Bacterial sulfate-reducing process in oil-polluted karst rocks

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The Perm region (the Western Urals, Russia) occupies an area of about 160,000 sq. km. The karstified rocks, i.e., limestone, dolomite, gypsum, anhydrite, and paleozoic rock salt, are either exposed or lie close to the surface in the area of about 30,000 sq. km. Oil deposits are distributed on the significant part of the territory of the region. A considerable number of them is located within the drainage area of the rivers, where the rivers water is weakly protected from pollution due to the intense karst development.

Turaevka and Kamenka rivers flow on the territory of Irensky carbonate-sulphate karst district. Part of the riverbeds are underground and discharge as karst springs. Kokuyskoye oil field occupies part of the territory of Irensky carbonatesulphate karst district; its oil-producing wells are located in the drainage area of Turaevka and Kamenka rivers.

Until the 90s of the 20th century the water in the rivers was clean and used as potable one. Numbers of accidental spills of oil and technical fluids on the surface and leaks of oil through broken sides of oil-producing wells led to pollution of karstified rocks with oil and oil products. Now water of Turaevka and Kamenka rivers contains saturated and unsaturated hydrocarbons, their acids, ethers, alcohols, and halogenated derivatives. The bottom of the rivers are covered with a thin layer of dark brown oil tar for several tens of meters downstream their discharges from the rocks, and subaqual springs in the riverbeds periodically discharged with oil. A strong smell of hydrogen sulfide coming from the water of these rivers, as well as the deposition of elemental sulfur, covering the underwater part of the river plants, are detected.

To our minds, this features indicate the development of bacterial sulfate-reducing process:

 $2SO_4^{2-} + 5Corg + 2H_2O = 2H_2S + 5CO_2,$

where oil hydrocarbons serve as carbon and energy sources. Herewith the release of carbon dioxide into river water enhances the dissolution of carbonate rocks.

Oil spills in the karst areas may increase the processes of carst development and were accompanied by bacterial sulfate reduction process in the gypsum rocks.

This work was financially supported by the Russian Foundation for Basic Research (project 16-35-00104 mol_a).

²²²Rn emanations from selected metamict minerals

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Radiation Damage. Emanation Coefficient of ²²²Rn

Metamict minerals contain uranium and thorium that degrade the crystal structure of the minerals mainly by α -decay events. This presentation reports the relantionship between the results of ²²²Rn emanations and absorbed α -dose for a representative group of metamict oxides, phosphates and silicates [1]. The radon isotope ²²²Rn (T_{1/2} = 3.64 d) belongs to the ²³⁸U decay series, and occurs as an inert gas that is detectible in U bearing mineral phases. The α -decay of ²²⁶Ra (E_a = 4.77 MeV) is accompanied by recoil of the ²²²Rn nucleus with an energy of 86 keV. Emanation coefficients of ²²²Rn (e₂₂₂, expressed in percentage) measure the number of radon atoms released per the number of radon atoms produced within the ²³⁸U decay series for a given mineral. This ratio provides a quantitative measure of the quality of the mineral's internal structure.

Results

The ²²²Rn emanation coefficients for the presented minerals vary widely from 5 x 10⁻⁵% (uraninite) to 2.5% (turkestanite). Emanation coefficients for ²²²Rn generally decrease with increasing total absorbed α -dose, D_T (Fig. 1).



Figure 1: ²²²Rn emanation coefficients (e_{222}) for metamict minerals vs. total absorbed α -dose.

Figure 1 also shows that ²²²Rn emanations produce visible peaks for metamict phases having considerable concentrations of ²³²Th in excess of 2.8 wt.% and D₂₃₂ > 26 x 10¹⁵ α -decay mg⁻¹ (TUR, FMU, BRA, MPE, and THO). Excluding these observations, the relationship between e₂₂₂ and total dose (D_T) values can be fitted by an exponential function. Metamict oxides showed the lowest ²²²Rn emanation coefficients for the highest absorbed α -dose.

[1] Malczewski & Dziurowicz (2015) Am. Mineral. 100, 1378-1385.