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GENESIS OF CARBONATE MINERALS IN THE UPPER CARBONIFEROUS SANDSTONES IN CENTRAL POLAND

INTRODUCTION

Carbonate minerals of the Upper Carboniferous sandstone from the boreholes located between Warsaw and Dęblin have been studied. This rocks form in fluvial and deltaic environments (Waksmundzka, 1998). The amount of carbonate cement oscillated between 0 and 38.0 volume % in the studied rocks. Carbonates: siderite, dolomite, Fe-dolomite, ankerite i Fe-calcite form mainly porous cement, rarely basic one. Carbonate cements have been examined using a polarization microscope with a cathodoluminescence (CL) device and a scanning electron microscope (SEM) and chemical microprobe (EDS ISIS). X-ray diffraction (XRD) and fluid inclusions have been also analyzed. The stable isotopic determinations were conducted by Professor S. Hałas in Lublin.

CHARACTERISTICS OF CARBONATE MINERALS

Siderite appearing in the sandstones represents a variety of $FeCO_3$ with different $MgCO_3$. Rarely there are varieties containing manganium. The average amount of siderite in the Carboniferous sandstones is 4 volume %. Two generations of diagenetic siderite have been identified, the early siderite generation having the lower content of $MgCO_3$ than the late one (Kozłowska, 1997). The early siderite forms very fine crystalline specimens or spherulites, while the late generation crystallized as rhombohedrons or replaced detrital feldspars. In the early siderite crystals fluid inclusions have not been identified. The $\delta^{18}O$ values of early siderite vary from –15.43 to –4.18‰$_{PDB}$ and average is –8.6‰$_{PDB}$. The $\delta^{13}C$ values are from 1.37 to –16.12‰$_{PDB}$, average –5.51‰$_{PDB}$. The homogenization temperatures of fluid inclusions in the late siderite vary from 46 to 97.5°C. The $\delta^{18}O$ values of the late siderite generation oscillate between –13.97 to –3.44‰$_{PDB}$, average –8.5‰$_{PDB}$. The $\delta^{13}C$ values in range from –3.78 to –13.89 ‰$_{PDB}$, in average –9.62 ‰$_{PDB}$, seem to be lower in comparison to $\delta^{13}C$ values of the early siderite.

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Dolomite, **Fe-dolomite and ankerite** are the minerals of an isomorphic series of $CaMg(CO_3)_2$ – $Ca(Fe,Mn)(CO_3)_2$ and they mostly represented ankerite. The average amount of dolomite, Fe-dolomite and ankerite in the Carboniferous sandstones is 1 volume % of the rocks. Ankerite occurs very often as isolated rhombohedral crystals or as a basic cement. Some of the rhombohedrons can be named as saddle dolomite (ankerite). The homogenization temperatures of fluid inclusions are in the range of 55–129°C. The $\delta^{18}O$ values of Fe-dolomite and ankerite cements oscillate between –13.96 to –1.19‰$_{PDB}$, average –6.63‰$_{PDB}$. The $\delta^{13}C$ values vary from –0.92 to –14.19‰$_{PDB}$, average –7.44‰$_{PDB}$.

Fe-calcite was identified only in deltaic sediments by the author, where its average content is 3 volume % of rock. Fe-calcite forms pore cements most frequently and basic cement locally. Only one phase fluid inclusions were identified in Fe-calcite what can suggest minimum temperature below 50°C of calcite cement crystallization (Goldstein, Reynolds, 1994). The $\delta^{18}O$ and $\delta^{13}C$ values are equal to –13.62 and –12.08‰$_{PDB}$, –5.05 and –6.52 ‰$_{PDB}$, respectively.

FORMING OF CARBONATE MINERALS

Siderite of early generation forms as the first carbonate cement in the Carboniferous sandstones. This mineral precipitated in eodiagenesis, in anoxic environments such as: lakes, swamps and flood plains in the sediment rich in reactive minerals containing iron under low dissolved sulphate conditions. Higher content of $MgCO_3$ in the studied fluvial siderites can be connected with transformation of detrital magnesian minerals by meteoric porous water infiltration. It is possible that the early siderite crystallized in the temperature of range from 15 to 40°C (Rezaee, Schulz-Rojahn, 1998). Assuming the crystallization temperature of 25°C, the counted $\delta^{18}O$ value of porous water from which siderite is precipitated has oscillated between –17.71 to –6.06‰$_{SMOW}$, average –10.44‰$_{SMOW}$. These values suggest the porous water of meteoric composition strongly reduced in ^{18}O isotope. The obtained $\delta^{13}C$ values show that the porous waters were enriched in carbon generated in microbial methanogenesis zone (Morad, 1998).

In mesodiagenesis in the conditions of the progressive burial, other carbonate minerals precipitated in the following order: Fe-calcite, dolomite, late siderite, Fe-dolomite and ankerite.

Fe-calcite created at the beginning of mesodiagenesis in temperature of about 50-80°C, before the ankerite cement. It is possible that plagioclase grains, subjected to dissolution and albitization, were the calcium source. The assumed temperature range of calcite formation, points to $\delta^{18}O$ values of the porous water ranging from about –5.5 to about –1‰$_{SMOW}$. It proves that calcite precipitated from the porous water of the composition of a little modified meteoric water. The $\delta^{13}C$ values suggested that carbon could have formed in thermal decarboxylation organic matter zone (Morad, 1998).

Siderite of late generation precipitated in mesodiagenesis in the temperature range of about 60-85°C, locally simultaneously with ankerite. The formation of the high magnesium late diagenetic siderite is most likely connected with a high concentration of magnesium in the formation water. Altered minerals rich in Mg^{2+} could be the source of magnesium, or magnesium could be liberated from kerogen during burial processes. The crystallization temperatures of siderite show that this mineral precipitated from the porous water of $\delta^{18}O$ values oscillating between –6.85 to –0.68 $‰_{SMOW}$. The oxygen data show that the late siderite crystallized from the porous water of the composition of meteoric water enriched in ^{18}O isotope in comparison to the meteoric water from which precipitated the early diagenetic siderite. The low values of $\delta^{13}C$ suggest that the main source of carbon in isotopic composition of the late siderite is the organic matter subjected to decarboxylation and producing carbon strongly enriched in ^{12}C (Morad, 1998).

Dolomite formed most likely at the beginning of mesodiagenesis. **Fe-dolomite** and **ankerite** crystallized in temperature below 70°C. The occurrence of saddle dolomite (ankerite), one of the diagenetic geothermometers, points to the high crystallisation temperature. Due to no traces of an early diagenetic calcite in the studied Carboniferous sandstones, the formation of dolomite and ankerite should not be connected with dolomitization of calcite in late diagenetic stage. The calculated isotopic composition of the porous water from which precipitated Fe-dolomite and ankerite widely oscillated from –5.01 to 10.03$‰_{SMOW}$ for the crystallization temperature in range from about 80 to about 120°C. It is quite possible to accept that $\delta^{18}O$ values for the porous water of carbonate crystallization fall even in the narrower range from 0 to 2$‰_{SMOW}$. The $\delta^{13}C$ values in Fe-dolomite and ankerite isotopic composition suggested that carbon originated from two different sources - thermal decarboxylation of organic matter and microbial methanogenesis zone what Morad (1998) announces.

The replacement of one carbonate minerals by the other in the studied Carboniferous sandstones is a wide-spread process in mesodiagenesis. The effects of the early siderite replacement by the late one or the late siderite and Fe-calcite by ankerite in the rocks may be observed, as well as the effects of the carbonate dissolution as the reaction of progressive sediment burial leading to creation of a secondary porosity. According to Morton and Land (1987), carbonate cement dissolution results from the inflow of acid waters and CO_2 produced in a process of organic matter thermal maturation in siltstones. Only traces of the carbonate dissolution were observed in the studied cements.

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