

## Is oxygen-17 of atmospheric nitrate a tracer of industrial pollution?

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The oxygen isotopic composition of atmospheric nitrate ( $\Delta^{17}\text{O-NO}_3$ ,  $\delta^{18}\text{O-NO}_3$ ) provides useful information about the oxidation pathways of nitrogen compounds in the atmosphere resulting in the formation of nitrate. Oxygen-17 contents (expressed as  $\Delta^{17}\text{O}=\delta^{17}\text{O}-0.52*\delta^{18}\text{O}$ ) may be anomalously enriched in atmospheric nitrate as a result of the interaction with ozone ( $\text{O}_3$ ), whereas other oxidants ( $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{NO}_3$ ) contribute insignificant amounts of  $\Delta^{17}\text{O}$ . We postulate that in addition to the ability of  $\Delta^{17}\text{O}$  as a proxy of oxidation pathways in the atmosphere,  $\Delta^{17}\text{O}$  may also constitute a potential tracer for industrially derived atmospheric nitrate in close proximity of some anthropogenic emission sources.

The Athabasca Oil Sands Region (AOSR) in northeastern Alberta, Canada, holds one of the World's largest heavy oil reserves. The processing and upgrading of oil sands has raised concerns about potential environmental impacts of industrial nitrogen (N) emissions on neighbouring aquatic and terrestrial ecosystems. Stable isotope techniques may help to assess such impact in the case where industrial emissions are isotopically distinct from background values. Atmospheric nitrate in bulk deposition and throughfall was collected using ion exchange resins over ~6 months time periods from summer 2007 to summer 2011. Nitrate deposition rates, nitrogen and the triple oxygen isotopic compositions ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$ ) of atmospheric nitrate in bulk deposition and throughfall were determined. Nitrate emitted in  $\text{PM}_{2.5}$  (particles with a diameter  $<2.5 \mu\text{m}$ ) from one of the major emission stacks was also analyzed for  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  and was not anomalously enriched in oxygen-17 ( $\Delta^{17}\text{O-NO}_3 \approx 0\text{‰}$ ), providing a potential tracer of industrially derived nitrate [1].  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of atmospheric nitrate deposition showed distinct trends towards lower values with increasing nitrate deposition rates in all sampling periods. This relationship between the oxygen isotopic composition and atmospheric nitrate deposition rates allowed for the estimation of industrial contributions to atmospheric nitrate deposition in the AOSR [2].

[1] Proemse, Mayer, Chow & Watson (2012), *Atm. Env.* 60, 555-563. [2] Proemse & Mayer (2012), in: K. Percy (Ed) *Developments in Environmental Science*, 11, 243-266.

## Gas-solutions interaction in hydrothermal ore forming processes

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The heterogenic fluid participates in the ore forming process at many hydrothermal deposits. The origin of such a fluid is usually explained by the phase separation of a homogeneous gas-saturated water-salt fluid. An alternative model of ore-forming process in which a heterogeneous fluid occurs by mixing a water-salt solution and the gas fluid is discussed in this report.

A thermodynamic modeling of the adiabatic process of interaction of water-salt fluid (1M NaCl) with gaseous  $\text{CO}_2$  at 350o C, 1 kb was carried out. According to this model the process of increasing of carbon dioxide amount in the system accompanied by the gas phase appearance at  $\text{CO}_2$  concentration of about 3m. The gas volume increases with the addition of  $\text{CO}_2$  to the system up to 8 m. Meanwhile the water proceeds into the gas phase, the salt concentrations and ionic strength of the solution increase. Synchronously gold solubility decreases by about 20%.

Thermodynamic modeling characterizes only one aspect of the process of aqueous fluid with the gas mixing, but this process is much more complex.

The process of gas passing through the liquid increases the interphase, which leads to a number of inter-fluids border effects. Such process is called "barbotage", it is easy-to-realize technically and it is used in series of technological processes.

Barbotage is broadly used in technologies for heating and mixing of aggressive liquids, as well as for solutions scavenging. Barbotage generates the gas emulsions and leads to formation of large interfacial area at liquid - gas interphase boundary. It promotes the intensifications of heat- and mass-exchange processes and deeper gas-liquid chemical interaction. Spontaneous formation of scores of small bubbles can cause a cavitation. Barbotage facilitates also the flotation process.

The signs of the barbotage participation in some natural hydrothermal ore-forming systems are demonstrated in the report. The gas-liquid interaction must be considered upon the study of hydrothermal ore deposits.

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