

## Nitrogen chemistry and speciation in geothermal waters, Iceland

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Nitrogen is an element of biogeochemical importance, and may occur in various oxidation states in geothermal fluids including gaseous and aqueous dinitrogen ( $N_2$ ), gaseous or aqueous ammonia ( $NH_3$ ), aqueous nitrate ( $NO_3^-$ ), aqueous nitrite ( $NO_2^-$ ) and organic nitrogen. Overall redox disequilibrium is generally observed for various redox species in geothermal waters, such disequilibrium serving as a potential inorganic energy source for chemosynthesis.

Considerable focus has been made on the speciation and reaction energies associated with H, O, S, Fe and C compounds whereas N-containing compounds have received less attention. The object of this study was to determine the distribution and the main reactions among the various nitrogen species in geothermal surface- and ground waters in Iceland, as well as to quantify the inorganic energy sources deriving from these chemical reactions and potentially available for microorganisms in their metabolism.

Samples of geothermal water were collected from geothermal springs and wells at various locations in Iceland and analysed for their major dissolved element composition including various redox sensitive elements like  $H_2S$ ,  $SO_4$ ,  $H_2$ ,  $O_2$ ,  $CH_4$ ,  $CO_2$  and DOC as well as aqueous nitrogen species including  $N_2$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $NH_4$ , and  $N_{total}$ . The sampled waters ranged in temperature from 2 to 125°C and pH of 2.48 to 9.72. The concentrations of various nitrogen species were in the range <0.1 – 204  $\mu\text{mol/L}$ , <0.1 – 0.66  $\mu\text{mol/L}$  and <0.1 – 8.51  $\mu\text{mol/L}$  for ammonia, nitrite and nitrate, respectively. The redox potential for various redox pairs differ by up to 1200 mV indicating redox disequilibrium, with the N-compounds also being at disequilibrium. Aqueous speciation and calculations of excess chemical energies (chemical affinity) involving nitrogen species were further carried out. These results indicate that the many nitrogen bearing reactions provide positive excess energy (chemical affinity) to its surrounding, both acting as  $e^-$  acceptors and donors as well as being linked to other redox pairs including H, O, S and C containing compounds. Examples of possible nitrogen containing compound reaction paths and their associated excess chemical energies will be demonstrated.