

## Carbon and hydrogen isotope fractionation of organic pollutants in aquifers

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The enormous world wide exploitation, handling and transportation of hydrocarbons led to a widespread contamination of aquatic subsurface systems. Consequently, cost effective, nonintrusive remediation strategies such as natural attenuation have emerged as promising approaches for cleaning contaminated groundwater. Within this concept it is important to predict the fate of contaminants and, in particular, to differentiate between destructive (biodegradation) and non-destructive (sorption, dilution, dispersion, volatilization) attenuation processes. Quantifying intrinsic bioremediation actually relies on a broad basis of hydrogeological, geochemical and microbiological data. Although these attempts have been important for identifying main subsurface processes, there have also been remarkable limitations. Especially in highly heterogeneous aquifers inaccurate mass balances of contaminants, electron acceptors and end products make the assessment of degradation processes more difficult.

Recent studies on compound specific isotope analysis have demonstrated, that isotope fractionation is a powerful tool to provide insight into the fate of hydrocarbons in contaminated aquifers. Both in laboratory and field studies enrichment of the heavier isotope ( $^{13}\text{C}$ ,  $^2\text{H}$ ) in the residual non-degraded substrate was observed during biodegradation for aromatic (Meckenstock et al., 1999; Steinbach et al., 2002) as well as for chlorinated hydrocarbons (Sherwood Lollar et al., 2001). As described in the Rayleigh equation [ $\ln(^{13}\text{C}/^{12}\text{C})_t / (^{13}\text{C}/^{12}\text{C})_0 = (1/\alpha - 1) \ln f$ ] the change in isotopic composition can be correlated with the extent of biodegradation via the kinetic fractionation factor  $\alpha$ . The latter is derived from laboratory studies and in conjunction with isotopic variations in the substrate the extent of degradation can be estimated.

The presentation will focus on new applications of carbon and hydrogen isotope ratio measurements to trace the biodegradation of hydrocarbons in the subsurface. Observed isotope fractionations were used to calculate the extent of biodegradation independent of abiotic attenuation processes.

### References

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## Glass inclusions in early crystals from Burfell picrite, Iceland

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Homogenised glass inclusions in chrome-spinel and olivine from the picrite lava shield Burfell, SW Iceland, form a continuous series of compositions ranging 13.6-9.9 wt.% MgO in the spinel, and 11.2-8.4 in the olivine. Calculations indicate that the pressure range of formation was about 17 to 7 kb. The  $\text{K}_2\text{O}$ -concentration varies 0.01-0.05 wt.%, i.e. 5 times, which might suggest either continuous fractional melting of a single source, in which case MgO and  $\text{K}_2\text{O}$  should vary inversely, or the mixture of two magmas, K-rich and K-poor. Since there is no correlation between  $\text{K}_2\text{O}$  and MgO, or between measured and calculated temperatures-of-inclusion and  $\text{K}_2\text{O}$ , the latter model is indicated. This is in agreement with Gurenko & Chaussidon (1995) who postulated two melts beneath the Reykjanes peninsula, enriched and depleted. However, in view of the above, their contention that the two types of melt were derived from the continuous melting of a single mantle source cannot be right.

All the inclusions from Burfell classify as depleted, but a single inclusion out of the total of 29 is "high-CaO"-melt, similar to inclusions from a picrite in N-Iceland (Sigurdsson et al. 2000) that were attributed to a wehrlite source as opposed to lherzolite.

There is an almost-complete separation between the spinel and olivine inclusions, the former contain  $\text{MgO} > 11\%$ , the latter  $\text{MgO} < 11\%$ . Plotting  $\text{K}_2\text{O}/\text{TiO}_2$  vs.  $\text{K}_2\text{O}$ , the spinel inclusions may be interpreted as primary melts, or mixtures thereof, whereas the olivine inclusions reflect different degrees of crystallization. The spinel inclusions suggest clinopyroxene control in the spinel-lherzolite stability field, whereas the olivine inclusions reflect olivine + plagioclase control at lower pressures. Decompression-melting of spinel lherzolite is incongruent, with especially clinopyroxene dissolving and olivine precipitating. The absence of olivine inclusions from this higher-pressure stage suggests that the olivine was precipitated on the conduit walls as the melt ascended, whereas the smaller-sized chromite crystals made it to the surface. This also indicates that olivine and chrome spinel sample in their glass inclusions different parts of the melting column.

### References

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