High spatial resolution Cl isotope analyses of apatites using NanoSIMS

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In order to elucidate isotopic compositions and origins of Cl in magmas and biogenic products, and related interactions such as assimilation of seawater components and diagenesis, we measured Cl isotopes in crystal and micro-inclusion apatites using NanoSIMS 50 (Cameca, Gennevilliers, France) at Atmosphere and Ocean Research Institute, Japan. The analytical technique is as follows[1]. Two combinations of EMs were applied to measure ^{35}Cl and ^{37}Cl: EM3 & EM4a; or EM4b and EM5. Running in a cycling mode among three magnetic fields, for instance, two single collection datasets ($^{37}Cl_{EM4a}/^{35}Cl_{EM4a}$, $^{37}Cl_{EM5}/^{35}Cl_{EM5}$) and one multi-collection dataset ($^{37}Cl_{EM5}/^{35}Cl_{EM4a}$) are obtained, where subscripts show corresponding EM detectors. Considering the average of $^{37}Cl_{EM4a}/^{35}Cl_{EM4a}$ and $^{37}Cl_{EM5}/^{35}Cl_{EM5}$, high reproducibility and precision are expected because total counts increase and analytical artifacts due to difference between detectors' sensitivity are offset. 5-μm to 10-μm spots were applied for analyses of the following apatites: "Morocco", an apatite crystal collected from Imilchil/Errachidia region in Morocco[1]; "Trichognathus", a Mississippian conodont from the Illinois Basin region in North America (the $^{238}U/^{206}Pb$ isochron age: 323 ± 36 Ma)[2]; "Cono2.7", one of index conodonts from Langkawi Island, northern Malaysia (the $^{232}Th/^{208}Pb$ isochron age: 429 ± 50 Ma)[3]; 5-μm apatite inclusions in zircons, and a few hundred-μm apatite crystals from Torihama dacite, SW Japan (the $^{238}U/^{206}Pb$ isochron age of zircons: 271 ± 58 ka)[4]; and 5-μm to 10-μm apatite inclusions in Efremovka CV3 chondrite. $\delta^{37}Cl$ values in Trichognathus were heterogeneous, and 2.6–5.7‰ higher than the value in Morocco whose reproducibility was 2.3‰ (1σ; N=6) during the session, while Cono2.7 showed $\delta^{37}Cl$ values indistinguishable from Morocco. There were no apparent correlations between Cl abundance and $\delta^{37}Cl$ values in Trichognathus, suggesting that mass independent fractionation processes of Cl during seawater-conodont interactions may have produced relatively high Cl isotopic ratios. This technique was also applicable to micro-inclusions. For Torihama samples, Cl counts in apatite inclusions were three-orders of magunitude higher than sorrounding zircons, thus we could avoid contaminations on $\delta^{37}Cl$ values in inclusions completely. Those values were not distinguishable from Morocco, indicating their typical magmatic origins. The data of inclusions in the chondrite will be also discussed.

[1] Kagoshima et al. (2014) *AGU Fall Meeting*, Abstract #V34A-04. [2] Sano & Terada (2001) *GRL* **28**, 831–834. [3] Ueki & Sano (2001) *Geohem. J.* **35**, 307–314. [4] Sano et al. (2002) *JVGR* **117**, 285–196.