of HCO₃⁻ in natural waters will cause a higher solubility of the heavy REE compared with the light REE (Herrmann, 1978).

The behaviour of the REEs can be significantly influenced by pH. A decrease in pH will favor solution of the REEs and their transport either as complexes or as free ions. An increase in pH can result in one or all of the three processes: precipitation of the REEs as hydroxides or carbonates, exchange of the REEs for H⁺ on accessible mineral exchange sites, and adsorption onto the surface of minerals (Balashov et al., 1964). We believe the third process is most likely occurring in Vântului Cave as we found the pH to vary downstream from 5.1 to 8.

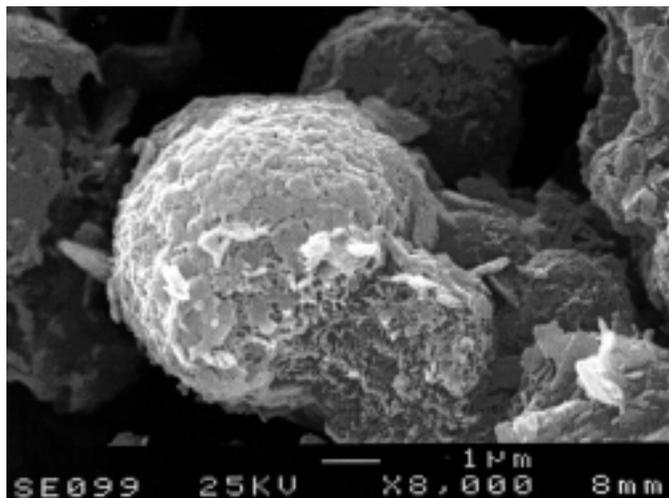


Figure 4. Botryoidal-shaped agglomerates covered by clusters of thin platy crystals.

The ferromanganese oxide surfaces have an ability to absorb appreciable quantities of ions from solution, particularly favoring the cations of transition metals and REEs.

The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the black coatings are ~ 0.512207 , an identical value to that found in two other samples from above the cave (bauxitic and red residual clay). The similarity of this ratio to that of karst-bauxite sediments suggests the REEs were readily removed from above the cave by percolating water and concentrated in the cave environment. The REEs were incorporated into the black ferromanganese coatings by coprecipitation with particulate iron colloids or other nodular phases.

The possible sources of the REEs (based on $^{143}\text{Nd}/^{144}\text{Nd}$ ratio) in the black coatings from Vântului Cave are dominated by continental input, the main source being an Upper Jurassic igneous rock ($\epsilon_{\text{Nd}}(0) = -10.5$). The $\epsilon_{\text{Nd}}(0)$ of about -1.39 found in all samples suggests there is an additional source of Nd to this area with a higher $\epsilon_{\text{Nd}}(0)$, possibly Nd released from weathering of some young rhyolitic rocks that outcrop in the central part of the Padurea Craiului Mountains.

The conclusions presented here will remain tentative until further work can establish more precisely the behavior of the REE and Nd isotopes in the black coatings from Vântului Cave. Nevertheless, they do provide an indication of the potential of Nd isotopes, in particular, as a tool with which to approach paleochemistry studies in the cave environment.

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