

Electromagnetic emission in mineral and rock dehydration

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Abstract. The article considers regularities of radiofrequency electromagnetic radiation from minerals and rocks, with samples being heated in a vacuum to 20° C- 1000° C. The examples of electromagnetic emission correlation with electric conductivity, thermoluminescence and thermographic analysis during physic-chemical processes resulting from diagenesis, catagenesis and metagenesis have been provided.

1. Introduction

In 1970 a geological and physical exploration team was organized at the department of Solid State Physics, Electrophysical Faculty (SSP EPF), Tomsk Polytechnical University. Salnikov V.N., teaching assistant of SSP department, was appointed to head it. Based on variable anomalies of natural field, the first measurements of the earth's impulse electromagnetic field were conducted under the supervision of A.A. Vorobyev in the Altai and ore mine "Kommunar" in summer surveying season, 1971 [1].

Consequently, the research objective was set up – "Which physico-chemical processes, apart from fracturing as a result of rock decomposition due to earthquakes, can cause electromagnetic emission in the Earth's shells?" In 1971 the plan of laboratory investigations, aimed to detect electromagnetic emission caused by physico-chemical processes which occur due to rock and mineral heating, was proposed. In Laboratory of Dielectric and Semiconductor Physics V.N. Salnikov and his students made a circuit for electrical conductivity operating set-up to measure electromagnetic radiation. It is measured upon heating naturally occurring and man-made dielectrics in a vacuum at temperatures of 20 °C -1000 °C simultaneously with conductivity and separately. The procedure and methods of mineral and rock properties investigations are provided in [2]. The experimental results in measuring electric conductivity of muscovite and rock samples being heated and cooled in temperature interval of 20 °C-1000 °C have been obtained. Variation in electric conductivity timed to occurrence of impulse electromagnetic radiation at radio-frequencies between 247,5 kHz and 35,8 mHz has been detected. The changes in electrical conductivity and electromagnetic emission maxima correspond to vaporization temperature of weakly-bound water (about 100° C), electrical activity of mica surface centers (20-450 ° C), temperatures of muscovite crystallization in hydrothermal process (480-160 ° C), phase transitions 550-590 °C and constitutional water release (780-800-1000 ° C)

In addition to three known water types in crystals - constitutional water, crystallization water and adsorbed water, N.P. Ermakov (1972) distinguishes the fourth type, trapped or mother water, which is geometrically captured in mineral pores. Removal of this water by means of heating in inclusion

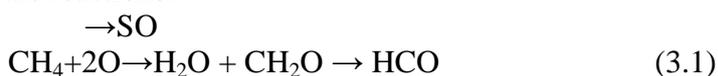


disintegration (dehydration) leads to significant reduction in mineral specific gravity and considerable loss at calcination [3]. It has been stated that electromagnetic emission in heated samples of quartz, orthoclase, mica and rocks which contain these minerals can be detected due to separation of mineral-forming solutions. This separation brings about volume change, polarization, current magnitude impulse change in minerals in the intervals of mineral and ore formation temperatures (Figure 1, 2, 3).

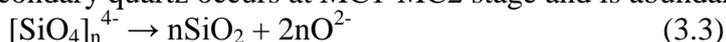
2. Materials and methods

Self-organization effects resulting in the formation of time-ordered varied structures can occur during certain nonlinear chemical reactions in the lithosphere due to metasomatism, metamorphism and hydrothermal process. Thereby, the speed of nonlinear reaction product formation depends on reactant concentrations. Of particular interest in analyzing hydrogeological consequences of catagenesis of sedimentary rocks is mesocatagenesis (MC1-MC3). It is a so-called “thermal furnace”, where considerable transformations of mineral and organic matter including water solutions take place at the temperature of 80-160 °C [4].

In studying physico-chemical conditions of the considered catagenesis grade the question arises concerning the source of oxygen necessary for oxidation of organic matter, for instance, in the reactions:



Silicon is of great significance for the studied physico-chemical processes. Our attention was attracted by the fact that in underground waters of oil-gas bearing basins adjacent to oil deposits there is a great deficiency of silicon, whereas country rocks are subjected to silicification. During regional catagenesis of Permian and Carboniferous deposits in Kuzbass secondary quartz occurs at MC1-MC2 stage and is abundant at later catagenesis stages:



As reactions 3.1-3.3 proceed simultaneously and involve the common element – oxygen, and its release in the reaction 3.3 contributes to oxidation of dispersed organic matter, it is possible to deal with coupled reactions when there is interdependence of mineral and organic matter transformations (equation 3.1, 3.2). Silicon-oxygen tetrahedron turns into bent SiO_2 molecule according to rock silicification mechanism, consequently forming geochemical barriers for hydrocarbon gases. During catagenesis in silicate rocks, exoelectron emission accompanied by acoustic emission is brought about. For the described catagenesis conditions hydrocarbon-silicate interaction is the main factor. In petroleum geochemistry, it has been shown that mineral catalysts are of great importance for thermodynamic destruction of organic matter. Their activity is due to ions of aluminium, iron, silicon and acid interlayer water in minerals (Khant, 1982; Tikhomirov, 1978; Dinisenko, 1974).

In energy terms hydrocarbon-silicate interaction reactions can occur since Si-O and O-H dissociation energy is equal to 224 and 462 kJ/mole, respectively; and corresponds to energy level of hydrocarbon transformation:

- $\text{CH}_3\text{—H}$ (453 kJ/mole),
- $\text{C}_2\text{H}_5\text{—H}$ (407,4 kJ/mole),
- $\text{CH}_3\text{—R}$ (252 kJ/mole).

Physico-chemical analysis shows that between hydrocarbons and rock-forming silicates spontaneously proceed reactions which are accompanied by heat release over the range of 480.8 kJ/mole and are similar to that given below:



In these reactions, oxygen is intensively removed up to 10...20 %. One ton of hydrocarbons can affect nearly 10 m³ of rocks (Dinisenko, 1974). In hydrocarbon migration paths this effect causes leaching of rocks in Kuzbass. The deposited silicon interacts easily with alkali-hydroxide-water solutions resulting in secondary silicate formation at the later stages of catagenesis.

3. Results and discussion

In studying electric conductivity-temperature dependence, the experiments showed that exponential electric conductivity-temperature relationship in complex compounds such as minerals and rocks is not consistent (Figure 1). What causes inconsistency of electric conductivity-temperature dependence of minerals and rocks?

Deviation of mineral and rock conductivity from exponential law due to change of element number (n) and temperature (T) of exothermic and endothermic reactions can be caused by the following reasons:

– Vaporization of weakly-bound water and semi-bound water (dewatering) at temperature of 0-420 ° C;

– Dehydration at higher temperatures (zeolite and constitution water separation)
 $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}] \times [\text{FOH}]_2 \rightarrow \text{AlSi}_3\text{O}_5;$

muscovite mullite

– Disintegration of gas-liquid inclusions in minerals (decrepitation);

– Oxidation-reduction reactions involving exothermic and endothermic effects;

– Piezo-effect which determines dielectric polarization;

– Polymorphous transformations, for example, α - β inversion at 573 ° C;

– Natural radiation which causes energy accumulation in mineral defects and release of stored energy upon heating by light, heat, radio frequency impulse electromagnetic radiation (Schottky and Fresnel defects);

– Artificial radiation exposure to charged particles, gamma-rays, x-rays and other types of rays that result in electric state;

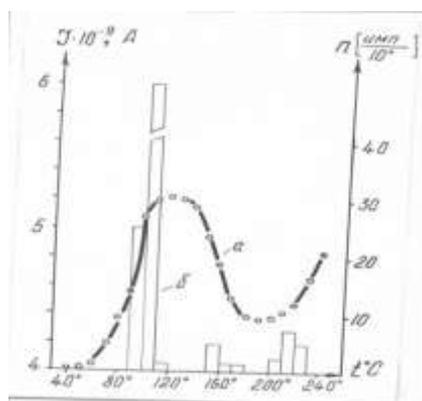


Figure 1. Temperature dependence of electromagnetic impulse intensity (a) and current rate change (b) in the interval of weakly-bound water (granite, 715-M sample, Shindinskiy Khrebet).

– Formation of new phase in heterogeneous dielectric system matrix, formation and decomposition of solid solutions, for instance, $\text{NaCl} + \text{KCl} + t = \text{solid solution}.$

Let us consider modeling of conductivity anomalies in $\sigma = f(T^\circ)$ or $\lg\sigma = f(-)$ dependence. While dielectric being heated, conductivity anomalies occur both in impurity and intrinsic range which is determined by basic ions of the crystal lattice. It should be reminded that electric conductivity-temperature dependence is analytically expressed as follows:

$$\sigma = A \exp\left(-\frac{U}{kT}\right), \text{ where } A = \dots$$

On heating dielectric in which there are no phase transitions of the first and the second type, charge (q) – constant; ion mobility (lattice parameter) δ and their quantity (n) change insignificantly with temperature increase (T); particle vibration frequency (ν) does not practically change until melting point.

In chemical reactions, we deal with self-sustained oscillations which are determined by reacting substance amount over time, i.e. reaction intensity increases with increase in temperature or time, and then reaching extremum, it decreases. Temperature changes depending on heat absorption or heat release reaction effects. Redistribution of heat in samples, supplemented by furnace effect or on the contrary, its absorption by the system, traces a curve, passing over maximum or minimum. Therefore, in accordance with whatever physic-chemical process (related to phase transition of the first type) is, it is advisable to substitute n or T_1 in a pre-exponential variable for normal law of distribution or Gaussian law in electrical conductivity formula (Rytov, 1978).

It is concerned with the case of modeling, whereas in reality it can be much more complicated and does not follow Gaussian law at the moment of phase transition. The mathematical scheme of Bernourlli problem contains a number of specific issues which may represent model situations for defining electric conductivity at the period of I type phase transition occurrence: shot effect (Schottky effect) in a vacuum; random walk; intensity fluctuations.

Nine modifications of electric conductivity temperature dependence deviation from exponential law were first presented by V.N. Salnikov in [2].

Formation and decomposition of defect complexes are always accompanied by neutralization of definite amount of ΔQ_x charges in a dielectric sample being heated.

Hence, f potential between unlike defects and their complexes drops by Δf , additional charge ΔQ_x is required for its restoration. Intensity of internal electrical field between defect complexes reaches 10^6 V/sm.

For a single neutralization event:

$$C_x = \frac{Q_x}{\Delta f}; \text{ where } C_x = \dots$$

C_x – capacitance of two mica plates or crystal faces, or a defect sample; S – plate area; d – distance between plates; ϵ – specific inductive capacity of medium; E_0 – dielectric constant

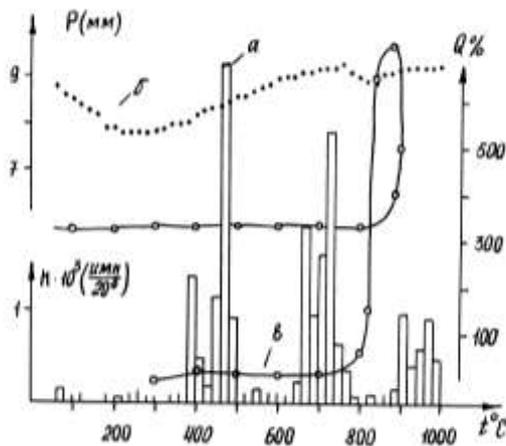


Figure 2. Temperature dependence of electromagnetic pulse (EMP) intensity of Sogdiodon muscovite mica: a – EMP intensity; b – vacuum change in a system while EMP measuring (according to V.N. Salnikov); c – heaving of mica as a result of zeolite and constitutional water loss according to the research done by E.K. Lashava, 1948.

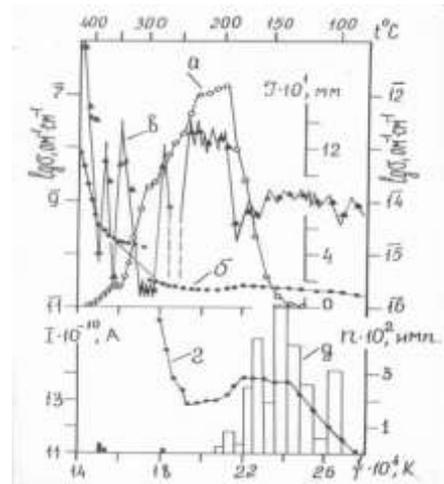


Figure 3. Correlation of electric conductivity with thermoluminescence of microcline samples: a – thermoluminescence; b – electric conductivity dependence at high temperatures; c – electric conductivity dependence on cooling, after sample being heated to 800°C; d – conduction current change upon heating; д – electromagnetic pulse intensity at 0,15-30MHz frequency band.

For example, in muscovite during neutralization immediate increase in C_x capacitance occurs between electrodes which host dielectric (Figure 2). Mica heaving in course of constitutional water separation, and its splitting results in decrease in C_x capacitance between mica plates, while f potential and electrical field intensity (E) increases. It is supposed that intensity of internal field (EIF), produced by defect-adsorbed charges alters according to formula:

—

E_0 – internal field intensity, produced by adsorbed charges in defect spacing or pore counter-surfaces at the moment of emission (charge) termination; t – time of charge (emission or quantum diffusion); τ – time constant of defect-adsorbed charge accumulation, i.e. Maxwellian dielectric relaxation time.

Dielectric relaxation time is dependent on volume resistivity ρ_v and dielectric capacity ϵ :

or —

The formula shows that the more volume charge relaxation time (i.e. time of its retention by dielectric) is, the less electrical conductivity is, and the bigger dielectric capacity which is the ratio of capacitance of a capacitor filled with dielectric C to capacitance of a capacitor C_0 , which is filled with vacuum between plates. Consequently, the formula is written as: —

Volume charge relaxation may take place both due to slow diffusion resulting from conduction and fast relaxation which is accompanied by electrical breakdown, cold emission induced emission, electromagnetic signal generation.

4. Summary and conclusion

Based on experiments in electrical conductivity, electromagnetic radiation and results of differential thermal analysis (DTA) of carbonaceous rocks of Yangoyakhinskoe ore deposit and Paleozoic deposits of gas-oil fields in Tomsk Oblast, we have detected the stages of decarbonatization which can be used to determine mineralization and diagenesis conditions. In DTA curves of limestones it is possible to observe one minimum at 960°C, which is due to CaCO_3 decomposition to CaO and CO_2 . In case of dolomite two minima can be observed: the first is related to decomposition of solid solution $\text{CaMg}(\text{CO}_3)_2$ to CaCO_3 and MgCO_3 , which in turn, decomposes to MgO and CO_2 (780 °C); the second occurs due to CaCO_3 decomposition to CaO and CO_2 (Figure 4).

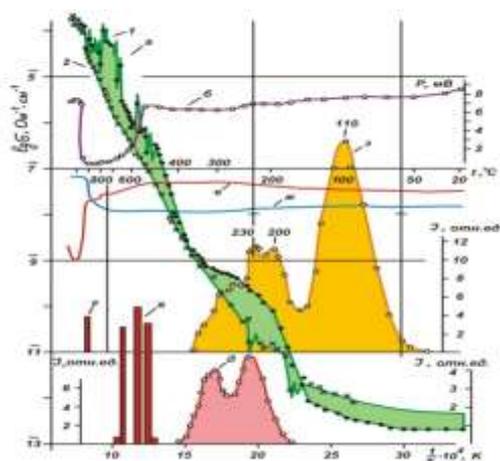


Figure 4. Conductivity-temperature dependence of limestone sample (a): 1) heating; 2) cooling; vacuum change in a system (b); electromagnetic impulses while heating (c); electromagnetic impulses in cooling (d); natural thermoluminescence (e); differential thermal analysis (f); differential thermal analysis on weight loss (g); gamma-thermoluminescence (sample 1052) (h).

Application of electro-physical methods can define kinetics of solid solution decomposition more precisely and introduce new method to determine temperature of geological processes. The integral analysis of electro-physical properties of carbonaceous rocks, different stages and lithogenesis phases can decipher the history of rock formation and transformation. Detection of evolution regularities of carbonaceous substance exposed to thermal and electrical field using electro-physical methods can be applied to differentiation and correlation of Paleozoic carbonaceous deposits of gas-oil fields.

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