

Trace element and *REE* anomalies in Quaternary organic-rich deltaic deposits

D. J. Huisman
B. J. H. van Os

NITG-TNO, Geological Survey of the Netherlands, P.O. Box 157,
2000 AD Haarlem, The Netherlands

The low-gradient deltas of large river systems form extensive interfaces between fresh and saline water systems. Re- and transgressions over such delta plains cause alternating marine and continental diagenetic environments over large areas. Moreover, changes in ground water regime through fluctuations in sea level or river dynamics may result in variations in the redox-state of sediments, and thus cause additional diagenetic processes.

In order to investigate the effects of these diagenetic processes we studied heavy metal, As, V, U, Y and *REE* enrichments in organic-rich layers from the Plio-Pleistocene Rijn-Maas-Schelde delta in the Southern Netherlands, and the associated mineral phases. The organic deposits studied include peat from laterally extensive coastal marshes, and peat, gyttja and organic-rich clays from local basins, river fens and palaeosols from Late Pliocene and Early Pleistocene fluvial deposits. Despite the fluvial origin, the S-contents of these deposits are locally high (up to 12%). Sulphide-related As-contents may reach levels up to 900 ppm.

The anomalies

S and As are more abundant in all organic layers than in sand and clay layers. In most of the organic-rich

layers (36 out of 45), enrichments occur of various combinations of the elements Co, Cr, Cu, Mo, Ni, Pb, V, U, Y, Zn and the *REE* (see Fig. 1). The chondrite-normalized *REE*-patterns from these enrichments are similar to the patterns of clay, but show an additional positive Ce-anomaly. Some of the peat and browncoal layers show depletions of Ba and, less frequently, Cr and V.

Observed diagenetic mineral phases

The presence of pyrite was determined in all samples studied microscopically and by electron-microprobe. Additionally, $(\text{Fe,Ni,Co})\text{S}_2$ ('Bravoite') and PbS (Galena) were found. Large pyrite nodules (up to several cm) from some of the organic-rich layers show large variations in trace element contents, and many showed extremely high contents of As (max. 3700 ppm), Co (max. 2400 ppm), Ni (max. 2700 ppm), Pb (max. 660 ppm) and Mo (max. 90 ppm). These high concentrations were probably caused by pre-concentration of these elements in Fe,Mn-oxides in a terrestrial environment. In a later phase, the elements were released into groundwater when the Fe,Mn-oxides were reduced, and subsequently they were immobilized and possibly further enriched in pyrite or as separate sulphides. Differences in pyrite

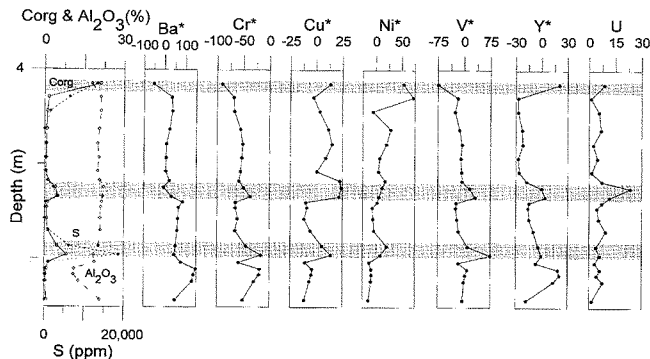


FIG. 1. Example of metal enrichments related to organic rich layers (shaded) in Pliocene clay. Elements with asterisks: difference between actual concentration and (Al-based) detrital background.

morphology and composition within single samples indicate that there have been several stages of sulphide formation.

We could not identify the mineral phases related to the enrichments of Y, REE, Cr, V and U. However, it is most likely that Y and REE are present as phosphates. The positive Ce-anomaly indicates that these elements were pre-concentrated in Fe, Mn-oxides in an oxidizing environment. Subsequent reduction of these oxides and the onset of sulphidization caused the immobilization of Y and REE as phosphates that were released by the degradation of organic matter during sulphate reduction.

Origin of the anomalies

From the above it can be concluded that anomalies of As, Co, Cu, Ni, Pb, Zn and Mo as found in the organic-rich layers of the Plió-Pleistocene Rijn-Maas-Schelde delta are related to pyrite and specific sulphides that are formed in several stages (Fig. 2). Part of the sulphidization takes place before burial during marine transgressions over continental organic deposits, with sulphate derived from sea water and Fe from local, continental sources. Because of the low gradient of the delta and the relative proximity of equivalent marine deposits such transgressions can be as short-termed as spring tides or storm floods. After burial, pyrite formation in organic layers continues whenever marine transgressions causes saline groundwater intrusions, and associated downward percolation of SO_4^{2-} -rich water. Moreover, fluctuations in groundwater level as a result of episodic or cyclic changes in sea level or river regime can cause changes from reduced to oxic environment. During oxic periods the oxidation of pyrite may have several consequences. Firstly, Fe-oxides are formed which incorporate part of the trace elements from the (oxidized) pyrite, and may concentrate and take up additional trace elements, including Y and REE, from groundwater. Secondly, the decrease in pH associated with sulphide oxidation promotes weathering of primary minerals. As a result of these weathering processes major and trace elements, including Ba, Cr and V are released. Thirdly, the elevated SO_4^{2-} -levels may cause precipitation of gypsum and baryte.

Pyrite oxidation in overlying deposits could induce secondary pyrite formation in deeper reducing organic layers. Reducing conditions could persevere during a regression phase in the peat or organic layers whereas other parts of the sediment body become

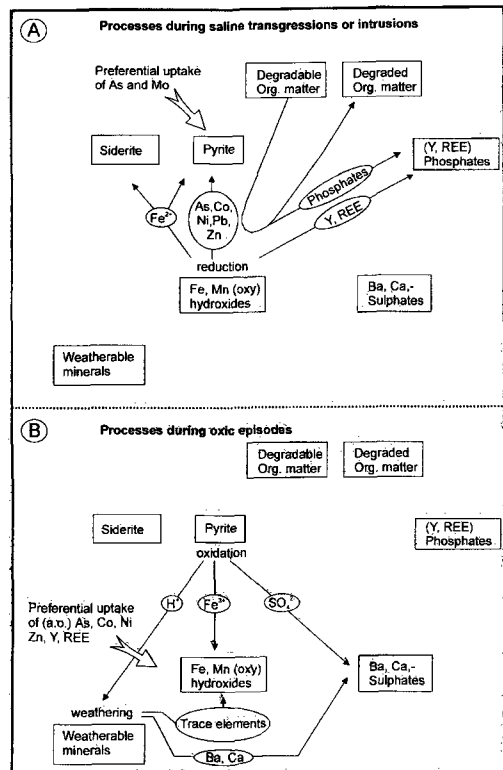


Fig. 2. Diagenetic processes causing trace-element enrichments in organic-rich subsurface layers. A: During saline transgressions and intrusions. B: during oxic periods.

oxidized. As U, Cr and V are mobile under oxidized conditions and immobile under reduced, the presence of Cr, V and U-enrichments in these layers indicates that at least one episode occurred, in which this organic layer remained reduced while the surrounding sediment was oxic or suboxic.

Because of the cyclic occurrence of transgressions and regressions during the Quaternary, the repeated redistribution of trace elements has led to the extreme enrichments found in the Rijn-Maas-Schelde delta deposits. The suites of trace elements enriched in organic layers by the processes described above is very typical, as it consists of elements that are mobile under oxic conditions and immobilize during reduction, as well as elements that are mobile under reduced conditions and immobilize during oxidation. This type of element enrichments in organic-rich sedimentary sections may be diagnostic for all large-scale deltaic environments.