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Characterization of CO2-induced (?) bleaching phenomena in German red bed sediments by combined geochemical and evolved gas analysis

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We investigated varied coloured Buntsandstein and Rotliegend sandstones in Central Germany (Thuringian Vorderrhön, Altmark) by thermogravimetric/pyrolytic (DEGAS– directly coupled evolved gas analysis) and geochemical (ICP-MS/OES) means to evaluate geochemical/mineralogical characteristics of red bed rocks and their presumably altered, bleached modifications. Commonly bleaching of primary red bed sediments is regarded as a result of fluid-rock reactions by the participation of CO_2.

This study is performed in the framework of the special research program "GEOTECHNOLOGIEN" (funded by the German Ministry of Education and Research – BMBF) and is part of two BMBF sponsored projects – "COMICOR", an analogue study on potential effects of CO_2-bearing fluids on Buntsandstein and Rotliegend deposits in Hesse and Thuringia and "CLEAN", an enhanced gas recovery (EGR) pilot project in cooperation with GDF SUEZ E&P Deutschland GmbH. The intention of CLEAN is to evaluate the feasibility of EGR techniques and the suitability of depleted natural gas reservoirs for potential industrial CO_2 sequestration projects.

According to rock colour variations two slices of handspecimens (M49, A1) were split into 12 and 15 equally sized samples for analytical work.

The medium grained Lower Buntsandstein sample M49 from Thuringia is of fluvial origin and partially bleached with transitions from red (unbleached) to light colours (bleached). Bulk rock geochemistry of red bed and bleached subsamples of M49 are almost similar, including rare earth element (REE) content. Only the content of iron and related metals is depleted in bleached samples compared to the red bed types. All PAAS normalized pattern of M49 show positive Eu and slightly negative Ce anomalies, most likely caused by the presence of apatite and illite in the rocks.

The degassing behavior observed by DEGAS of M49 subsamples is mainly controlled by the breakdown of sheet silicates, hydroxides and hydrates, as well as of carbonates and sulphates. DEGAS pattern show no obvious systematic differences between the varied coloured zones of this specimen.

Sample A1 consists of totally bleached medium grained, lithoclast rich Rotliegend sandstone which was deposited on a flood plain with braided rivers and aeolian dunes. Subsamples of A1 are grouped into three zones - all are bleached, with colours ranging from white to dark grey.

Grey and dark grey zones (A1-1 to A1-6, A1-15) are cemented by Ca-rich carbonates and contain microscopically identified bitumina. In contrast the pore space of white zones (A1-7 to A1-14) is filled by anhydrite. These mineralogical differences are also reflected in the bulk rock geochemistry. In comparison to grey rocks white subsamples are depleted in iron and related elements as well as in REEs.

Moreover, correlations between rock colour and degassing behavior exist. White samples display typical degassing signatures of sulphates, whereas dark grey zones reveal minor sulphate content, but also the presence of an additional S-species (sulphide) and CO_2 (carbonate). Similar features were obtained regarding the specification and abundance of hydrocarbon components. In all samples of A1 methane, ethane and carbonylsulphide were detected, with higher contents in the more whitish parts. In grey rocks an additional, long-chained hydrocarbon component occurs. The relevance of this species is not yet resolved and will be investigated further in more detail.

Mass spectrometric gas analytical and related geochemical data confirm major differences in rock composition of Buntsandstein and Rotliegend samples, mainly caused by primary rock composition and by the involvement of

variable fluid composition during burial diagenetic alteration.

In this study DEGAS was applied for the first time to characterize sandstone geochemistry. Our results constrain that this method might be a complementary analytical tool appropriate for petrological sedimentary research.