

## CO<sub>2</sub> induced geochemical reactions at the pore scale

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In many geologic systems pore space is conceptualized as a containment and delivery system for fluids, not unlike a pipe network that delivers water through a city. However, in rocks exposed to reactive fluids, pore networks are not static. The pore network undergoes constant reshaping as minerals dissolve and precipitate. Despite the importance of pore network structure on many fundamental geologic processes, the physical characteristics of pore networks in rocks are poorly understood, in part due to their dynamic nature. Sub-micron sized pores in fine-grained rocks, such as shales and mudstones, require advanced techniques for quantification and characterization. Small angle neutron scattering, a technique that provides statistical data on the topology and architecture of pore networks, was combined with high-resolution imaging, and gas sorption measurements to characterize and quantify the pore network structure in 5 fine-grained rocks. In these rocks a large fraction (up to 80%) of the pore volume and surface area is contained within pores <20 nm in diameter. When two of these rocks were reacted with CO<sub>2</sub> under conditions relevant to CO<sub>2</sub> sequestration or enhanced oil recovery, mineral dissolution and precipitation changed the structure of the pore network with an overall loss of pore connectivity. This study demonstrates the application of neutron scattering to the study of pore networks in fine-grained rocks and the reshaping of these pore networks by mineral reaction.

## The Río Mundo dolostones (Spain): Implications for MVT and hydrocarbon formation

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Dolomitic rocks constitute a potential natural resource as they may host base-metal and hydrocarbon deposits. The study of the dolomitization associated with a Zn-(Pb) Mississippi Valley-type (MVT) deposit in the Río Mundo area (Albacete, SE Spain) may be a breakthrough for mining and hydrocarbon companies, as it is an excellent example to unravel relationships between dolomitization, fluid flow, fractures, host-rock porosity, ore deposition and hydrocarbon accumulation. Petrographical and C/O stable isotope data from carbonates (dolomites and calcites) have been used in order to study these associations. The MVT mineralization consists of sphalerite with hydrocarbon fluid inclusions, galena, pyrite and marcasite. It is hosted by Middle Jurassic dolostones, which are found below Upper Cretaceous age rocks. The hydrothermal dolomitizing event was essential for the ore genesis as it increased the rock porosity up to ~25%. Host limestones have δ<sup>18</sup>O values between +27.55 and +27.83‰ (SMOW) and δ<sup>13</sup>C from +2.32 to +3.16‰ (PDB). Pervasive dolomitization resulting from interaction with hydrothermal fluids have δ<sup>18</sup>O values between +25.07 and +26.89‰ and δ<sup>13</sup>C from -0.53 to +0.61‰. The limited δ<sup>18</sup>O shift may be explained by interaction of regional limestones with a <sup>18</sup>O-enriched dolomitizing fluid at low fluid/rock ratio and constant temperature. δ<sup>13</sup>C values indicate that hydrothermal fluids were enriched in <sup>12</sup>C, compatible with the presence of hydrocarbons trapped in sphalerite and porosity-filling organic matter. Although part of the ore is disseminated within dolostones (δ<sup>18</sup>O: +25.85 to +26.34‰; δ<sup>13</sup>C: -2.31 to -0.15‰), most massive brown to reddish sphalerite zoned crystals appear associated with vein-dolomite (δ<sup>18</sup>O: +25.13 to +26.93‰; δ<sup>13</sup>C: -0.75 to +0.59‰) filling fractures. The overlap of the different dolomite isotopic signature ranges suggests an isotopic resetting or the occurrence of a single dolomitizing event. The mineralization and hydrothermal dolomitization event must have occurred during Upper Jurassic to Lower Cretaceous times.