

## Fluid mixing and deep dissolution of carbonates

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The presence of cavities filled with new minerals in carbonate rocks is a common feature in oil reservoirs and lead-zinc deposits. Since groundwater equilibrates rapidly with carbonates, the presence of dissolution cavities in deep carbonate host rocks is a paradox. Two alternative geochemical processes have been proposed to dissolve carbonates at depth: hydrogen sulphide oxidation to sulphuric acid, and metal sulfide precipitation. However, textures indicate that the minerals filling the cavities grew in open spaces, sulphides are not the only minerals found in the cavities, and barren dissolution breccias exist. Therefore, dissolution of carbonates is not directly linked to sulphide precipitation.

Reactive transport simulations are needed to reconcile observations with conceptual models. Three different scenarios of mixing were simulated. They correspond to proposed models for the formation of Mississippi Valley Type ore deposits. All three include a dilute groundwater and a brine, both saturated with respect to calcite. The results show that mixing two warm solutions saturated in carbonate results in a new solution that dissolves the host rock. Mixing is in general more effective in dissolving carbonates than H<sub>2</sub>S oxidation or metal sulphide precipitation (Fig. 1). Variations in the proportion of the end-member fluids can also form a supersaturated mixture and fill the cavity with a new generation of carbonate. Therefore, mixing is consistent with the wide set of textures and mineral proportions observed as cavity infillings. Reactive transport calculations were performed with the code RETRASO, developed under a contract with ENRESA.

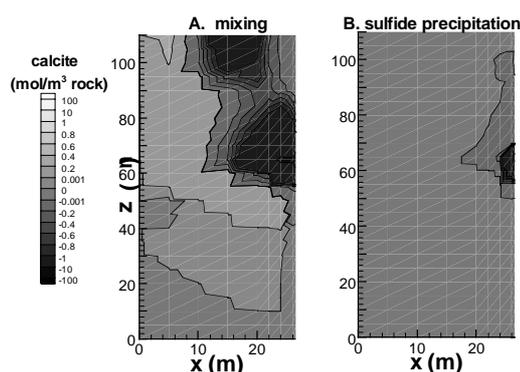


Figure 1. Contour plots of amount of calcite dissolved (dark grey) and precipitated (light grey) in mol/m<sup>3</sup> comparing the effects of mixing and sulphide precipitation after 0.150 Ma.

## Comparison of residence time indicators (<sup>3</sup>H/<sup>3</sup>He, SF<sub>6</sub>, CFC-12 and <sup>85</sup>Kr) in shallow groundwater: a case study in the Odense aquifer, Denmark

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Different residence time indicators (<sup>3</sup>H/<sup>3</sup>He, <sup>85</sup>Kr, SF<sub>6</sub> and CFC-12) were used to characterise the shallow groundwater of a semiconfined sand aquifer. The investigated site is located on the Island of Funen in the city of Odense, Denmark. Geologically the site is located in a complex setting of Quaternary glaciofluvial sand aquifers with confining clay tills. The investigated wells have 5-14 m screened intervals in sands below the confining clay layer at depths ranging from 18 to 56 m.b.s.. Sand "windows" at the surface with high recharge rates occur locally. The aquifer has pronounced anaerobic conditions, (O<sub>2</sub>: < 0.1 mg L<sup>-1</sup>; Eh: < -33 mV).

The groundwater dating aims to study the aquifer susceptibility to contamination, and the dynamics of the shallow aquifer system. As a first approximation the tracers measurements were interpreted assuming piston flow. The resulting ages range between 17 and 32 years and agree reasonably well. However, discrepancies between these apparent tracer ages indicate that additional processes have to be taken into account. Degradation under reducing conditions leads to CFC ages that are too old compared to the other tracers. Hydrodynamic dispersion seems to be of minor importance in the area under investigation. A comparison of <sup>3</sup>H/<sup>3</sup>He ages with estimates from <sup>85</sup>Kr and SF<sub>6</sub> indicates diffusive loss of <sup>3</sup>He and/or an admixture of older (tracer free) water components in the deepest parts of the aquifer.