Fractionation of chlorine isotopes between ice and groundwater: Identification of freezing processes

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Fractionation of chlorine isotopes has been measured extensively in natural systems and in laboratory experiments [1,2], and used to determine the origin of solutes in groundwaters. In this study, the fractionation factor for chlorine isotopes between ice and groundwater was determined in laboratory experiments, and detailed information was collected on chemical and isotopic changes during freezing.

Freezing experiments were carried out in a column containing Na-SO_4 groundwater from Palmottu, Finland with a Cl concentration of 100 mg/L. The groundwater was frozen at temperatures between -2 and -3 °C. At the termination of the experiment, the ice column was cut into ten segments. Chemical and isotope (δ^2H, $\delta^{18}O$, and $\delta^{37}Cl$) analyses were performed on the thawed ice segments, the original groundwater and the final residual solution.

The difference in chlorine isotopic composition measured in the original and final waters (0.83 vs. 0.87‰) was within the analytical uncertainty of ±0.1‰. $\delta^{37}Cl$ could not be determined in the top two ice segments formed during the early stages of freezing due to insufficient chloride. Relative to the inital groundwater, the chlorine signatures measured in the next six ice segments showed an enrichment in ^{37}Cl, and $\delta^{37}Cl$ was observed to decrease with progressive freezing. No fractionation was measured between the last two ice segments and water. The average $\delta^{37}Cl$ value of 1.4‰ from the top four ice segments was used to calculate a fractionation factor of 1.0005.

With progressive freezing, a gradual depletion in the oxygen isotopic composition was observed, similar to the trend seen in $\delta^{37}Cl$. This positive correlation between $\delta^{37}Cl$ and $\delta^{18}O$ in ice may aid in the recognition of groundwater compositions which have been influenced by freezing processes (e.g. development/degradation of permafrost conditions) in the past.

References

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