Feature

Surprises from the top of the mantle transition zone

Recent studies of chromite deposits from the mantle section of ophiolites have revealed a most unusual collection of minerals present as inclusions within the chromite. The initial discoveries were of diamonds from the Luobosa ophiolite in Tibet. Further work has shown that mantle chromitites from ophiolites in Tibet, the Russian Urals and Oman contain a range of crustal minerals including zircon, and a suite of highly reducing minerals including carbides, nitrides and metal alloys. Some of the minerals found represent very high pressure phases indicating that their likely minimum depth is close to the top of the mantle transition zone. These new results suggest that crustal materials may be subducted to mantle transition zone depths and subsequently exhumed during the initiation of new subduction zones—the most likely environment for the formation of their host ophiolites. The presence of highly reducing phases indicates that at mantle transition zone depths the Earth's mantle is 'super'-reducing.

The transition zone between the Earth's upper and lower mantle is located at between 410 and 660 km depth and is identified from an increase in seismic wave velocities at its upper and lower boundaries. This is as a result of an increase in density in response to a change in the mineralogy of the mantle. Olivine (as α-olivine) and pyroxenes and garnet in the upper mantle are converted respectively into β-olivine (wadsleyite) and the phase majorite in the transition zone. Our knowledge of the mantle transition zone has been gained almost exclusively from the work of geophysicists and experimental petrologists, and actual samples from this part of the deep mantle are extremely rare. In fact they have been restricted to tiny inclusions located inside natural diamonds. Very recently this has all changed and a series of newly published studies have extended our knowledge of the Earth's hidden depths enormously and have brought with them some great surprises. These results were presented by Jing-sui Yang, Paul Robinson and colleagues of the Chinese Academy of Geological Sciences in Beijing, and Bill Griffin and colleagues at Macquarie University, Australia at a scientific meeting in Beijing in 2014 and more recently the details of their work have been published (see Suggestions for further reading, below).

The first surprise was where the mantle transition samples were found. They were found as inclusions in the mineral chromite in the rock chromitite. Chromitite is the ore of chromium and is predominantly made up of the mineral chromite accompanied by small amounts of silicate minerals. Chromitites form in two different types of geological environment. Extensive deposits of chromitite are found in large layered mafic igneous intrusions such as the Bushveld Complex of South Africa and the Great Dyke of Zimbabwe. In these localities the chromitites have formed as a consequence of crystal fractionation and occur as magmatic layers in the pyroxenites and peridotites of the lower part of the intrusion. These chromitites are known as 'stratiform chromitites' because of their layered nature. The other type of setting for chromitites is in the mantle section of ophiolites. In this case the chromitites appear to have formed in dykes, again as a result of fractional crystallization, but in this case from a transient magma migrating through the upper part of the sub-ophiolite mantle. These accumulations of chromitite are often tabular in shape, frequently deformed into pods, and are known as 'podiform chromitites'. They are usually

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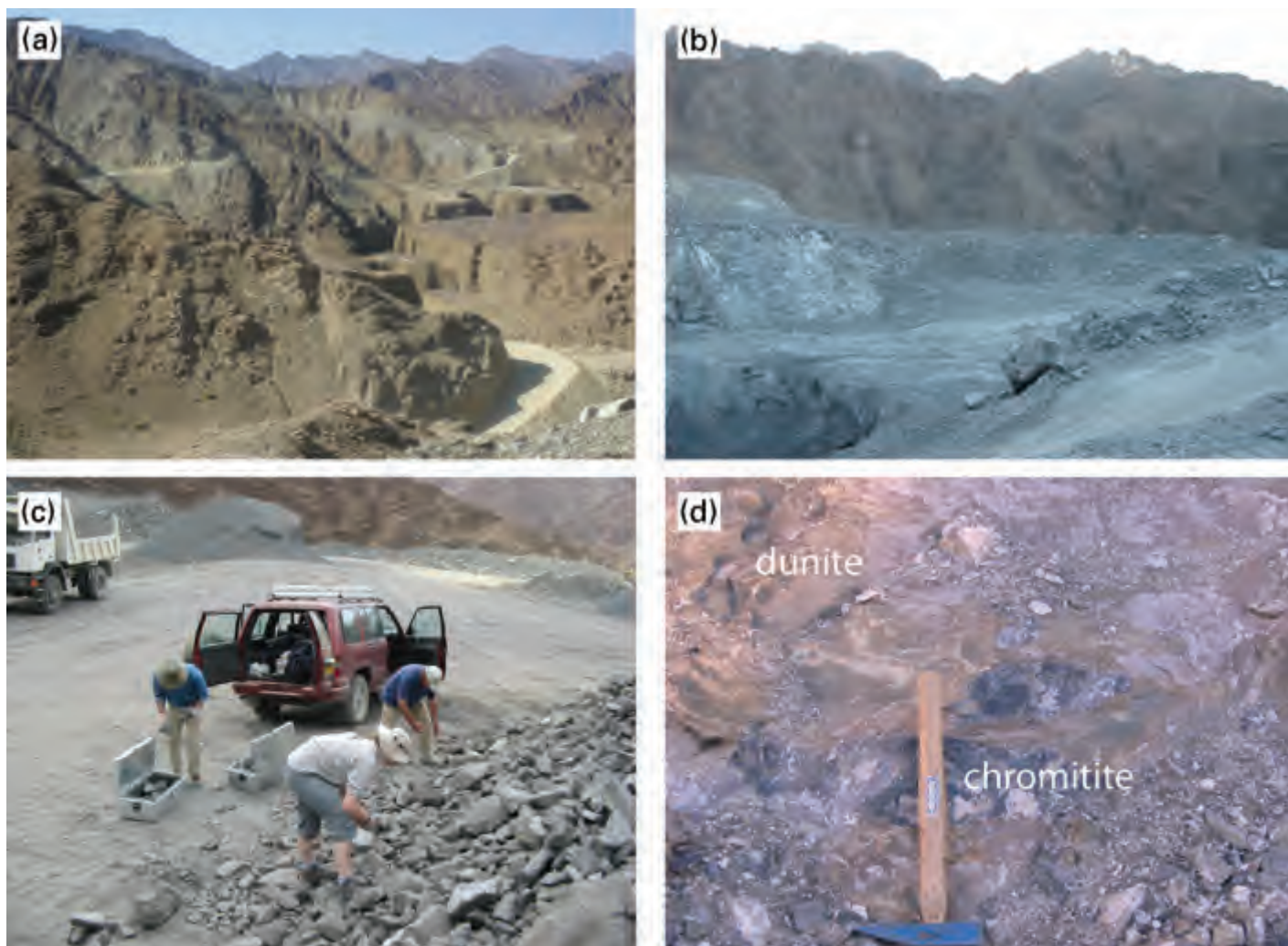
much smaller than the stratiform occurrences. It was in the podiform chromitites of the Jurassic–Cretaceous (*c.* 175–126 Ma) Luobusa ophiolite in Tibet that the most dramatic discoveries of mantle transition zone minerals were first made. This started with the remarkable discovery of diamond.

Diamonds in ophiolites

Diamond in ophiolites and in ophiolitic chromitites was initially thought to be a geological impossibility, because ophiolites represent the remnants of shallow ocean lithosphere, whereas diamonds represent crystallization in the deep mantle. Thus the first reports of diamonds in ophiolitic chromitites were treated with great scepticism. The most probable explanation was that there had been anthropogenic contamination—the diamonds had been introduced into the sample at some stage in the rock crushing process—perhaps through inadequate cleaning of the crushing equipment. This is of course a serious issue and should be addressed. However, it is first important to understand how the deep mantle minerals were

discovered. Groups in Germany under Paul Robinson and in China under Jing-sui Yang collected chromitites by the ton. I know, because almost ten years ago I went into the field with Paul Robinson when he was extending his study into the Oman ophiolite. I helped to transport about half a tonne of chromite in the back of my struggling four-wheel drive, along a rough road from a remote mine in the Oman mountains back to his more fragile hire-car on the main road (Fig. 1). These very large samples were then treated using industrial scale mineral separation processes to recover the very small volumes of mineral inclusions from the chromitite. An exceptional 1-ton sample from Luobusa yielded about 1000 grains of diamond but the normal diamond occurrence in chromitites is much less, at about 0.03 g per tonne (30 ppb). Four different mineral separation techniques are used to separate the minerals into up to 13 different groups on the basis of their physical properties. It takes about 1 month to separate the mineral inclusions from 1 tonne of rock and about 7 months for one person to hand-pick the concentrate. But using this painstaking methodology it has been possible to recover not

Fig. 1. The Shamis chromitite orebody in Wadi Rajmi, Oman from which deep mantle minerals were recovered. **a.** The Wadi Rajmi access road showing wadi gravels in the foreground and mantle harburgites making up the higher peaks. **b.** The Shamis II open cast pit. Mantle harzburgites in the background. **c.** Collecting samples in large volume. **d.** Pods of chromitite in dunite at the Shamis II pit.

only diamond, but a wide range of minerals from chromitites from ophiolites in several different parts of the world.

The matter of whether the diamond was a contaminant has now also been resolved after a massive search for diamond *in situ* in chromitite samples. Again this was the result of a hugely labour-intensive exercise. Forty pieces of chromitite were cut into 4 cm² shapes and polished using very fine diamond discs. In total the equivalent of 24000 polished sections were examined, and over the period of a year six diamonds were found *in situ*, proving that the diamonds had come from the chromitites. The diamonds observed were between 0.2–0.5 mm in diameter, hosted in generally round patches of amorphous carbon. These grains are larger than those used in the polishing (< 0.04 mm) and so can safely be regarded as part of the original rock and not introduced during grinding and polishing. In addition, *in situ* grains of moissanite (silicon carbide) and corundum have also been found in chromite grains.

Minerals from the continental crust in the deep mantle

The second of the great surprises to emerge from this novel scientific study is that minerals which began their life in the Earth's continental crust are now being recovered from the top of the mantle transition zone. Robinson and colleagues, in a paper published in 2015 describe a wide range of silicate minerals, metal alloys, carbides, oxides and sulphides which have been recovered from ophiolites in Tibet (Luobusa, Dongqiao), Russia (Ray-Iz) and Oman (see Table 1). About 20 of these minerals are crustal in origin and the tectonic implications of this finding are hugely important.

Of particular importance amongst the crustal minerals are phases such as quartz and its high pressure polymorph coesite. Also the mineral zircon— important because it can be dated using U-Pb decay. Here we need to be careful however, because it is just possible that the zircon could be a primary mineral in the oceanic crust. Nevertheless, a careful investigation by Robinson and his team showed that the zircons from the Luobusa, Dongqiao and Oman ophiolites have the same geochemical signature as zircons typically found in the granites of the continental crust. Thus they are deeply buried crustal fragments. The results of U-Pb geochronology on separated zircons shows that whilst the Tibetan ophiolites were formed at about 175–180 Ma the measured zircon ages are between 380 and 2695 Ma, indicating the incorporation of much older continental crust. In Oman the ophiolite formed at about 96 Ma and the measured U-Pb zircon ages are 84–1411 Ma suggesting the incorporation
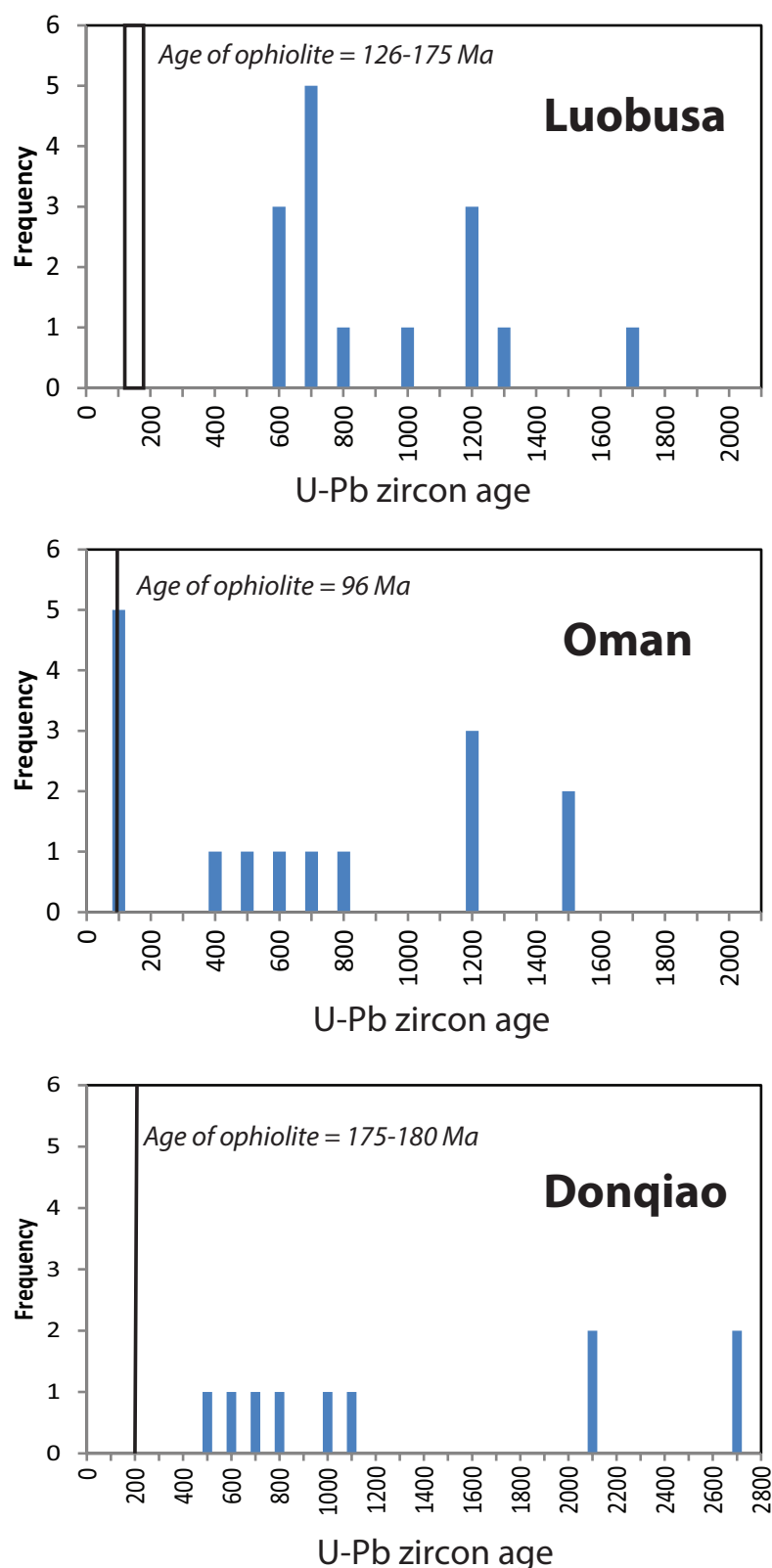

Fig. 2. Histograms of U-Pb zircon ages for zircons recovered from the Luobusa, Oman and Donqiao ophiolites (data from Robinson *et al.*, 2015)

of a mixture of contemporary and older continental crust (Fig. 2).

A further surprise is the observation that the diamonds found in these samples are most probably of crustal origin. Carbon isotope measurements of the diamonds showed a very negative signature ($\delta^{13}C$ = −18 to −28‰), much more negative than is typical for the more normal diamonds recovered from kimberlites. A highly negative carbon isotope signature is found in many forms of organic matter and 'chromitite diamonds' may be composed of former living carbon originating at Earth's surface.

Minerals formed under super-reducing conditions

Another group of minerals which are prominent in those recovered from ophiolitic chromitites are those formed under highly reducing conditions. This includes minerals occurring as native elements (diamond, native Cr and native Al), carbides (moissanite (SiC) and tungsten carbide), Ti-nitrides, and a variety of metal alloys, some Fe-rich and associated with Ni and Cu, and the mineral wüstite (FeO), and others rich in the platinum group elements (PGE) particularly Os, Ir and Ru. A list of the more common mineral species is given in Table 1.

Many of these minerals are thought to have formed under 'super-reducing' conditions in the mantle. The oxidation state of the mantle can be described by reference to a series of oxygen producing/consuming reactions known as buffer curves. Measurements are made on a logarithmic scale. Normal upper mantle has an 'oxygen fugacity' as it is called, equivalent to that of the equilibrium between the minerals quartz, fayalite (Fe-olivine) and magnetite (Q-F-M). The oxygen fugacity of the upper mantle is thought to decrease with depth to values close to the equilibrium between native iron and the mineral wüstite (FeO). This is the I-W buffer curve, which is five log units lower that the QFM buffer. Some of the reduced species found in the chromitite mineral assemblage indicate even lower conditions than this. For example phases such as moissanite (SiC), native Si and the phase $FeSi_2$ suggest conditions as low as eight log units below that of the iron–wüstite buffer curve, which is thirteen log units lower than the normal upper mantle. This is super-reducing and is indicative of the environment from which these minerals have come. Some of these super-reducing minerals, in particular alloys rich in Os, are amenable to Re-Os isotopic dating and can provide minimum ages for the crystallization of some of the PGE-rich alloys. Although this work is in its infancy, this approach may provide a means of estimating when these phases crystallized in the super-reducing environments which they now record.

Table 1. Reduced and highly reduced mineral phases found in ophiolitic chromitites

Mineral Group	Mineral name	Formula
Native elements	Diamond	C
	Native Cr	Cr
	Native Al	Al
	Native Fe (and associated wüstite)	Fe, (FeO)
	Native Si	Si
	Native Ta	Ta
Carbides	Tungsten carbide	WC, W-(Co)-C
	Moissanite	SiC
PGE and base metal alloys	Os-Ir-Ru alloys	Os_5Ir_4Ru (variable)
	Os-Ir alloys	Os_3Ir_2, Ir_2Os
	Pt-Fe-Ni-Cu alloys	$Pt_7(FeCuNi)_3$ (variable)
	Fe-Cr-(Ni) alloys	Fe_7Cr_2Ni, Fe_9Cr
	Fe-Si alloys	$FeSi$, Fe_3Si_7
	Fe-Ti alloys	
Nitrides	Ti-nitrides	Ti_2N, Ti_2N_3
	B-nitrides	BN
Sulphides	Pyrite	FeS_2
	Chalcopyrite	$CuFeS_2$
	Troilite	FeS
	Arsenopyrite	FeAsS
	Ni-sulphides	Ni_3S_2, NiS
	Molybdenite	MoS_2
	Galena	PbS

Evidence for mantle transition zone depths

A particular reason why the recovery of crustal minerals from mantle chromitites is important is that they hold clues to the depth from which these minerals have been recovered. It has already been noted that diamond is associated with some mantle chromitites. Thus the presence of diamond at temperatures of say 1400 °C indicates that these samples formed at a minimum pressure of about 5 GPa, or *c.* 150 km depth (Fig. 3). A critical mineral assemblage at Luobusa is an intergrowth at the micron scale of the minerals coesite (a high pressure form of quartz) and kyanite on an Fe-Ti metal alloy. The texture of this intergrowth suggests that the coesite is pseudomorphing after the phase stishovite (an even higher pressure version of silica) which is stable above 11 GPa (*c.* 330 km depth) at 1400 °C. An indication of an even deeper origin are chromite grains which have exsolved needles or grains of the minerals diopside, enstatite, Fe-carbide and SiO_2—all with preferred orientations. These results have been interpreted, on the basis of laboratory studies, as the recrystallization of a high-pressure precursor of chromite, with a different crystal structure, but which formed at pressures of > 12.5 GPa, near the top of the

mantle transition zone. This is the best evidence we have for these samples coming from the top of the mantle transition zone.
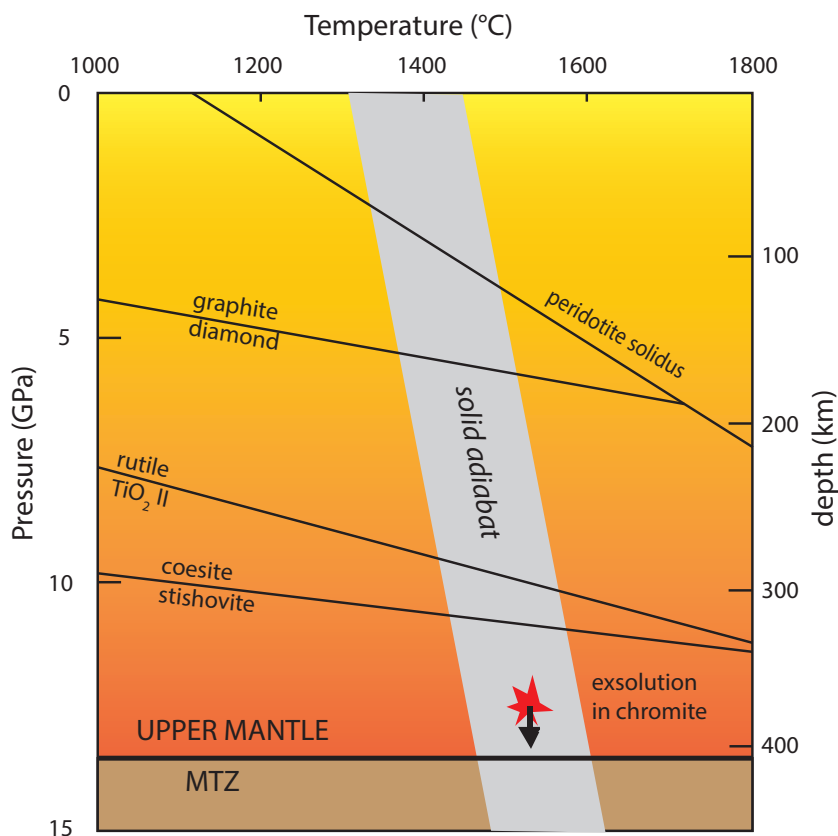
Further evidence for very great depths comes from highly detailed work on mineral inclusions within the SiO_2-phase coesite. These are minerals preserved on the nanometre scale and so are only detected using transmission electron microscopy. Dobrzhinetskaya and colleagues reported in 2009 the presence of the phase $TiO_2 II$, a high pressure form of rutile, cubic boron-nitride and titanium nitride. At these temperatures $TiO_2 II$ forms at pressures above 10 GPa, and cubic boron-nitride and titanium nitride are stable up to pressures of 60 and 40 GPa respectively, indicating that a possible upper limit on the depth of these samples is very great indeed.

Tectonic processes

One of the principal challenges of these new discoveries about the deeper mantle is to understand how upper crustal materials can be found at the top of the mantle transition zone and to understand the equally intriguing question of how they might be brought back to the surface again. There are several models and these need to be examined in the light of some new thinking around the origin of ophiolites.

The results of seismic tomography have shown us that slabs of ocean crust are subducted deep into the Earth's mantle. Subducted slabs and broken slab fragments have been imaged penetrating into the mantle transition zone and perhaps coming to rest there, creating what may be a 'slab graveyard'. Other images show slabs passing through the mantle transition zone even deeper into the lower mantle. If these slabs are also able to carry sediment with them then this would seem to provide a mechanism whereby crustal minerals such as quartz, corundum, zircon and perhaps organic carbon to form diamond are emplaced in the deeper mantle.
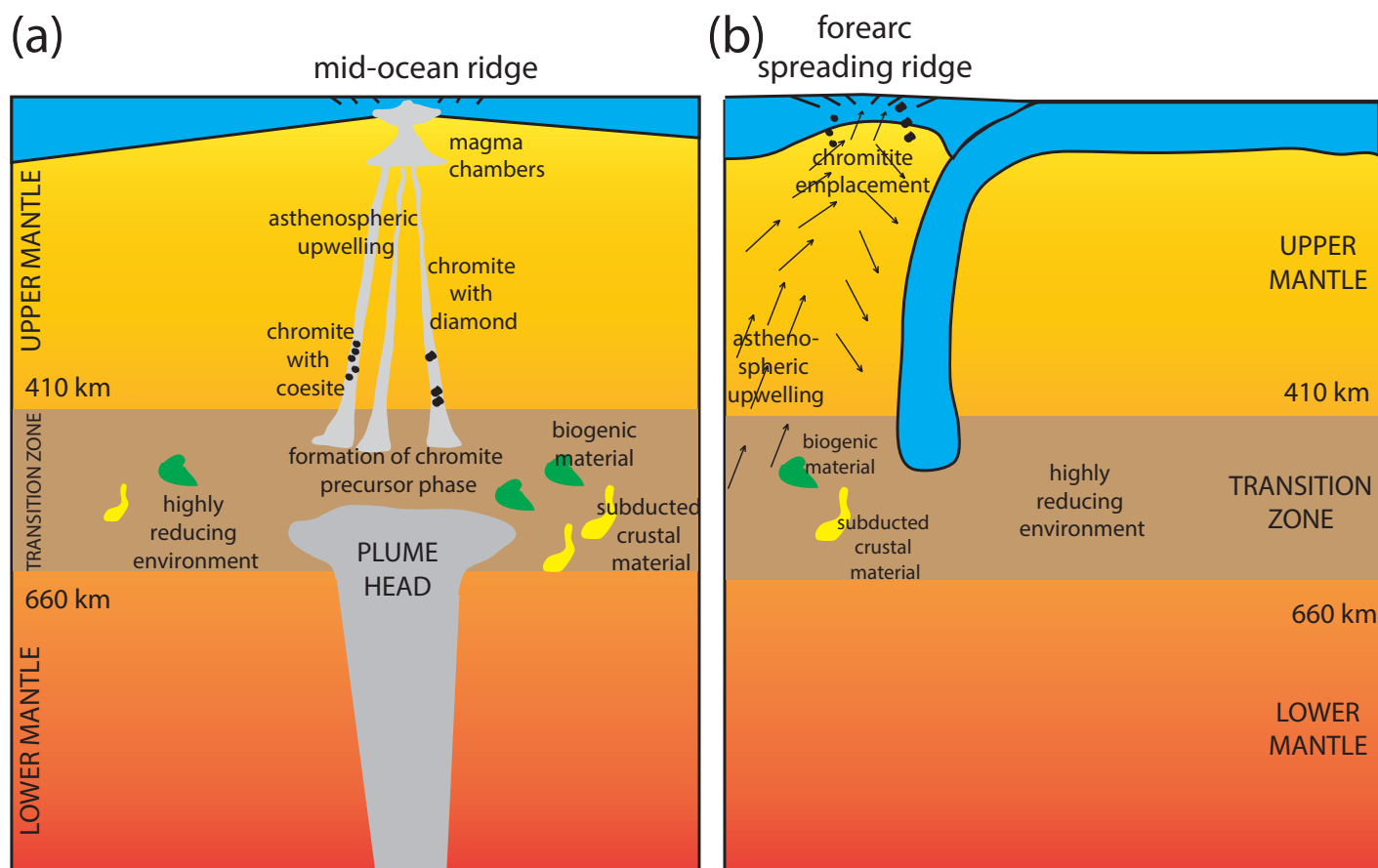
So there is a mechanism—subduction—for the transport of crustal materials into the deep mantle. What is much more contentious is a mechanism for their return to the Earth's surface. What is needed is flow within the mantle capable of transporting materials from a deep level to a shallow level such that they end up in the sub-oceanic mantle beneath a spreading ridge. Yang and colleagues proposed that this might happen in a mantle plume, located beneath a spreading ridge (Fig. 4a). In this model a mantle plume rises from the lower mantle into the mantle transition zone where it collects a mixture of crustal materials brought there through earlier subduction and super-reducing minerals from the transition zone itself. These are then carried through the upper mantle on the upwelling plume to be incorporated in the magma systems beneath a spreading ridge. Whilst

Fig. 3. Pressure temperature grid showing the important phase changes preserved in the mineral inclusions found in ophiolitic chromitites.

workable, this model requires the happy coincidence of mantle plume and spreading ridge, which is not often observed. Furthermore, this model predicts that chromite in other plume lavas, such as those in ocean islands, might also be the host to very deep mantle minerals. These have not yet been reported.

In my view, there is a better model and this arises from new ideas about the origin of ophiolites. In recent years it has become clear that ophiolites form in a number of different tectonic settings and that, contrary to what we previously thought, those associated with oceanic spreading centres are rather rare. Much more common are ophiolites associated with subduction. These are the 'supra-subduction zone' ophiolites that tend to be the host of highly Cr-rich chromitites of the type described here from Tibet, Russia and Oman. Supra-subduction zone ophiolites are thought to form during the process of subduction zone initiation, that is, they represent sea floor spreading associated with the creation of a new subduction zone. As the ocean crust fractures and a newly formed subducting slab descends into the shallow mantle—a process known as slab roll-back—asthenospheric mantle from below rises into the space created by the descending slab and an episode of spreading is initiated at the front of the newly forming arc: the forearc environment. It is the rocks which form in this setting which we now think are most commonly found as ophiolites (Fig. 4b). What

(a) mid-ocean ridge

(b) forearc spreading ridge

Fig. 4. Mechanisms by which minerals from the mantle transition zone might be brought into the shallow oceanic lithosphere. **a**. The plume model of Yang *et al*. (2015). **b.** the slab rollback model of McGowan *et al*. (2015).

our new results from the mantle transition zone seem to be telling us is that the mantle upwelling beneath the forearc may rise from very deep in the mantle, as deep as the top of the mantle transition zone itself and far deeper than anyone had anticipated. Thus in this model, as a new slab descends into the mantle, compensating asthenospheric mantle rises from the mantle transition zone bringing with it—encapsulated and protected in sturdy grains of chromite—a mixture of mantle transition zone minerals and those crustal minerals which have come to rest there. These minerals ultimately find a new home in those mantle chromitites typical of depleted ophiolitic mantle.

In detail there may be some subtle differences between the diverse tectonic environments reported in these new studies. For example, in Tibet the ophiolites may record a long period of subduction as India and Asia converged and it is possible that the subducting slab penetrated the mantle transition zone, prompting further mantle upwelling which brought old crustal material to the surface. However, in Oman, the subduction may have only lasted about 3 Ma. In this case young zircons may not have been derived from the mantle transition zone but rather have been carried upwards from the surface of the newly subducting slab by the mantle upwelling through a local slab tear, to carry shallow subducted

sediment back to the surface. The variable age of the crustal materials derived from the mantle transition zone, as recorded by zircon ages (Fig. 2), suggests that the processes recorded may represent multiple cycles of subduction and long-lived residency in the deep mantle.

A final puzzle is that of the origin of the chromite itself, the host to this remarkable array of minerals. Did it nucleate in the deep mantle and encapsulate its hosts in the mantle transition zone, did it form much later at shallow levels in the mantle as has more commonly been assumed, or is it shallow-formed, subducted and then returned to the shallow mantle? McGowan and colleagues have shown that Luobusa chromitites have the same major and trace element chemistry as ophiolitic chromitites from Turkey. From this they infer that the Luobusa chromitites were formed at shallow levels in the mantle, were subducted (because of the presence of high pressure phases) and then exhumed. What is unexplained in this model is how the crustal xenocrysts and mantle transition zone minerals were encapsulated within the chromite. In addition it does not explain the exsolution textures observed indicating a former, compositionally different, high pressure form of chromite. Whilst chromite is only stable to 12.5 GPa (albeit at 2000 °C), a phase with a very similar

structure is stable up to 20 GPa and so it is possible that the precursor to the chromites now observed in sub-ophiolitic mantle had a very deep origin.

Wider implications

It has taken the protagonists of these novel studies some years to gain wide acceptance of their ideas. However, the major criticisms have now been answered and the science has been very carefully documented and so it is time for the Earth Science community to reflect on the significance of these findings. They are two-fold. First, we now know that crustal materials (in what volumes we are not sure) can be returned to at least mantle transition zone depths within the Earth through subduction. This is highly relevant to the current debate on crustal recycling. Second, we have been alerted to the possibility that maybe only the upper part of the Earth's mantle is oxidized and that below the upper 250 km the mantle is highly reducing. This too is an important observation and relevant to modern discussions about the evolution of the Earth's oxygenic atmosphere.

Acknowledgements

Suggestions for further reading

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