

Materials science

Diamonds from warm water

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There is a revival of interest in growing diamonds hydrothermally in the laboratory, but it has met with questionable success. One dream is to grow large diamond crystals in mild conditions, at about 500 °C and 1 kbar (a thousand atmospheres), in the manner so successful with quartz and emerald. A more reasonable expectation may be the extension of our knowledge about how natural diamonds grow. On page 513 of this issue¹, Zhao and colleagues present the latest efforts to grow diamond under relatively low pressure and temperature, using a solution of nickel and carbon in water.

Carbon can be made into diamond directly by compression, both in industry and in nature (in meteorite impacts, for example). That requires a pressure above about 120 kbar and a temperature of about 2,000 °C. At lower pressure and temperature (50 kbar and 1,400 °C), indirect, static conversion via solutions of carbon in iron and/or nickel occurs on a large scale every day in factories all over the world, to produce small, abrasive diamond grains with metal inclusions. If diamond is still stable at core-of-the-Earth pressures (3.6 Mbar), and if there's enough carbon present in the iron down there, we might expect the same process to produce large diamond crystals (perhaps even Scott Fitzgerald's "Diamond as big as the Ritz"). But there is a third route, the hydrothermal process, which may be responsible for most natural diamonds.

Most diamonds that we know about have come into the crust along paths that tapped at least the upper mantle, and perhaps the deeper mantle too. There are still many mysteries in the genesis of natural diamonds, but it is clear that they are remarkably free of metallic elements (that is one way to differentiate synthesized from natural diamond gemstones). So metal-carbon solutions do not appear to be involved in diamond growth in the mantle and above.

Other inclusions in natural diamonds (such as silicates and sulphides) are a prolific source of information about the growth environment. But more pertinent to hydrothermal synthesis is the clear evidence for carbon, hydrogen and oxygen in the form of various liquid phases of the C-H-O system. The presence of oxygen and hydrogen in diamond has been known for a long time², but characterization of 'coated diamond' — a poor-quality, fibrous diamond layer overgrown on a more homogeneous base — strongly supports the presence of liquid C-H-O phases during diamond growth³. The chemistry of graphite in equilibrium

with water in this system has been clearly established⁴, and it is a reasonable assumption that, with increased pressure, diamond would form from the same chemistry. The very small diamonds found in metamorphic rocks⁵ probably grew from similar C-H-O liquids.

It is pertinent that the major breakthrough in diamond synthesis after the early high-pressure successes was chemical vapour deposition of diamond⁶ at less than one atmosphere and 1,000 °C, in the C-H and C-H-O systems. It can also be grown from metal-C-H systems at similar pressure and temperature⁷. The mechanism depends on the presence of atomic hydrogen, which is probably not involved in hydrothermal growth, but the idea of a broad continuum of diamond stability is still valid. Diamond deposition also occurs in molten NaOH in the presence of nickel and carbon^{7,8}, and carbon with a high level of *sp*³ bonding (as in diamond) can be deposited by the reaction of Al₄C₃ and CCl₄ in a molten halide melt at a pressure of just one atmosphere⁹. The problem is how to capitalize on these clues.

Zhao *et al.*¹ appear to have achieved diamond-on-diamond deposition under hydrothermal conditions in the presence of nickel and vitreous carbon, at 800 °C and 1.4 kbar. Their problem is proving that there is new growth of diamond in the presence of diamond seeds. The same difficulty was faced by the early workers in chemical vapour deposition, and there are still sceptics who question whether any success was achieved in that technique until the Russians grew crystals visible to the eye.

A common problem in this field is diamond fever, a disease that enables one to see diamonds where they are not. Many have succumbed to this affliction. But the authors are aware of the

problem and have brought all their resources (electron microscopy, energy-dispersive X-rays, Raman scattering, and their intuition) to bear on the grains they have produced. They conclude that "...aggregates, tens of micrometres in size, of small diamond crystals can be grown in a hydrothermal environment from a mixture of carbon, water and metal...".

They are reasonably sure that there were no big 'sports' in their original seed distribution, and that the anhedral 15-micrometre particle in Fig. 1a on page 513 is new diamond. If this grain grew from a sub-micrometre seed, the same growth rate would produce the Cullinan diamond in about 30 million years; compare that with a time of only about 200 days extrapolated from currently available growth-rate data for gem-quality diamonds grown by the thermal-gradient method from metal-carbon solutions. But even if the aggregates of Fig. 1b are sintered from the original seeds, the result is interesting. If reproduced by others, it will confirm that hydrothermal diamond growth is possible, and so may be involved in forming natural diamonds. That could explain why natural diamonds contain no metal.

There are unanswered problems, like the destiny of the nickel and its role in the process, and how to find a reliable method to distinguish seeds from new growth. Be sceptical, but this result looks like the state-of-the-art from a hydrothermal system. □

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Figure 1 Industrial diamond grit. These diamonds could have crystallized in the Earth's mantle from a watery solution.

IMAGE
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