# The Effects of Dissolved Chloride on the $Fe^{3+}/\sum Fe$ of Rhyodacitic Melt

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We have conducted a series of experiments designed to evaluate intrinsic effects of the dissolved chlorine on the equilibrium $Fe^{3+}/\sum Fe$ in hydrous, chloride-rich rhyodacite liquids. Experiments were conducted at series of controlled $fO_2$ in an IHPV at 950°C and 130 MPa. The $Fe^{3+}/\sum Fe$ values of the run-product glasses were measured with synchrotron μ-XANES spectroscopy on beamline 13ID-D at the Advanced Photon Source, Argonne National Laboratory.

Data from experiments indicate that the addition of dissolved chloride increases the equilibrium $Fe^{3+}/\sum Fe$ of the melt relative to values predicted by several popular algorithms that equate $Fe^{3+}/\sum Fe$ with $fO_2$ and bulk melt composition. The deviation of the observed $Fe^{3+}/\sum Fe$ values from their predicted "equilibrium" values suggests that the interaction of dissolved chloride with Fe in the melt alters the activity-composition relationships for FeO and $FeO_{1.5}$ in the melt. Calculated $G^{ex}$ associated with the $FeO_{1.5}$ and FeO components of the melt systematically vary as a function of the imposed experimental $fO_2$.

Data from these experiments imply that hydrous Fe-poor melts with intermediate silica and fairly modest chloride contents (i.e., ≤ 0.75 wt%) may display rather oxidized $Fe^{3+}/\sum Fe$ values despite possessing a relatively reduced equilibrium $fO_2$. The data further suggest that any empirical or thermodynamic model of the $Fe^{3+}/\sum Fe$ in silicate liquids must include terms to account for the non-ideal behaviour of $\gamma FeO_{1.5}/\gamma FeO$ that is associated with the presence of dissolved chlorine in the melt.

# Jack Hills zircons record a thermal event coincident with the hypothesized Late Heavy Bombardment

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## Introduction

The Late Heavy Bombardment (LHB) is a hypothesized period of intense bombardment of the inner solar system at ca. 3.9 Ga, inferred from disturbed lunar ages. Major thermal effects to the Earth's crust are expected from LHB-impact scenarios, but unambiguous terrestrial evidence of this event is unknown, probably owing to the sparse geologic record from this period. However, detrital zircons from Jack Hills, Western Australia span the period 4.3-3.0 Ga, including the time period of the LHB, and may record evidence for this event.

## Results and Discussion

We investigated the trace element chemistry of the Jack Hills detrital zircon record for the period 4.0 – 3.8 Ga in search of apparent changes in thermal conditions consistent with the LHB. The Ti-in-zircon temperature ($T^{xlln}$) distribution is well established for Hadean detrital grains, clustering about an average value of ~680°C – likely indicating near water-saturated granitic melting conditions. The average $T^{xlln}$ does not change appreciably through the period 4.0-3.8 Ga, but between 3.91-3.84 Ga, there is a notable group of low-Ti zircons with apparent $T^{xlln}$ extending well below the granite solidus. Further investigation revealed that this period contains two groups of zircons with clearly distinguishable trace element signatures. Group I resembles the Hadean Jack Hills zircons in Ti, Hf, Ce, U, and Th/U, whereas Group II contains lower Ti, Ce, and Th/U along with higher Hf and U. Group II also displays a high degree of U-Pb concordance compared to the 4.0-3.8 Ga Jack Hills zircons as a whole, despite their high U contents. We interpret Group II as originating from the solid-state recrystallization of originally magmatic (perhaps even Group I-like) zircon during a thermal event ca. 3.9 Ga. This thermal excursion is also seen in epitaxial growths on Hadean zircon cores found in previous studies.

## Conclusion

A group of Jack Hills zircons at ca. 3.9 Ga appear recrystallized, and likely record a significant thermal event in the source terrane. Although an endogenic cause for this thermal event cannot be definitively ruled out, these observations may constitute the first terrestrial evidence for the LHB.