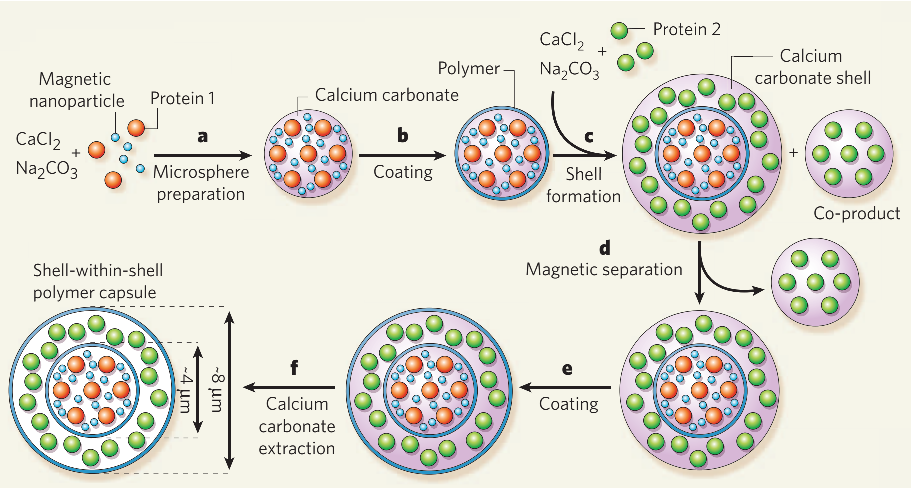

Figure 1 | Polymer shells within shells. Kreft *et al.*[1] have prepared polymeric shell-within-shell capsules. **a**, The authors prepared calcium-carbonate microspheres in which magnetic nanoparticles and a protein were embedded. **b**, The spheres acted as templates for a polymer film. **c**, The authors then deposited a thick shell of calcium carbonate in which a different protein was embedded, and (**d**) separated the desired material from co-products using a magnet. **e**, A second polymer layer was deposited on the outer sphere. **f**, Finally, the authors extracted the calcium carbonate to leave behind a polymeric shell-within-shell structure, with different proteins trapped in separate compartments. (Figure adapted with permission from ref. 1.)

surrounded by a separate solution of the other polymer. Such a system lacks a semi-permeable membrane to separate the two solutions, but has the advantage that the whole thing can easily be triggered to break down using various stimuli, such as heating; this is potentially useful for applications in which the capsule is being used as a delivery system. In comparison, Kreft and colleagues' approach yields physically robust shells, but these could, in principle, be made with degradable polymers.

Kreft *et al.* comment[1] that one of the long-term goals of their work is to produce drug-delivery systems that can release drugs in a controlled manner, or in response to a biological trigger. For this application, biodegradable multilayered materials are especially useful. Interestingly, several such polymeric materials are about as compliant[6] as cell and nuclear membranes[7] — that is, their tendency to revert back to their original shape upon the removal of a distorting force matches that of their biological counterparts. Physical properties such as compliance are surprisingly important in determining the compatibility of materials with biological systems. For example, it is now known that flexible objects are less prone to being engulfed by phagocytic cells, which clear foreign particles from the bloodstream and often prevent drug-delivery systems from working[8]. The ability to eliminate rigidity from drug-delivery systems makes Kreft and colleagues' decalcification approach[1] even more attractive.

A grander challenge for LbL assembly is to prepare functional mimics of nucleated cells. Perhaps the ingredients for transcribing DNA into messenger RNA could be trapped in the synthetic nucleus of a cell mimic; the RNA could then be translated into proteins in the surrounding 'cytoplasm'. This is undoubtedly ambitious, but such systems might help answer a fundamental question of biology: why do cells store DNA in a nucleus? Regardless of the directions pursued, Kreft and colleagues' mild method for the LbL assembly of nucleated systems and compartmentalized reactions is likely to stimulate the work of materials scientists for years to come. ■

Catherine Picart is at the Université Montpellier 2, Montpellier, CEDEX 5, 34095, France. Dennis E. Discher is in the Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA.
e-mail: discher@seas.upenn.edu

1. Kreft, O., Prevot, M., Mohwald, H. & Sukhorukov, G. B. *Angew. Chem. Int. Edn* **46,** 5605–5608 (2007).
2. Tang, Z., Wang, Y., Podsiadlo, P. & Kotov, N. A. *Adv. Mater.* **18,** 3203–3224 (2006).
3. Neu, B. *et al. J. Microencapsulation* **18,** 385–395 (2001).
4. Johnston, A. P. & Caruso, F. *Angew. Chem. Int. Edn* **46,** 2677–2680 (2007).
5. Long, M. S., Jones, C. D., Helfrich, M. R., Mangeney-Slavin, L. K. & Keating, C. D. *Proc. Natl Acad. Sci. USA* **102,** 5920–5925 (2005).
6. Richert, L., Engler, A. J., Discher, D. E. & Picart, C. *Biomacromol.* **5,** 1908–1916 (2004).
7. Dahl, K. N., Kahn, S. M., Wilson, K. L. & Discher, D. E. *J. Cell Sci.* **117,** 4779–4786 (2004).
8. Beningo, K. A. & Wang, Y. L. *J. Cell Sci.* **115,** 849–856 (2002).

EARTH SCIENCE

Old diamonds and the upper crust

Ian S. Williams

Was the early Earth a blackened landscape of congealed lava, or was it cool enough for oceans to form? The discovery of diamonds in the oldest-known relics of surface rocks adds new élan to this debate.

The earliest era of Earth's history — between the creation of the planet about 4.5 billion years ago and the formation of the oldest known rocks 500 million years later — is the geological equivalent of the Dark Ages. The formal name given to the period, the Hadean, matches the long-held view that during this time Earth's entire surface, or at least large tracts of it, was a hellish, seething mass of molten lava. In contrast to that picture, recent studies of the oldest known relics of surface rocks, tiny and rare crystals of the trace mineral zircon ($ZrSiO_4$), indicate that it took less than 200 million years for Earth's surface to cool sufficiently for water to condense. Menneken and colleagues' discovery[1] (page 917 of this issue) that some of those ancient zircon crystals contain tiny diamonds turns the field on its head once more. The results lend succour to the view that the initial hot phase was long-lived, and will invigorate questioning of the cool-Earth concept.

As Earth grew in the dust cloud around the proto-Sun, probably colliding with a planet the size of Mars during the process, surface temperatures would have reached in excess of 6,000 °C (ref. 2). When the surface eventually cooled, solid rocks started to form, but what those rocks were like, and when the formation process started, are controversial questions. The problem is one of preservation. Intense meteorite bombardment destroyed much of the early crustal rock, and with it evidence of Earth's early environment. In addition, Earth is an active planet on which crustal rocks are continuously destroyed by weathering and erosion, and recycled deep into the interior through plate tectonics. These processes have been going on for at least 3.8 billion years, and so very few crustal rocks older than 3.7 billion years — and none older than 4.03 billion years — are known.

The only surviving relics of Earth's crust from those first 500 million years of the planet's history are zircon crystals, mostly recovered from slightly less ancient sedimentary rocks[3]. Zircon is a tough mineral: it is both chemically and physically inert under a wide range of geological conditions. As a result, zircon grains formed in old igneous and metamorphic rocks are commonly recycled unchanged into younger rocks.

Figure 1 | Treasure trove. Menneken and colleagues[1] found diamonds in zircons, the earliest known remnants of Earth's crustal rocks that occur in conglomerates at Jack Hills in Western Australia.

Hadean zircon grains are small (less than 0.3 mm in diameter) and rare: so far only two rocks, both from Western Australia, have been found with an 'abundance' of the grains (which means about 1 part per million by weight). Fortunately for those studying the early Earth, these tiny grains carry a remarkable amount of information about the rocks in which they crystallized. That information can be extracted through a range of modern techniques that allow growth zones in individual zircon grains to be analysed on a scale of a few micrometres.

For example, uranium, thorium and lead isotopes provide an accurate measure of a grain's age[3]; zoning textures[4] and patterns of rare-earth elements[5] distinguish igneous from metamorphic growth; and microinclusions of other minerals show the mineralogy of the original host rock[5]. The more titanium a zircon grain contains, the higher its crystallization temperature was[6]; and the greater the grain's enrichment in the oxygen isotope ^{18}O, the more the magma from which the zircon crystallized interacted with liquid surface water[7,8]. The hafnium isotopic ratio ^{176}Hf/^{177}Hf indicates whether that magma was purely mantle-derived (high initial value) or contained a crustal component (low initial value)[8,9]. Finally, xenon isotopes, among them the fission products of the extinct plutonium isotope ^{244}Pu, provide some of the most direct evidence available that Earth formed with a plutonium–uranium ratio similar to that of the Sun[10].

Some of the conclusions reached on this basis have been challenged, principally on the grounds that some of the compositions measured do not accurately reflect the temperature or the primary chemical and isotopic compositions of the magmas from which the zircons crystallized. But a majority view prevails. Hadean zircons are mostly of igneous origin, and crystallized in a series of events that occurred mainly between 4.25 and 4.00 billion years ago; crystallization temperatures averaged only about 680 °C (ref. 8); the host magmas had compositions similar to granites, and were produced by the melting of mixtures of crustal and mantle rocks; and the crustal rocks had interacted with liquid water at or near Earth's surface. All in all, this is convincing evidence that there were at least some periods during Earth's early history when its surface was cool.

The discovery by Menneken *et al.*[1] of microdiamond inclusions in about 1 in 20 zircons, ranging in age from 4.3 to 3.1 billion years, that were randomly selected from the original Jack Hills conglomerate site in Western Australia[3] (Fig. 1), will necessitate a careful reassessment of these conclusions. Diamond is a mineral that forms only at high pressures, whether these are transient (during, for example, a meteorite impact) or sustained (through deep burial, for instance). It is therefore not found in low-temperature granite magmas such as those in which the Hadean zircons are inferred to have crystallized.

Assuming that the zircon did crystallize at temperatures of about 680 °C, pressures exceeding 3.5 gigapascals would have been needed for diamond to be stable in the magma source. This pressure is equivalent to burial more than 100 kilometres below Earth's surface. But the Jack Hills zircons show no other evidence of such high pressures — whether transient in the form of shock features, or sustained in the form of relics of other high-pressure minerals, metamorphic overgrowths or rare-earth element compositions indicative of high-pressure growth. If the evidence of the diamonds is correct and the Hadean zircons did crystallize from magmas at high pressure, then those magmas could not have been crustal melts. This would undermine other inferences based on the assumption that the zircons preserve their original chemical and isotopic compositions — including the deduction that the early Earth was cool.

Menneken *et al.*[1] present two possible explanations for the presence of diamonds in zircons of such a wide age range. Either the diamonds formed during a single high-pressure event about 4.3 billion years ago and were then recycled into younger rocks, or they were incorporated into the Hadean zircons by an undefined process that was repeated several times during the first billion or so years of Earth's history. Neither of these explanations is entirely convincing, and the implications for surface temperatures on the early Earth are not discussed.

A possible explanation that does not contradict the evidence for a cool early Earth is that the diamond was introduced to the zircon not as diamond, but as graphite precipitated into fractures and other imperfections in the zircon grains. De Corte *et al.*[11], for example, have studied microdiamond inclusions in zircon from rocks subjected to ultra-high pressure in the Kokchetav Massif in northern Kazakhstan. They concluded that the original carbon that the diamonds were formed from was precipitated through the reaction of carbon dioxide with a reduced carbon phase such as methane.

One can conceive of a process in which a segment of early crust containing zircon from low-pressure igneous rocks of different ages became impregnated with carbon-rich fluids, possibly produced by reactions involving an atmosphere enriched in carbon monoxide, carbon dioxide and methane[12]. Rapid deep burial of those rocks by subduction (horizontal tectonics), sagduction (vertical tectonics) or mantle overturn[12] could then have formed diamond in zircon of various ages during a single event, possibly without changing the zircons' chemical and isotopic compositions. During subsequent uplift, metastable diamond trapped in zircon grains could have been preserved, with some partly reverting to graphite — as indeed is observed[1].

Whether the diamond was indeed produced by such a relatively rapid process, or was of long-lived mantle origin, could be tested by examining its carbon isotopic composition and whether nitrogen is present as single nitrogen atoms (indicating little time spent in the mantle at relatively low temperatures) or nitrogen pairs and tetrahedra (long residence time at relatively high temperatures)[13]. Such tests will be needed to further the lively debate on whether the early Earth was hot, or not. ■

Ian S. Williams is in the Research School of Earth Sciences, The Australian National University, Canberra, ACT, 0200, Australia.
e-mail: ian.williams@anu.edu.au

1. Menneken, M., Nemchin, A. A., Geisler, T., Pidgeon, R. T. & Wilde, S. A. *Nature* **448,** 917–920 (2007).
2. Benz, W. & Cameron, A. G. W. in *Origin of the Earth* (eds Newsom, H. E. & Jones, J. H.) 61–67 (Oxford Univ. Press, New York, 1990).
3. Compston, W. & Pidgeon, R. T. *Nature* **321,** 766–769 (1986).
4. Cavosie, A. J., Wilde, S. A., Liu, D., Weiblen, P. W. & Valley, J. W. *Precamb. Res.* **135,** 251–279 (2004).
5. Maas, R., Kinny, P. D., Williams, I. S., Froude, D. O. & Compston, W. *Geochim. Cosmochim. Acta* **56,** 1281–1300 (1992).
6. Watson, E. B. & Harrison, T. M. *Science* **308,** 841–844 (2005).
7. Wilde, S. A., Valley, J. W., Peck, W. H. & Graham, C. M. *Nature* **409,** 175–178 (2001).
8. Trail, D. *et al. Geochem. Geophys. Geosyst.* **8,** Q06014 doi:10.1029/2006GC001449 (2007).
9. Amelin, Y., Lee, D.-C., Halliday, A. N. & Pidgeon, R. T. *Nature* **399,** 252–255 (1999).
10. Turner, G., Harrison, T. M., Holland, G., Mojzsis, S. J. & Gilmour, J. *Science* **306,** 89–91 (2004).
11. De Corte, K. *et al. Island Arc* **9,** 428–438 (2000).
12. Kramers, J. D. *J. Geol. Soc.* **164,** 3–17 (2007).
13. Taylor, W. R., Canil, D. & Milledge, H. J. *Geochim. Cosmochim. Acta* **60,** 4725–4733 (1996).