A cool early Earth

John W. Valley*
William H. Peck*
Elizabeth M. King*
Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin 53706, USA
Simon A. Wilde
School of Applied Geology, Curtin University of Technology, GPO Box U1987, Perth, Australia

ABSTRACT

No known rocks have survived from the first 500 m.y. of Earth history, but studies of single zircons suggest that some continental crust formed as early as 4.4 Ga, 160 m.y. after accretion of the Earth, and that surface temperatures were low enough for liquid water. Surface temperatures are inferred from high $\delta^{18}O$ values of zircons. The range of $\delta^{18}O$ values is constant throughout the Archean (4.4–2.6 Ga), suggesting uniformity of processes and conditions. The hypothesis of a cool early Earth suggests long intervals of relatively temperate surface conditions from 4.4 to 4.0 Ga that were conducive to liquid-water oceans and possibly life. Meteorite impacts during this period may have been less frequent than previously thought.

Keywords: Archean, zircon, oxygen, isotopes, meteorites, impacts.

INTRODUCTION

The young Earth (4.5–3.8 Ga) was highly energetic. Sources of heat, both internal and external, were significantly greater than at any time since. The combined energy of planetary accretion, gravitational settling of Earth's metallic core, meteorite impacts, and possibly collision with a Mars-size body was sufficient to melt the entire Earth during its accretion, dated as 4.56–4.45 Ga (Halliday, 2000). Furthermore, before 4.4 Ga, the heat produced by radioactive decay was approximately five times higher than today, not including the effects of short-lived nuclides (Pollack, 1997). Although these events surely caused massive melting before 4.45 Ga, estimates of surface temperatures after 4.45 Ga depend critically on the magnitudes of meteorite bombardment and atmospheric insulation, which are uncertain.

The most direct evidence of past temperatures on the surface of Earth comes from oxygen isotope compositions ($\delta^{18}O$) in rocks; however, no rocks have been identified from the earliest Earth. Dating of lunar rocks (Snyder et al., 2000) indicates a crust by ca. 4.4 Ga, but no such evidence exists on Earth. The oldest known rocks on Earth formed at 4.0 Ga (Bowring and Williams, 1999), and the oldest water-laid sediments are 3.8–3.6 Ga (Nutman et al., 1997; Whitehouse et al., 1999). The absence of rocks older than ca. 4 Ga, taken with other evidence, has been interpreted to suggest a hot early Earth, sometimes called Hadean or ''hell-like,'' in which any crust was destroyed by meteorite impact or melting, all water was vaporized, and the atmosphere was steam rich (see Pollack, 1997).

The only terrestrial materials that are known to be older than 4 Ga are detrital and xenocrystic zircons from Western Australia (see Compston and Pidgeon, 1986; Wilde et al., 2001; Peck et al., 2001; Mojzsis et al., 2001), including a recently discovered crystal from the Jack Hills, Western Australia, with an age of 4.404 Ga (Wilde et al., 2001). At present, these isolated zircon crystals are the only direct evidence of conditions on the earliest Earth.

ZIRCONS

Zircon is a common trace mineral in granitic rocks that preserves detailed records of magma genesis. Zircons also form in mafic rocks or during metamorphism. Zircons provide reliable crystallization ages, magmatic $\delta^{18}O$ values, and magmatic rare earth element (REE) compositions, and may contain inclusions of other cogenetic minerals. These characteristics can be preserved even when a crystal has been removed from its host rock by weathering, transported as a detrital grain, deposited, hydrothermally altered, and metamorphosed (Valley et al., 1994). In well-defined situations, zircons provide information of even earlier events, before magmatic crystallization. Thus, studies of zircon can provide important ground truth for models of the early Earth.

Archean Zircon Record

Figure 1 shows the $\delta^{18}O$ of zircons with measured U-Pb ages of 2.6 to 4.4 Ga (see text and Table DR-1[1]). Figure 2 shows histograms of $\delta^{18}O$ for these samples in comparison to olivine and zircon from Earth's mantle. Several conclusions can be made. There is no systematic trend for $\delta^{18}O$ versus the age of the Archean magmas that represent 40% of the age of Earth. Values average close to the primitive value of Earth's mantle (5.3‰ ± 0.3‰ based on zircon xenocrysts in kimberlite, Fig. 2B; Valley et al., 1998), in high-temperature equilibrium with the value of mantle-derived olivine from peridotite xenoliths and from oceanic island basalts (Fig. 2A; Mattey et al., 1994; Eiler et al., 1997). The average value for Archean igneous zircons from four continents, exclusive of the Jack Hills (Fig. 2C), is 5.6‰, which would be in high-temperature equilibrium with a basalt (whole rock) of ~6‰ or a granite of 6.5‰–7.5‰. The distribution is slightly skewed toward higher values. High values of 7‰–8‰ are found even in the oldest zircon crystal (Fig. 1). Thus, the processes affecting the $\delta^{18}O$ of magmatic zircons show no evidence of change during this period. The relative constancy of $\delta^{18}O$ in Archean zircons is in contrast to zircons younger than 2 Ga, which have magmatic values from 0‰ to 13.5‰ due to evolution of Earth's crust to contain more high $\delta^{18}O$ sediments, evolved ''S-type'' magmas, and hydrothermally altered rocks (Peck et al., 2000).

---

*E-mail: Valley—valley@geology.wisc.edu. Present addresses: Peck—Department of Geology, Colgate University, Hamilton, New York 13346, USA; King—Department of Geography-Geology, Illinois State University, Normal, Illinois 61790, USA.

[1] GSA Data Repository item 2002034, Table DR1, Values of $\delta^{18}O$ and U-Pb ages of zircons from Archean igneous rocks, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

Geology; April 2002; v. 30; no. 4; p. 351–354; 3 figures; Data Repository item 2002034.

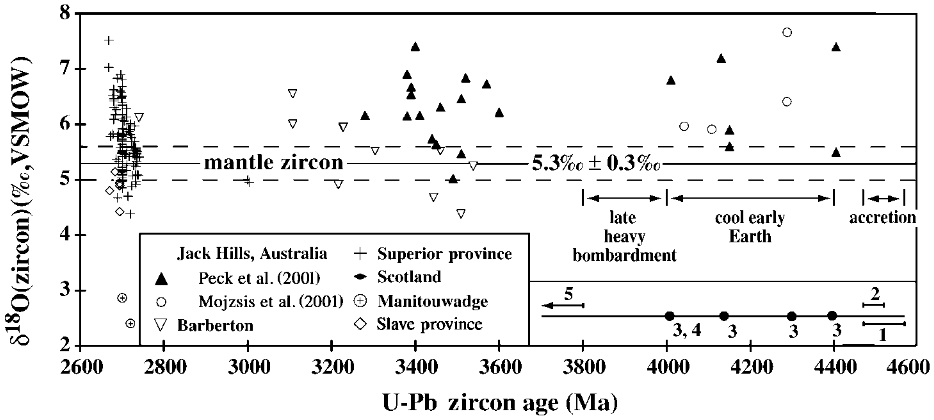

Figure 1. Crystallization age (U-Pb) and δ^{18}O for Archean magmatic zircons. Distribution of magmatic δ^{18}O values does not change throughout Archean. Most magmas had primitive δ^{18}O value similar to that in mantle today (mantle zircon), but some zircon values are as high as 7.5‰. High-δ^{18}O zircons and host magmas resulted from melting of protoliths that were altered by interaction with liquid water at low temperatures near surface of Earth (see text). Time line (inset, lower right) shows: (1) accretion of Earth, (2) formation of Moon and Earth's core, (3) minimum age of liquid water based on high δ^{18}O zircon, (4) Acasta gneiss, and (5) Isua metasedimentary rocks. VSMOW is Vienna standard mean ocean water.

Jack Hills Detrital Zircons

The distribution of δ^{18}O values measured in Jack Hills detrital zircons (Peck et al., 2001; Wilde et al., 2001; Mojzsis et al., 2001) matches that of younger Archean samples (Fig. 1). The only unusual aspect of the oldest zircons is their age. The higher Jack Hills δ^{18}O values (6‰–8‰) are the same as those of zircons from syntectonic to posttectonic sanukitoids (see King et al., 1998) and plutons intruded into metasedimentary rocks (Fig. 2, C and D). In younger granites, such high-δ^{18}O zircons are known to form in magmas with δ^{18}O (whole rock) values to 10‰ (Valley et al., 1994), indicating burial and melting of rocks that were subjected to low-temperature alteration, weathering, or diagenesis (Taylor and Sheppard, 1986; Gregory, 1991). It is significant that such alteration requires liquid water near the surface of Earth. High δ^{18}O values are routinely found in younger granitoids and interpreted to result from interaction of low-temperature liquid water with their protoliths. We conclude that this is also the best interpretation for the protoliths of magmas that formed Jack Hills zircons.

Figure 1 shows that the higher values of δ^{18}O are evenly distributed throughout the Archean, including the value of 7.4‰ ± 0.7‰ from two analyses of the core of the 4.4 Ga Jack Hills zircon (Peck et al., 2001). Because of the unique significance of this single zircon crystal, all processes to account for the high δ^{18}O value have been considered. Possible scenarios include: (1) formation in a meteorite, (2) fractional crystallization of the host granitic magma from a primitive terrestrial melt at 4.4 Ga, (3) exchange of the protolith of the granitic magma with steam rather than liquid water, and (4) exchange of the protolith with liquid water.

Any model should consider the features of this 4.4 Ga zircon: finely concentric magmatic zoning as revealed by cathodoluminescence; REE patterns that include negative Eu and positive Ce anomalies, and heavy-REE enrichments to ∼10 000 times chondrites; zoning in δ^{18}O that correlates to trace element zoning (7.4‰ vs. 5.0‰); inclusions of SiO_2 that indicate a quartz-saturated granitic magma; and a Pb-Pb age of 4.404 ± 8 Ga with >99% concordant U-Pb ages (Peck et al., 2001; Wilde et al., 2001).

Could the 4.4 Ga Jack Hills zircon be extraterrestrial in origin? Zircons as old as 4.32 Ga occur in lunar granophyre (Meyer et al., 1996; Snyder et al., 2000); however, the combination of high δ^{18}O values, quartz saturation, and enriched REE compositions are not consistent with formation on the Moon or in any known meteorite. Furthermore, meteoritic zircons are very rare on Earth. The close similarity of the 4.4 Ga crystal to other zircons in the same rock suggests that they all formed on the same planetary body. Clearly, the Jack Hills zircons did not all come from meteorites.

The chemical compositions of Jack Hills zircons are characteristic of those from continental-type crust on Earth, such as might have chemically differentiated from the mantle in a tectonic environment similar to Iceland today. However, there are no known high-δ^{18}O reservoirs in the mantle. Rare high values in young mantle-derived basalts either result from crustal contamination or from subduction of hydrothermally altered crust (Eiler et al., 1997). It is possible to raise the δ^{18}O of a magma by 1‰–2‰ through fractional crystallization and separation of low-δ^{18}O mafic minerals (Taylor and Sheppard, 1986). However, this process would not be sufficient to explain the δ^{18}O of 8‰–10‰ for the magma inferred from the Jack Hills sample. Furthermore, at magmatic temperatures, the δ^{18}O of a zircon in equilibrium with such an evolving magma would be constant because the fractionation, Δ^{18}O (magma-zircon), would increase at approximately the same rate as δ^{18}O (magma) due to the increasing felsic component of the melt. Thus, high δ^{18}O zircons suggest supracrustal input to magmas.

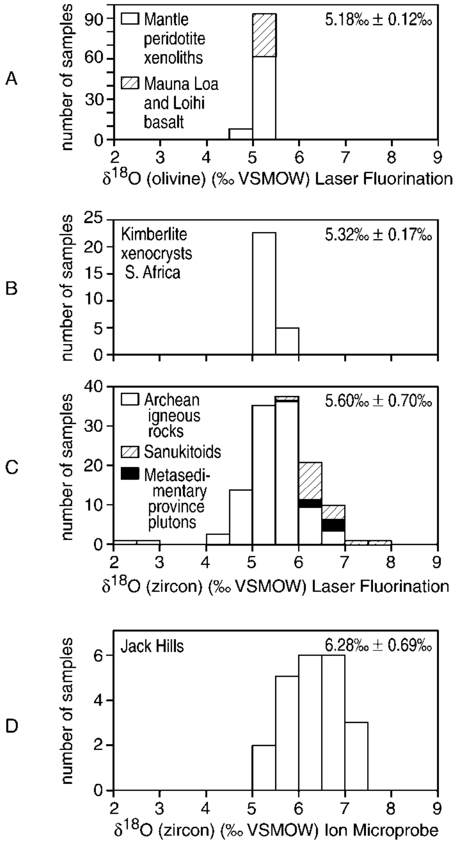

Figure 2. Histograms of δ^{18}O. A: Olivine from mantle xenoliths (Mattey et al., 1994) and Hawaiian basalts (Eiler et al., 1997). B: Zircon xenocrysts from kimberlites in South Africa (Valley et al., 1998). C: Zircons from igneous rocks of Superior province, Canada (King et al., 1998). D: Ion microprobe analyses of single zircons from Jack Hills, Western Australia (Peck et al., 2001). Superior province histogram (C) peaks at mantle δ^{18}O value with tail toward higher values. Jack Hills zircons (D) are higher in δ^{18}O than mantle. VSMOW is Vienna standard mean ocean water.

SURFACE OF EARTH AT 4.4–4.0 Ga

The constancy of δ^{18}O for zircons over the period 4.4–2.6 Ga (Fig. 1) suggests that the magmatic processes and protoliths at 4.4–4.0 Ga were similar to those at 3.8–2.6 Ga. This similarity would not be expected if the older rocks formed in the absence of water and younger rocks were derived from hydrothermally altered material (see also Campbell and Taylor, 1983). Liquid-water oceans were required by 3.8–3.6 Ga to precipitate chemical sediments found in Greenland (Nutman et al., 1997; Whitehouse et al., 1999), and by 3.5 Ga, sedimentary rocks, stromatolites, and pillow basalts indicate widespread submarine conditions. Thus, the constancy of $\delta^{18}O$ and the presence of granitoids suggest not only that there were oceans back to 4.4 Ga, but also that surface temperatures were not too dissimilar from those of younger periods.

Limits on temperature for near-surface alteration of the protolith of the high-$\delta^{18}O$ 4.4 Ga magma can be calculated from the $\delta^{18}O$ of the early hydrosphere, the fractionation of $^{18}O/^{16}O$ between basalt (or granite) and water, and the stability of liquid water versus steam. Temperatures must have been in the range that would elevate $\delta^{18}O$ by exchange with surface waters. Compositions of hydrothermally altered upper ($\delta^{18}O > 6‰$) and lower ($\delta^{18}O < 6‰$) ocean crust have not significantly changed through time, suggesting that $\delta^{18}O$ (seawater) $\approx 0‰$ for at least the past 3.6 b.y. (Gregory, 1991). If fully equilibrated, $\delta^{18}O$ (basalt) is 8‰ at ~200 °C in equilibrium with liquid water ($\delta^{18}O = 0$) and 250 °C with steam. These are common temperatures for seawater alteration of the upper ocean crust (Gregory, 1991). Thus a seawater-dominated hydrothermal system will raise the $\delta^{18}O$ of basalt to 8‰ only at ''low'' temperatures below 200 °C for liquid water oceans. Meteoric waters are lower in $\delta^{18}O$ than seawater and thus exchange with fresh water would make calculated temperatures lower. If the amount of water was limited or exchange was not fully equilibrated, then the temperature estimate would also be lower.

The question arises, could such exchange be dominated by steam at 100–250 °C? If no oceans existed on modern Earth and all water formed a steam atmosphere, the atmospheric pressure would be ~270 bar (Zahnle et al., 1988), which is above the critical point of water (220 bar). A boiling-ocean and steam-atmosphere system would be buffered in pressure and temperature along the liquid-vapor phase transition, and today's ocean volume would require temperatures above the critical point of water (~374 °C depending on salinity) to completely vaporize. The temperature for H_2O as 100% steam (>374 °C) is significantly above the range (<200 °C) indicated by the high $\delta^{18}O$ (zircon) values. Furthermore, the processes by which large volumes of crust become hydrothermally altered require that fluids recirculate and that the ratio of water to rock be $\gg 1$ (by weight) in order to raise $\delta^{18}O$ in protolith of zircon-forming magmas. Steam is known to discharge readily from hydrothermal systems, but not to recharge them. It is unlikely that a low-density vapor efficiently penetrated to sufficient depths in the crust to alter the protolith of the 4.4 Ga zircon-forming magma. Thus, the best explanation of existing data is that surface temperatures were below ~200 °C at 4.4 Ga. This temperature is in the range of liquid water for a modern-size hydrosphere and is low enough to cause partial or complete condensation of a steam atmosphere to form oceans.

IMPLICATIONS OF A COOL EARLY EARTH

The conclusion that liquid water was prevalent as early as 4.4 Ga is consistent with the energetic nature of early Earth, but provides an important boundary condition. Significant uncertainties exist in models for the sources and timing of the early high-energy events. Low surface temperatures and liquid water are easier to reconcile with these models if: (1) core formation and the genesis of the Moon were earlier than 4.45 Ga, allowing more time for cooling; (2) if the Moon formed by some process other than impact by a Mars-size body; (3) if atmospheric insulation was low; or (4) if the meteorite bombardment of Earth from 4.4 to 4.0 Ga was less intense than has been proposed.

The formation of the Moon and segregation of Earth's core were recently dated as 4.5 Ga by Halliday and coworkers (see Halliday, 2000), and although the impact model for forming the Moon is widely accepted, significant questions persist (see Jones and Palme, 2000). If the Moon did form by impact, a large, relatively late addition to the heat and mass of Earth is indicated. Alternatively, capture of a planetesimal would not cause additional heating of Earth. Either nonimpact or an earlier date are consistent with Xe-closure estimates that suggest that Earth has not melted since 4.45 Ga, but that a major disturbance occurred before that time (see Podosek and Ozima, 2000). Planet-scale closure to rare-gas escape would not date a melting event, but rather would record the later solidification of crust sufficient to retard outgassing. Thus, considerable cooling had already occurred by 4.45 Ga.

The nature and timing or even existence of magma oceans is uncertain (Newson and Jones, 1990). Although it is possible that Earth was fully melted before 4.45 Ga, crystallization of such a magma ocean has been modeled to occur on the scale of 1–10 m.y. in the absence of atmospheric insulation (Spohn and Schubert, 1991; Pollack, 1997).

Before 4.45 Ga, the hydrosphere was surely 100% vapor, but the nature of this atmosphere depends on the composition and quantity of volatiles. Large impacts might have stripped Earth of its atmosphere, facilitating radiative cooling. Conversely, a thick insulating atmosphere might have absorbed radiated energy, raising surface temperatures by more than 100 °C (Abe et al., 2000). Even with significant insulation, Earth's surface could have cooled to within the stability of liquid water as indicated by high $\delta^{18}O$ zircons. Cooler surface conditions would be enhanced by lower solar luminosity.

Meteorite Bombardment

The most significant addition of energy to the surface of Earth from 4.4 to 3.8 Ga may have been meteorite impacts. Although the crater record on Earth has been destroyed by tectonics, the rate of early meteorite bombardment of the inner Solar System can be estimated by examination of craters on well-preserved surfaces of the Moon and Mars. On the Moon, where craters have been dated, the time-integrated flux of meteoritic material from 4.4 to 3.8 Ga is estimated by surveying crater density, measuring the addition of siderophile elements such as Ir to the lunar crust, and determining the extent of impact stirring or gardening of the crust (Arrhenius and Lepland, 2000; Hartmann et al., 2000). However, the relation of meteorite flux to age is not uniquely determined. Hartmann et al. (2000) reviewed these studies and estimated that the meteorite flux was 2×10^9 times greater at the beginning of accretion of the Earth than today (Fig. 3, dashed line), and the flux declined rapidly such that most of Earth's mass was acquired during the first 10–100 m.y.

Accretion of the Earth was essentially complete by ca. 4.45 Ga; however, two models exist for the subsequent period. A high meteorite flux has long been recognized ca. 3.9 Ga, suggesting higher flux for the period 4.45–3.9 (Fig. 3, dashes). However, recent Ar-Ar dating of lunar impact glasses supports earlier proposals of an alternate hypothesis, that late heavy bombardment at 3.9 Ga was caused by processes in the outer Solar System, by deflection of asteroids, or by collisions of geocentric material (Tera et al., 1974; Cohen et al., 2000). If Earth was subjected to a spike of meteorite bombardment ca. 3.9 Ga, then interpolation between 3.9 and 4.5 Ga would be incorrect, and the period from 4.4 to 4.0 Ga might have been relatively tranquil (Arrhenius and Lepland, 2000; Hartmann et al., 2000), consistent with cooler surface temperatures (Fig. 3, solid line).

The evidence for liquid water is consistent with a cool early Earth and heavy bombardment at 4.0–3.8 Ga. The four high-$\delta^{18}O$, pre–4.0 Ga zircons each must be younger than the time of liquid water interaction with their magmatic protoliths; hence, these dates are shown as minimum ages at the top of Figure 3. The chemically precipitated sedimentary rocks from Greenland could have been deposited at 3.6 or 3.8 Ga (Nutman et al., 1997; Whitehouse et al., 1999). At present, there is no zircon evidence for liquid water during the

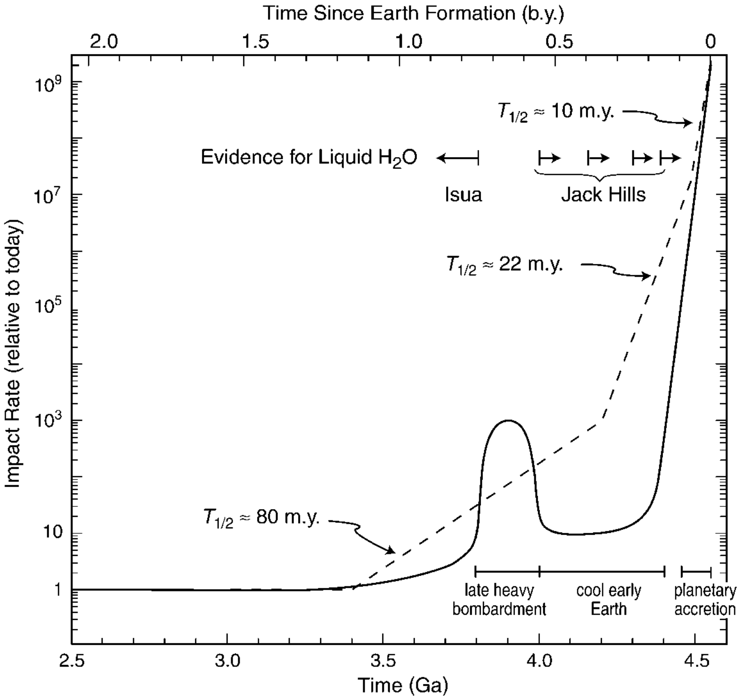

Figure 3. Estimates of meteorite-impact rate for first 2 b.y. of Earth history. Two hypotheses are shown: exponential decay of impact rate (dashes, Hartmann et al., 2000) and cool early Earth–late heavy bombardment (solid curve, this study). Approximate half-life is given in million years for periods of exponential decline in flux. In either model, spikes occurred owing to isolated large impacts. Evidence for liquid water comes from high-δ^{18}O zircons (>4.4 to >4.0 Ga) and sedimentary rocks (Isua, 3.8–3.6 Ga). The cool early Earth hypothesis (solid curve) suggests that impact rates had dropped precipitously by 4.4 Ga, consistent with relatively cool conditions and liquid water.

late heavy bombardment, and more data are being sought. The earlier period, 4.4–4.0 Ga, is called Hadean by some. However, we suggest that Earth was not ''hell-like'' then and may have been hospitable to the earliest life.

ACKNOWLEDGMENTS

We thank Mary Diman, Colin Graham, Henry Pollack, Mike Spicuzza, Allan Treiman, and two reviewers for comments on and assistance with various aspects of this paper. Research was funded by the National Science Foundation (EAR-99-02973) and the Department of Energy (93ER14389).

REFERENCES CITED

Arrhenius, G., and Lepland, A., 2000, Accretion of Moon and Earth and the emergence of life: Chemical Geology, v. 169, p. 69–82.

Bowring, S.A., and Williams, I.S., 1999, Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada: Contributions to Mineralogy and Petrology, v. 134, p. 3–16.

Campbell, I.H., and Taylor, S.R., 1983, No water, no granites—No oceans, no continents: Geophysical Research Letters, v. 10, p. 1061–1064.

Cohen, B.A., Swindle, T.D., and Kring, D.A., 2000, Support for the lunar cataclysm hypothesis from Lunar meteorite impact melt ages: Science, v. 290, p. 1754–1756.

Compston, W., and Pidgeon, R.T., 1986, Jack Hills, evidence of more very old detrital zircons in Western Australia: Nature, v. 321, p. 766–769.

Eiler, J.M., Farley, K.A., Valley, J.W., Hauri, E., Craig, H., Hart, S.R., and Stolper, E.M., 1997, Oxygen isotope variations in ocean island basalt phenocrysts: Geochimica et Cosmochimica Acta, v. 61, p. 2281–2293.

Gregory, R.T., 1991, Oxygen history of seawater revisited: Timescales for boundary event changes in the oxygen isotope composition of seawater, *in* Taylor, H.P., et al., eds., Stable isotope geochemistry: San Antonio, Texas, Lancaster Press, p. 65–76.

Halliday, A.N., 2000, Terrestrial accretion rates and the origin of the Moon: Earth and Planetary Science Letters, v. 176, p. 17–30.

Hartmann, W.K., Ryder, G., Dones, L., and Grinspoon, D., 2000, The time-dependent intense bombardment of the primordial Earth/Moon system, *in* Canup, R.M., and Righter, K., eds., Origin of the Earth and Moon: Tucson, University of Arizona Press, p. 493–512.

Jones, J.H., and Palme, H., 2000, Geochemical constraints on the origin of the Earth and Moon, *in* Canup, R.M., and Righter, K., eds., Origin of the Earth and Moon: Tucson, University of Arizona Press, p. 197–216.

King, E.M., Valley, J.W., Davis, D.W., and Edwards, G.R., 1998, Oxygen isotope ratios of Archean plutonic zircons from granite-greenstone belts of the Superior province: Indicator of magmatic source: Precambrian Research, v. 92, p. 365–387.

Mattey, D., Lowry, D., and Macpherson, C., 1994, Oxygen isotope composition of mantle peridotite: Earth and Planetary Science Letters, v. 128, p. 231–241.

Meyer, C., Williams, I.S., and Compston, W., 1996, Uranium-lead ages for lunar zircons: Evidence for a prolonged period of granophyre formation from 4.32 to 3.88 Ga: Meteoritics and Planetary Science, v. 31, p. 370–387.

Mojzsis, S.J., Harrison, T.M., and Pidgeon, R.T., 2001, Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4300 Myr ago: Nature, v. 409, p. 178–181.

Newson, H.E., and Jones, J.H., 1990, Origin of the Earth: Oxford, Oxford University Press.

Nutman, A.P., Mojzsis, S.J., and Friend, C.R.L., 1997, Recognition of $\geq$3850 Ma water-lain sediments in West Greenland and their significance for the early Archean Earth: Geochimica et Cosmochimica Acta, v. 61, p. 2475–2484.

Peck, W.H., King, E.M., and Valley, J.W., 2000, Oxygen isotope perspective on Precambrian crustal growth and maturation: Geology, v. 28, p. 363–366.

Peck, W.H., Valley, J.W., Wilde, S.A., and Graham, C.M., 2001, Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high δ^{18}O continental crust in the early Archean: Geochimica et Cosmochimica Acta, v. 65, p. 4215–4229.

Podosek, F.A., and Ozima, M., 2000, The xenon age of the Earth, *in* Canup, R.M., and Righter, K., eds., Origin of the Earth and Moon: Tucson, University of Arizona Press, p. 63–72.

Pollack, H.N., 1997, Thermal characteristics of the Archaean, *in* deWit, M., and Ashwal, L., eds., Greenstone belts: Oxford, Oxford University Press, p. 223–232.

Snyder, G.A., Borg, L.E., Nyquist, L.E., and Taylor, L.A., 2000, Chronology and isotopic constraints on lunar evolution, *in* Canup, R.M., and Righter, K., eds., Origin of the Earth and Moon: Tucson, University of Arizona Press, p. 361–395.

Spohn, T., and Schubert, G., 1991, Thermal equilibration of the Earth following a giant impact: Geophysical Journal International, v. 107, p. 163–170.

Taylor, H.P., and Sheppard, S.M.F., 1986, Igneous rocks; I. Processes of isotopic fractionation and isotope systematics, *in* Valley, J.W., et al., eds., Stable isotopes in high temperature geological processes: Mineralogical Society of America Reviews in Mineralogy, v. 16, p. 227–271.

Tera, F., Papanastassiou, D.A., and Wasserburg, G.J., 1974, Isotopic evidence for a terminal lunar cataclysm: Earth and Planetary Science Letters, v. 22, p. 1–21.

Valley, J.W., Chiarenzelli, J.R., and McLelland, J.M., 1994, Oxygen isotope geochemistry of zircon: Earth and Planetary Science Letters, v. 126, p. 187–206.

Valley, J.W., Kinny, P.D., Schulze, D.J., and Spicuzza, M.J., 1998, Zircon megacrysts from kimberlite; oxygen isotope variability among mantle melts: Contributions to Mineralogy and Petrology, v. 133, p. 1–11.

Whitehouse, M.J., Kamber, B.S., and Moorbath, S., 1999, Age significance of U-Th-Pb zircon data from early Archean rocks of west Greenland: A reassessment based on combined ion-microprobe and imaging studies: Chemical Geology, v. 160, p. 201–224.

Wilde, S.A., Valley, J.W., Peck, W.H., and Graham, C.M., 2001, Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 gyr ago: Nature, v. 409, p. 175–178.

Zahnle, K.J., Kasting, J.F., and Pollack, J.B., 1988, Evolution of a steam atmosphere during Earth's accretion: Icarus, v. 74, p. 62–97.

Manuscript received July 31, 2001
Revised manuscript received December 12, 2001
Manuscript accepted December 19, 2001

Printed in USA