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Stable isotope analysis of carbonates from the W-Hungarian natural CO_2 occurrence

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Carbone capture and storage is becoming more vital in the last years because the concentration of carbon-dioxide is constantly increasing in the atmosphere in relation with anthropogenic emissions. To reach the long-term safety of CO_2 geological storage, it is needed to be aware of the geological environment, its behavior, and the influence of the complex physical and chemical reactions on the investigated system. The study of natural CO_2 occurrences can help us to understand and predict what processes are likely to occur in CO_2 geological storage reservoirs in geological time scales. In the presented work we provide a detailed insight into the stable isotope composition of different carbonate minerals of a natural CO_2 reservoir from the Mihályi Répcelak area, W-Hungary. The study of stable isotope systems provides important information on the time of CO_2 flooding and the origin of CO_2. We measured the C and O isotope composition of different carbonate minerals, ankerite, dawsonite and siderite, as well as the H isotopes in dawsonite. The measurements both on separated mineral grains and whole rock sample were carried out. The analyses of C and O stable isotopes in separated carbonates was performed with Thermo Finnigan Delta Plus XP mass spectrometer. H stable isotope measurement was conducted on whole rocks applying LWIA-24d type laser analyser. Using the obtained isotopic values the δ13C values of CO_2 in equilibrium with dawsonite and the δ18O values of water in equilibrium with carbonate minerals were calculated. The results of C and O isotopes are the following: δ 13CPDB values on average are ankerite: 1.86 ‰ dawsonite: 1.53 ‰ to 1.56 ‰ siderite: 2.07 ‰ and δ 18OSMOW values ankerite: 22.15 ‰ dawsonite: 19.46 ‰ to 19.54 ‰ siderite: 22.99 ‰V̇alues of δDSMOW for dawsonite vary between -73.14 ‰ and -74.31 ‰Ṫhe calculated value of δ13C of CO_2 in equilibrium with dawsonite ranges between -4.55 and 2.58 ‰Ṫhese values indicate magmatic origin for carbon (magmatic origin: -4 to 7 ‰. The calculated δ18O values of water in equilibrium with dawsonite range from -1.39 ‰ to 2.04 ‰ depending on model temperature (70 °C- 98 °C). These results indicate the water origin of dawsonite formation what are meteoric origin. The water isotopic composition has been derived on three independent ways, among which the dawsonite hydroxyl component measurement was done first time to our knowledge. In summary the CO_2 which was present during the formation of carbonate minerals had magmatic origin, whereas the percolating water likely had meteoric origin modified due the prolonged water-rock interaction.