

## Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills, Australia: Implications for the Hadean Earth

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We welcome a discussion on the origin of mineral inclusions in detrital zircons from Jack Hills, Australia, which have previously been interpreted to be primary and magmatic and, hence, to constrain the composition of the earliest crust.

In our recent paper (Rasmussen et al., 2011), we used multiple lines of evidence to suggest that at least some, and possibly most, of the inclusions in zircons from Jack Hills formed after deposition. In-situ U-Pb dating of xenotime and monazite inclusions showed they formed during two discrete metamorphic events (Rasmussen et al., 2010), whereas monazite-xenotime and Ti-in-quartz thermometry indicates that at least some monazite, xenotime, and quartz inclusions are metamorphic. Based on the lack of apatite inclusions in Jack Hills zircons relative to common igneous rocks, we argued that apatite was once much more abundant but had been pseudomorphed by matrix minerals during metamorphism. We concluded that zircon is susceptible to fluid-mediated alteration and cautioned against the use of muscovite and quartz inclusions to infer the composition of the host melts of the Hadean zircons.

Hopkins et al. (2012) question our scholarship for failing to cite previous work that apparently discusses the resetting of isotopic systems in phosphate inclusions. The paper by Caro et al. (2003), which they quote as an example, actually applies to short-lived <sup>146</sup>Sm–<sup>142</sup>Nd chronometry on rocks from the 3.7–3.8-Gyr Isua greenstone belt in West Greenland, and mentions nothing about phosphate inclusions in zircon or isotopic resetting. This paper is therefore not relevant to the discussion. However, another paper by Caro et al. (2008) may be more relevant. It reports <sup>146</sup>Sm–<sup>142</sup>Nd systematics for Hadean zircon grains from Jack Hills, suggesting that there was post-crystallization disturbance of the <sup>147</sup>Sm–<sup>143</sup>Nd system and concomitant light rare earth element (LREE) enrichment. Caro et al. (2008, p. 262–263) state “... the presence of primary inclusions of apatite, monazite or xenotime could also produce LREE-enrichment in the grains. However, primary inclusions cannot account for the Sm–Nd systematics of the Jack Hills composite as these are essentially contemporaneous of zircon formation (Trail et al., 2004) ...”. Instead, they speculate that the source of the disturbance is present either in secondary rims or as secondary REE-rich minerals located along fractures and/or pitted grain surfaces. Clearly, Caro et al. (2008) do not consider that resetting of isotopic systems in phosphate inclusions occurred, because they imply the inclusions are primary. Hopkins et al. (2010) speculate that very high radioactivity associated with monazite may cause volume changes that can overcome the confining pressure of the host phase. Unfortunately, there is no evidence presented to support this proposal. In addition, we dated mainly xenotime inclusions, which are significantly less radioactive than high-Th monazite and therefore even less likely to undergo radiation-induced crystal damage.

In regard to the origin of the muscovite inclusions, we noted that in Jack Hills zircons, they occupy randomly oriented, hexagonal-shaped domains with pyramidal or rounded terminations and aspect ratios of 1:1.5–1:3.5, typical of apatite inclusions in magmatic zircons. Hopkins et al. (2008, 2010) do not address the preponderance of muscovite and

quartz inclusions or paucity of apatite, not only in Hadean zircons but also in younger Archean zircons from Jack Hills. This distribution points to a common process that has affected all detrital zircons from Jack Hills. We suggest that apatite inclusions were dissolved either in the host granitic rocks, during erosion and sedimentation of their enclosing zircon grains or during deformation and metamorphism following zircon deposition. We envisage that the molds after primary apatite were subsequently filled with metamorphic minerals matching those in the matrix of the host metasedimentary rock (e.g., quartz, muscovite, monazite, xenotime).

In relation to the heterogeneous Si/Al ratios in muscovite inclusions, we suggest an alternative explanation. The case for geotherms of ~60 °C/km in the Hadean presented by Hopkins et al. (2008, 2010) rests upon the analysis of minute muscovite inclusions, many apparently <5 μm, within zircon crystals. Under the conditions used for electron probe microanalysis, Monte Carlo modeling indicates a spatial resolution of 3–4 μm and a depth resolution of 1.5–2 μm for muscovite. Under these conditions, there is a real possibility that X-rays will be generated from enclosing zircon or other grains; e.g., quartz, within multi-phase inclusions. Therefore, the muscovite analyses should be subjected to a quality control filter. For structural formulae calculated on the basis of 11 oxygen atoms per formula unit (apfu), it is generally accepted that (Ca + Na + K) > 0.9 apfu is required for acceptable analyses (e.g., Zane and Rizzo, 1999). Only three of the 17 analyses reported by Hopkins et al. (2008, 2010) meet this criterion (67\_3.2, 67\_15.16, and 73\_6.9). Of these three analyses, 67\_3.2 is also suspect, having 1.1 apfu (Ca + Na + K) and >0.09 apfu Ca. The analysis of muscovite composition by Zane and Rizzo (1999) finds minimal substitution of Ca (<0.045 apfu) in muscovite from granitic rocks. The two “acceptable” analyses reported by Hopkins et al. (2008, 2010) have 3.12 and 3.16 apfu Si and fall within the range of our analyses of metamorphic muscovite from Jack Hills. Our failure to address the bimodal distribution of Si pfu (note ‘per formula unit’ and not ‘plaque-forming unit’) values reported by Hopkins et al. (2008, 2010) therefore reflects our reservations about the quality of the analyses and lack of evidence for an igneous origin for the muscovite inclusions.

In conclusion, we reject the claim of omission and will let the readers decide upon the level of our scholarship. We maintain that the use of mineral inclusions in Jack Hills zircons to infer initial magma chemistry is problematical and urge caution in their use to determine the composition of the earliest crust.

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