

U-series studies on the Opalinus Clay, northern Switzerland.

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The Opalinus Clay (OPA) in northern Switzerland is considered as potential host rock for a deep geological repository for radioactive waste (spent fuel and high level vitrified waste). We studied the systematics of ^{238}U , ^{234}U and ^{230}Th in rock samples of the OPA from two locations: Benken exploratory bore hole (Zürcher Weinland) and Mont Terri Rock Laboratory (canton of Jura). These long-lived radionuclides provide information regarding their long-term, in-situ behaviour in the OPA which may be used as a proxy for some transuranium species.

At Benken the OPA along with underlying clay-rich formations forms a thick and undisturbed sequence of very low permeability with stagnant, reducing pore water. If U is heterogeneously distributed then steady-state bulk ($^{234}\text{U}/^{238}\text{U}$) disequilibrium is expected, provided that the diffusion rate of ^{234}U is significant compared to its decay constant. In theory this would enable an estimate about mobility of ^{234}U . Sampling was carried out on a cm-scale to study mobility over short distances and elucidate possible small-scale lithological control and on homogenized, 25 cm long portions of a 2 meter long drill-core section to provide information on transport over a longer distance (m-scale samples).

At Mont Terri, the Mesozoic sedimentary sequence, which contains the OPA, forms an overthrust anticline. Erosional incision that commenced around 2.5 Ma ago has caused infiltration of young, meteoric waters into the Lower Dogger Limestone (LDL) that overlies the OPA (Bossart and Wermeille 2003). As a result, reducing and stagnant pore water of the OPA has been exposed to the oxidizing aquifer at the OPA/LDL interface. This hydrogeological setting provides a unique opportunity to study the behaviour of long-lived U-series radionuclides and gives insight into processes that govern their transport in the OPA. We investigated rock samples from 5 boreholes drilled along a profile from the LDL aquifer away in the OPA. Two sampling approaches were used. Samples were taken on a m-scale and on a cm-scale to provide information on possible interactions between the oxidizing LDL and the reducing OPA and to investigate the behaviour on a small-scale, respectively.

The rock samples underwent first leaching by aqua regia followed by total HF digestion. ^{238}U , ^{234}U and ^{230}Th concentrations and ratios were determined using MC-ICP-MS. In all studied samples U was enriched in the HF digestion fraction which has a high U/Th ratio. A study by SEM-EDS points to tiny zircon grains (sub-micron up to several microns in size) as the main U-rich phase. This fraction consistently has ($^{234}\text{U}/^{238}\text{U}$) < 1. The aqua regia leach fraction was enriched in Th, and complementary to the HF fraction, having ($^{234}\text{U}/^{238}\text{U}$) > 1. Within error limits, the bulk ($^{230}\text{Th}/^{234}\text{U}$) are consistently in equilibrium. Most of the cm-scale samples show a striking negative correlation between total U content and bulk ($^{234}\text{U}/^{238}\text{U}$). Variations on the cm-scale between clay and carbonate-sandy layers are shown by β -scanning to correspond to variations in U and/or Th content, with the (dominant) clay being much richer.

Data obtained from the cm-scale samples of the OPA from Mont Terri give concentration patterns and activity ratios similar to those from Benken. A clear negative correlation between the bulk U content and bulk $(^{234}\text{U}/^{238}\text{U})$ is observed for most samples. In contrast, the m-scale samples (25 cm average) from Benken all have very uniform bulk $(^{234}\text{U}/^{238}\text{U})$ of one.

The m-scale samples from Mont Terri reveal a distinct trend in the bulk $(^{234}\text{U}/^{238}\text{U})$ and decrease from 1.035 (± 0.003 2SE) at the OPA/LDL interface to equilibrium ($(^{234}\text{U}/^{238}\text{U}) = 1$) inwards the OPA.

We explain the bulk $(^{234}\text{U}/^{238}\text{U})$ disequilibria in the cm-scale samples by a very slow diffusive redistribution of ^{234}U . This process is driven by in-situ production from the rock matrix. The negative correlation between bulk $(^{234}\text{U}/^{238}\text{U})$ and total U content suggests that ^{234}U migrates from regions of higher supply of ^{234}U towards those of lower supply which is, in most cases, equivalent to transfer from clayey towards carbonate-sandy portions of the rock. Due to the quasi-steady-rate of this production the diffusion of ^{234}U is likely to operate at a near-steady-state. This behaviour is in accordance with the suggestion proposed by various authors that the mobility of ^{234}U is enhanced due to its oxidation to U^{VI} as a result of α -recoil (Rosholt et al. 1963). The major factor determining ^{234}U in-situ supply rates are the small-scale lithological variations which regulate its diffusive flux and control the observed bulk rock $(^{234}\text{U}/^{238}\text{U})$. The mobility of ^{234}U in the OPA is limited to the cm-scale as inferred from the m-scale (25 cm average) core samples from Benken having an equilibrium bulk $(^{234}\text{U}/^{238}\text{U})$. These results indicate that the mobility of U in the OPA has been limited to less than 25 cm in the last ca. 1 Ma. The progressive decrease in bulk $(^{234}\text{U}/^{238}\text{U})$ in the m-scale samples of the OPA from Mont Terri is interpreted in terms of slow diffusive redistribution of U between the LDL and the OPA. We explain the observed trend by in-diffusion of U with $(^{234}\text{U}/^{238}\text{U}) > 1$ from the LDL into the OPA. This is accompanied by U scavenging by Fe-oxyhydroxides or precipitation at a moving front of U reduction potential. Bulk $(^{230}\text{Th}/^{234}\text{U})$ equilibrium suggest that this process has almost reached steady-state. The bulk $(^{234}\text{U}/^{238}\text{U})$ indicate an upper limit for the penetration of U into the OPA of ca. 5-6 m.

Our study indicates that in undisturbed portions of the OPA only a very limited redistribution of U-series radionuclides has occurred in the last ca. 1 Ma. This is emphasized by the homogenized 25 cm long sections of the Benken bore core all having $(^{234}\text{U}/^{238}\text{U})$ in equilibrium. Nevertheless, the observed mobility of ^{234}U is surprising considering the reducing potential of the OPA pore water. This fact is explained by oxidation of $^{238}\text{U}^{\text{IV}}$ to $^{234}\text{U}^{\text{VI}}$ as a consequence of α -decay.

M-scale samples of the OPA from Mont Terri prove that upon intrusion of oxidizing conditions into the OPA a larger scale mobility of U is expected. Even then however, the mobility of U isotopes in the OPA is inhibited by their (co-)precipitation.

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