Structural Differences in Calcite in Lower Pennsylvanian Carbonate Oil Reservoirs of the Volga-Ural Region, Russia, Revealed by Electron Paramagnetic Resonance and Cathodoluminescence Microscopy

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Abstract

This paper reports on the structural and geochemical differences in diagenetic calcites from oil-water contacts determined by various methods. The differences in calcites were revealed by electron paramagnetic resonance (EPR) spectroscopy on the basis of the ratio of sulfur-oxygen radiation centers and impurity of manganese ions. The data obtained correlate well with the results of the analysis of extracted calcite grains divided using cathodoluminescence microscopy. A relationship was established between important diagenetic events in the basin history, and calcite structural features were established. Content of manganese Mn^{2+} in the lattice of calcite and the color of luminescence allow parameters of the oxidation-reduction potential of the calcite precipitation to be evaluated. According to EPR studies, there is a steady increase in the proportion of Mn^{2+} from the early stages of diagenesis to changes in rocks associated with oil migration and oil charge events, including time of stabilization of the oil-water contact zone. The same tendency is valid for the relation of SO_3^- paramagnetic centers with respect to SO_2^- centers, where the share of SO_3^- centers is increasing.

Keywords: diagenesis, calcite cement, carbonate reservoir, oil-water contact

Introduction

Oil-water contacts are the most reaction-prone areas of oil deposits [1], [2], [3], where the rocks show significant changes in the mineral composition and structure. Chemical and biochemical reactions at the boundary between water and oil produce CO_2 and organic and inorganic acids, which significantly affect the mineral dissolution and precipitation processes in rocks [4], [5], [6]. Carbonate rocks from oil-water contacts are characterized by enhanced intensity of diagenetic processes, such as leaching, recrystallization, calcite cementation, dolomitization, and silica cementation [1].

Oil-water contacts are rarely well characterized by core material, since they have no economic interest due to the lack of prospects of oil recovery from them.

The study area was the Akanskoe oilfield located in the Nurlatsky district of the Republic of Tatarstan, in the east of the European part of the Russian Federation. Tectonically, the oil field is located in the east of the Russian Platform, within the Volga-Ural Anticline, on the eastern side of the Melekesskaya Depression (Fig. 1). We studied core samples represented by shallow-marine limestones of the Bashkirian Stage of the Carboniferous System, which were collected from a depth of 992-997 m. The samples contained oil reservoir rocks and an oil-water contact. The study primarily focused on the oil-water contact zone.
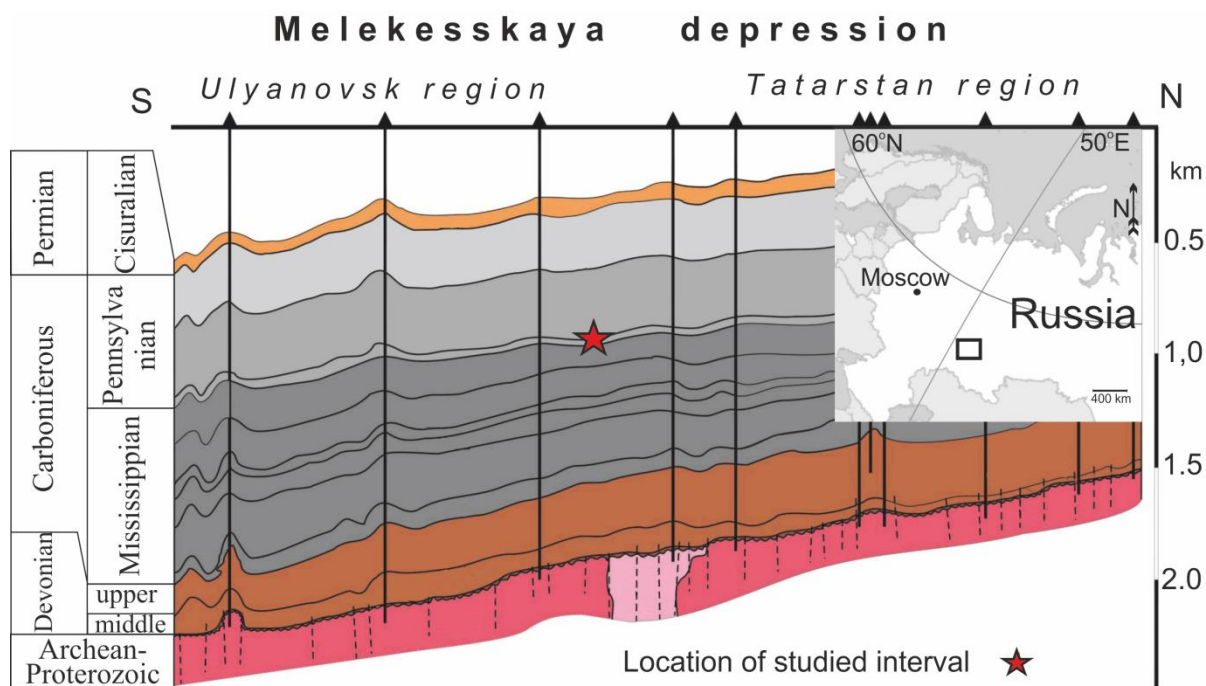
Fig. 1. Schematic geological profile of the Melekesskaya depression: (modified after Gorunova, 2009).

Methods

Investigation of sedimentary rocks involves paying particular attention to post-sedimentary changes in the rocks. This enables determination of the direction and staging of diagenetic processes during the development of the sedimentary basin [7]. Conventional optical microscopy studies, which are frequently used for this purpose, do not provide a complete picture of the environment and chemistry during the processes of mineral formation. Therefore, it is necessary to use other analytical methods to identify the typomorphic features of secondary minerals. These methods include electron paramagnetic resonance (EPR) spectroscopy and cathodoluminescence microscopy (CL). EPR is often used to study the diagenetic transformations of the structural components of limestone.

The method allows the identification of subtle crystallochemical features of genetically distinct calcites [8], [9], [10], [11], [12]. These crystallochemical features in calcites include the paramagnetic centers SO_2^-, SO_3^-, and Mn^{2+}, which are isomorphically incorporated into the calcite structure to position of CO_3^{2-} and Ca^{2+} and provide important genetic information about the environment of mineral formation.

EPR studies were conducted at the Kazan Federal University (Kazan, Russia) on a CMS8400 spectrometer (frequency 9.4 GHz, room temperature). The specimens were ground in an agate mortar to approximately 0.1 mm particles. EPR patterns were recorded at room temperature both electron-hole and Mn^{2+} centers EPR spectrum at range of magnetic field 5 mT and 80 mT respectively.

The EPR spectrum of Li^+ was used as a reference for the position of the lines, with a G-factor of 2.0023.

In addition to EPR, the same calcites were analyzed by cathodoluminescence microscopy.

The method is based on identifying the extent and nature of calcite luminescence caused by the excitation of atoms of the mineral crystal lattice by bombarding electrons. The method is quite good for the identification of the zonal structure and spatiotemporal sequence of calcite cement formation.

In addition, the nature of grain luminescence allows some genetic interpretation of the conditions in the calcite cement growth environment.

CL was conducted with a "hot cathode" CL microscope (type HC1-LM) at the Ruhr-University Bochum, Germany. The acceleration voltage of the electron beam was 14 kV and the beam current were set to a level gaining a current density of ~9 μA mm^{-2} on the sample surface. Further details of the analytical procedure are provided in Christ *et al.* [13].

Results

Prior to the analyses, the most representative specimens with a clearly visible sequence of calcite cement alterations that could be reliably isolated for investigation were sampled. Usually, these were sample fragments with large leaching caverns in which the alteration of calcite types from the walls to the centers of the chambers was clearly visible.

Macroscopically, a sequence of calcite deposition from dense rock areas to chamber cavities is readily observed in samples (Fig. 2):

- calcite grains in dense limestones (Ca-1, Ca-2, Ca-3);
- intensively recrystallized dense calcite (Ca-4a);
- calcite with abundant hydrocarbon inclusions (Ca-4b);
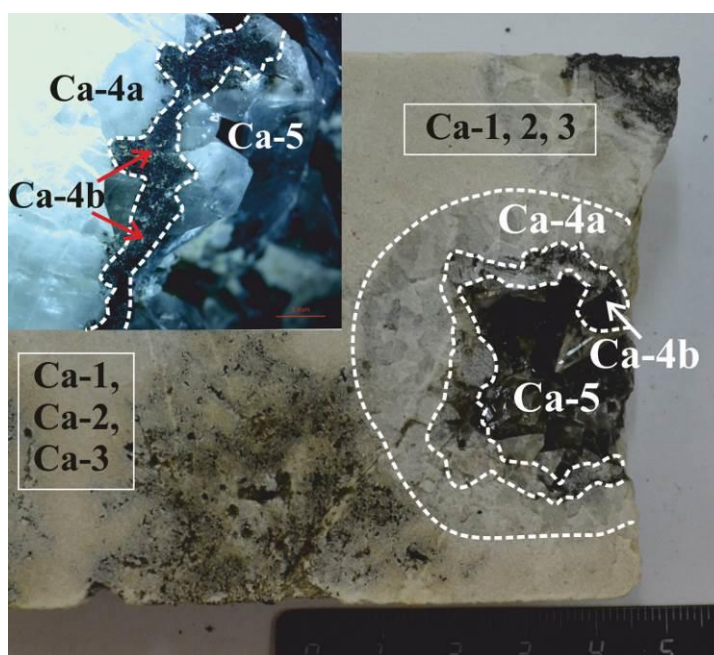- transparent calcite covering the chamber walls (Ca-5).

Fig. 2. The positions of morphologically different secondary calcites in limestones from oil-water contacts.

EPR studies

EPR studies of samples demonstrated that the identified morphological types of calcite grains are characterized by certain defects in their crystal structure (Table 1).

Table 1. The content of Mn^{2+} isomorphous impurities and paramagnetic SO_2^- and SO_3^- centers in the crystalline textures of morphologically distinct calcites (by amplitude, arbitrary units per gram of rock).

Types of calcite grains	The content of paramagnetic centers (Rd / mg)		
	Mn^{2+}	SO_2^-	SO_3^-
Calcite grains of dense, least modified limestone (Ca-1, Ca-2, Ca-3)	1008.9-1128.2	121.4-129.6	39.7-81.4
Calcite grains of dense, strongly recrystallized limestone (Ca-4a)	2363.0	38.34	318.1
Calcite grains with hydrocarbon inclusions (Ca-4b)	3029.3	0.00	279.6
Transparent calcite grains (Ca-5)	3181.9-4569.3	0.00	396.3-526.9

Sedimentary and diagenetic calcites (Ca-1, Ca-2, and Ca-3) obtained from slightly altered rock areas are characterized by the predominance of SO_2^- centers over SO_3^- centers (Fig. 3).

The manganese lines of these calcites in the EPR spectra are narrow. Importantly, in dense rock areas, it is impossible to distinguish the calcites that constitute the structural components of

limestones and the cements formed during the early and late diagenesis of sediments. Identification is only possible by analysis of thin sections under an optical microscope and by investigation of thin sections using cathodoluminescence microscopy. For calcite grains, similar data were obtained in the areas of manifestation of the secondary leaching process and partial recrystallization. However, the content of SO_2^- centers is noticeably reduced, and the concentrations of Mn^{2+} ions that isomorphically replace Ca^{2+} in the mineral crystal lattice are increased (Table 1).

In the areas of intensive rock recrystallization, in which calcite provides complete metasomatic replacement of components of limestones (including cement and organic residues), much higher levels of isomorphic Mn^{2+} ions are observed in the grains of newly formed calcite (Ca-4a).

Simultaneously, a change in the ratio of the content paramagnetic centers occurs.

The concentrations of SO_2^- centers in the crystal structure of calcites are significantly reduced.

In contrast, the concentrations of SO_3^- centers are increased and become dominant. An EPR analysis of large, transparent, scalenohedral calcite crystals (Ca-5) grown on the chamber walls showed that the crystals are characterized by the lack of SO_2^- centers. In this case, the concentrations of SO_3^- centers are significantly higher than those in the sedimentary–diagenetic (Ca-1, Ca-2, Ca-3) and metasomatic (Ca-4a) calcites discussed above. Furthermore, the content of impurity Mn^{2+} ions replacing Ca^{2+} in the structure is increased by several orders in scalenohedral calcite grains (Ca-4).
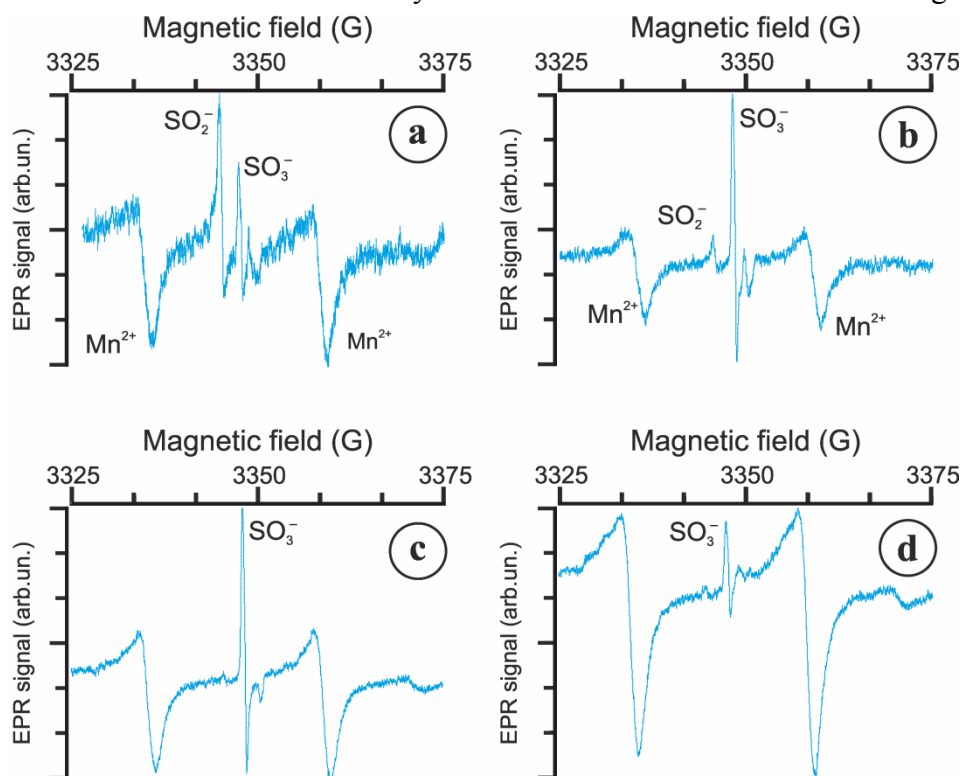

Fig. 3. EPR spectra of studied calcites: (a) calcites from dense, least modified, areas of limestones (Ca-1, Ca-2, Ca-3); (b) intensively recrystallized grains of calcite (Ca-4a); and (c) and (d) grains comprising transparent crystals of calcite (Ca-5).

Cathodoluminescence microscopy

Investigation of selected calcite types by cathodoluminescence microscopy clarified some patterns in the qualitative content of Mn^{2+} ions in calcites, which defines the nature of the luminescence.

For example, it was determined that at least two calcite types sequentially alternating with each other can be distinguished in limestone areas (that are not affected by secondary processes) in the cement that binds the structural elements (Ca-1) (Fig. 4A and B). For example, the first cement type identified by cathodoluminescence microscopy is ubiquitous and nonluminescent calcite (Ca-2).

In general, the presence of this calcite in carbonate rocks formed in normal shallow-marine environments is quite typical and common, and the lack of luminescence is usually caused by the presence of Fe^{3+} ions in the calcite structure [14]. In addition, bright orange luminescence of calcite

(Ca-3) is observed in the spatiotemporal sequence of calcite cement formation. The bright luminescence is caused by the presence of Mn^{2+} ions in the calcite structure. This alternation of calcite cement is also commonly observed and is a characteristic of marine carbonate sediments [15].
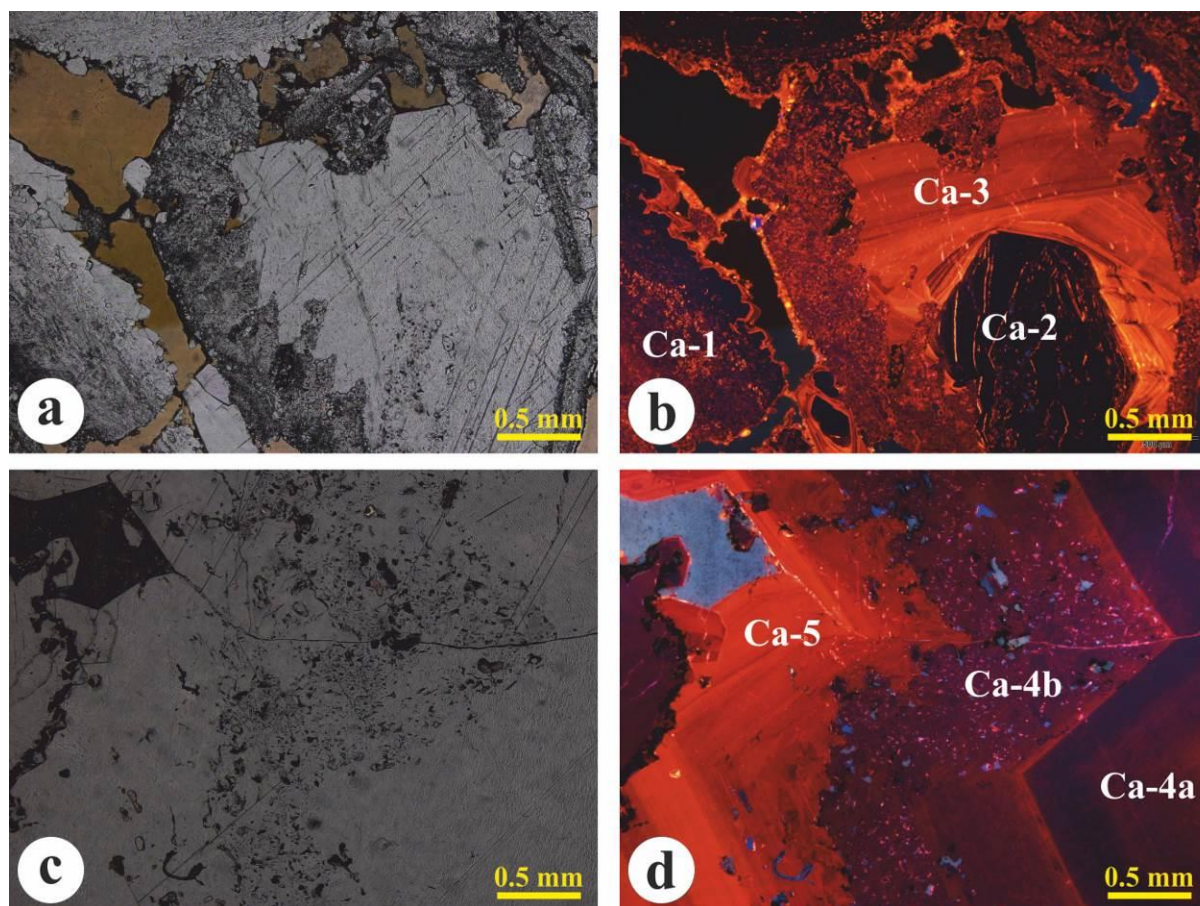
This calcite often shows the evidence of corrosion.

Fig. 4. Cathodoluminescence properties of different paragenetic phases placed against transmitted light photomicrographs. (A/B) Host sediment (Ca-1), nonluminescent blocky spar calcite (Ca-2), and bright orange luminescent blocky spar calcite cement (Ca-3). Note the complex zoning of Ca-3. (C/D) Cement phase Ca-4a, 4b, and 5. Note the sharp boundary between phases 4a and 4b and the corrosive boundary with the overlying phase Ca-5. Ca-4b is interpreted as a paragenetic phase coeval with oil migration based on numerous hydrocarbon inclusions. Note the complex zoning of phase Ca-5.

The next calcite type in the sequence of post-sedimentary mineral formation is blocky calcite (Ca-4).

This calcite type typically forms rather coarse-grained aggregates that are clearly distinguishable both under the microscope and in hand specimens. This cement type usually has dark red and brown-red luminescence. We suggest that this calcite is divided into two types: Ca-4a (true blocky calcite) and Ca-4b (calcite with abundant hydrocarbon inclusions; Fig. 4C and D). In this case, the external borders of this calcite toward younger calcite are always heavily corroded. Slit voids with hydrocarbons adsorbed on their walls can be often observed. The next and final stage of calcite cementation is blocky sectorial calcite (Ca-5) with bright orange luminescence. This type of calcite is clearly distinguishable both in thin sections and hand specimen in the form of drusy aggregates covering the walls of chambers and pores. The bright luminescence results from an increased concentration of Mn^{2+} ions in the structure, which is confirmed by the EPR data [15].

Interpretation and Discussion

Based on these findings, it is possible to establish the sequence of carbonate rock transformations that occurred along with post-sedimentary changes. For example, the major diagenetic stages are well tracked. After accumulation of the sediment, structural limestone elements underwent minor changes, whereas the cement was already subjected to the active influence of pore solutions during the early stages of diagenesis. For example, the lack of luminescence in calcite Ca-2 is caused by the presence of Fe_3^+ and indicates an early stage of rock diagenesis in an oxidizing or nearly oxidizing environment [16].

This is confirmed by the presence of breccia and carbonates with traces of subaeral exposure. This type of limestone strata confirms the possibility of diagenetic cementation under the influence of meteoric fluids saturated with oxygen. The next important, quite natural stage in the history of post-sedimentary rock transformation is the change from an oxidizing environment to a reducing environment. This stage is probably associated with the time of late sediment diagenesis. This is evidenced by the appearance of calcite cement with bright orange luminescence. The inability to reliably confirm the difference between Ca-2 and Ca-3 cements by EPR results from the difficulty in recognizing these two calcite types, because they are visually indistinguishable in samples (they are only recognizable using cathodoluminescence microscopy). In this regard, the EPR data on the content of Mn^{2+} and SO_2^- and SO_3^- centers in these calcites were averaged.

In our opinion, Ca-4a and Ca-4b cements were formed during the oil migration and accumulation stage.

For example, metasomatic calcite (Ca-4a) was formed during the stage preceding migration of hydrocarbons and was probably associated with the CO_2-rich fluids that dissolved some of the calcium carbonate and redeposited it on the chamber walls. Almost ubiquitous corrosion of the preceding, late-diagenetic cement (Ca-3) indicates dissolution processes resulting from a high content of CO_2. The same processes probably caused the metasomatic alteration of original limestones and intensive recrystallization. Subsequently, during the stage of active migration and accumulation of hydrocarbons, a calcite was formed that contained abundant oil inclusions and bitumen adsorbed on the faces of growing grains. The high degree of similarity between the Ca-4a and Ca-4b calcites, both in hand specimen and in the luminescence color under the microscope, suggests that these calcites are associated with the same stage of post-sedimentary basin history. However, the absence of hydrocarbons from one calcite (Ca-4a) and the presence of hydrocarbons in the other (Ca-4b) enable their division into separate subtypes. Formation of the coarsely crystalline calcite (Ca-5) covering the cavernous walls may be associated with the formation and stabilization of the oil-water contact zone.

A significant portion of the active oxygen was consumed by the oxidation of hydrocarbons, which facilitated the development of a reducing environment and inclusion of Mn^{2+} into the calcite structure.

This is confirmed by the EPR data and the bright orange luminescence observed in cathodoluminescence microscopy.

Conclusions

The crystallochemical differences observed between genetically different calcites of oil-water contact zones suggest the following conclusions:
1. The calcite cements Ca-2 and Ca-3 formed during early and late diagenesis and were observed almost ubiquitously in all studied samples.
2. The predominance of SO_2^- centers over SO_3^- centers from the least altered rock areas, and generally indicates the predominance of reducing conditions during sedimentation and diagenesis of sediments. However, the cathodoluminescence data demonstrate that oxidizing environments associated with the formation of calcite cement Ca-2 could also have been present during early diagenesis.

3. The elevated content of Mn^{2+} ions in secondary, clearly grained calcites Ca-4a, Ca-4b, and Ca-5, indicates a stronger reducing environment during their formation compared to that of sedimentary–diagenetic calcites Ca-1, Ca-2, and Ca-3.
4. Large calcite crystals covering the cavernous walls (Ca-4a, Ca-4b, and Ca-5) formed during deep diagenesis with the involvement of hydrocarbon fluids. The presence of compositional variations in the calcite suggests that the mineral-forming medium actively evolved as a result of periodic carbonation and migration and accumulation of hydrocarbons.

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