

## A case-study of $^3\text{He}$ - $^3\text{H}$ dated groundwaters to reconstruct atmospheric $^{36}\text{Cl}$ inputs

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$^3\text{H}$ - $^3\text{He}$  systems of groundwaters allows precise dating of modern recharges and determination of mixing % with older groundwaters. In this study, we show the benefit of this method to reconstruct the  $^{36}\text{Cl}$  inputs from rainfall for a mid latitude setting (Venice, Italy). The sampled groundwaters have been dated using  $^3\text{H}$ - $^3\text{He}$  and  $^{14}\text{C}$  (Mayer *et al.* this volume). Comparison between tritogenic  $^3\text{He}$  and  $^3\text{H}$  record of Vienna (IAEA) enabled us to determine mixing % between modern ( $^3\text{He}$ - $^3\text{H}$ - dated) and old ( $^{14}\text{C}$ - dated) component in mixed recent groundwaters. The large span of residence times allowed building a coherent attenuation signal of  $^{36}\text{Cl}$  on the whole last 50 years, since nuclear tests in the 1950<sup>s</sup>, when a large amount of  $^{36}\text{Cl}$  was introduced in the atmosphere, inducing a thousand fold increase of the input signal. The built attenuation curve shows a maximum peak value of 7, 960 at.  $\text{m}^{-2} \cdot \text{s}^{-1}$  and a current deposition between 123 and 251 at.  $\text{m}^{-2} \cdot \text{s}^{-1}$  with maximum attenuation between bomb pulse and 1980 and slower lowering between 1980 and current deposition rate. Moreover,  $^{36}\text{Cl}$  in old groundwaters, corrected for decay and addition of secular neutrogenic  $^{36}\text{Cl}$ , allowed to estimate natural deposition up to 12, 000 BP, with a local mean value of 53 at.  $\text{m}^{-2} \cdot \text{s}^{-1}$ . Gap between current and calculated natural deposition rate was investigated. A possible way of overproduction by stratospheric activation of CFCs by neutron is proposed. Finally, our samples and a wide range of literature data were compared to investigate the impact of the latitude on the attenuation of the bomb pulse.

## Dynamics of mineral precipitation in mixing zones in porous media

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Stimulating *in situ* precipitation of minerals to immobilize metal contaminants is a promising approach for subsurface remediation. However, predicting and controlling the spatial/temporal distribution of reactant mixing and precipitates remains a challenge. Fluid flow, dispersive/diffusive transport of reactants, biogeochemical reactions and changes in porosity-permeability are tightly coupled, in a non-linear fashion, and at multiple scales.

Chemical gradients within the mixing zones will determine local reaction rates, products, and possibly changes in hydrodynamic characteristics of the porous media. Transients in mineral precipitate distributions that arise from these gradients in multi-component mixing zones can influence: 1) the longer term outcomes of reactions in the affected region, and 2) the ability of models that employ volume averaging at some scales to predict changes in local properties of the system, such as extent and rates of reactions.

We have conducted physical experiments, along with model simulations, to investigate the dynamics of mineral precipitation in two types of mixing geometries in porous media. One is double diffusion where reactants, calcium and either carbonate or phosphate, mix in gel or granular media through diffusive transport. Precipitation band formation occurs as expected, but with evolving local structures that affect permeability and chemical conditions on either side of the precipitation zone. The process coupling also affects the precipitation products. In the second type of mixing geometry, carbonate ion is formed *in situ* by enzymatic hydrolysis of urea in a porous media column where calcium is introduced along with the urea. A precipitation zone forms downstream of the head of the immobilized enzyme zone, which causes reduction in permeability and flow, changes in the chemical composition along the column, and eventually compression of the reaction and precipitation zone. Both examples illustrate challenges in controlling precipitation events as well as in predicting mixing and precipitation using volume averaging modeling approaches. Modeling results for the experiments from a fully coupled, fully implicit reactive transport simulator will also be presented.