

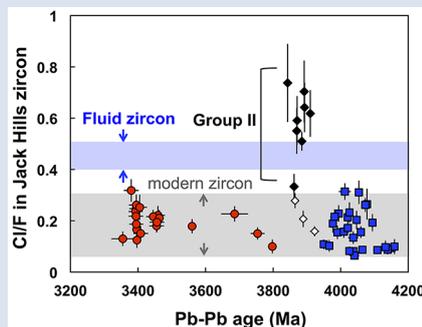
Zircon halogen geochemistry: Insights into Hadean-Archean fluids

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Abstract



Understanding the distribution of halogens in rocks can potentially trace ancient lithosphere, hydrosphere, and atmosphere interactions. Although no sedimentary rocks older than 3.8 Ga are known, insights into sediment-atmosphere exchange on early Earth could be obtained from knowledge of halogen contents in ancient zircons. Here we present the first study of halogen abundances in Jack Hills zircons together with younger zircons of known provenance to provide geologic context. The relatively low (*ca.* 0.1–0.6 $\mu\text{g/g}$) chlorine concentrations in most Hadean and Archean Jack Hills zircons are similar to the average concentration in younger igneous zircons. In contrast, significant Cl enrichments are found in a subset of *ca.* 3.9–3.8 Ga zircons ($[\text{Cl}]_{\text{average}} = 1.43 \pm 0.27 \mu\text{g/g}$) that appear to record halogen transport under hydrothermal conditions. Such Cl-bearing fluids in early Earth history may reflect extraction of halogens from the interior to near surface environments.

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Introduction

Earliest Earth remains one of the great frontiers for fundamental discovery as little is known about key events such as the mechanisms and timing of life's origin. Given that >3.8 Ga rocks are exceedingly rare and no rock older than 4.03 Ga is known (*cf.* O'Neil *et al.*, 2008), constraining conditions on early Earth has largely relied on the only materials identified from the Hadean eon: ~4.4 to 3.8 Ga detrital zircons (Mojzsis *et al.*, 2001; Peck *et al.*, 2001; Harrison *et al.*, 2008; Holden *et al.*, 2009; Bell *et al.*, 2011). Oxygen isotopes, rare earth element (REE) patterns, crystallisation temperatures, and inclusions in detrital zircons from the Jack Hills, Western Australia, are suggestive of the presence of recycled crustal material that had interacted with liquid water at low temperature (*e.g.*, Watson and Harrison, 2005; Trail *et al.*, 2011; Bell and Harrison 2013; Harrison *et al.*, 2017) and show how experimental calibrations can permit zircon to act as an environmental monitor of lithosphere and surface processes. On the other hand, the lack of a known sedimentary record older than 3.83 Ga (Manning *et al.*, 2006) limits our understanding of the volatile evolution on earliest Earth. To address this issue, one approach is to trace those volatile components that partition at measurable levels into zircon. Previous investigations of oxygen isotopes and trace elements in Jack Hills zircons (*e.g.*, Mojzsis *et al.*, 2001; Cavosie *et al.*, 2005; Trail *et al.*, 2007; Bell *et al.*, 2011) indicate two distinctive protolith sources: Group I and Group II (Bell and Harrison, 2013). Group I is similar in most respects to >3.9 Ga and <3.8 Ga Jack Hills zircons,

with magmatic Th/U and average Ti-in-zircon temperatures *ca.* 680 °C. Group II is a distinctive subset of the zircons with ages 3.9–3.8 Ga that show distinctive chemistry relative to Group I (lower Th/U, P, and Ce; higher U and Hf). Their Ti-in-zircon temperatures are mostly subsolidus, and these zircons are either dark and homogeneous in cathodoluminescence or display patchy zoning. The Group II characteristics imply recrystallisation during thermal events (Hoskin and Black, 2000). Such episodes may have provided a mechanism for volatile transport in early fluids. Given the significance of halogens in lithosphere-hydrosphere-atmosphere interactions, we focus here on their abundances in Jack Hills zircons and examine fractionations between nominally mobile (Cl) and immobile (F) halogens in a variety of reservoirs (*e.g.*, magmatic and metamorphic systems).

Samples and Methods

Our Jack Hills zircon suite ranges in U-Pb age from 4.2 to 3.4 Ga (Table S-2). Oxygen isotope ratios and REE patterns in some of these zircons have been investigated previously and shown to lack secondary alteration (Table S-2, S-3, and S-4, Fig. S-7 and S-8; Bell *et al.*, 2011, 2014, 2016; Bell and Harrison, 2013). Given the possible felsic parent sources of Jack Hills zircon (Bell *et al.*, 2018), zircons from igneous (I-type) and sedimentary (S-type) granitoids from the Phanerozoic Lachlan Fold Belt (LFB), Australia, and Mesozoic batholiths of southern California, USA, were also investigated as

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analogues for establishing geologic provenance. Detection limits ($[F] = 0.78 \pm 0.07 \mu\text{g/g}$ and $[Cl] = 0.12 \pm 0.02 \mu\text{g/g}$ with 2 se.; Fig. S-4) were determined by analysing synthetic zircons grown in halogen-free conditions by the 1 atm flux method (e.g., Trail *et al.*, 2016). We also synthesised zircon grains in a halogen-rich fluid to explore Cl (and F) partitioning in zircon and to produce an analogue of recrystallised zircon (see Supplementary Information for experimental details).

The *in situ* analyses of Cl and F in zircon were performed using the CAMECA *ims1290* ion microprobe. Analytical details are described in the Supplementary Information. Mud Tank zircons implanted with known F or Cl isotopic dosages were analysed as concentration standards. Cracks/inclusions in samples were identified *via* secondary and backscattered electron SEM imaging. Analysis zones were limited to regions without cracks or inclusions.

Results

Young zircons (1.1–0.1 Ga) display uniform F concentrations (Fig. 1) within uncertainty ($1.80 \pm 0.11 \mu\text{g/g}$), except AS3 zircon (Duluth Complex, Minnesota), which we attribute to enrichment during hydrothermal alteration (Takehara *et al.*, 2018). All the post-Archean zircons in this study exhibit systematically low Cl contents, some of which cannot be resolved from the baseline. The average concentration is determined as $0.31 \pm 0.04 \mu\text{g/g}$.

Fluorine concentrations in all 58 Jack Hills samples are slightly higher than those in zircons from the LFB and southern Californian granitoids ($2.28 \pm 0.19 \mu\text{g/g}$). Chlorine concentrations and Cl/F ratios in Jack Hills zircons appear to vary with age (Fig. 1). Significantly high Cl concentration ($[Cl]_{\text{average}} = 1.19 \pm 0.32 \mu\text{g/g}$) is observed in a subset of zircons within a narrow age range of 3.9–3.8 Ga. Archean grains with ages from 3.8 to 3.4 Ga display Cl contents identical to the young zircons ($[Cl]_{\text{average}} = 0.34 \pm 0.04 \mu\text{g/g}$), pointing to a magmatic environment with halogens levels roughly similar to modern igneous systems. Two Jack Hills zircons older than 3.9 Ga yield exceptionally high Cl contents (RSES 178-7.14 and RSES 178-8.8 with Pb-Pb ages of 4012 Ma and 4073 Ma, respectively), although the halogen measurements on the other 25 grains are within error of the range of 0.1–0.6 $\mu\text{g/g}$ in the young zircons.

Halogens in Jack Hills Zircons: Primary or Secondary?

Given that mobile elements can be substituted into the zircon lattice during secondary alteration (e.g., Bell *et al.*, 2016), care must be taken to ascertain that Cl and F concentrations reported for Jack Hills zircons do not represent post-crystallisation hydrothermal alteration. In our study, U-Pb ages in all Cl-rich zircons are concordant within $\pm 10\%$ (Bell and Harrison, 2013) indicating little Pb loss or U gain after 3.8 Ga. In addition, two indices, including $(\text{Sm}/\text{La})_N$ (Hoskin, 2005) and the LREE-I [$= (\text{Dy}/\text{Nd}) + (\text{Dy}/\text{Sm})$; Bell *et al.*, 2016], can test for possible alteration effects leading to crystalline degeneration. The high values of both indices for all grains (except one Archean zircon) are indicative of crystalline zircon, including the Cl-rich grains (see Bell *et al.*, 2016) (Fig. 2). The halogen abundances are interpreted as reflecting concentrations present during crystallisation from their primary sources magmas. The distribution of oxygen isotopes in our samples ($\delta^{18}\text{O}_{\text{ave}} = 5.87 \pm 0.17$; Fig. S-7)

is consistent with the prevailing populations for their corresponding time periods (Cavosie *et al.*, 2005; Trail *et al.*, 2007; Bell *et al.*, 2016) and no obvious correlation between $\delta^{18}\text{O}$ and Cl concentration is observed. The prominent excursion of Cl content in multiple 3.9–3.8 Ga zircons is higher than that seen thus far in post-Archean grains.

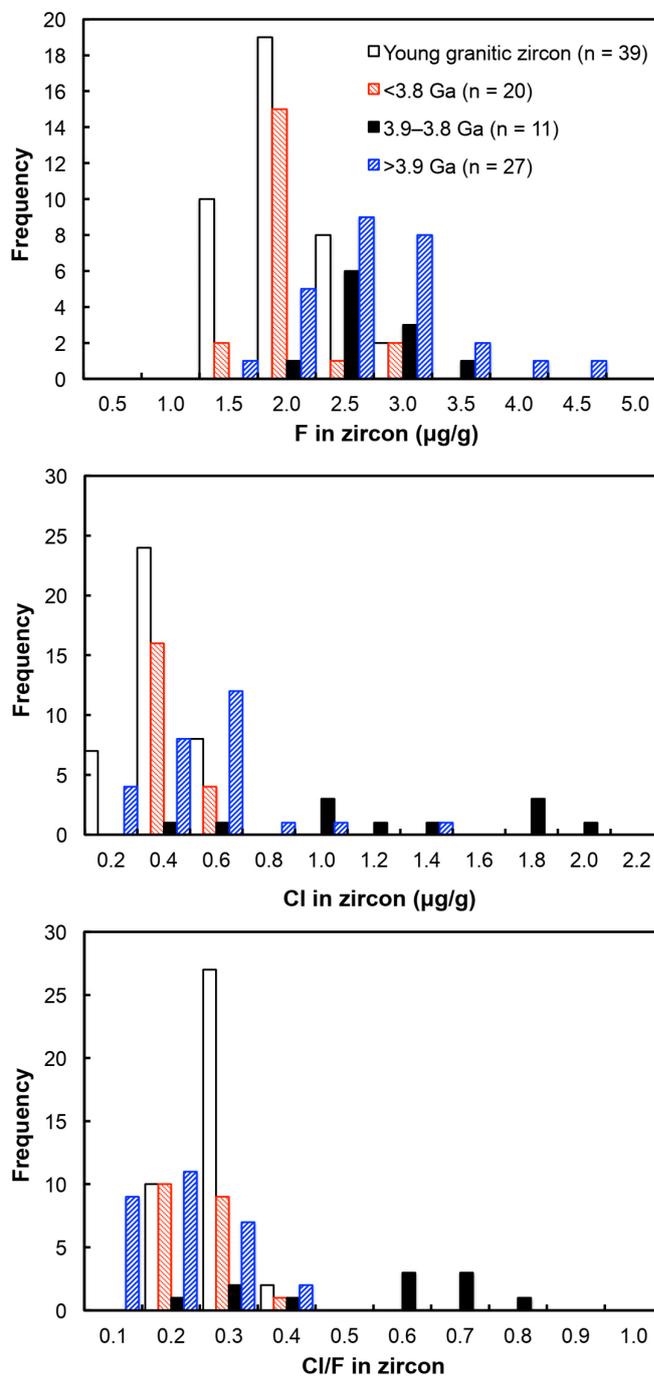


Figure 1 Fluorine concentrations in Jack Hills zircons ($[F]_{\text{average}} = 2.28 \pm 0.19 \mu\text{g/g}$) are generally indistinguishable from those in young granitic zircons ($[F]_{\text{average}} = 1.80 \pm 0.11 \mu\text{g/g}$). Elevated Cl concentrations observed in eight 3.9–3.8 Ga zircons (black columns) yield distinctly high Cl/F ratios ($\text{Cl}/\text{F} > 0.3$) when compared with other Jack Hills zircons.

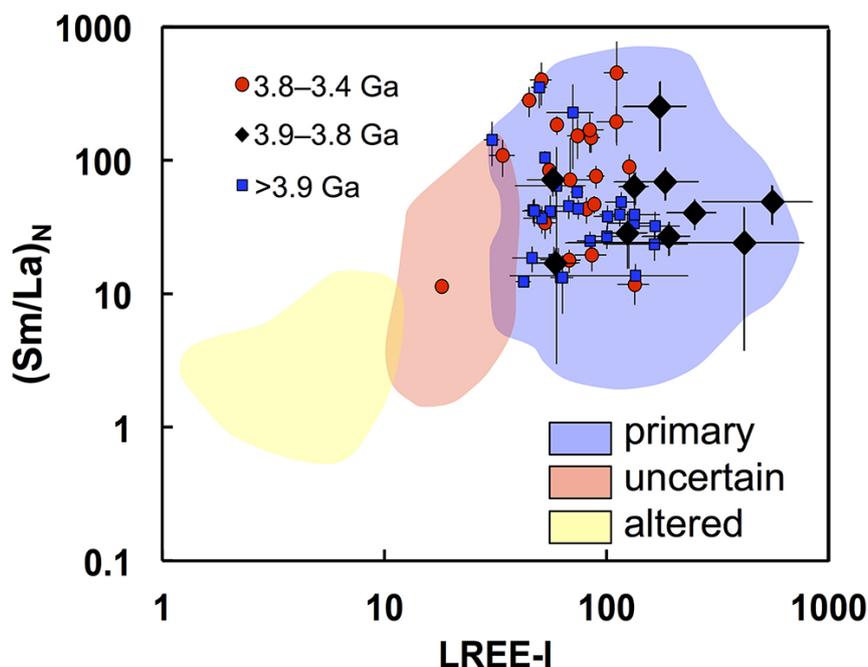


Figure 2 High values of $(\text{Sm/La})_N$ and LREE-I $[(\text{Dy/Nd}) + (\text{Dy/Sm})]$ in Jack Hills sample grains imply that most of samples, especially Cl-rich zircons, are primary. The elevated Cl concentrations in zircons therefore derived from primary sources.

Group II Zircons: Recrystallisation in Cl-rich Fluids?

Bell and Harrison (2013) classified 3.9–3.8 Ga Jack Hills zircon grains into two categories. Group I exhibits temperatures and compositions similar to other igneous zircons across the age spectrum, and Group II shows high U, lower (Th/U) ratio (<0.25), and anomalously low Ti ($1.82 \pm 0.47 \mu\text{g/g}$). The concordant U-Pb ages in Group II zircons and their igneous protolith similar to Group I suggest that they formed by transgressive recrystallisation, in which recrystallisation occurs across the entire zircon under high temperatures (Hoskin and Black, 2000). The distribution of halogens in the Jack Hills zircons is consistent with this classification. The *ca.* 3.9 Ga zircons in this study contain three Group I zircons ($[\text{Cl}]_{\text{average}} = 0.58 \pm 0.28 \mu\text{g/g}$) and eight Group II zircons ($[\text{Cl}]_{\text{average}} = 1.43 \pm 0.33 \mu\text{g/g}$) (Table S-2), in which two Group I zircons (RSES 56-3.17 and RSES 181-2.10) display Cl contents identical to the young zircons, and the other Group I zircon (RSES 178-20.20) has a Cl concentration higher than the young zircons, but consistent with the lowest level of Cl contents in Group II zircons (Fig. 3a).

Significant differences in Cl/F ratios are observed between Group I zircons and Group II zircons (Fig. 3b). The Jack Hills zircons with the age of 3.8–3.3 Ga and 4.2–3.9 Ga display Cl/F ratios within the range of young magmatic zircons (0.02–0.30). In addition, in the period of 3.9–3.8 Ga, no distinguishable difference of Cl/F ratios in three Group I zircons are found compared to other Jack Hills zircons. However, Cl/F ratios of Group II zircons are distinctively higher (0.33–0.74) than the ratios of young magmatic zircons.

The Ti-in-zircon crystallisation temperatures (T^{zln}) of each Jack Hills zircon are obtained using a protocol developed in previous studies (Watson and Harrison, 2005; Harrison *et al.*, 2008). As shown in Figure 4, the Jack Hills samples group into two clusters based on their T^{zln} and Cl/F ratios. All the Cl-rich Group II zircons exhibit distinct T^{zln} below the nominal granite solidus ($\sim 650 \text{ }^\circ\text{C}$), with an average T^{zln} of $596 \pm 17 \text{ }^\circ\text{C}$. In contrast, the T^{zln} among all other Jack Hills zircons with low Cl/F ratios overall cluster about an identical average of 680

$^\circ\text{C}$, indistinguishable from the Hadean distribution (Watson and Harrison, 2005).

A possible mechanism to interpret the low Ti contents and other characteristics of Group II zircons is metamorphic transgressive recrystallisation of originally igneous zircons (Bell and Harrison, 2013). High temperature transgressive recrystallisation results in flushing the more incompatible trace elements (*e.g.*, Ce) from the mineral, an increase in compatible elements (*e.g.*, Hf, U), and homogeneous dark textures (Hoskin and Black, 2000). These characteristics are all consistent with the chemistry and internal structure of Group II zircons. Moreover, transgressive recrystallisation of zircon occurs during metamorphism at temperatures up to 600 $^\circ\text{C}$. Such conditions can be achieved by the presence of hydrothermal fluids which can quickly elevate and maintain local temperatures for significant durations (Hoskin and Black, 2000). Zircon recrystallisation can occur in the contact or absence of fluids, although the elevated Cl concentrations and Cl/F ratios in Group II Jack Hills zircons relative to magmatic zircons strongly suggest the involvement of Cl-rich fluids at *ca.* 3.9 Ga, which would additionally enhance zircon recrystallisation given high solubility of ZrO_2 in saline fluids relative to pure H_2O (Bernini *et al.*, 2013).

We can roughly estimate Cl content in fluids during Group II recrystallisation based on the analysis of synthetic zircon synthesised in a Cl- and F-bearing aqueous fluid. The zircon synthesised from a fluid with 4000 $\mu\text{g/g}$ Cl and 2000 $\mu\text{g/g}$ F displays a Cl concentration of $\sim 1 \mu\text{g/g}$ and a Cl/F ratio of 0.46, demonstrating that Cl can substitute into zircon when crystallising in fluid-rock systems (Table S-1). The Cl/F ratio is relatively low compared with ratios in Group II zircons, which could be attributed to the high temperature (1300 $^\circ\text{C}$; 1 GPa) of the experiment relative to Hadean conditions ($\sim 680 \text{ }^\circ\text{C}$) and/or the different Cl/F ratios compared to the natural fluid ratios. The partition coefficient ($D_{\text{zircon-fluid}}$) of $2.3 \pm 0.2 \times 10^{-4}$ implies fluids with Cl contents of 4×10^3 – $1 \times 10^4 \mu\text{g/g}$ during Group II recrystallisation. This is similar to Cl concentrations in some brine hydrothermal fluids in the present day (*e.g.*, Stefánsson and Barnes, 2016), though significantly lower than that in modern deep crustal fluids (*e.g.*, Bodnar, 2003). Future systematic experiments are required for precise estimates on $D_{\text{zircon-fluid}}$ under different P-T conditions.



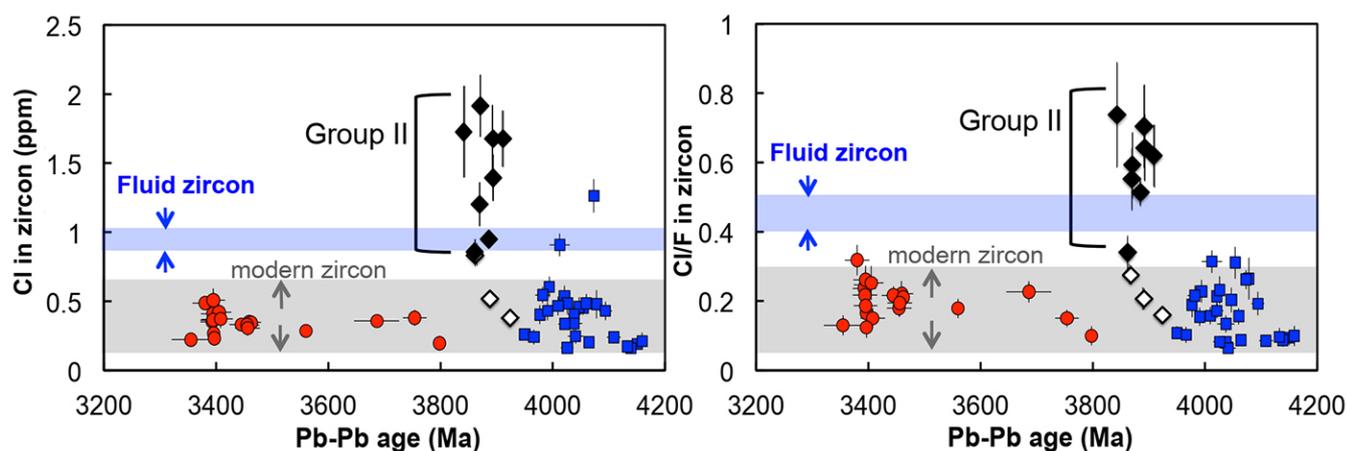


Figure 3 (a) Chlorine distribution and (b) Cl/F fractionation in Jack Hills zircons are mainly identical to the ranges determined from modern magmatic zircons in this study (red circles: <3.8 Ga zircons; white diamonds: 3.9–3.8 Ga Group I zircons; blue rectangles: >3.9 Ga zircons; grey bar: modern zircon ranges) except Group II zircons crystallised at 3.9–3.8 Ga (black diamonds). A synthetic zircon grown in an aqueous-rich fluid exhibits Cl content and Cl/F ratios (blue bars) that fall within the range of Group II.

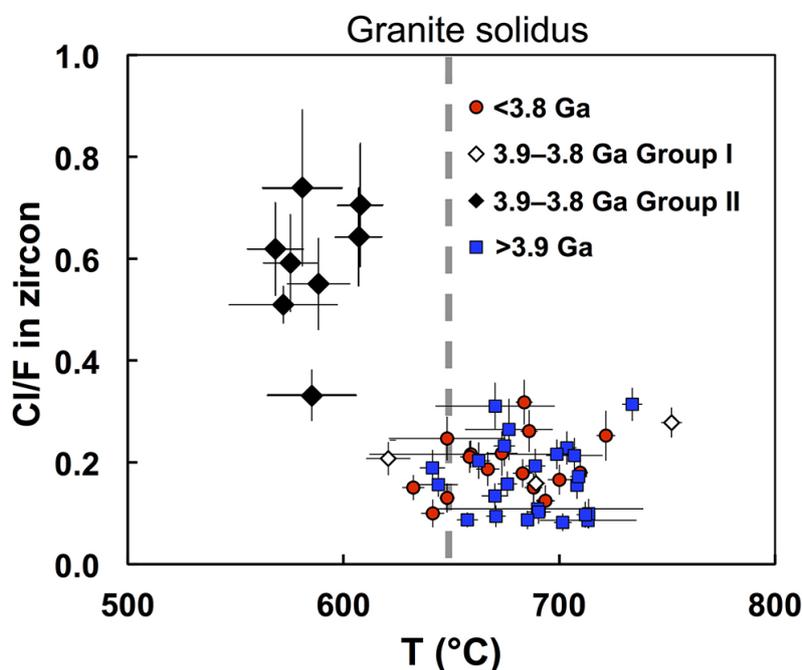


Figure 4 Chlorine-rich Group II zircons are characterised by Ti-in-zircon temperatures below granite solidus. The clearly distinguished cluster of Group II from other magmatic zircons suggests the mechanism of Group II as solid state recrystallisation involving Cl-bearing fluids.

Implications and Conclusions

Studies of Bulk Silicate Earth (BSE) halogen abundances suggest the anomalous depletions observed in volatile halogens (Cl, Br, and I) relates to their volatility during condensation from the solar nebula (Lodders, 2003; Sharp and Draper, 2013). However, these putative depletions were rendered moot by a recent analysis of the abundances of Cl, Br, and I in meteorites, which indicate much lower average abundances in primitive chondrites (Clay *et al.*, 2017) than previously thought. Given the large proportion of heavy halogens in the crustal reservoirs (80–90 % of BSE; Burgess *et al.*, 2002), notwithstanding contributions from a late veneer (*ca.* 1 % Earth mass) or complete mantle degassing (maximum estimated extraction efficiency is ~50 %; Allègre *et al.*, 1996), additional halogens transported from deep Earth would still be required, likely *via* early fluids.

The enrichment of Cl in all Group II Jack Hills zircons indicates the presence of fluids with Cl concentrations similar to modern metamorphic fluids. The average $\delta^{18}\text{O}$ identical to prevailing populations of other Jack Hills zircons suggest that rather than recycled crustal material, which would yield distinctly high $\delta^{18}\text{O}$ values, the Cl-bearing fluids occurred inside of nascent crust, either in the deeper crust or near the surface following impacts. Whether the ~3.9 Ga recrystallisation arises from meteoritic, meteoric or deep sourced fluids, the elevated Cl concentration in Group II zircons provides the first insight into halogen transfer and cycling through metamorphic fluids on early Earth.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1905>.



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