Sulfur speciation in quenched melts by Micro-XANES – The nature of S(IV+) in glasses

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Although Sulfur occurs only as a trace element in magmatic systems its behavior is directly related to a variety of important geological processes (e.g. formation of ore deposits, global cooling by S-rich explosive volcanism). The solubility of sulfur depends strongly on its oxidation state that may vary from S^{2-} to S^{6+}, and thus shows strong dependence on the oxygen fugacity in the system. XANES measurements at the S K-edge provide unique information on the sulfur species present. The fine structure at the S K-edge is dominated by localised 1s-2p transitions, which are strongly dependent on the electronic configuration of S [1]. Spectra were recorded at the ESRF ID 21 micro-focus beamline using a combination of broad and focused beams (200 µm and 0.8 µm diameter). We determined the S speciation in glasses in a variety of naturally occurring composition synthesized at 1 GPa, 1100 to 1350 ^{o}C (dry conditions) and at 200 MPa and 1050°C (5 wt% dissolved H_2O). Of special interest was the detection of a S^{4+} species at intermediate redox conditions, i.e. the transition from S^{2-} to S^{6+}, as found by [2] in natural samples. The presence of such an intermediate species has important consequences on the thermodynamic treatment of sulfur equilibria in magmas. Synthetic samples were equilibrated at various oxygen fugacities and sulfur saturated conditions. In addition, disequilibrium samples were made, resulting in a continuous transition from S^{2+} to S^{6+} from the rim to the center of the samples. The presence of S^{4+} was observed only in a few oxidized samples. However, our experiments show that the S^{4+} is related to beam damage induced by the electron-microprobe analysis, which preceded the XANES analysis. Furthermore, time-dependent XANES measurements indicate strongly that S^{4+} is also formed during the acquisition of the XANES spectra, which is particularly the case when using the focused beam. Due to this effect the S species in the disequlibrium samples were not analysed by collecting the complete XANES. Instead, scans across the samples were performed by resonant excitation at the energy position of each species. These profiles gave no indication for the presence of S^{4+}. Finally, we have used the intensities of the respective resonances for S^{2-} and S^{6+} to determine the sulfur oxidation state in the glasses as a function of the oxygen fugacity during the synthesis.

References

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Controls on microbial activity and compositional alteration of crude oil during in reservoir biodegradation

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Biodegradation of crude oil and natural gas in petroleum reservoirs is of great economic relevance and plays an important role in the biogeochemical carbon cycle. Petroleum reservoirs are an outstanding habitat of the deep subterranean biosphere where hydrocarbons – the main constituents of crude oil and natural gas – are present in abundance to function as potential microbial carbon and energy sources. The effects of biodegradation on oil and gas composition are well-documented while only little is known about the underlying processes. It is, however, clear that geologic environments with significant accumulations of hydrocarbons, particularly petroleum reservoirs, are mostly anoxic. Limitations of microbial activity in petroleum reservoirs are poorly understood and are subject of ongoing investigations. Temperature is generally regarded as being very important with a threshold for biodegradation of approximately 80°C. Little is known about the availability of electron acceptors and nutrients.

This contribution will present new approaches to better assess and understand processes associated with hydrocarbon degradation in subsurface reservoirs by employing advanced analytical techniques (petroleum and stable isotope geochemistry). Model experiments with individual hydrocarbons as pure substrates or crude oil as a complex mixture of substrates provide insight into substrate specificities of numerous pure cultures of denitrifying and sulphate-reducing hydrocarbon-utilising bacteria. On this basis it can be shown that different patterns of hydrocarbon degradation in different oil fields most likely reflect differences in the respective microbial consortia. A new concept explaining observed patterns of compositional alteration will be suggested, which is based on the hypothesis that bioavailability of individual petroleum constituents is a crucial control of microbial activity. This is supported by the patterns of stable isotope fractionation associated with the oxdiation of light hydrocarbons which allow the conclusion that diffusive transport of hydrocarbons exerts a main control on biodegradation rates, bioavailability of substrates and thus on microbial activity in a reservoir. Our results from various petroleum systems have strong implications with respect to the validity of the conventional perception of biodegradation as a process removing different compound classes sequentially resulting in more or less similar patterns of compositional alteration in any biodegraded oil reservoir.