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

T. M. Harrison,[1,2]* J. Blichert-Toft,[3] W. Müller,[4] F. Albarede,[3] P. Holden,[2] S. J. Mojzsis[5]

Valley *et al*. review the lines of evidence on which we drew to conclude that continental crust formed much earlier than previously thought. Their comment contains some misrepresentations that we correct, but new information they provide appears to bolster our hypothesis. Nothing in their comment refutes the presence of continental crust or plate boundary processes prior to 4 billion years ago.

Although nothing in their comment precludes the existence of continental crust or plate boundary processes before 4 billion years ago (Ga), Valley *et al*. (*1*) provide new data that appears to bolster our case that the very early Earth may have had more in common with the present than is widely believed (*2*). Several misrepresentations of our work require correction.

Valley *et al*. (*1*) point to their experience that ancient zircon cores can show "differences in concordant ages…from 0 up to 400 million years," which could complicate the assessment of crystallization age. Although pathologic effects, such as excess ^{231}Pa (*3*), always need to be assessed, we are confident that our approach is adequate to assess the reliability of assignment of $\varepsilon_{Hf(T)}$. We do not disagree with their call for electron beam imaging. Given space limitations, however, we chose to leave such documentation for a follow-up study. Although imaging can be helpful, the practice of inferring three-dimensional (3D) properties from a 2D section is something of an art form, and we caution against overreliance on pattern recognition.

Valley *et al*. (*1*) may be implying that our interpretation—that the majority of the Hadean Jack Hills zircons formed in a continental environment—was specifically informed by δ^{18}O values as high as +15 per mil (‰). Nowhere in this or other papers do we state this. They go on to support our view that "many Jack Hills igneous zircons have δ^{18}O = 6.5 to 7.5 ‰…interpreted to indicate burial and melting of high δ^{18}O protoliths that resulted from low temperature alteration…and probably oceans at Earth's surface." Although they go on to assert that the Jack Hills zircons could have been any altered supracrustal rocks, they do not specify the occurrence of materials yielding low zircon crystallization temperatures that would not be related to plate boundary processes (e.g., hot spots would not meet this requirement).

Valley *et al*. (*1*) appear to agree with the self-evident conclusion that quartz inclusions in zircon indicate formation in silica-saturated magmas. It is unclear to us, however, whether they are arguing that these "granitic magmas such as tonalite, trondhjeimite, or granodiorite" formed outside of a plate boundary environment.

We are delighted by the report (*1*) of Ti-in-zircon temperatures from felsic (663 ± 63°C) and mafic (761 ± 57°C) igneous rocks (the relatively high [U] of Jack Hills zircons preclude a kimberlitic origin). Specifically, the range reported for mafic zircons of 704 to 818°C is skewed to higher temperatures than the 655 to 705°C peak that we recognize in the Jack Hills zircon population (*4*), underscoring our interpretation that "the vast majority [of Jack Hills zircons] formed in a continental environment." That Valley *et al*. (*1*) believe the overlap of Jack Hills Ti thermometry with that for all rock types is permissive of derivation from mafic and felsic protoliths is puzzling. Although a *t* test would show that the Jack Hills population could not be distinguished from the felsic population in figure 2 (*1*), we are confident that the same test would show it is distinctively different from the mafic population, with which it overlaps by only 1°C. We invite these authors to provide an example of a detrital population of ~680°C zircons derived exclusively from a mafic protolith.

Valley *et al*. (*1*) reiterate our summary of the potential complications in using zoned zircons to assess ε_{Hf} with reference to our mixing model but provide no new insights into this issue. If, as they state, "scatter of 18 ε_{Hf} units" could be easily created by incorrectly assigning an age to a Hf isotope composition, then why is the observed distribution of data in the negative ε_{Hf} field [figure 2 in (*2*)] essentially confined to the triangular region between the average continental Lu/Hf and ε_{Hf} = 0, rather than randomly scattered? In contrast to previous studies, we went to great lengths to evaluate the effect that such complexities could have on Hf isotope results, particularly those that deviate significantly from $\varepsilon_{Hf(T)} = 0$. Using the time-resolved signal from the laser ^{176}Hf/^{177}Hf analyses [figure S1 in (*2*)], the relative [U] of cores and rims in the context of the mixing model that we derived, as well as imaging studies, we filtered out those data that were susceptible to calculation artifacts [see SOM in (*2*)]. In any case, use of our refined analytical method, in which coupled measurements of HF and Pb isotopes are made during laser drilling, should clearly resolve this issue.

Finally, Valley *et al*. (*1*) state that our arguments do not yet "uniquely support the hypotheses of plate tectonics and subduction by 4.5 to 4.4 Ga or of complete differentiation of continental crust before 4 Ga…", but we made no such claims (*2*). Rather, we hypothesized, "Jack Hills zircons are largely of continental origin, and our preferred interpretation is that a major differentiation event occurred at 4.4 to 4.5 Ga, producing continental crust and a complementary depleted mantle reservoir. Because the production of modern continental crust is intimately connected with orogenic magmas, our interpretation implies that plate boundary interactions may have begun within the first ~100 My of Earth history." We stand by our view that the simplest explanation of all evidence gathered from >4 Ga zircons is that the Hadean Earth functioned in a broadly similar fashion as today. The comments of Valley *et al*. (*1*) only strengthen the case for our hypothesis.

[1]Department of Earth and Space Sciences and Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095, USA. [2]Research School of Earth Sciences, Australian National University, Canberra, A.C.T. 0200 Australia. [3]Ecole Normale Superieure, CNRS UMR 5570, 69364 Lyon Cedex 7, France. [4]Department of Geology, Royal Holloway University of London, Egham, TW20 0EX, UK. [5]Department of Geological Sciences, University of Colorado, Boulder, CO 80309, USA.

*To whom correspondence should be addressed. E-mail: mark.harrison@anu.edu.au

References

1. J. W. Valley, A. J. Cavosie, B. Fu, W. H. Peck, S. A. Wilde, *Science* **312**, 1139 (2006); www.sciencemag.org/cgi/content/full/312/5777/1139a.
2. T. M. Harrison, J. Blichert-Toft, W. Müller, F. Albarede, P. Holden, S. J. Mojzsis, *Science* **310**, 1947 (2005).
3. R. R. Parrish, S. Noble, *Revs. Min. Geochem*. **53**, 198, Mineralogical Society of America, Washington, DC, J. M. Hanchar, P. W. O. Hoskin, Eds. (2003).
4. E. B. Watson, T. M. Harrison, *Science* **311**, 779c (2006).

27 February 2006; accepted 27 April 2006
10.1126/science.1125408