Cryptokarsts (Belgium)

***Description*:** The cryptokarsts in Southern Belgium (Figure 1) occur in folded Lower Carboniferous limestones. Their sedimentary infill comprises Eocene/Oligocene marine clays/sands, followed by a wide range of Neogene continental deposits, from fluviatile, palustrine and lacustrine environments (Ertus, 1990; Nicaise, 1998 in De Putter et al., 2002).

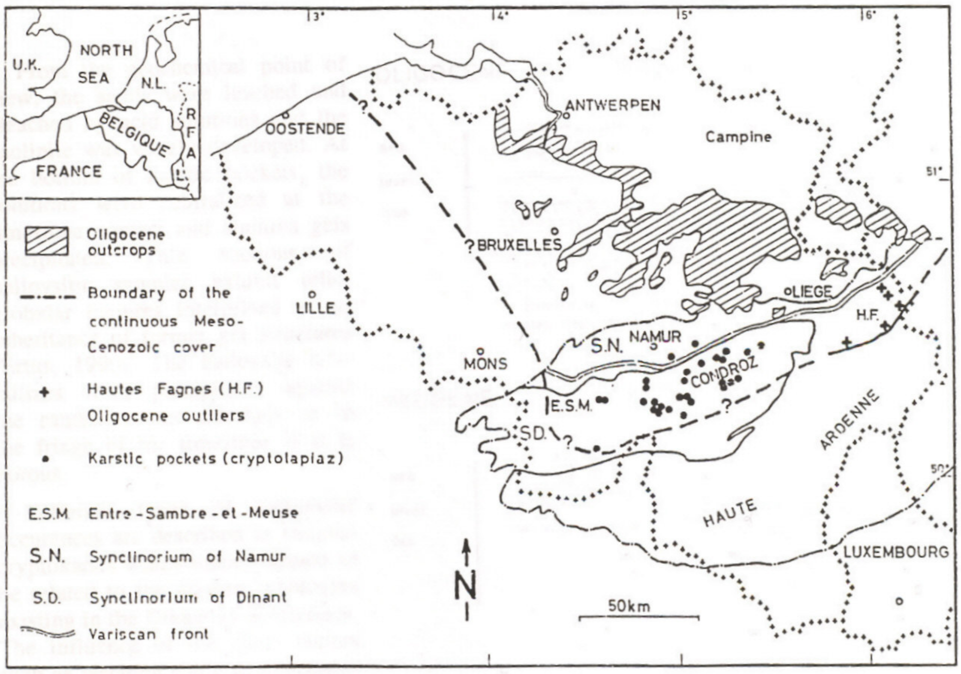

Figure 1: Sketch map of the Entre-Sambre-et-Meuse and Condroz areas in Belgium. Location of some important karstic pockets (Dupuis, 1992).

With the regression and fall of sea level after the deposition of the permeable sandy marine sediments of Upper Eocene or Oligocene age, the dissolution of the carbonate substratum began, leading to local karstic subsidence. Due to this, lakes and/or ponds were formed on the paleosurface and organic-bearing Neogene sediments were progressively deposited. At the same time, the sands were leached and blanched by acid solutions (pH 2-4) generated by the oxidation of organic matter and/or from the weathering of pyritic brown coal. At the limestone contact in the base of the karstic hollows, the acid solutions were neutralized and (silica) gels precipitated. Halloysite (hydrous kaolinite) crystallized from these gels at the sand/limestone interface and in the fringe of the porous limestone (see Figure 2 for a summary of the evolution of the cryptokarsts).

Mineralization of halloysite occurred at the carbonate wall, resulting in the sequential fixation of trace elements (Pb, Th, REE, U), controlled by their solubility.

By investigating the different wall-sediments composed of halloysite, karstfilling sediments, internal silicified limestone, kaolinite-rich halloysite and external silicified limestone (Figure 3), the following observations were possible:

- The halloysite samples are depleted in most incompatible elements, except for Pb. Depletion is weak to moderate for Ba, U, middle REE and heavy REE, but stronger for Th, light REE, Zr and Hf.

- The internal silicified limestones have variable, although generally low, trace element contents. Depletion is weak for Ce and Pb, moderate for Ba, U, middle REE and heavy REE and stronger for light REE, Zr and Hf.

- The kaolinite-rich halloysite and external silicified limestone show heavy depletion in Zr and Hf and are strongly depleted in Ba, Th, Nb and enriched in REE.

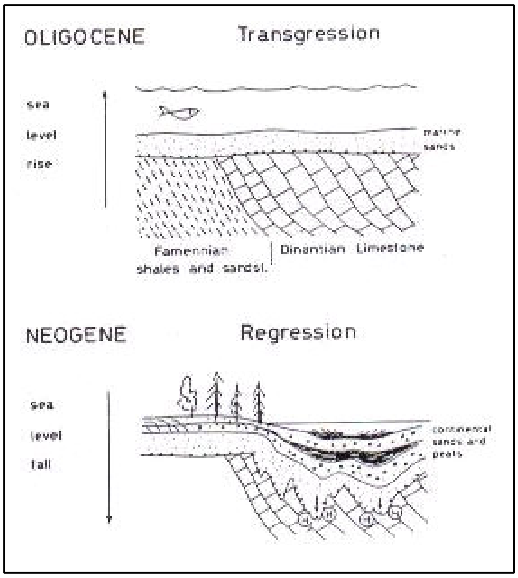

Figure 2: Sketch summarizing the evolution of the cryptokarsts of the Entre-Sambre-et-Meuse and Condroz areas in two main steps (Dupuis, 1992).

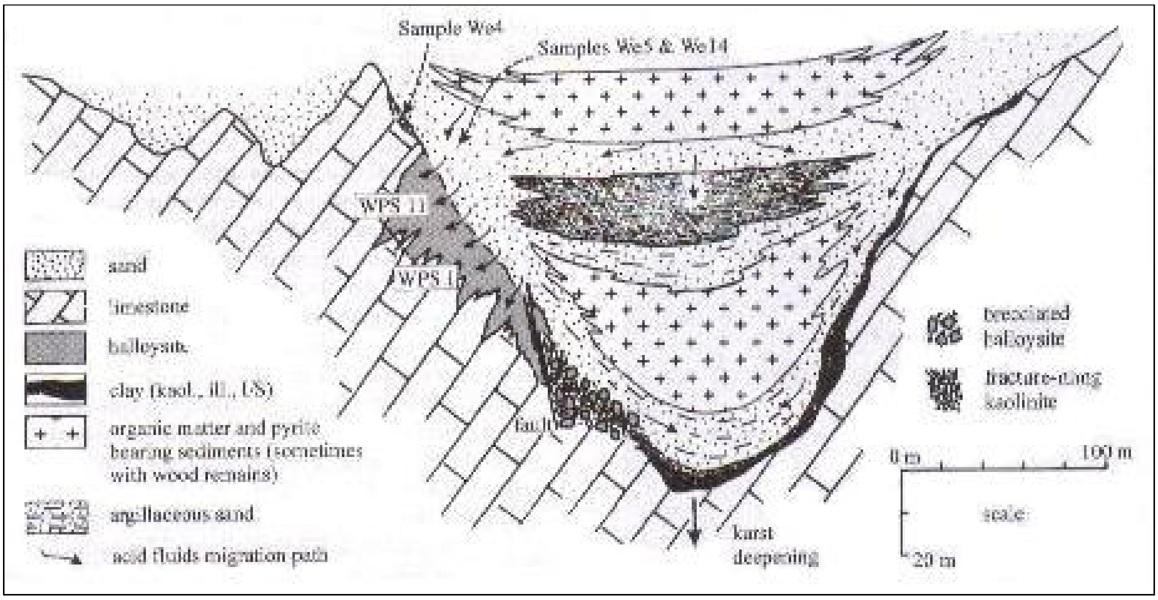

Figure 3: Composite section of the Weilen (S; Belgium) halloysitic Neogene cryptokarst, with acid fluids migration path (drawing modified from Nicaise, 1998 in De Putter, 2002).

Other important remarks are:

- Concerning U and Th: On the one hand, the Th-solubility is low in the assumed pH range (pH: 2-4) and mostly controlled by complex formation. Apart from the organic complexes, for which there is no relevant data, it is known that complexes such as $ThH_2PO_4^{3+}$, ThF_2^{2+} and $Th(SO_4)_2$ can form in the relevant pH-range. On the other hand, in the pH range between 2 and 4, and in oxidizing conditions, mobile UO_2^{2+} was most probably the dominant U species, while uranyl complexes such as UO_2F^+ and UO_2SO_4 possibly increased the U mobility in fluids. Carbonate complexes are dominant at higher pH (from pH>4 onward) (Langmuir, 1978 in De Putter, 2002). Moreover at the end of the cryptonisation sequence, relatively small U-rich automorphic (Ce, Nd) monazite crystals formed on the kaolinite flakes and an obvious trend of Th/U ratio decrease is observed with increasing depth.

- Concerning Pb: This element migrates downward and is trapped in (Ce, Pb, Co) sulfo-aluminosilicates and (Mn, Pb, Ce) amorphous oxihydroxides in both the karstfilling and the internal silicified limestone. In the layered (Mn, Pb, Ce) rich aggregates, Pb is associated with the Mn-rich laminae, rather than with the Ce-rich ones (other associations of these elements due to coupled Mn and Co, Ce, Pb oxidation reactions were described by Michard & Renard, 1975 in De Putter, 2002).

- REE were mobilized in the karsts' sedimentary infill due to the dissolution of their mineral carriers (detrital clays among others). They most probably migrated downward as both inorganic and organic complexes. The relative importance of REE-species in groundwater is strongly dependent on both the pH and the REE atomic number.

Relevance: All these results suggest that the sandy sediments in contact with the karstic carbonate wall, and the carbonate wall itself, have acted as a kind of geochemical 'barrier'. This case shows that even in natural, i.e. intrinsically uncontrolled and unmonitored, systems, radionuclide (U, Th, REE, Pb) migration paths are often limited in space. Various processes combine to trap these elements, all of which are present in radioactive waste (De Putter et al., 2002).

Position(s) in the matrix tables: Mudrocks, RN retardation at low temperature, chemical.

Limitations**:** The ratios of Th/U here are close to normal crustal values (Th/U = 3-4); while the ratio in a radioactive waste disposal would be significantly higher; there is thus no contribution to knowledge about the effect of appreciably higher ratios.

Quantitative information**:** No PA relevant parameter data are available.

Uncertainties**:** Uncertainties relate to the initial boundary conditions of the analogue systems.

Time-scale**:** The endokarstic features are dated as early Cretaceous. The trigger mechanisms for the karst formation developed during Aptian and Albian times before the Cenomanian and Turonian trangressions. The cryptokarstification itself happened during the Thanetian.

PA/ safety case applications: No known applications.

Communication applications: No known applications.

References**:**

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Added value comments: None suggested.

***Potential follow-up work*:** None recommended.

Keywords: halloysite, carbonates, mineralization, Neogene,

Reviewers and dates: Laurent Wouters & Astrid Verheyen (April, 2004)