

studying non-uniform calcium dynamics in more complex systems, such as brain neurons.

Tour and colleagues' work provides a host of opportunities for the development of further chemical tools. A wish list for next-generation designs might include calcium-responsive groups with brighter fluorescence and more rapid turn-on responses; ratiometric readouts of fluorescence that allow the concentration of ions in nanometre-sized calcium bursts to be measured; and a choice of coloured reporters, so that different kinds of sensor can be used and identified in the same experiment. A range of sensors with different binding affinities for calcium would also be useful, as calcium-ion concentrations vary depending on the cell type.

Furthermore, the discovery and optimization of new peptide motifs that recognize small molecules should lead to sensors that bind with improved selectivity to proteins tagged with those peptides; this will improve the signal-to-noise ratios of sensors in localized cellular regions and allow multiple probes to be used that recognize different tags<sup>3-7</sup>. The authors' general concept could also be exploited to

visualize protein regions by using methods other than fluorescence, such as electron microscopy, magnetic resonance imaging, positron emission tomography and ultrasound. Different reporters could also be used, so that other metal ions, naturally occurring organic compounds and enzyme-reaction products can be detected. By opening the door to such possibilities, Tour *et al.*<sup>1</sup> have taken a step towards the most ambitious goal of all — developing chemical probes that can visualize specific features of living systems with molecular resolution. ■

Christopher J. Chang is in the Department of Chemistry, University of California, Berkeley, 532A Latimer Hall, Berkeley, California 94720, USA. e-mail: chrischang@berkeley.edu

1. Tour, O. *et al.* *Nature Chem. Biol.* **3**, 423–431 (2007).
2. Griffin, B. A., Adams, S. R. & Tsien, R. Y. *Science* **281**, 269–272 (1998).
3. Hauser, C. T. & Tsien, R. Y. *Proc. Natl Acad. Sci. USA* **104**, 3693–3697 (2007).
4. Ojida, A. *et al.* *J. Am. Chem. Soc.* **128**, 10452–10459 (2006).
5. Prescher, J. A. & Bertozzi, C. R. *Nature Chem. Biol.* **1**, 13–21 (2005).
6. Chen, I. & Ting, A. Y. *Curr. Opin. Biotechnol.* **16**, 35–40 (2005).
7. Guignet, E. G., Hovius, R. & Vogel, H. *Nature Biotechnol.* **22**, 440–444 (2004).

indicate that a rock has spent a long time in an environment with a higher Rb/Sr ratio. High Rb/Sr ratios are characteristic of the continental crust, but can also come about through the melting of mantle rock. Because of its large ionic radius, rubidium fits poorly into the crystal structures of mantle minerals, and so becomes concentrated in melted rock fractions much more effectively than strontium does. This effect is strongest at low melt fractions, so high Rb/Sr ratios could also be the signature of small amounts of melt that formed in one region of the uppermost part of the mantle (the asthenosphere) and migrated into another part (the lithosphere). This process, known as mantle metasomatism, has become increasingly favoured by mantle geochemists<sup>4</sup>. As a result, the burden of coming up with incontrovertible proof has shifted onto those who argue that some volcanic mantle upwellings contain recycled continental material.

Previous assessments have had to rely on extrapolations of isotope-ratio and trace-element trends in various extruded rocks to an endpoint thought to correspond to values found in the continental crust. As the range of ratios covered by the data was small, and their distance from the inferred continental ratio large, this procedure was akin to wagging a large dog with a small tail. One could not know if the ratio of the distant inferred end-point of the trend really did represent the continental crust, or something well short of it — a metasomatized mantle region, for example.

The breakthrough presented by Jackson *et al.*<sup>2</sup> is an extension of the range of observed <sup>87</sup>Sr/<sup>86</sup>Sr ratios (and the correlated neodymium isotope ratio <sup>143</sup>Nd/<sup>144</sup>Nd) in volcanic extrusions well into the region of typical old continental rocks (Fig. 1, overleaf). Even so, these isotope ratios might, in principle, be explained by rocks processed through an extreme version of the metasomatic model. But the authors also ascertain values of various other tell-tale trace-element ratios that are a factor of four lower than those found in metasomatized rocks, and are entirely characteristic of an origin in the continental crust<sup>5</sup>.

## GEOCHEMISTRY

# The lost continents

Albrecht W. Hofmann

**Once subducted into the mantle, material from Earth's continental crust seems to disappear. But its distinctive isotopic signature has been found back at the surface — in volcanic rocks on a Pacific island.**

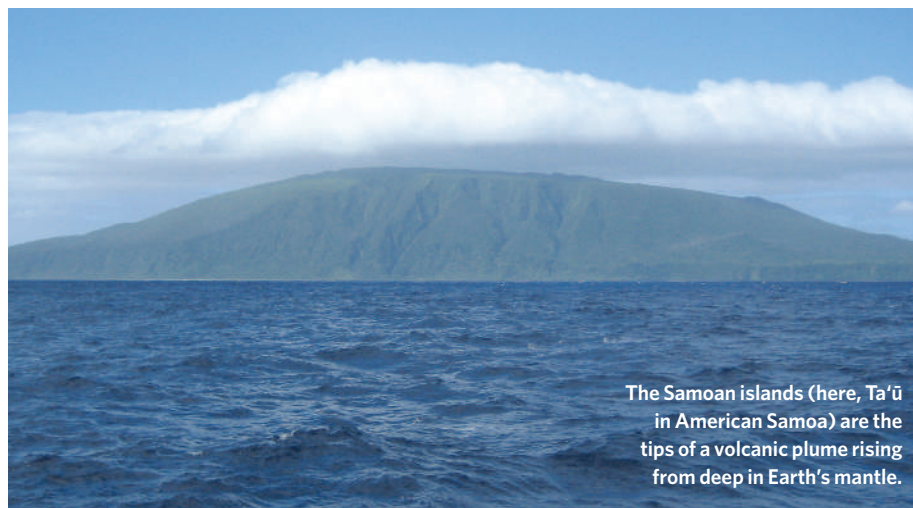
Plate tectonic theory requires that much of Earth's crust returns to the underlying mantle through the process known as subduction. Most of this subducted material is solidified volcanic lava — basalts — from oceanic crust (see, for example, ref. 1). But continents do not completely escape this fate; material eroded from the continental crust is deposited on the ocean floor as a veneer of sediments up to a few hundred metres thick. This layer is subducted, when the time comes, along with the basaltic crust.

But what happens to the continental material after that? Does convection in the mantle stir it around so that it loses its distinctive identity? Or does at least some of it reappear in volcanic rocks formed at ocean ridges or at isolated 'hotspots' of volcanic extrusion under the sea? Jackson *et al.*<sup>2</sup> (page 684 of this issue) have found what might be a 'smoking gun' for the second option. In unprecedented studies of the isotopic and trace-element compositions of basalts dredged from the flanks of a Samoan island, they find almost unequivocal evidence for traces of recycled ancient continental crust in extruded volcanic rocks.

Samoa, a chain of islands in the South Pacific just east of the International Date Line,

is thought to owe its existence to a plume of volcanic material rising from the deep mantle. It has long been singled out as a possible harbour of traces of recycled continental material because its rocks contain more radiogenic strontium (<sup>87</sup>Sr, produced by  $\beta$ -decay of the very long-lived rubidium isotope <sup>87</sup>Rb) relative to normal strontium (<sup>86</sup>Sr), than is usual<sup>3</sup>.

Moderately increased <sup>87</sup>Sr/<sup>86</sup>Sr ratios



The Samoan islands (here, Ta'ū in American Samoa) are the tips of a volcanic plume rising from deep in Earth's mantle.

S. R. HART

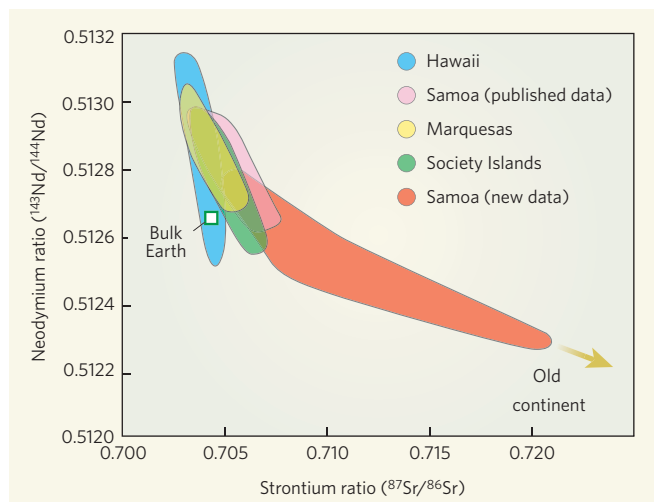
One possible loophole in this interpretation is that the continental isotopic and trace-element signature might have been picked up by the basalts in transit from their melting site in the mantle, at depths of 100 km or so, through the original Pacific Ocean floor — which is itself covered with predominantly continent-derived sediment. Jackson *et al.* effectively counter the spectre of such 'crustal contamination' through non-recycled material by analysing actual Pacific sediments near Samoa, finding that the lead isotope ratios of these samples are incompatible with those of Samoan lavas.

If the origin of the Samoan magma source is now settled, one may reasonably infer that other nearby ocean islands of similar isotopic composition (known as enriched-mantle 2, or EM2)<sup>6</sup>, such as the Society Islands (including Tahiti) and the Marquesas, have similar sources. This would be a mixture of mantle rocks and recycled oceanic crust, with a sprinkling of sediment derived from ancient upper continental crust and subducted along with the rest of the package. Similarly, a few other ocean islands, such as Pitcairn, might contain small amounts of recycled pelagic sediment.

The troubling point remains, however, that even if all EM-type volcanoes contain recycled sediments, instances in which this can be recognized are rare. After all, wherever subduction occurs, sediments are likely to enter the mantle. Jackson and colleagues<sup>2</sup> point out that if the current rate of sediment subduction (0.5–0.7 km<sup>3</sup> per year) is representative of the past 4 billion years, the total amount of subducted sediment will make up only about 0.15% of the mass of the mantle. That might

not seem much, but it is about a third of the present-day mass of the continents.

These sediments are also rather highly enriched in incompatible elements (those most likely to be removed by mantle melting), up to a factor of about 100 compared with primitive mantle compositions. They are even more enriched when compared with present-day mantle, which has been depleted in these same elements by the removal of continental crust. Thus, in the present-day mantle, possibly



**Figure 1 | Adopting continental values.** The strontium and neodymium ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$  in volcanic rocks from several mantle 'hotspots' or plumes. High strontium and low neodymium ratios are both characteristic of ancient continental rocks, but possibly also of mantle regions enriched by infiltration of small amounts of mantle melt. Data for Hawaiian islands are representative of most ocean island volcanoes, which show isotopic evidence for normal mantle enrichment and depletion processes. Published data from Samoa, the Marquesas and the Society Islands, all island groups in the South Pacific, deviate from the normal mantle trend (which also contains the composition of the total 'bulk' Earth) in the direction of high  $^{87}\text{Sr}/^{86}\text{Sr}$  values, indicating that they might contain recycled continental material. Jackson and colleagues' data<sup>2</sup> (red) greatly extend this trend. Together with other 'continental' geochemical indicators, these data strongly support the continental recycling hypothesis for this (relatively rare) class of volcano. (Isotope data assembled from ref. 7.)

10–20% of the highly incompatible elements rubidium, uranium and thorium might have been reinjected into the mantle from crustal sources by sediment subduction. And the very fact that the mantle is isotopically remarkably heterogeneous demonstrates that convective stirring is not particularly efficient.

Given all these factors, I find it remarkable that so little of the subducted sediments can be recognized in recycled form in both mid-ocean ridges and hotspot volcanoes. Much of the budget of subducted trace elements must therefore either be short-circuited back to the surface during subduction-related volcanism, or be hidden in a relatively stable place such as the subcontinental lithosphere. That is a question for another day. For now at least, such material has at last been identified in one place where it does appear.

Albrecht W. Hofmann is at the Max Planck Institute for Chemistry, Postfach 3060, 55020 Mainz, Germany.  
e-mail: hofmann@mpch-mainz.mpg.de

1. Widom, E. *Nature* **443**, 516–517 (2006).
2. Jackson, M. G. *et al.* *Nature* **448**, 684–687 (2007).
3. White, W. M. & Hofmann, A. W. *Nature* **296**, 821–825 (1982).
4. Workman, R. K. *et al.* *Geochem. Geophys. Geosyst.* **5**, doi:10.1029/2003GC000623 (2004).
5. Hofmann, A. W., Jochum, K. P., Seufert, M. & White, W. M. *Earth Planet. Sci. Lett.* **79**, 33–45 (1986).
6. Zindler, A. & Hart, S. R. *Annu. Rev. Earth Planet. Sci.* **14**, 493–571 (1986).
7. <http://georoc.mpch-mainz.gwdg.de>

## ELECTROSTATICS

# Colour discrimination

Like charges repel, unlike charges attract. The simplest way to show this is to charge up different pieces of insulating plastic by rubbing them on your shirt and watching what they do when brought up close to one another. Amit Mehrotra and colleagues use a similar idea to separate a mixture of red and blue sand grains falling into a hollow acrylic cylinder, purely through the different amount of charge each is carrying (A. Mehrotra *et al.* *Phys. Rev. Lett.* **99**, 058001; 2007).

The red and blue grains were all of the same size and positively

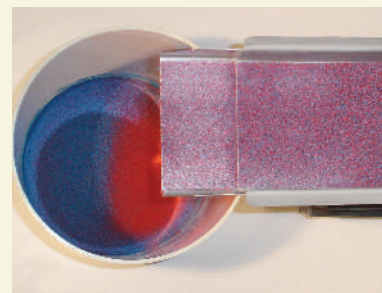
charged, with the charge density of the blue grains being about six times that of the red. The authors also made the cylinder positively charged by rubbing it lightly with nitrile gloves. The grains were mixed up on a vibratory feeder, and then discharged into the cylinder from a metal chute.

On entering the cylinder, the charged grains separated spontaneously into red and blue components (pictured). Oddly, however, it was the more positively charged blue grains that moved towards the positively charged

cylinder walls — rather than being more strongly repelled, as basic electrostatics would seem to demand.

The authors show through simulations that the sand particles are not, in fact, going against the grain. The effect is caused by negative charges induced on the underside of the metal chute, whose concentrated attraction causes a 'beard' of falling sand grains to grow on the lip of the chute. This beard is sufficiently repulsive that the more highly charged blue grains levitate more strongly off the end of the chute, resulting in two falling streams separated according to colour.

Pretty as it is, the experiment also



has a practical aspect. The ability to separate grains by how much charge they carry, rather than by charge sign, could have applications in technologies that exploit electrostatic charging — aerosol drug delivery, xerography and filtration, for example.

Richard Webb