Geochronology

Diamond dating anomalies

Martin H. Dodson

DIAMONDS are particularly interesting samples of the Earth's mantle. Because of their unique combination of chemical stability and mechanical strength, impurities which they incorporate at their birth are protected almost indefinitely against interactions with the surrounding mantle. Some diamonds are known to be 2–3 thousand million years (Gyr) old^{1,2}, but direct dating of diamonds by the potassium–argon method has not been attempted until fairly recently^{3,4}, despite the great sensitivity of modern equipment for argon isotope analysis. Expectations, however, in geochronology are easily confounded; Ozima and co-workers, in a series of papers^{4–6} culminating in the one on page 226 of this issue⁶, show that forming diamonds can incorporate large amounts of 'excess' radiogenic argon in association with potassium, so that what began as a dating project has ended as a study of ancient mantle fluids.

Because of previous indications that excess argon would be a problem³, Ozima and his colleagues decided to use an 'isochron' method (see figure) to date a suite of ten samples from Zaire called 'cubic' diamonds. These curious stones are polycrystalline aggregates with a rather fibrous structure and roughly cubic in shape, some having clear octahedral cores. It seemed likely that they are of uniform age and share the same initial argon isotope composition, essential conditions for the isochron method. In the event the stones yielded⁴ a respectable linear array on the potassium–argon isochron diagram — indicative of uniform age — but a thoroughly unrespectable age of 6 Gyr, apparently making them 1.5 Gyr older than the Solar System.

Obtained from a single sample, this result would simply have been rejected as being due to excess radiogenic argon. The linearity of the isochron plot, however, made such an idea hard to accept, for it required that the excess argon was incorporated in exact proportion to the potassium. This seemed unlikely, because normally the contrast in chemistry between potassium and argon ensures that the Ar/K ratio in a new mineral grain is both lower (commonly zero) and more variable than in its surroundings.

A more fundamental explanation was therefore sought, and it was suggested⁴ that the potassium had an anomalously high abundance of the parent ⁴⁰K. However, it was soon shown⁵ that potassium in Zaire diamonds is isotopically indistinguishable from that found in any other terrestrial material. Thus the diamonds

must either have incorporated a pre-solar component (diamonds have been found in meteorites) or have been isotopically contaminated in a very unusual way.

The question is now resolved in this issue⁶ in favour of contamination during crystal growth, by mechanical entrapment of an argon-rich fluid. The clinching evidence comes from the argon–argon (or argon-39) method, in which samples are irradiated with fast neutrons, converting a small proportion of ³⁹K to ³⁹Ar. The ratio ⁴⁰Ar/³⁹Ar in gas extracted from the

Isochron plot for cubic diamonds from the earlier paper by Ozima and co-workers⁴. The ⁴⁰Ar and K contents of samples are plotted as ratios to their ³⁶Ar contents, which are assumed to be constant through time. Because ⁴⁰K decays radioactively to ⁴⁰Ar, data from samples formed at the same time, with uniform 'initial' argon-isotope composition (⁴⁰Ar/³⁶Ar), but variable K/³⁶Ar, would all fall on a straight line whose slope gives the age of the samples. The intercept shows the initial ⁴⁰Ar/³⁶Ar, in this case close to zero (-700 ± 900), suggesting that no ⁴⁰Ar was trapped in the forming diamonds. The ³⁹Ar data of Ozima and co-workers in this issue, however, show that these diamonds entrapped, as they grew, a variable mixture of fluids, one with high, fairly uniform Ar/K, another with low ⁴⁰Ar/³⁶Ar.

samples corresponds to the radiological daughter–parent ratio ⁴⁰Ar/⁴⁰K in the conventional method. The gas is usually extracted in stages while the sample is heated to successively higher temperatures; changes in apparent age during this step-heating procedure show differences between the locations of ⁴⁰Ar and ³⁹Ar within the sample. (Furthermore, during neutron irradiation ³⁸Ar is produced from chlorine and ³⁷Ar from calcium, so the concentrations of these elements may also be determined by argon isotope analyses.)

In their new paper, Ozima *et al.*⁶ present step-heating analyses of four irradiated diamond samples. The 'age' from their isochron plot is again close to 6 Gyr, with little indication of changes during step-heating. More important, they find an excellent correlation of chlorine with ⁴⁰Ar. Ozima *et al.* point out that similar

correlations obtained from fluid inclusions in the upper crust reflect leaching of argon and chlorine from crustal rocks. Evidently these diamonds provide evidence for analogous processes in the mantle, and the gases extracted from them consist of mixtures, in varying proportions, of a chlorine-free component with ⁴⁰Ar/³⁶Ar of about 340 and a component with ⁴⁰Ar/Cl of 8 or 9. Rather less convincing is the attempt, by means of a correlation diagram for radiogenic ⁴⁰Ar/K against Cl/K, to separate the ⁴⁰Ar into an excess component and an *in situ* radiogenic component (with a calculated age in the range 0–3 Gyr).

Navon *et al.*⁷ (see also ref. 8) recently presented elemental analyses for Zaire cubic diamonds rich in sub-micrometre inclusions, interpreting them in terms of volatile-rich fluids roughly comparable with potassic magmas. Ozima *et al.* give potassium, chlorine and calcium abundances which are broadly consistent with those of Navon *et al.*, and provide complementary argon-isotope data. The significance of these inclusions for the understanding of mantle processes⁸ would be hard to exaggerate, and it is clear that there must be further attempts to date them. Reported success in dating of fluid inclusions in crustal rocks⁹ suggests that the Rb–Sr method could be worth a try.

Finally, do the problems encountered in dating of diamonds have serious implications for more conventional applications of the potassium–argon method? The answer is, probably not. In these diamonds the potassium–argon system is evidently dominated by a rather homogeneous ⁴⁰Ar-rich fluid which has been incorporated mechanically during crystal growth, mixed with small amounts of a low ⁴⁰Ar/³⁶Ar component. Thus the system does not satisfy one of the most fundamental requirements for successful dating, that the radiometric clock must be reset by a process of chemical differentiation between parent and daughter elements. In ordinary rocks and minerals the immense difference between the chemical properties of potassium and argon ensures that this condition can usually be satisfactorily met, with the likelihood of obvious inconsistencies in the data if it is not. □

1. Kramers, J.D. *Earth planet. Sci. Lett.* **42**, 58–70 (1979).
2. Richardson, S.H., Gurney, J.J., Erlank, A.J. & Harris, J.W. *Nature* **310**, 198–202 (1984).
3. Ozima, M., Zashu, S. & Nitoh, O. *Geochim. cosmochim. Acta* **47**, 2217–2224 (1983).
4. Zashu, S., Ozima, M. & Nitoh, O. *Nature* **323**, 710–712 (1986).
5. Podosek, F.A. *et al.* *Nature* **334**, 607–609 (1988).
6. Ozima, M., Zashu, S., Takigami, Y. & Turner, G. *Nature* **337**, 226–229 (1989).
7. Navon, O., Hutcheon, I.D., Rossman, G.R. & Wasserburg, G.J. *Nature* **335**, 784–789 (1988).
8. Menzies, M.A. *Nature* **335**, 769–770 (1988).
9. Darbyshire, D.P.F. & Shepherd, T.J. *J. geol. Soc. Lond.* **142**, 1159–1177 (1985).

Martin H. Dodson is in the Department of Earth Sciences, University of Leeds, Leeds LS2 9JT, UK.