Helium isotope signatures in rocks, minerals, and related groundwater: Residence time of He in a sandstone – shale interlayering (Molasse Basin, N. Switzerland)

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In a rock-water system, an apparent residence time for He can be derived from the ratio of the He concentration in pore water to the He production in minerals given that 1) the rock-water system is at steady state and 2) the He flux from external sources is negligible. This second condition is crucial and needs to be assessed by the identification of the He sources in a given hydrologic environment.

In the Permo-Carboniferous shale – sandstone inter-layering (PC-NCH; Molasse Basin, northern Switzernland) we investigated He and Ar isotopes and the parent element concetrations of whole rock samples and mineral separates. Shale and sandstone layers are similarly abundant in this ca. 800m thick low-permeability sequence.

In the shales, the parent elements U, Th, and Li are mainly concentrated in biotite, muscovite, clay minerals, and organic matter with ~95% of the produced He being lost from these phases. Hence, the ^{4}He/^{3}He ratio in the pore water can be assumed to be similiar to that of the *in situ* production ($1.3x10^7$), provided that there is no external influx of He. Groundwater in the bounding aquifers has almost equal ^{4}He/^{3}He ratios (Pearson *et al*., 1991) so that such an external source can be excluded. This is also supported by the ^{40}Ar/^{36}Ar ratios.

Quartz, plagioclase and microcline have ratios of ~1 of measured ^{4}He to mineral-produced ^{4}He, and ^{4}He/^{3}He ratios are identical with those of the bulk rock ($1.3x10^7$). The low Li-content of these minerals cannot account for such ratios and they must have trapped their He from the pore water. This is supported by the higher ^{3}He (~30x) and ^{4}He (~4x) contents obtained for quartz and plagioclase of the sandstones compared to their production capacity. This further suggests that these minerals trapped He that was generated in the shales and migrated via the pore water into the sandstones.

Measurements of the migration of He-atoms through quartz crystals showed that equilibrium between internal (gas-fluid vesicles) and external He-concentrations is achieved during ~10 Kyr under PC-NCH temperature (70°C). By applying this new approach to constrain He isotope concentrations in pore waters across the entire PC-NCH cross section, similarly high concentrations were obtained, suggesting long He residence times in the order of tenth of millions years in the PC-NCH.

Distribution of mercury in soil near Idrija mercury mine, Slovenia

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The distribution of mercury in soil near Idrija mercury mine was investigated. Soil samples were collected from 4 locations along the Idrija River. Location 1 is upper reaches of the mine and 2 is the nearest point of the mine. Locations 3 and 4 are 5 and 10 km lower reaches of the mine, respectively. At each location, soil samples were taken by core sampler at interval of ca. 30 m from the riverside toward a hill perpendicular to the river. The individual core samples were separated with layer and used for determination.

T-Hg in soil was determined by CVAAS after wet digestion at 230°C using H_2SO_4-HNO_3-$HClO_4$ mixture. For MeHg determination, soil samples were treated with KOH-ethanol solution and MeHg eluted in the liquid was extracted with toluene as dithizonates and determined by GC-ECD. Chemical composition of soil samples was determined by WD-XRF.

T-Hg in surface soil ranged 0.8 to 480 mg kg^{-1} (dry basis) and the highest value was observed in location 2. The surface T-Hg concentration tended to decrease with distance from the river toward hill, which suggests the main source of Hg in study area is the transported Hg with river from the mine. The vertical variation of T-Hg in location 4 suggests a recent dispersion of Hg, in which the surface soils at 1st and 2nd points from the river showed the lowest concentration of Hg, while at 3rd and 4th points the highest concentration was observed at the soil surface and the value decreased with depth. MeHg concentration ranged 0.8 to 16 $\mu g\ kg^{-1}$ (dry basis) and the lowest value was observed at location 2. The MeHg % of T-Hg in surface soil increased with the distance from the riverside toward hill. From the observations, it was suggested that the dispersed mercury from river is subject to methylation in the forest area. The dispersion of Hg was also discussed with the results of XRF determination.