

**IMPLICATIONS OF HADEAN MINERALOGICAL DIVERSITY FOR ORIGIN OF LIFE STUDIES.** E. A. Bell<sup>1</sup>, D. Trail<sup>1,2</sup>, T. M. Harrison<sup>1</sup>, and P. Boehnke<sup>3,4</sup>; <sup>1</sup>Department of Earth, Planetary & Space Sciences, UCLA, Los Angeles, CA 90095, <sup>2</sup>Department of Earth & Environmental Sciences, University of Rochester, Rochester, NY 14627, <sup>3</sup>Department of the Geophysical Sciences, University of Chicago, Chicago, IL 60637, <sup>4</sup>Chicago Center for Cosmochemistry, Chicago, IL

**Introduction:** Because the Hadean eon (pre-4.03 Ga) is defined by the absence of a terrestrial rock record, acquiring knowledge of what minerals then existed must necessarily be by implication. Neither of the two approaches thus far utilized – thought experiment [1] and documenting primary inclusions in Hadean detrital zircons [2] – is likely to provide a complete inventory, but the former has the potential for serious misdirection.

The presence or absence of key mineral phases during the Hadean has significant implications to the plausibility of certain pathways to life. For example, the RNA World hypothesis posits an evolutionary stage in which self-replicating RNA molecules arose before the emergence of DNA and proteins [3]. Each nucleotide in RNA contains a ribose sugar with attached bases (ACGU) and two phosphate groups. Thus a postulated paucity of terrestrial phosphate minerals on early Earth as a source of reactive phosphorous [4] could have forestalled biopoiesis. The observation of leachable apatite inclusions in Hadean Jack Hills zircons [5] suggests otherwise. Although ribose is unstable in many environments, aqueous solutions containing high borate concentrations stabilize that molecule [6,7,8]. Several authors have argued that borate minerals didn't exist in sufficient quantities when the prebiotic synthesis processes that led to RNA occurred [1,9]. However, laboratory partition experiments coupled with B contents of >4 Ga zircons [10] suggest that Hadean crustal B concentrations were similar to modern Earth.

**Hadean mineral speculations:** Hazen [1] concluded that Hadean Earth supported fewer than 10% of the ~4800 known mineral species and that the “relative Hadean mineralogical parsimony is a consequence of the limited modes of mineral paragenesis prior to 4 Ga”. Four criteria were enumerated that eliminated minerals from consideration as significant Hadean phases. These assumptions are: (1) rare minerals today were never widely distributed or volumetrically significant, (2) minerals arising primarily at convergent boundaries didn't exist because plate tectonics had not yet initiated, (3) biologically-mediated minerals were absent because all life is post-Hadean, and (4) redox-sensitive minerals requiring a high  $f_{O_2}$  didn't predate the Great Oxidation Event. We note that i) since only one quarter of known minerals are documented from >25 localities [1], criterion (1) is also true for all but ~15% of the presently known mineral species, ii) while

there is absolutely no evidence that plate tectonics was not operating on Earth during Hadean times, there is evidence that it may have been [11], and iii) while there is absolutely no evidence that life did not arise during the Hadean, there is some evidence that it might have [12,13]. While redox-sensitive minerals requiring an  $f_{O_2}$  higher than the hematite-magnetite buffer were likely rare on Hadean Earth, local conditions might have supported them in microenvironments [e.g., 13].

**Observed Hadean minerals:** We have thus far identified fourteen minerals as primary inclusions in Hadean Jack Hills zircons [2]. They are: quartz, plagioclase, alkali feldspar, muscovite, biotite, hornblende, sphene, apatite, monazite, ilmenite, rutile, Fe-oxides,  $Al_2SiO_5$ , and graphite [2]. About two-thirds of all documented primary inclusions are quartz and muscovite and thus there appears little question that I- and S-type granitoids coexisted during the Hadean and that the quartz-deficient TTGs were not a significant source [cf. 1].

As a comparator, we surveyed a large number of zircons from Phanerozoic I-, S-, and A-type granitoids and found them to host thirty-one distinct mineral inclusions (i.e., a 0.65% occurrence rate relative to the known total), ranging from the expected granitic species (e.g., quartz, feldspars, micas) to the surprising (e.g., NaCl, Cu). However, as any one locality contains only three to nineteen included mineral species ( $10 \pm 4$ ), the Jack Hills suite could be viewed as reflecting similar mineralogic diversity as today. If a similar scaling relationship exists between these two populations and their respective global mineralogic domains, even comparing overall mineral occurrence rates (i.e., 32:15) would imply that a minimum of 2,000 (i.e.,  $15/0.0065$ ) minerals were present during the Hadean. But many of the ~4,800 known minerals form by fluid interactions in the upper few km of crust, a zone almost exclusive of zircon formation. Thus not finding zeolites, sulfates, borates or other such inclusions in Hadean zircons is not evidence they didn't then exist, but rather that they either haven't yet been observed or were not amenable to capture.

**Summary:** Geochemistry provides no significant limitation on the type or abundance of minerals that may have been present on Hadean Earth. Speculations in the literature that claim to impose such restrictions risk inhibiting thought regarding possible scenarios for the emergence of life on Earth.

**References:**

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