The Coupling Of The Oxidation Of Reduced Sulfur Compounds With The Reduction Of FE(III)-Minerals

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The oxidation of reduced sulfur compounds in the presence of Fe(III)-minerals in the sediment of acid mining lakes is seemingly a important effect for the neutralization of these habitates.

Our youngest studies show now high turnoverrates from schwertmannite to goethite and resulting from this a release of sulfate in a depth between 3-9cm in the lakesediment.

In this reason we investigated the turnover rates from sulfid with iron(III)-(hydr)oxides in laboratory experimentes, to quantify these processes.

Therefore we constructed a fluidized-bed reactor which allows us to determine well defined concentrations of the sulfide input into the reactorvolume at various acidic pH-levels, where the Fe(III)-(hydr)oxides get reduced. With online-detection of H_2S and pH at the outflow we can calculate the turnoverrates of different Fe(III)-(hydr)oxides in the presence of sulfide.

Analysing the samples at the outflow with ionchromatography we want to detect some intermediates of the sulfurcircle (thiosulfate, tetrathionate).

Using new microelectrodes, we investigated the intermediates of the sulfurcycle (and their turnoverrates) with “in situ”-measurements inside the reactor.

We also use these new elektrodes to investigate the intermediates inside of undisturbed sedimentcores of an acidic lignite mining lake to investigate the in situ chemistry of such sediments.

The poster will show the reactor and some of our results and allows some statements about the chemistry inside them.

References

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Chemical and isotopic variations in hydrocarbons from a metamorphic black shale sequence (100-500°C)

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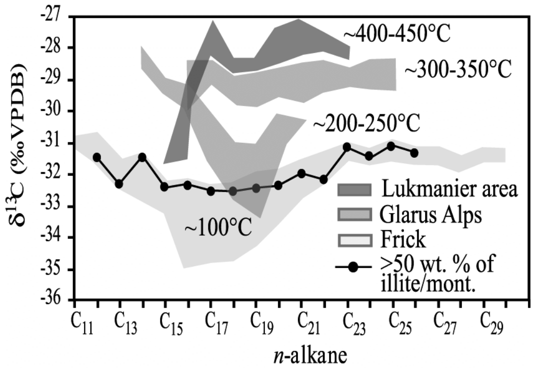
We present the first molecular and isotopic results of hydrocarbons (HC) from a prograde metamorphic Liassic black shale sequence in the Swiss Alps. The studied samples range from unmetamorphosed (~100°C) to low staurolite-grade (~500°C) sediments. Between 100°C and 300°C, the HC distributions show: (1) an increase of naphthenic envelopes; (2) irregular *n*-paraffin profiles; (3) lower contents of $C_{<15}$ and $C_{>25}$ compared to mid-chain *n*-alkanes; (4) a decrease of Pr/Ph ratios; (5) substantial amounts of C_{17} to C_{28} alkylcyclohexanes; (7) an occurrence of C_{14} to C_{20} alkenes; (8) the disappearance of steranes and hopanes and (9) a predominance of bibenzyl and methyl-benzenes. Above 350°C, we note a decrease of naphthenic envelopes and a degradation of the $C_{>23}$ alkylcyclohexanes. The progressive ^{13}C-enrichment (up to 8‰) of the $C_{>17}$ n-alkanes (Fig. 1) points to a substantial sensibility of these compounds to prograde metamorphic processes. At 200-250°C, the ^{13}C-enrichment (up to 4‰) of the $C_{<17}$ *n*-alkanes indicates thermal cracking of these compounds. This is supported by thermodynamic data indicating that $C_{<17}$ *n*-alkanes can not achieve metastable equilibrium in a mineral-CO_2-H_2O-CH_4 system at ~200°C. Above 350°C, the ^{13}C-depletation (up to 4‰) of the same components points to a generation of ^{13}C-depleted higher compounds. The disappearance of $C_{>23}$ alkylcyclohexanes above 350°C suggests that long-chain alkylcyclohexanes were thermally destroyed to form $C_{<17}$ n-alkanes. The ^{13}C-depletetion is in line with a origin of alkylcyclohexanes from fatty acids preserved in the aluminosilicates structures.

Figure 1: $\delta^{13}C$ values of *n*-alkanes.



These results show the utility of a combined biomolecular and isotopic approach to evaluate the relative importance of destruction, (hydrolytic) transformation and generation of hydrocarbons in a metamorphic system.