A new high-precision method for determining stable chlorine isotopes using UV-LA-MC-ICP-MS

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Chorine is the dominant anion in many geological fluids and one of the main volatile components on Earth. It has high partition coefficients in aqueous fluid (Bureau et al. 2000) and is enriched in seawater, pore fluid and sediment, but depleted in the mantle. Chlorine has two stable isotopes: ^{35}Cl and ^{37}Cl. The isotope ratios of ^{37}Cl/^{35}Cl are usually expressed by δ-notation relative to Standard Mean Ocean Chloride (SMOC) as

$\delta^{37}Cl = [(^{37}Cl/\ ^{35}Cl)sample / (^{37}Cl/\ ^{35}Cl)SMOC\ -1] \times 1000$. (Eggenkamp 2014)

Their large relative mass difference suggests that these isotopes should fractionate during reactions between aqueous chloride solutions and solid phases in which Cl is at least partly covalently bound. Taken together, the δ^{37}Cl also may provide a good tracer of subducted materials into the mantle. Measurement of chlorine isotope ratios has been performed by the gas source isotope ratio mass spectrometry (IRMS) (Kaufmann et al., 1984), the positive and negative thermal ionization mass spectrometry (P-TIMS / N-TIMS) (Xiao and Zhang 1992; Desaulniers et al., 1986) and the inductively coupled plasma mass spectrometry (ICPMS) (Fietzke et al., 2008).

We report a new rapid high-precision determination method of chlorine isotope ratios in halite and AgCl pellet formed from seawater and igneous rock samples. Use of a 266 nm ultra violet–femtosecond laser ablation (UV-FsLA) provided quantitative sampling of halite and AgCl, and enabled precise determination of ^{37}Cl/^{35}Cl isotope ratios (δ^{37}Cl) coupled with a multiple Faraday collector–inductively coupled plasma mass spectrometer (MFC-ICPMS). We used ^{36}Ar$^+$/^{38}Ar$^+$ as an external standard for the mass bias corrections between ^{39}K$^+$–^{41}K$^+$, ^{36}Ar^{1}H$^+$–^{38}Ar^{1}H$^+$–^{40}Ar^{1}H$^+$, and ^{35}Cl$^+$–^{37}Cl$^+$ with isobaric overlap corrections between K$^+$, ArH$^+$, and Cl$^+$ ions. Sulfur (^{36}S$^+$) isobar on ^{36}Ar$^+$ was indirectly monitored and corrected by a baseline modelling using ^{36}Ar$^+$/^{38}Ar$^+$ measurement. Those combined to accomplish an accurate and high-precision measurement of ^{37}Cl$^+$/^{35}Cl$^+$ ratios. Using the new analytical protocol, δ^{37}Cl in the natural halite samples were analyzed by direct laser ablation. The δ^{37}Cl in igneous rocks were analyzed by AgCl powder pellets produced after pyrohydrolysis separation and co-precipitation of the separated Cl with silver. The external reproducibility of δ^{37}Cl measurement was ±0.2 ‰2SD (2-standard deviation) for halite and ±0.3 ‰2SD for AgCl rivaling to the gas source isotope ratio mass spectrometry. The new analytical protocol enabled a precise and rapid δ^{37}Cl analysis of igneous rock samples from AgCl with as small as 4 μg chlorine. This is also the first report analyzing a high-precision δ^{37}Cl *in situ* from halite of the same amount of chlorine.

Keywords: stable chlorine isotopes, UV-LA-MC-ICP-MS