comes to bromine chemistry than surfaces that have been exposed to the atmosphere, such as the upper level of the snowpack. This points to the potential importance of acidic conditions, shown in laboratory studies to play a role in the generation of reactive bromine. Specifically, it is possible that ice samples derived from ocean water are buffered by the marine carbonatebicarbonate system, and so are less acidic than snow samples exposed to atmospheric gases such as nitric and sulfuric acid. If so, this points to a potential anthropogenic influence on polar bromine chemistry, given that human activities generate atmospheric acids.

The study by Pratt *et al.* illustrates one way in which bromine can be released into the Arctic atmosphere. There is observational evidence that other pathways are also likely to be important, including the

recycling of reactive bromine by snow and salty particulates generated during storms^{9,10}. The extent to which meteorological conditions govern the relative importance of these processes is unclear, but wind is required in both cases. Equally uncertain is the chemistry involved in bromine generation, in particular the significance of spatial and temporal variations in surface acidity, salinity and morphology.

Pratt and colleagues⁴ report significant bromine release from real-world snow. The findings lend much more confidence to the suggestion that halogens released from icy surfaces help to explain polar ozone depletion events. Summer-time and multi-year sea ice are at record low levels in the Arctic, being replaced by additional open ocean and first-year sea ice, both of which are often covered with salty snow. Whether the rising fraction of young sea ice will enhance

snowpack bromine production and release, and concomitant changes in atmospheric chemistry, remains to be seen.

 \Box

Jon Abbatt is in the Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada.

e-mail: jabbatt@chem.utoronto.ca.

References

- 1. McNeill, V. F. et al. Atmos. Chem. Phys. 12, 9653-9678 (2012).
- 2. Abbatt, J. P. D. et al. Atmos. Chem. Phys. 12, 6237-6271 (2012).
- 3. Simpson, W. R. et al. Atmos. Chem. Phys. 7, 4375-4418 (2007).
- 4. Pratt, K. A. et al. Nature Geosci. 6, 351-356 (2013).
- Barrie, L. A., Bottenheim, J. W., Schell, R. C., Crutzen, P. J. & Rasmussen, R. A. *Nature* 334, 138–141 (1988).
- Vogt, R., Crutzen, P. J. & Sander, R. A. Nature 383, 327–330 (1996).
- 7. McConnell, J. C. et al. Nature 355, 150-152 (1992).
- 8. Abbatt, J. P. D. et al. J. Phys. Chem. A 114, 6527-6533 (2010).
- Yang, X., Pyle, J. A. & Cox, R. A. Geophys. Res. Lett. 35, L16815 (2008).
- 10. Jones, A. E. et al. Atmos. Chem. Phys. 9, 4639-4652 (2009).

Published online: 14 April 2013

MANTLE GEODYNAMICS

Older and hotter

Volcanic rocks erupted at mid-ocean ridges can record the temperature of the underlying mantle. Ancient crust in the Atlantic Ocean formed from anomalously hot mantle, possibly warmed by continental insulation before the opening of the ocean basin.

Charles Langmuir

he distribution and history of temperature in Earth's interior are central to our understanding of Earth's structure and evolution. Such data are pertinent to mantle convection, the history of uplift and subsidence of continental margins, and, through volcanism, the chemical compositions of ocean and atmosphere with possible impacts on the biosphere. Although there are various ways to constrain the current distribution of mantle temperature. information on ancient temperatures has been particularly hard to come by. Writing in Nature Geoscience, Brandl et al. use the compositions of basalts from the ancient oceanic crust in the Atlantic and Pacific oceans to provide constraints on mantle temperatures in the past.

Volcanic rocks erupted at mid-ocean ridges are ultimately produced by melting of Earth's mantle. Higher mantle temperatures cause a greater fraction of the mantle to melt, changing the chemical compositions of the erupted melts. In the ocean-ridge setting, hotter mantle generates magma with lower sodium and aluminium and higher iron contents. The compositions of volcanic rocks sampled from mid-ocean ridges can

therefore be used to infer the temperature of the underlying mantle at the time the rock formed.

Compositional variations in volcanic rocks sampled from present-day ocean ridges reveal that mantle temperatures during the generation of the lavas vary from about 1,300 °C to 1,500 °C, with the highest mantle temperatures largely associated with mantle hotspots^{2,3}. Older samples of oceanic crust — originally formed at a mid-ocean ridge but now distributed across the ocean basins due to plate tectonic movements - have been suggested to provide a record of mantle temperatures in the past^{2,4,5}. However, older samples can only be obtained by drilling through hundreds of metres of sediments to penetrate the volcanic basement of the ocean basins, and published data have been limited⁵.

Brandl *et al.*¹ rectify this problem by carefully resampling more than 500 basalt glasses that range in age from 3 to 165 million years. The samples are taken from 45 drill sites in the Atlantic and Pacific oceans as part of the Ocean Drilling Program. To assess ancient mantle temperatures, they analyse the chemical

compositions of the samples and compare them to existing data drawn from presentday ridge samples⁶. The results show that the oldest samples from the Atlantic Ocean are uniformly low in sodium and high in iron contents, in contrast to younger Atlantic ridge basalts that mostly have higher sodium and lower iron. The data thus suggest a regular, temporal change in mantle temperature beneath Atlantic ridges. Quantifying the effect suggests the mantle was 100-150 °C hotter some 150 million years ago, when the Atlantic Ocean basin first formed. This drastic temperature change over such a relatively short time span — compared with the 4,500-million-year history of the Earth — is too large to result from the normal evolution of Earth's interior temperature, and must have a different cause.

Brandl *et al.*¹ suggest that continental insulation can explain the high mantle temperatures. Before the African continent broke away from the Americas about 180 million years ago, the continents were a single supercontinent, named Pangaea. This massive land mass could have served as an insulating blanket over the mantle, causing the temperature of the underlying mantle

to rise⁷. When the supercontinent rifted, the high mantle temperatures would have led to extensive melting and the formation of a mid-ocean ridge that erupted volcanic rocks with chemical compositions that were characteristic of this high mantle temperature. As the ocean basin opened further, Africa and the Americas drifted apart, and the mid-Atlantic ridge sampled cooler mantle, leading to a progressive change in the composition of the ocean crust.

To test this scenario, Brandl *et al.*¹ examine the present-day rifting environment of the Red Sea, which marks the ongoing breakup between Africa and Arabia. Mantle temperatures beneath the Red Sea seem higher than normal, too. Moving away from the Red Sea into the Indian Ocean, where the mid-ocean ridge is much older, the mantle temperatures seem to decline, consistent with the idea of continental insulation.

One question with respect to the ancient samples is statistical significance. There are only four drill holes that sample the ancient crust in the Atlantic Ocean, compared with over a thousand sampling sites along the present-day Mid-Atlantic Ridge. The high apparent temperatures could therefore be a sampling fluke. However, the compositions of all four of the samples older than 100 million years overlap with the extreme, hot end of the compositional data array of present-day ridges worldwide (Fig. 1). The only present-day samples that record such hot mantle temperatures are those erupted at ridge segments above the Iceland hotspot.

Apart from the Iceland region, less than 5% of the 241 ridge segments sampled around the globe overlap in compositional space with the ancient samples. That all four ancient sites occupy the extreme portions of the present-day array is then statistically significant. Furthermore, most of the ancient samples were not located near ancient hotspot tracks, so the higher temperatures cannot be attributed to an ancient Iceland-like hotspot. Nevertheless, questions remain as to whether the ancient samples are representative of hemispherewide conditions. The ancient sample sites span only 10° of latitude, a small swath of less than 10% of the vast extent of ancient Atlantic Ocean crust. Much greater sample coverage is necessary to confirm the result of high temperatures associated with the rifting of the entire Atlantic basin.

An enigmatic feature of the new data is the fact that three of the four oldest sites from the Pacific Ocean have a similar chemical signature to the old Atlantic sites. These data imply higher mantle temperatures beneath the Pacific Ocean, too. Yet, the Pacific Ocean samples formed several thousand kilometres away from the nearest continental margin.

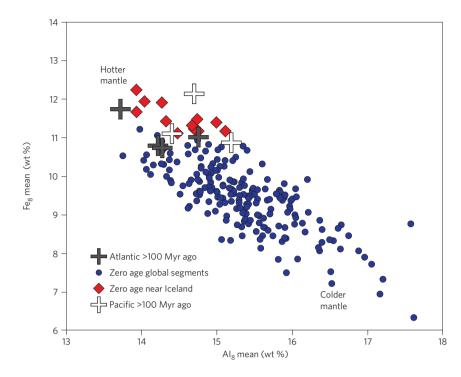


Figure 1 | Chemical compositions of ancient ocean crust in the Atlantic and Pacific oceans compared with modern ocean ridge segments. Mean drill hole compositions of ancient crust from the Atlantic (black crosses) and Pacific (white crosses) oceans plot at the extreme (hot) end of the compositional spectrum of modern ridge segments (blue dots and red diamonds^{10,11}). Young ocean crust forming near Iceland also exhibits extreme compositions, caused by the Iceland hotspot. The ancient ridge samples have compositions consistent with high mantle temperatures, yet most are not influenced by hot spots. For the Atlantic Ocean, Brandl *et al.*¹ suggest the raised mantle temperatures recorded in the ancient samples were caused by continental insulation. Data are averages from Brandl *et al.*¹ and from present-day ridge segments corrected for inter-laboratory bias¹⁰ and normalized to 8% MgO.

Unlike the Atlantic samples, the Pacific data show no systematic change in mantle temperature with time and the raised mantle temperatures cannot result from continental insulation. Other factors must therefore also contribute to ancient temperature variations beneath the ocean basins.

There is some debate as to whether variations in the chemical compositions of mid-ocean ridge basalts truly reflect variations in mantle temperature. Some insist instead that variations in mantle composition are the ultimate cause⁸, which may be the case at least in some regions⁹. The abundant evidence for high temperatures beneath most hotspots is not consistent with this interpretation, but the relative roles of mantle temperature and mantle composition remain to be fully resolved.

Brandl and colleagues¹ suggest that ancient oceanic crust in the Atlantic Ocean formed from anomalously hot mantle that was warmed by the insulating effect of the continents. The data show that our view of the temperature and composition of the mantle based on present-day mid-ocean ridge magmas is not the whole story, and

a great deal could be learned by sampling the composition of old oceanic crust more systematically. Based on the available data, much of the ancient oceanic crust seems to have been generated under conditions that are rare beneath present-day ridges.

Charles Langmuir is in the Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, USA. e-mail: langmuir@eps.harvard.edu

References

- Brandl, P., Regelous, M., Beier, C. & Haase, K. *Nature Geosci.* 6, 391–394 (2013).
- 2. Klein, E. & Langmuir, C. J. Geophys. Res. 92, 8089-8115 (1987).
- Kein, E. & Langmuir, C., Klein, E. & Plank, T. AGU Monograph 71, 183–280 (1992).
- 4. Keen, M., Klein, E. & Melson, W. Nature 345, 423-426 (1990).
- Humler, E., Langmuir, C. & Daux, V. Earth Planet. Sci Lett. 173, 7–23 (1999).
- Lehnert, K., Su, Y., Langmuir, C. Sarbas, B. & Nohl, U. Geochem. Geophys. Geosys. http://dx.doi.org/10.1029/1999GC000026 (2000).
- 7. Anderson, D. L. Nature 297, 391–393 (1982).
- 3. Niu, Y. & O'Hara, M. J. Petrology 49, 633-664 (2008).
- 9. Zhou, H. & Dick, H. Nature 494, 195-200 (2013).
- Gale, A., Dalton, C., Langmuir, C., Su, Y. & Schilling, J.-G. Geochem. Geophys. Geosys. http://dx.doi.org/ 10.1029/2012GC004334 (2013).
- Gale, A., Langmuir, C. & Dalton, C. AGU Fall Meeting abstr. DI21A-1947 (American Geophysical Union, 2010).