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Jan PARAFINIUK[1]

SHIFT OF THE SULPHUR ISOTOPE COMPOSITION OF SULPHATE MINERALS FROM THE MIOCENE EVAPORITES OF THE CARPATHIAN FOREDEEP IN POLAND AND UKRAINE

Miocene evaporite sequence in the Carpathian Foredeep plays important role as a useful correlation marker and deposits of economic significance. Most of the evaporites are generally considered to be Badenian, although Eggenburgian and possible Karpatian salts are also known. They represent almost complete set of marine evaporate facies: sulphate facies (gypsum and anhydrite), halite, and potash facies (mainly K and Mg sulphates) but the transitions between them are not clear and can be only sporadically observed. Nevertheless, evaporate facies form quite regular spatial pattern within the Miocene Carpathian foreland basin. The most abundant evaporite minerals are Badenian gypsum and anhydrite. Gypsum occurs in the marginal, northern part of the foredeep forming a belt 20-60 km wide and a few tens meter thick. Usually gypsum section may be divided into two parts: a lower member dominated by autochtonous, bottom-grown selenites or giant intergrowths and an upper one composed of microcrystalline clastic gypsum. All the economic native sulphur deposits of Poland and Ukraine are located within these gypsum. Towards central part of Carpathian Foredeep gypsum is gradually replaced by anhydrite developed as laminated, nodular and brecciated varieties with common redeposition features. Halite facies was deposited in narrow axial part of the evaporite basin on the Polish and Ukrainian territory. Halite deposits extend along the northern part of the Carpathians and in many cases are tectonically disordered by the front of the overthrusting nappes. Potash facies has not been found in the Polish part of the Carpathian Foredeep but it forms economic deposits in Western Ukraine (Kalush, Stebnyk). Geology of these deposits is complex since they have been strongly affected by the overthrusting Carpathians (Koriń, 1994). Potash deposit in the Stebnyk mine is of Eggenburgian age. Its large thickness, reported to be more than 1000 m, is caused by tectonic deformations of the sedimentary layer 100-120m thick. The stratigraphic position of deposit in the Kalush mine remains subject of controversy. The evaporatic sequence of this deposit up to 500 m thick has been lately regarded as Badenian. In mineral composition of these deposits K-Mg sulphates predominate significantly over chlorides, thus the Ukrainian potash deposits are well known as classic examples of

[1] *Institute of Geochemistry, Mineralogy and Petrology, Warsaw University, al. Żwirki i Wigury 93, 02-089 Warszawa, Poland, e-mail janpar@geo.uw.edu.pl*

the sulphate type of potash evaporites. Their principal constitutes are langbeinite and kainite whereas carnallite and sylvite are present in smaller quantities. Occurrence of polyhalite, kieserite, anhydrite, leonite, picromerite, syngenite and many others sulphate minerals were also reported from these deposits.

One of the principal modern tools in examining the origin of evaporite formation is determination of sulphur isotope composition in the sulphate minerals. For the Badenian evaporites of the Carpathian Foredeep several hundreds of isotopic analyses were carried out. Available isotopic data have been contribiuted here to elucidate some aspects of hydrological evolution of the Miocene basin during precipitation of evaporites.

The majority of sulphur isotope data (ca. 400 analyses) is related to gypsum and anhydrite of the sulphate facies. Average $\delta^{34}S$ value for gypsum and anhydrite was estimated as 21.6±0.5‰ (Peryt et al., 2002). This value is typical for the Miocene marine evaporites elsewhere as well as for contemporaneous evaporites reflecting sulphur isotope ratios in modern sea water. Relatively narrow range of $\delta^{34}S$ values is specific for giant intergrowths and selenic gypsum whereas for the clastic gypsum up to few per mil spread was recorded. This fluctuation of sulphur isotopic composition, generally interpreted as a result of redeposition and recrystallization of previously precipitaded gypsum, is useful for constrains of the depositional enviromnents. There are no differences between $\delta^{34}S$ values of gypsum from marginal and anhydrite from inner parts of the foredeep.

For gypsum and anhydrite embedded in halite several tens analyses of sulphur isotopes ratios have been performed. Their $\delta^{34}S$ values are very similar to those from the sulphate facies. Anhydrite and gypsum from Wieliczka salt mine show values close to 22‰ (Claypool et al., 1980; Parafiniuk and Halas, 1997). Slightly higher values av. 22.6 and 22.7‰ reported for Wojnicz and Cieszanów boreholes, respectively (Cendon et al., 1999) resulted rather from recycling of previously formed evaporites than from shift in the isotopic composition of brine.

Sulphur isotope ratios in K-Mg sulphates of the Ukrainian deposits have been examined less extensively. However, available data show essential difference in their isotopic composition in comparison with sulphates of the previous facies. Basal anhydrite from the potash deposits has still $\delta^{34}S$ values about 21-22‰, as predicted for the Miocene evaporites, but for anhydrite from the beds of potash salts $\delta^{34}S$ values decrease to 16.7‰. Similar values 16-17‰ have been obtained for langbeinite, kainite, polihalite and other K-Mg sulphates. Neither isotopic fractionation trend among these minerals nor dependence of sulphur isotope composition on their crystallization sequence have been noticed. Moreover, no difference in sulphur isotope composition between Eggenburgian potash salts from Stebnyk and probably Badenian deposit in Kalush has been recognised. Subsequent transformation and weathering of K-Mg sulphates towards formation of secondary minerals like mirabilite, blödite or picromerite also did not change essentially their sulphur isotope ratios.

CONCLUSIONS

Sulphur isotope composition of the Miocene evaporites of the Carpathian Foredeep is quite uniform up to stage of the potash facies precipitation. Significant shift of $\delta^{34}S$ values recorded in K-Mg sulphates seems to be best explained in terms of change in the hydrological regime of the evaporation basin. Another possible mechanism of sulphur isotope fractionation is crystallization in a closed system. Since gypsum crystals are isotopically 1.65‰ heavier than parent brine, highly evaporated facies should reveal gradual decrease of their $\delta^{34}S$ values. Nevertheless, experimental data of Raab and Spiro (1991) suggest that such a decrease is correct only to the end of the halite facies and in evaporites of the potash facies even an opposite trend has been observed. The detected decrease of $\delta^{34}S$ values of sulphates from the Ukrainian potash deposits has also no connection with the most powerful sulphur isotope fractionation process, i.e. bacterial reduction of sulphates. In evaporate basin with intensive bacterial reduction the $\delta^{34}S$ value of sulphates from later facies should be higher than from the initial evaporation stages. The best interpretation for the sharp decrease in the $\delta^{34}S$ values of potash salts in the Carpathian Foredeep seems to be change of the hydrological regime of the evaporation basin from marine to lacustrine, due to disconnection from the open sea on the stage of precipitation of the potash salts. Evaporation of decreasing brine volume becomes more sensitive to modify its isotope composition in comparison to steady state conditions when the previous facies precipitated. Decrease of $\delta^{34}S$ value of the brine may be triggered by influx of older evaporites or weathering sulphates with lower $\delta^{34}S$ values from adjacent areas.

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