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THERMAL ANNEALING DERIVATIVES OF TECHNOGENIC GYPSUM BY ELECTRON PARAMAGNETIC RESONANCE

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ABSTRACT

Previously dehydration products EPR spectra of single crystals of gypsum ("Marino glass") have been studied in the temperature range from 100 to 425 ^{0}C [*Crystall. Reports, 2014, Vol. 59, No. 3, pp. 399*]. In this work, the subject of study was selected technogenic gypsum and its derivatives dehydration [Procedia Earth and Planet Sci. Vol. 15, 2015, P. 579].Temperature region of formation gypsum, alpha and beta phase states of bassanite and gamma-anhydrite, insoluble anhydrite were determined from the EPR spectra of radical ions and the atomic hydrogen. Obtained results may be used for the control in the technological processes of gypsum materials production, and scientific purposes.

Keywords gypsum, bassanite, gamma-anhydrite, insoluble anhydrite

INTRODUCTION

Many physical properties of gypsum are connected or controlled by water molecules. Therefore, a basic understanding of the structure of gypsum as conditions change, a complete description of the behavior of water molecules and the hydrogen bonds required [1].

In a series of experiments, the gamma-irradiation at room temperature, it was found that gamma-irradiation of calcium sulfate hemihydrates shows signals except the EPR free radical groups, a pair of extremely narrow lines separated by about 500 G, which may be interpreted as atomic hydrogen lines [2].

Gypsum, $CaSO_4 \cdot 2H_2O$, and dehydrated derivatives ($CaSO_4 \cdot xH_2O$, $0<x<2$) emit or absorb water under certain conditions. The width of the ESR central line SO_3^- occurring gypsum in the process of single crystal X-ray irradiation at 25 °C, decreases to 0.3 G as a result of annealing at 120 °C for 30 minutes [3]. This was accompanied by a decrease in weight of a sample and involves the formation of large areas in the dehydrated sample through separation of water molecules. When removing water molecules from the region of SO_3^- paramagnetic center disappears interaction between the electron spin S = 1/2 center and the nuclear spin angular momentum I = 1/2 hydrogen surrounding water molecules and therefore there is a narrowing of the EPR spectral lines. If you leave a sample in air, then is observed an increase in its weight and the disappearance of the ESR SO_3^- centers with narrow absorption lines. This reverse situation is a result of

the absorption of water molecules from the environment and restore the interaction between the electron spin S = 1/2 nuclear spin I = 1/2 environment of water molecules. This narrow line with g (I) = 2.0025 and a half-width of 0.3 G was attributed SO_3^-(I) ion-radical, passing from gypsum structure in the structure of gamma-anhydrite.
If the heat treatment at 100 °C to expose the powder sample (not a single crystal), then it is observed from another radiation EPR center SO_3^-(II) with g (II) = 1.9993 and a small line width [4]. However SO_3^-(II), in contrast to the center SO_3^-(I) in a single crystal, there is observed only after x-ray exposure in a narrow range 100-225 °C temperature annealing.

This is because the reduction in crystal size accelerates dehydration of gypsum and causes its conversion to γ-anhydrite. Intensive allocation of water creates a moist environment for the formation of γ-anhydrite with α-morphological modification. Therefore it can be concluded that the centers of the narrow lines SO_3^-(II) and SO_3^-(I) formed into morphologically different α - and β –modification of γ-soluble anhydrite.

Observed also a broad EPR lines on which background the narrow lines of the centers were recorded. Wide lines are attributed to water-containing components of the annealing product: gypsum and bassanite [4].

EPR lines of atomic hydrogen produced in the process of X-ray irradiation in the two systems are structurally different channels in the α- and β- modifications frame γ-$CaSO_4$, allow you to control the phase components of the annealing products gypsum and processes that take place between them, on the EPR spectrum at room temperature [4].

Morphologically differing crystals of gypsum "Marino" glass [3-5] and technogenic gypsum [6] are characterized by different size and shape of the crystals, as well as deferent degrees of defects in the structure. Natural single crystal gypsum "Marino" glass, crystallized in normal conditions, is characterized by a unit cell to set C2/c and a radiation centers (such as, two SO_4^- - ^1H and SO_3^- - ^1H) with super hyperfine splitting of the proton H (I=1/2) and without splitting SO_3^-, SO_2^- [3-5]. While well-faceted crystal morphology technogenic gypsum was crystallized at lack of humidity to set described by I2/a, and is characterized by radiation paramagnetic centers (G1-SO_3^-, G2-SO_4^-, G3 - CO_2^-) without super hyperfine splitting of proton water [6].

In situ investigation of formation and transformation of five different phases in the $CaSO_4$–H_2O system in the temperature range of 20-500 °C, crystal structure of the subhydrate β-$CaSO_4 \cdot 0.5H_2O$ and soluble anhydrite $CaSO_4$ has been made possible through the use of time resolved synchrotron radiation powder X-ray diffraction (SR-PXD) and advanced design of sample holder [7]. These investigations were performed with focus on the phase transitions studies under hydrothermal and dry conditions.

In this work, the subject of study was selected technogenic gypsum and its derivatives dehydration [6]. Temperature region of formation gypsum, α- and β- phase states of bassanite and gamma-anhydrite, insoluble anhydrite were determined from the EPR spectra of radical ions and the atomic hydrogen.

CARRYING OUT EXPERIMENTS

For annealing gypsum used space electric furnace SUOL with a quartz tube, closed on one side the supplying end of the flask with dry KOH, and the other outlet tube with a narrow end, which ensured the dryness and limit the water vapor pressure. The gypsum

sample was ground to sizes of 0.5–1.0 mm and placed in a quartz cell, which was mounted in the furnace quartz tube.
After thermal annealing, the cooled sample was ground in an agate mortar into a power with grain sizes of ~0.05 mm. A layer of the powder samples, uniformly distributed in a transparent paper, was mounted to the X-ray tube window and irradiated for 1 hour at 25°C [4]. The X-ray irradiation produced by URS-55A X-ray setup equipped with BSV-2 X-ray tube (Cu, 30 kV, 18 mA) at 25°C. The weight for recording the ESR spectra was 30–50 mg. A weighted sample was placed (in an organic ampoule) in the ESR spectrometer cavity. The ESR spectra were recorded by a X-band (9.13 HGz) PS.100X spectrometer (ADANI, Belarus) at 25 ^{0}C.

After each stage of annealing on ESR record in two ranges of magnetic field 400-4000 and 3214-3314 Gauss. The presence of non-structural inclusions in the form wide line of iron oxides (about 100 G) and line of surface electrons (with a width ~ 60 Gauss) were reflected in the EPR spectra.

EXPERIMENTAL RESULTS

The EPR radical ions. Record EPR spectra of radical ions radiation due to their rapid recombination was carried out without accumulation when scanning of 45 gauss, the amplitude modulation of 15 mG increments of 25 ℃ in the temperature range of 100 - 375 ℃ and 600 ℃ (Fig. 1). In the range of 100-200 ℃ in addition to the paramagnetic centers, the previously observed in the annealing products "Marino glass" [4], has induced signals from the surface radicals.

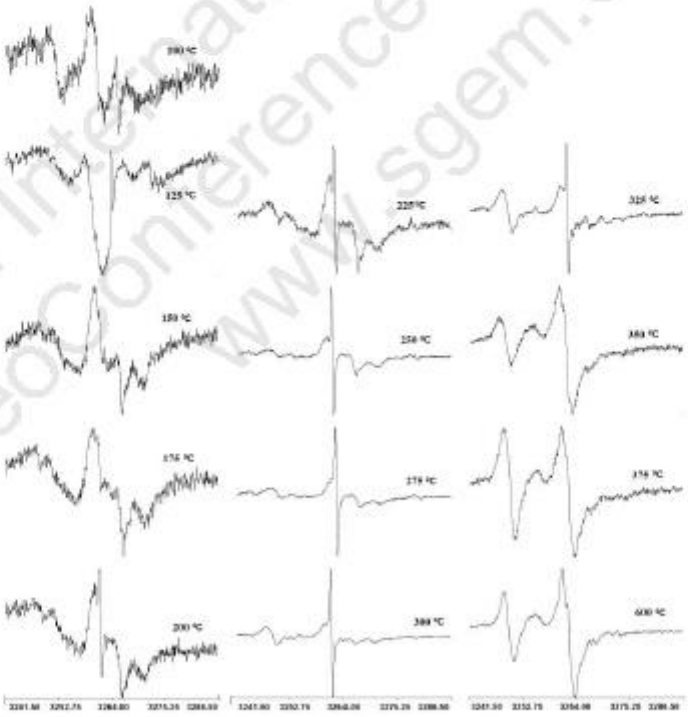

Fig.1. EPR scanning 45 G from vicinity of radical with the center of the magnetic field H = 3264 Gauss depending on temperature of isochronous technogenic gypsum annealing in the range 100-600 °C.

Changing the spectrum and intensity of the ion-radicals from the time of first registration, as a characteristic of preservation of the phase state during 3 months and after repeated exposure to X-ray radiation is shown in (Fig. 2). Samples were stored in ampoules under natural conditions, which have allowed us not only to repeat the recorded spectra after three months, but also to re-irradiate

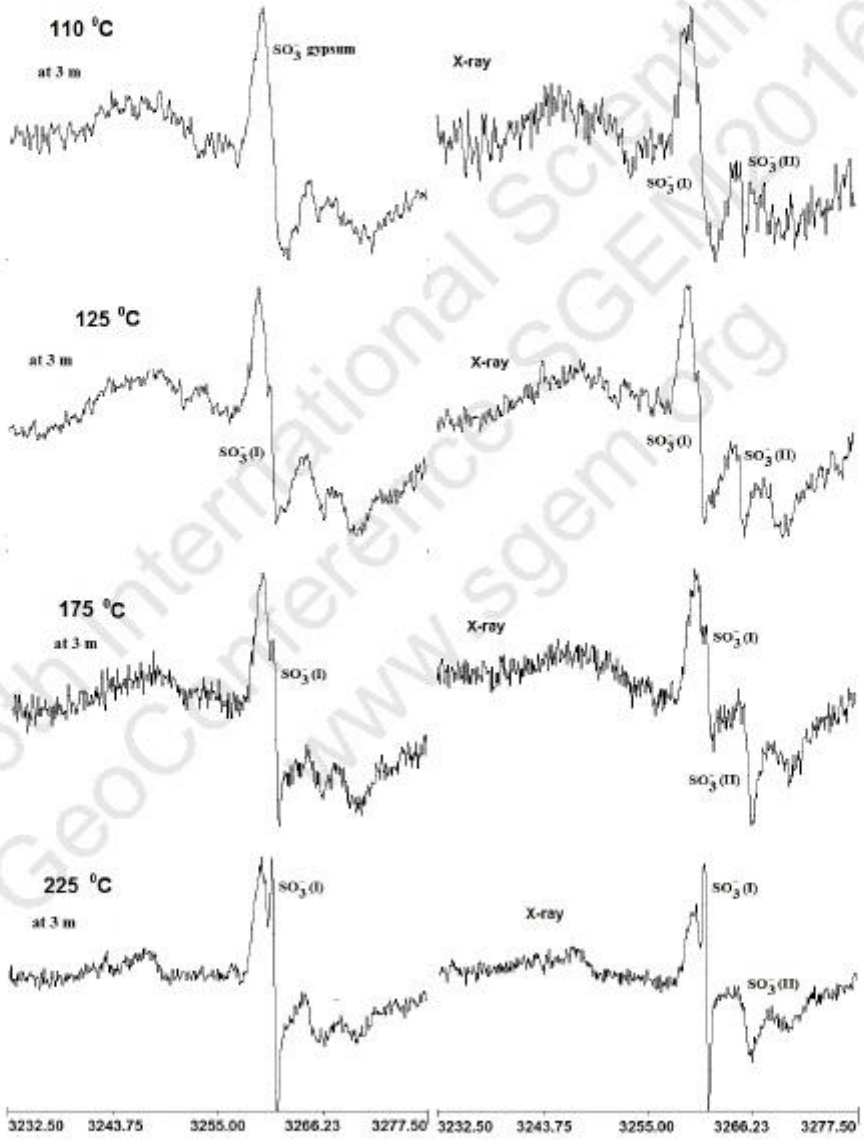

Fig.2. The EPR scanning 45 G from the vicinity of radical with the center of the magnetic field H = 3255 G after 3 months after first isochronous annealing technogenic gypsum at 110, 125.175 and 225 °C and additional X-ray radiation.

The intensity of narrow line SO_3^-(I) after 3 months decreases slightly, but then recovered after further exposure. Evidently is presented to establish equilibrium in the range of 100 - 225 °C and is observed a good safety SO_3^-(I) signal beta- modification soluble anhydrite after 3 months from the time of their formation. As a result of additional X-ray radiation the signal narrow line SO_3^-(II) center alpha modification bassanite recovers and increases the signal line narrow SO_3^- (I) beta modification gamma anhydrite. This indicates the stability of these preserving of paramagnetic centers.

EPR irradiated annealing the gypsum in an atmosphere of dry CO. Annealing was carried out as gypsum in an atmosphere of dry carbon monoxide (CO), and activating the X-ray radiation and recording the EPR spectra were performed in the air at room temperature (Fig. 3). Also EPR spectra were recorded in time in a day, two days after the first registration of the spectra.

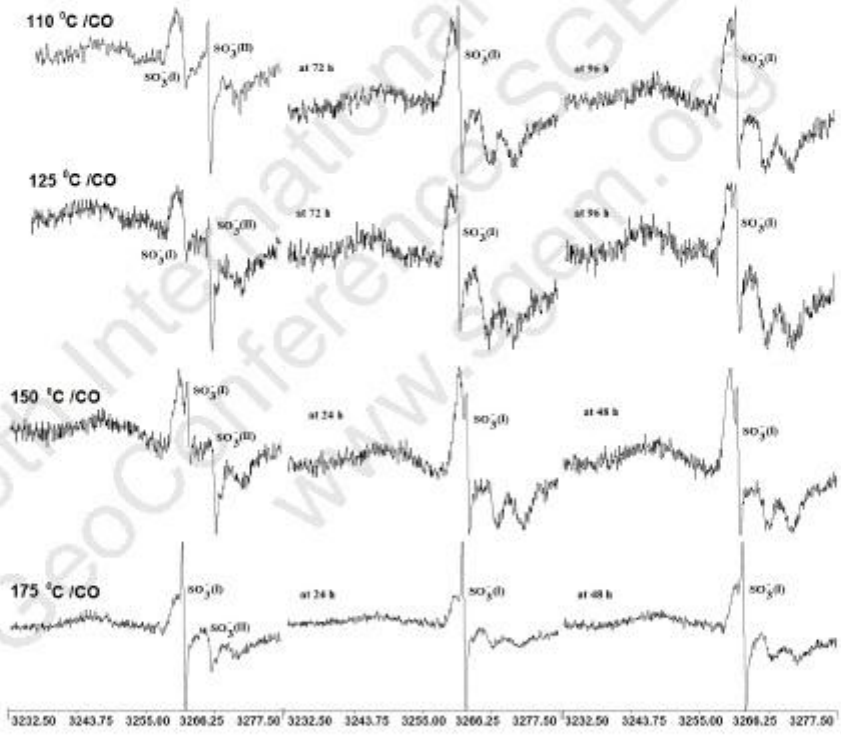

Fig. 3. EPR scanning 45 G from vicinity of radicals with the center of the magnetic field H = 3255 G after isochronous annealing technogenic gypsum an atmosphere of dry carbon monoxide at the range of 110 - 175 °C temperature. Every spectrum was recorded after going one, two or three days after their activation.

Effect on total carbon monoxide spectra in the appearance of ion radicals becomes apparent when comparing the spectra (Fig. 1) and (Fig. 3) obtained by annealing an atmosphere of dries air and carbon monoxide. Carbon dioxide capture free oxygen molecule. After annealing gypsum in an atmosphere of carbon monoxide were increased intensity of narrow line SO_3^-(II) alpha modification of the newly formed basanite at 110 and 125 °C. Then in the process of establishing the equilibrium state, the SO_3^-(I) line intensity is increased and the amount of beta modified gamma anhydrite is increased accordingly.

EPR atomic hydrogen. The number, intensity, and shape of the lines of atomic hydrogen depend on the annealing temperature. To obtain a reliable information, each EPR line of atomic hydrogen was recorded in the accumulation mode (n = 9) at field scanning of 10 G, time scanning of 60 s, and modulation amplitude of 4 mG. EPR scanning 10 G with the center of the magnetic field H = 2997 G the low-field line of atomic hydrogen depending on the temperature of isochronous technogenic gypsum annealing in the range 100-600 °C are presented on (Fig. 4).

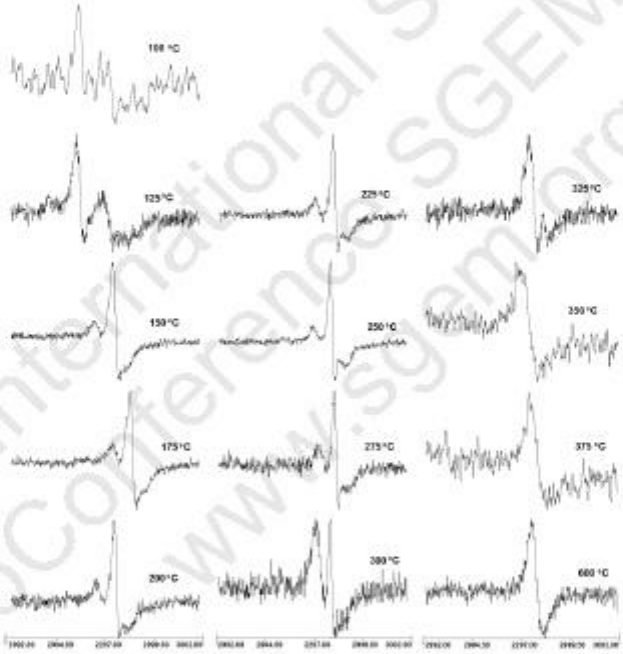

Fig.4. EPR scanning 10 G with the center of the magnetic field H = 2997 G the low-field line of atomic hydrogen depending on the temperature of isochronous technogenic gypsum annealing in the range 100-600 °C.

There is a certain similarity in shape and number of the EPR lines of atomic hydrogen in the annealing products gypsum "Marino Glass" [4] and technogenic gypsum. The difference between two genetically different samples gypsum depends on the humidity and temperature of dehydration. The hydrogen adsorption channels in the crystal structure depend on the quality of sorption surfaces of the channels or the quality of their physicochemical properties.

Annealing technogenic gypsum in an atmosphere of dry carbon monoxide was accompanied by an increasing and stabilization of atomic hydrogen in beta modification of the soluble anhydrite.

At low temperatures 100-150 °C in a "wet" annealing process forming α-hemihydrate and γ-CaSO4 (α) has a greater probability than β- modification hemihydrate and γ-anhydrite. Hydrogen atoms are responsible for more intense EPR spectrum, are in the channels of γ-CaSO4 (α) (Fig. 5) similar for both technogenic gypsum and gypsum "Marino Glass" [4].

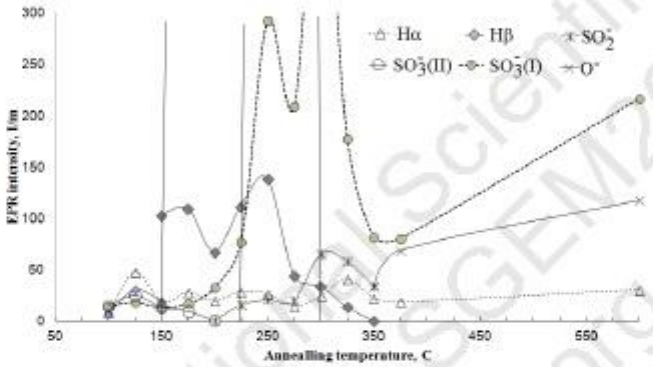

Fig.5. Change in the relative ESR intensity of low-field line of atomic hydrogen and radical ions in thechnogenic gypsum annealing products in the temperature range of 100–600°C. The line of atomic hydrogen (Hα and Hβ) and, correspondingly, radical ions SO_3^-(II) and SO_3^-(I) are indicated for the α and β phase modifications of the product. EPR SO_2^- and O^- radicals are indicated water-free area of soluble and insoluble anhydrite.

CONCLUSION

EPR is an effective method of study of the pore space, physical and chemical properties of nanoscale channels of the crystal structures through a system defects. The system defects gypsum and its thermal derivatives depend on the conditions of their formation, and acts as a sensitive indicator of the state of the environment.

The presence of a bassanite phase on the surface of Mars can be used to help constrain paleoclimates [8]. Low-temperature (258 K) XRD hydration experiments of bassanite resulted in the formation of gypsum in the presence of ice, suggesting that bassanite will not be present in association with H_2O ice. This behavior could simulate a potential hydration mechanism on the martian surface at higher latitudes as well as at depth in association with subsurface ice at lower latitudes.

In situ micro-Raman investigation of dehydration mechanism in natural gypsum (I2/a space group) were allow to conclude that bassanite formed from the dehydration of gypsum is satble and does not rehydrate to form gypsum under its experimental conditions [9].

Changing the number of lines of the EPR spectrum of the product of annealing gypsum and their intensity depending on the annealing temperature determined by the processes

of formation and transformation of the phase states of the product and water transfer between the channel systems of these states. The process of establishing equilibrium in the dehydration gypsum products depend on many factors and their analysis requires further experimental study and analysis of the results.

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