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Comment on "Heterogeneous Hadean Hafnium: Evidence of Continental Crust at 4.4 to 4.5 Ga"

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Harrison *et al.* (Reports, 23 December 2005, p. 1947) proposed that plate tectonics and granites existed 4.5 billion years ago (Ga), within 70 million years of Earth's formation, based on geochemistry of >4.0 Ga detrital zircons from Australia. We highlight the large uncertainties of this claim and make the more moderate proposal that some crust formed by 4.4 Ga and oceans formed by 4.2 Ga.

The proposal by Harrison *et al.* (*1*) of water-saturated granites (sensu stricto), differentiation of continental crust, and plate tectonics at 4.5 to 4.4 Ga is based on geochemical evidence from detrital zircons from the Jack Hills, Western Australia. We question such dramatic interpretations and draw less extreme conclusions. We interpret results for >4 Ga zircons to suggest the presence of granitic (sensu lato) crust by 4.4 Ga and oceans by 4.2 Ga. The composition of this crust is uncertain, although the preservation of these zircons requires at least some early buoyant crust.

The antiquity of >4 Ga zircons is not in question; however, imaging and multiple spot analyses within single crystals show that some zircons are complex and difficult to interpret. Of crystals with published cathodoluminescence (CL) images and multiple U-Pb age analyses made in core domains by ion microprobe, differences in concordant ages range from 0 to 400 million years (My), with the oldest age not always in the geometric center (Fig. 1, left) (*2*). Furthermore, many grains contain younger overgrowths or domains that are relatively featureless or have contorted CL zoning that suggest disturbance. Detailed electron beam imaging is essential to target in situ measurements and to correlate subdomains. For complex zircons, images should be published and available for critical examination (*2*–*6*).

Oxygen isotope ratios for Jack Hills zircons from 8 to 15 per mil (‰) have been interpreted as igneous and "S-type," implying partial melting of sedimentary protoliths (*7*). However, these high $\delta^{18}O$ values occur in zircons with extreme U-Pb disturbance, none have published CL images, and they may be metamorphic overgrowths (*7*, *8*). In contrast, all of our >4 Ga igneous zircons have $\delta^{18}O < 7.5‰$ (*4*, *5*). Furthermore, ∼5000 analyses of zircons from 1200 rocks of different ages show that S-type $\delta^{18}O$ (zircon) values above 7.5‰ are absent in igneous zircons from Archean rocks (*9*). Magmas in the Archean were remarkably constant in $\delta^{18}O$, consistent with continued growth of the crust until at least 2.5 Ga (*9*). All studies agree that many Jack Hills igneous zircons have $\delta^{18}O = 6.3$ to 7.5‰. Such mildly elevated values are interpreted to indicate burial and melting of high $\delta^{18}O$ protoliths that resulted from low temperature alteration and to require liquid water and probably oceans at Earth's surface (*6*, *10*). These protoliths could have been any altered supracrustal rock, including sediment or submarine basalt. Modern plate tectonic–style processes are not required to produce these features.

Harrison *et al.* (*1*) cite the presence of quartz inclusions in zircon as evidence of granite magmas. However, other studies (*2*–*4*) have reported on quartz and feldspar inclusions in these zircons and concluded that the zircons formed from silica-saturated and probably granitic magmas such as tonalite, trondhjeimite, or granodiorite—rocks that are common in younger Archean terranes.

Magmatic temperatures averaging 696°C are based on Ti thermometry on >4 Ga Jack Hills zircons and interpreted to indicate that melting as early as 4.3 to 4.4 Ga produced widespread water-saturated granites (*1*, *11*). However, Ti temperatures have also been reported for >4 Ga Jack Hills zircons (average 715°C ± 55°C) (*12*) and for zircons from wide-ranging felsic (663°C ± 63°C) and mafic (761°C ± 57°C) igneous rocks, including anorthosite (720°C ± 39°C), and megacrysts in kimberlite (758°C ± 49°C) (Fig. 2). Although variable TiO_2 activity, erratic intracrystalline Ti heterogeneity, and other uncertainties may require adjustment of temperature estimates, the Jack Hills Ti-in-zircon data are permissive of derivation from a wide range of both mafic and felsic host rocks.

Harrison *et al.* further suggest that new $^{176}Hf/^{177}Hf$ data for >4 Ga zircons indicate extreme differentiation of continental crust and mantle starting at 4.5 Ga (*1*). Following (*13*), the U-Pb age of each zircon is used to calculate, (εHf) assuming that the U-Pb age accurately represents the time Hf was acquired by the growing zircon. For a zoned zircon, this can be assured only if both measurements are made from the same domain. In contrast, Harrison *et al.* measured Hf by laser ablation (62- to 81-μm diameter holes) (*1*), and the zircon age determined by ion microprobe (∼25-μm diameter spot) was assigned to the measured $^{176}Hf/^{177}Hf$. This method marks an advance over whole grain analysis. However, the ion microprobe pits are shallower (1 to 2 μm) than the laser holes (up to 100 μm), and the volume analyzed by laser is more than 100 times as large. Harrison *et al.* modeled the hazards of analyzing a zoned zircon assuming that volumes analyzed are identical for Hf and U-Pb and showed possible errors from –7 to +5 in εHf in figure 1 of (*1*), but this is not the worst-case

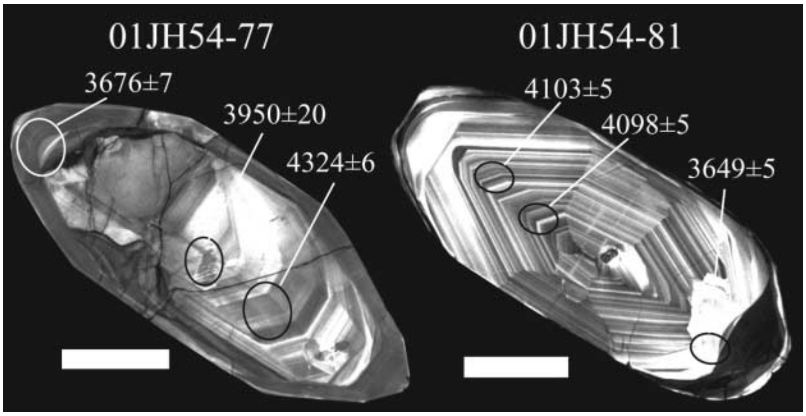

Fig. 1. Zircons 01JH54-77 and -81 from Jack Hills metaconglomerate showing sites of U-Pb analyses with age. Ages are in Ma and are >90% concordant. Scale bars, 50 μm. Additional analyses are shown in figure 5 in (*2*).

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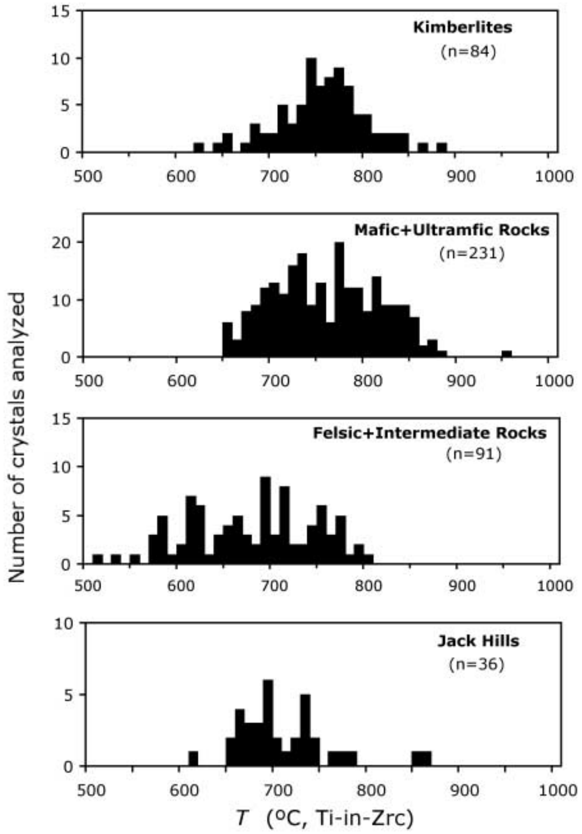

Fig. 2. Histograms for average Ti-in-zircon temperatures for individual zircons from kimberlite; mafic and ultramafic; felsic and intermediate composition rocks; and >4 Ga Jack Hills detrital zircons. Lithologic subsets of these groupings are more limited in range. For instance, Grenville anorthosites and gabbros average 720 ± 37°C ($n = 47$). From (*12*).

scenario. The effect of a 100-My error in age is to shift εHf by 2.2 to 2.5 units. A complex, disturbed zircon is shown in Fig. 1, left, with nearly concordant ages ranging from 4324 to 3950 Ma in its core. So what is the correct core age? If only one analysis is available for this zircon, in the extreme case, Hf could be either 374 My older or 374 My younger than the U-Pb age, and εHf could be in error by up to 9 units, either positive or negative. A total scatter of 18 εHf units could be created by analysis of many such crystals, similar to the range of data in figure 2 of (*1*). Although this is admittedly an extreme case, it illustrates the importance of fully characterizing each zircon and of analyzing exactly identical domains for both age and Hf. Modeling of possible Hf isotopic heterogeneity does not substitute for imaging and detailed analysis.

In summary, none of the data cited by Harrison *et al.* (*1*) uniquely support the hypotheses of plate tectonics and subduction by 4.4 to 4.5 Ga or of complete differentiation of continental crust before 4 Ga. We know that >4 Ga zircons contain a wealth of new information about this formerly unknown time on Earth and predict exciting discoveries, but such studies are in their infancy, and strong conclusions require strong evidence.

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