Intensive Degassing of Halogens on Early Earth Recorded in Jack Hills Zircons

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Understanding the distribution of halogens in rocks can aid tracking interactions among the lithosphere, hydrosphere, and atmosphere due to their volatility and incompatibility in most minerals. Although no sedimentary rocks older than 3.8 Ga [e.g., 1] are known, investigating halogens incorporated in ancient zircons could aid our understanding of the interaction between the atmosphere and lithosphere on early Earth.

We report Cl and F concentrations in Jack Hills detrital zircons with ages ranging ~3.3-4.1 Ga. Halogen concentrations in zircons from Lachlan Fold Belt (LFB) granitoids, southeastern Australia, were also measured for comparison. All measurements were performed on the CAMECA *ims*1290 at UCLA. The RSF values (Relative Sensitivity Factor; for quantification of concentrations) were determined by depth profiling analyses on F- or Cl-implanted zircons. In general, Cl and F in LFB zircons were resolved with the level of ppm to sub-ppm and all show identical F contents. Zircons from S-type LFB granitoids display uniformly higher Cl concentrations (~0.16 ppm) compared with I-type zircons (~0.08 ppm). We interpret the positive correlation between Cl content in zircons and ASI value of their parent rock as due to the involvement of surface reservoirs in the parent melts of S-type zircons.

In contrast to the LFB zircons, Cl concentration in Jack Hills zircons vary greatly. All the Jack Hills zircons younger than 3.8 Ga display Cl concentration and Cl/F ratio identical to those in LFB zircons. However, ~60% of igneous zircons from the period 4.1-3.8 Ga exhibit elevated Cl contents with the maximum concentration of ~0.8 ppm, indicating the presence of Cl-rich magma before 3.8 Ga and possibly providing a record of halogen transport and retention on the early Earth [2].

[1] Manning et al., (2006) *American Journal of Science* **306**, 303; [2] Clay et al (2017) *Nature* **511,** 614.