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RADIATION-INDUCED PARAMAGNETIC DEFECTS IN NATURAL BARITE

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ABSTRACT

Electron Paramagnetic Resonance (EPR) of paramagnetic defects in natural Barite were attempted to restore the properties of radiation – induced defects as genetic markers. Previously it was shown that structural defects of the crystal are entirely determined by the symmetry elements and translational symmetry of a regular system of points [1]. Point defects are formed due to vacancies of anions and cations of the structure [2]. The concentration of these defects depends from redox conditions of formation the minerals and the dose of the natural irradiation [3]. Valence state of the ion radicals may vary from diamagnetic to the paramagnetic state and vice versa.

Barite ($BaSO_4$), the most common barium mineral, occurs in depositional environments on sea floor, as well as in those on land including biogenic, hydrothermal, and evaporation on land and artificial technogenic.

Analysis of the EPR spectra of radicals and impurity ions in barite mineralization and host rocks led to the hypothesis: primary enriched barium solutions were replaced first with calcium, then iron- calcium and, but in the end - iron-containing fluids. At the same time gradually changing their redox potential and sulfate-reducing microbial community develops. Radiation and thermal stability of ESR centers barite has practical significance in various fields of science and industry.

The purpose of this study was to show possibilities of the electron paramagnetic resonance (EPR) method on the example of barite rocks identifying indicators going changes.

Keywords: barite, electron paramagnetic resonance, organic matter, radiation, annealing

INTRODUCTION

Combining the analysis of the conditions of layer-growth and symmetry elements of space groups in the process of crystal growth makes it possible, as shown in [1], specify the defects caused by the growth processes and the distribution of the impurity ions. The EPR spectra of single crystals of barite investigated in [1, 2]. These studies showed that all paramagnetic centers (PC) require charge compensation associated with vacancies nearest Ba^{2+} ions. The uses of thermo-radiation treatment and following monitoring of the EPR spectra have allowed revealing conditions of barite mineralization [3]. The mineral barite belongs to the orthorhombic system and refers to the space group Pnma - D_{2h}^{16} [4]. Atoms of barium, sulfur and oxygen, designated O1 and O2 are located in the plane of symmetry of the type 4 (c) (Fig. 1).

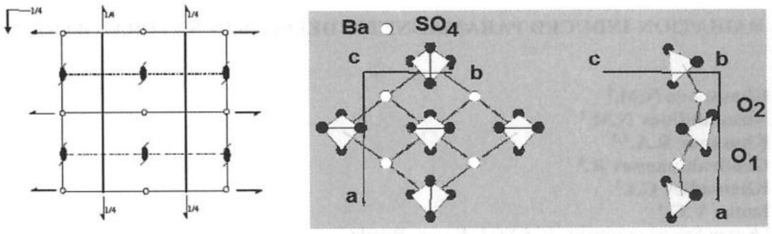

Fig.1. Elements of symmetry of the unit cell of the space group D_{2h}^{16}-Pnma and the projection of n-thick interlayer c/2 on a plane (001) and (010).

In the structure of the projection onto the plane (010) shows one layer c/2, but it is evident that the cell will include two layers thickness c/2. These two layers are converted into each other by means of the screw axis of the second order, the type of plane n, and a center of inversion. These packaging elements are not included in the symmetry of interlayer.

The purpose of this study was to show possibilities of the electron paramagnetic resonance (EPR) method on the example of barite rocks identifying indicators going changes.

The objects of research have become technogenic barite formed in the oil pipe, stratiform barite bacterial and algal inclusions and Barite morphogenetic type (concretions, secretions, and septary) in terrigenous sediments.

Monitoring was carried out on the EPR spectra of X-band spectrometer PC.100X (ADANI, Belarus) at room temperature. As an internal standard was used EPR spectrum Cr^{3+} ion in the crystal Al_2O_3, permanently installed in the side of the cavity opening.

Micro focus X-ray emitter firm RSM 50/50 Renis-M is used for irradiation. Isothermal annealing (30 minutes) was carried out in an electric furnace type SUOL with a tungsten tube in the top land area, equipped with drain pipe.

Sample preparation for EPR study. Rock preliminarily is triturated in an agate mortar. The weighted sample is placed in a plastic ampoule, a sealed on one side, and closed by tampon on the other side. This allows an ampoule to fill equal volume test sample and preserve samples for monitoring of the spectra depending on the time after irradiation or irradiation dose, since an ampoule is resistant to X-rays. Using powders makes universal EPR technique for studying mineral and organic matter (OM) in the rock. Identification of paramagnetic centers powders is produced with the assistance of the known parameters and models obtained in single crystals. Thus, the parameters of the EPR spectra of impurity ions, ion-radicals and free radicals are markers of the material composition of rocks and redox environments medium mineralization.

EXPERIMENTAL RESULTS

The technogenic barite was detected in thick viscous mass in the oil pipe. In the primary analysis of the ESR spectra of the mass was detected ion radical vanadium and free radical hydrocarbon, trace concentration of Mn^{2+} ion in the structure of the carbonate. Then, after chloroform extraction of hydrocarbons in the ESR spectrum was recorded

broad line of organic matter. After X-ray irradiation EPR signal PC consisting hole center close to the ion-radical O^-(I) (g_{xx} = 2.0186; g_{yy} = 2.0121; g_{zz} = 2.0093), electron center SO_3^-(I) (g_{xx} = 2.0034; g_{yy} =2.0024; g_{zz}= 1.9995) and SO_3^- (II) SO_3^-(I) (g_{xx} = 2.0076; g_{yy} =2.00224; g_{zz}= 1.9979) [2], belonging to barite was activated (Fig. 2a).

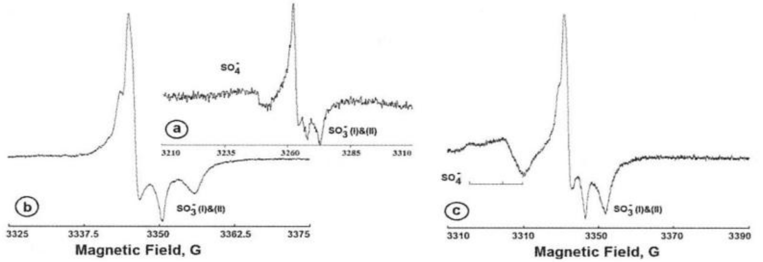

Fig.2. Record of the EPR spectrum of ion radicals in the technogenic barite performed: a) first - 08.02.2010; b) re-recorded - 04.25.2015; c) re-exposure x-ray radiation 25.04.2015 (3 hours).

The most surprising is that the EPR spectrum of the ion-radical SO_3^- (I) and (II) been preserved 5 years after exposure (Fig. 1b), which was a validation of their identification. The new exposure of the same sample after 5 years (Fig.2c) is accompanied by the appearance of the hole PC with parameters g- tensor {2.0186; 2.0121; 2.0093}. If we accept it's identification is similar to [1] hole centers SO_4^- (III), then the small anisotropy of the g-tensor is explained the substitution Ba^{2+} ion in one interlayer thickness (c/2) with PC (Fig.1) on isovalent impurity ions Ca^{2+} , Sr^{2+}. Substitution of barium ions smaller ionic radius can cause expansion of SO_4^{2-} tetrahedron and reduce cell parameters that were shown in [5]. It fits well into this model appearance SO_4^{3-} (g_{zz} = 2.0013; g_{yy} = 1.9975; g_{xx} = 1.9964) ion-radicals [2, 6].

Stratiform barite bacterial and algal structures

Three of the surface area of stratiform barite bacterial-algal structures were isolated and studied the EPR spectra of radical ions SO_2^- (g_{yy} = 2.0126; g_{zz} =2.0105; g_{xx}= 2.0033) and SO_3^-(I) (g_{xx} = 2.0034; g_{yy} =2.0024; g_{zz}= 1.9995) [2] (Fig. 3).

Predominance intensity SO_3^- (I) at ambient temperature signal indicates a predominantly oxidizing conditions given mineralization (see table).

Table. EPR intensity ion-radical SO_2^- и SO_3^-(I)

probe	SO_3^-			SO_2^-			SO_3^-/SO_2^-
№	25 °C	350 °C	600 °C	25 °C	350 °C	600 °C	25 °C
1	307.38	0	0	79.22	115.71	50.89	3.9
2	350.32	29.4	0	50.33	74.36	26.21	7.0
3	198.22	30.1	0	26.76	76.51	0	7.4

To determine the type of OM was undertaken to study the EPR spectra of samples annealed in a hydrogen atmosphere at 350 and 600 °C, in accordance with (Fig. 3).

Earlier in [2], it was found that SO_3^- (I) ion-radical crystal barite is stable to ~ 400 ^0C, and SO_2^- thermally stable to about 450 ^0C.

In this case SO_2^- radical ion is retained to 600 ^0C in the first two samples. The oxidation of iron ions Fe^{2+} -> Fe^{3+} and the formation of oxides, and the broadening of the free radicals take place in the sample №3.

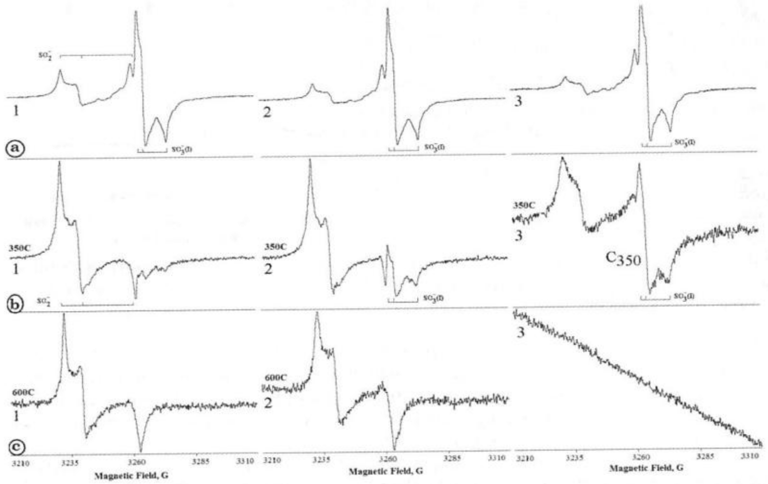

Fig.3. EPR spectra of radical ions SO_2^- and SO_3^-(I): a) at room temperature; b) after 350 ^0C annealing; c) after 600 ^0C annealing. Location selection is indicated by the numbers 1, 2, 3.

Annealing at 350 ^0C was marked by the broad line (C_{350}) on the background of the spectrum SO_3^-(I) ion-radicals in the sample №3, that the mere existence of such radicals testifies to their agents and the type of phytoplankton indicator of the low degree of "maturity" OM [7].

A notable feature of this stratiform barite is temperature stability and security SO_2^- radical ion, which is evidence of existence of bacterial and algal structures and specific hydro-chemical conditions of formation of authigenic stratiform mineralization. Apparently, in the barite mineralization created conditions for the development of sulfate-reducing microbial communities.

Stratiform barite in the Upper Jurassic terrigenous complexes

All samples studied barite mineralization, as noted in [3], are characterized by of PC SO_2^- (g_{yy} = 2.0126; g_{zz} =2.0105; g_{xx}= 2.0033) and SO_3^-(I) (g_{xx} = 2.0034; g_{yy} =2.0024; g_{zz}= 1.9995) [2] (Fig.4a). In the studied morphogenetic types of manifestations of barite mineralization was found obvious dominance of the centers, which indicates the formation of aggregates in the conditions of the oxidation potential of the environment characteristic of the bottom areas of sea basins.

The appearance of new lines O^-(I) (g_{xx} = 2.0186; g_{yy} = 2.0121; g_{zz} = 2.0093) и SO_4^{3-} (g_{zz} = 2.0013; g_{yy} = 1.9975; g_{xx} = 1.9964) [2] and the increase of the SO_3^- lines only 1.2 times was observed after irradiation of the sample №21 with X-rays (2 hours) (Fig.4b). There is a partial overlap of the lines SO_2^- and O^-. Intensity ion initial lines radicals SO_2^- and SO_3^- increased by 2 and 2.5 times, respectively, when another sample №35 irradiated with X-rays. In this case the appearance of new lines of this sample is not marked.

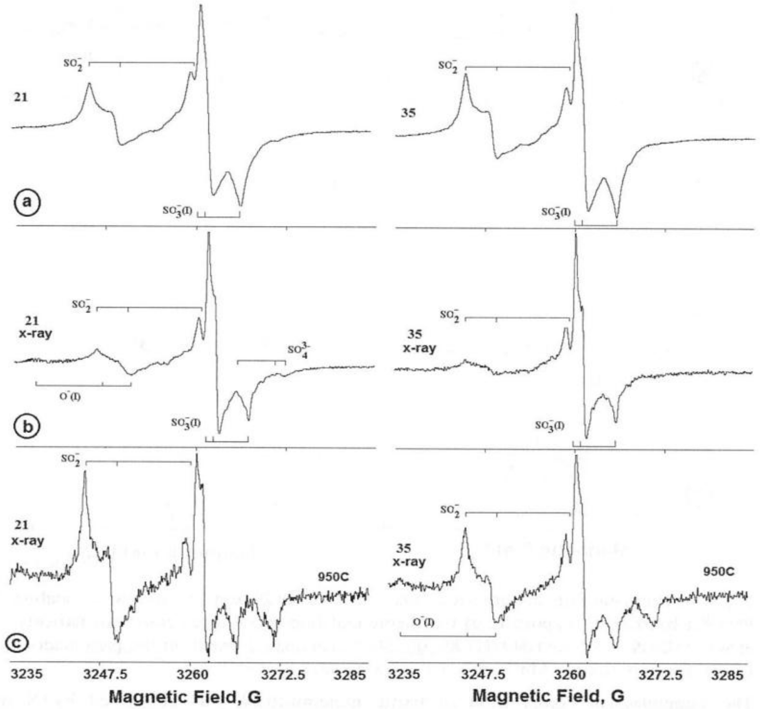

Fig.4. EPR spectra of radical ions barite mineralization of the sample 21 and 35: a) the original rock; b) after irradiation source rocks; c) after irradiation at 950 ^0C heated rocks.

The emergence of new lines O^-(I) (g_{xx} = 2.0186; g_{yy} =2.0121; g_{zz}= 2.0093) and SO_4^{3-} (g_{zz} = 2.0013; g_{yy} =1.9975; g_{zz}= 1.9964) as a result of irradiation heated at 950 ^0C samples are shown in (Fig.4c).

The thermal stability of ion radicals at 950 ^0C (Fig. 5a) and the intensification of the EPR lines after further irradiation (Fig.5b) says that in the structure of barite are resistant diamagnetic precursors centers firmly associated with key positions of the crystal lattice [8].

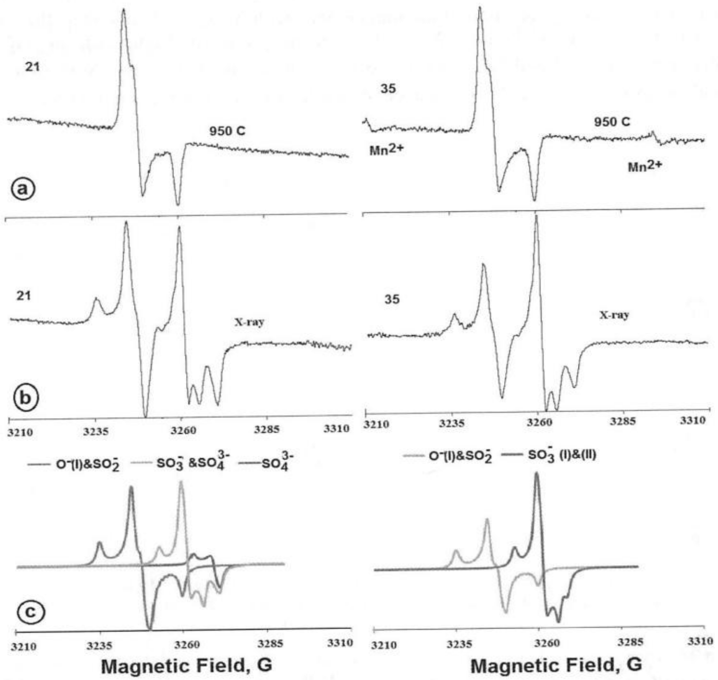

Fig.5. EPR radical ions in barite rock (sample number 21 and 35): a) after annealing at 950 ^{0}C; b) after re- exposure; c) the theoretical line spectral envelope ion radicals O^- &SO_2^-, SO_3^-& SO_4^{3-} and SO_3^-(I) & (II), SO_4^{3-}, calculated based on the parameters [2]. Line trace impurity ion Mn^{2+} are listed in carbonates host rock.

The mineralogical composition of barite mineralization was confirmed by X-ray diffraction pattern. Similarly in irradiated 60Co synthesized BaSO4: Eu, P was observed at 1173K thermoluminescence intensity maximum, EPR and fluorescence [9].

CONCLUSION

In natural conditions in the stratiform barite mineralization is observed SO_3^-(I) center and the second SO_3^-(II) center is required additional exposure. The formation of I and II centers can be associated with the vacancy O2 and O1, respectively, in the structure of SO_4^{2-} tetrahedron and a vacancy barium ion from the next interlayer with a thickness c/2 [1]. Both centers are formed without lowering the point symmetry as both oxygen O1

and O2, and the central ion S are in the plane of symmetry. Thermal stability of the SO_3^- (I) center is stored up to 400 ^{0}C (Fig.3b).

Thermal stability of another radical ion SO_2^-, also found in stratiform barite mineralization (Figure 3 and 4) depends on the physical, chemical and thermodynamic conditions of ore formation [3, 9].

The concentration of these defects depends from redox conditions of formation the minerals and the dose of the natural irradiation [3]. Valence state of the ion radicals may vary from diamagnetic to the paramagnetic state and vice versa.

Radiation resistance and activity centers is determined by the other two electron-hole centers almost axial values of the principal axes of the g-factor: SO_4^- hole and electron SO_4^{3-}, with the localization of the unpaired electron or hole in the place of substitution of barium, which is located in a thick interlayer growth c/2, by ions Sr, Ca, with a smaller ionic radius.

Thus, can be stated that in analysis samples of barite under the influence of thermal annealing and X-ray irradiation are redistributed electron charges of point defects in the system, which is possible only in conditions of existence of mobile charge carriers or electron excitations.

Analysis of the EPR spectra of radicals and impurity ions in barite mineralization and host rocks led to the hypothesis: primary enriched barium solutions were replaced first with calcium, then iron- calcium and, but in the end - iron-containing fluids. At the same time gradually changing their redox potential and sulfate-reducing microbial community develops. Radiation and thermal stability of ESR centers barite has practical significance in various fields of science and industry.

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