Halogens (Cl, Br and I) geochemistry in carbonates: Implications for salinity and diagenetic alteration of I/(Ca+Mg) ratios

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Halogens (Cl, Br and I) are concentrated in seawater and marine sediments of the Earth's surface reservoirs. For instance, Cl and Br concentrations and Cl/Br ratios in seawater are relatively uniform. The evaporation of seawater can elevate the Cl and Br concentrations while maintaining a constant Cl/Br ratio until the precipitation of halite. As a result, the Cl/Br ratio has been used to trace the origins of surface water, grounwater and brines in terms of salinity. With respect to iodine, I predominately occurs as IO_3^- and I^- in seawater, both of which are dissovled anions. In addition, based on thermodynamic considerations, the IO_3^-/I^- system serves as the most sensitive indicator of redox processes in the ocean. The laboratory-synthesized calcite demonstrate that IO_3^- is the only I species to substitute for CO_3^{2-} in the calcite lattice. Thus, I/Ca or I/(Ca+Mg) ratio in bulk carbonates was recently proposed as proxy to reconstruct subtle redox changes in the upper ocean water column.

We perform a pilot study on the halogens (Cl, Br and I) geochemistry using a case study of Middle Triassic marine dolomitization in South China. Our results show that the average Cl concentrations in limestone, dolomitic limestone, calcitic dolomite and dolomite are 88.3 ppm, 114.7 ppm, 121.3 ppm and 142.9 ppm respectively, and the corresponding Br concentrations are 1.15 ppm, 1.42 ppm, 1.59 ppm and 2.13 ppm, respectively. Both the concentrations of Cl and Br increased with the increasing dolomitization degree. The increasing tendency of Cl and Br is similar to the seawater evaporation trajectory before halite precipitation, indicating that dolomitization occurs in fluids with elevated salinity. As for the concentration of I, the mean values sharply decreased from 0.36 ppm in limestone to 0.13 ppm in dolomitic limestone samples, and it further lowered to 0.09 ppm and 0.08 ppm in calcitic dolomite and dolomite samples, respectively. The calculated I/(Ca+Mg) ratios dramatically dropped as the start of dolomitization. Thus, even though I/(Ca+Mg) ratios in carbonate recorded the redox conditions of fluids, while caution should be taken when applying this indicator to dolomite samples.