

Deep-earth methane and mantle dynamics: insights from northern Israel, southern Tibet and Kamchatka

William L. Griffin^{1*}, Sarah E.M. Gain¹, David T. Adams¹, Vered Toledo²,
Norman J. Pearson¹ and Suzanne Y. O'Reilly¹

¹ARC Centre of Excellence for Core to Crust Fluid Systems, EPS, Macquarie University, NSW 2109,
Australia

²Shefa Yamim (A.T.M.) Ltd., Akko, Israel

* Corresponding author.
Email: bill.griffin@mq.edu.au

Abstract

The oxidation state of fluids in Earth's mantle affects processes ranging from volcanism and the formation of the crust, to the generation of many types of ore deposits. In general, the lowest oxidation state of the mantle (and hence its fluids) is defined by the buffer reaction $2\text{FeO} \rightarrow 2\text{Fe} + \text{O}_2$. However, unusual mineral assemblages that require far more reducing conditions are found in volcanic rocks from a variety of geotectonic settings, raising questions about how such conditions can be generated in the mantle. Examples from northern Israel, Tibet and Kamchatka suggest that interaction between magmas and methane-hydrogen fluids derived from the deep Earth have generated highly reducing conditions within some volcanic plumbing systems. Such systems appear to be related to the margins of tectonic plates, including zones of continent-continent collision and/or deep oceanic subduction, and transform faults extending deep (up to 200 km) into the Earth's mantle. This represents an important but previously unrecognized fluid-transfer process within the mantle.

Foreword

This paper is both a condensation and an expansion of the 2015 Clarke Memorial Lecture, given by WLG at Macquarie University in August 2015, which summarized recent work by the ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS). We hope to provide both geologists and non-specialists with a glimpse into some recent exciting developments in Earth Science, and to show how the integration of observations at scales from microns to mountain ranges can give us a new picture of how Earth works. We are trying to understand processes not previously recognized, and the paper therefore contains

some “interesting” speculations, which we hope can generate (polite) discussion.

Introduction

The nature of the rocks in Earth's deep mantle (from the base of the crust to the top of the core; Fig. 1), and clues to their formation, are generally hidden beneath our feet in the vast space of inner Earth. However, small samples of the mantle are brought to the surface by some volcanic eruptions in which the magmas originated at depths of 250-100 km. Such magmas can rise to the surface at speeds of km/hour, entraining fragments of deep-seated rocks

and minerals (xenoliths and xenocrysts;

O'Reilly and Griffin, 2010). Larger samples

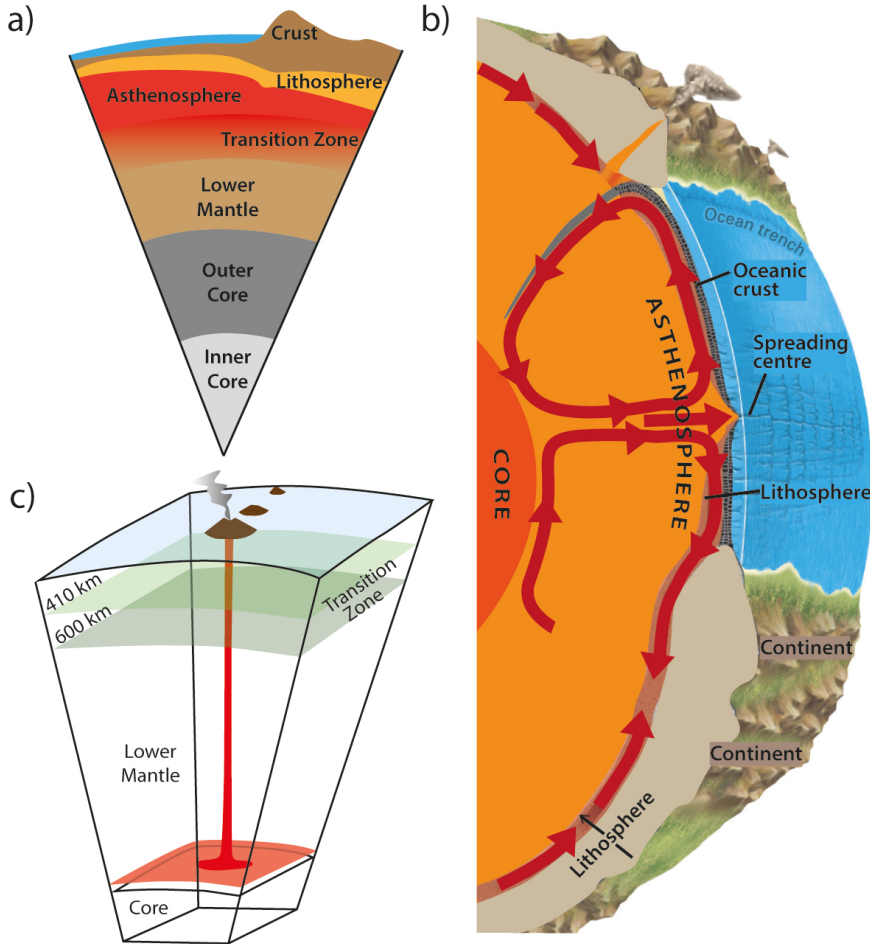


Figure 1. (a) Cross-section of Earth's interior, showing the divisions defined by mineralogy; (b) Cross-section emphasizing the convection of the mantle, driven by the heat in the core; (c) cartoon of deep-seated mantle plumes, in this case producing oceanic islands like Hawaii; smaller upper-mantle plumes may rise from the Transition Zone and produce much less magma.

of mantle rocks, tens to thousands of cubic km in volume, can be brought to the surface by geodynamic forces in regions where tectonic plates collide (e.g., Tibet, the Andes, New Guinea).

This report focuses on three locations that have yielded surprising discoveries about the nature of some mantle rocks and minerals and their conditions of formation deep in the mantle. Material from two of these areas

(S. Tibet, N. Israel) is being studied by the CCFS team, while recent discoveries in the Kamchatka Peninsula of NE Siberia provide important comparisons.

The Deep Earth and the Importance of Fluids

The large-scale structure and composition of Earth's convecting mantle (the

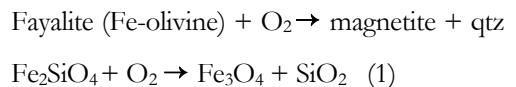
asthenosphere), extending from 100-200 km below Earth's surface to the outer edge of the core at ~2,900 km, are generally understood (Fig. 1). The uppermost (lithospheric) mantle is relatively cool and coupled to the crust; (10 to 40 km thick in oceanic and old continental regions respectively); these make up the lithosphere, and Earth's tectonic plates. The mantle is made up largely of ultramafic rocks – high in MgO and low in SiO₂. At depths between 410-660 km, in the Transition Zone, the dominant minerals (olivine, pyroxenes, garnet) go through a series of changes (phase transitions) to denser, higher-pressure forms, which dominate the mineralogy of the lower mantle (>660 km). The convection of the asthenosphere drives (or responds to) the movement of the tectonic plates that make up Earth's crust (Fig. 1b). In the upwelling parts of the convection system, decompression induces melting, with the production of a range of magma types, at relatively shallow levels of the asthenosphere. Where plates descend into the mantle at subduction zones, the introduction of water helps to cause large-scale melting, producing volcanic arcs – ranges of volcanoes like the Andes. Whether the whole mantle convects in the same way is still debated, but it is clear that material does emerge from the Transition Zone or even the core-mantle boundary, in the form of plumes, which bring hot mantle to near the surface. The results are visible in chains of volcanoes such as Hawaii; these “hotspot trails” reflect the movement of an oceanic plate over a stationary plume (Fig. 1c).

The role of fluids in all of these mantle processes is a major focus of the research program in the ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS). The presence of fluids helps to determine the viscosity of the convecting mantle, the temperatures at which it melts to produce magmas (which also are fluids), the nature of volcanic eruptions (explosive *vs* quiescent)

and the compositions of the magmatic products. We need to know the nature and distribution of different types of fluids in the mantle if we are to understand these processes.

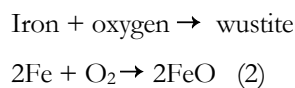
Oxidation-reduction (redox) reactions, in which oxygen is transferred from one mineral to another, or from a fluid to a rock or vice versa, play a vital role in many Earth processes, especially in the genesis of igneous rocks, and the movement and reaction of fluids at all levels of Earth's internal architecture. Redox reactions, as well as pressure (P) and temperature (T), can control which minerals are stable in rocks, and the distribution of water, carbon dioxide (CO₂), methane (CH₄), hydrogen and other components in fluids moving through the mantle and crust. Via such fluids, redox reactions also are very important in the formation of many types of ore deposits.

The “redox state” of a chemical system can be expressed in terms of the oxygen fugacity (f_{O_2}), which is simply the partial pressure of oxygen in an ideal gas of a given composition. It commonly is expressed as values relative to the f_{O_2} of a known reaction (a “buffer”; Fig. 2). For example, a relatively high oxygen fugacity (“oxidizing” conditions) would be defined by the reaction:



the “*FMQ*” buffer.

A much lower f_{O_2} (more “reducing” conditions) would be defined by a reaction such as:

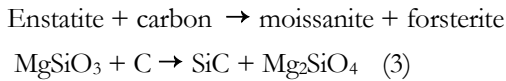


the “*IW*” buffer.

Most magmatic rocks in Earth's crust record f_{O_2} around the FMQ buffer; the upper

mantle tends to have lower fO_2 , and to become generally more reducing (lower fO_2) with depth (Fig. 2). The IW buffer is thought to represent a lower limit for fO_2 in the mantle, simply because mantle rocks contain so much FeO that it would be hard to reduce it all to Fe.

However, we do know that conditions more reducing than the IW buffer must occur locally in the mantle, partly because the mineral moissanite (silicon carbide, SiC) is found in some mantle-derived magmatic rocks such as kimberlites (the host rock of most diamonds) and even as rare inclusions in diamonds. The stability of moissanite is controlled by reactions such as:



As we study other mantle-derived rocks, we are finding that moissanite is unexpectedly common in the mantle, and can be accompanied by a wide range of other “super-reduced” minerals (e.g., metallic elements, carbides, nitrides) that require even more reducing conditions than moissanite itself. These occurrences raise two important questions: (1) what sort of processes can generate such conditions in Earth’s mantle? and (2) why didn’t these minerals react with the more oxidized mantle in which they are embedded?

Recent studies also have shown that remarkably similar super-reduced mineral assemblages can be found in mantle-derived rocks from completely different tectonic settings. This suggests the widespread operation of poorly-understood processes, not previously recognized in the mantle. Can the similarities and differences between some

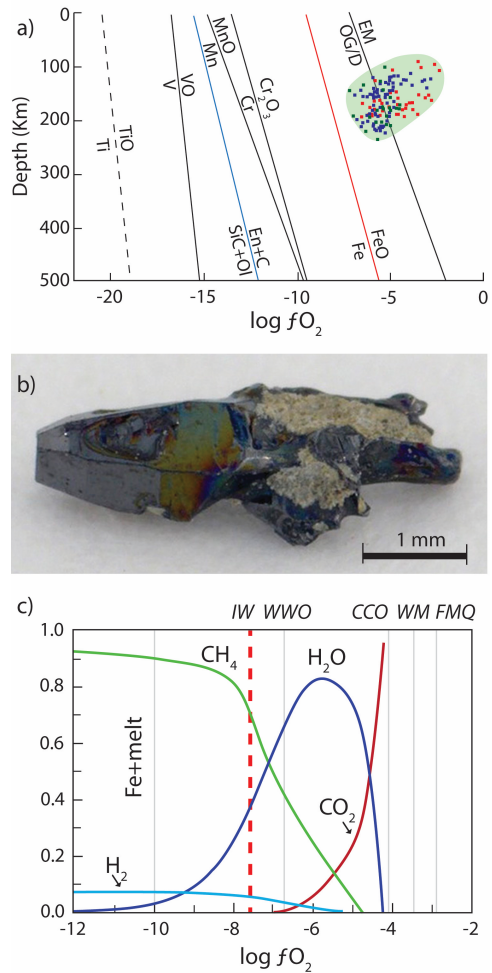


Figure 2. Oxidation-reduction (redox) reactions and their control on fluid compositions. (a) Oxygen fugacity vs depth (at 1500 °C) for some redox buffers; shaded field shows the range of fO_2 measured in rock samples from the upper (lithospheric) mantle, all above the Iron-Wustite (Fe-FeO) buffer; (b) a crystal (4.1 mm long) of moissanite from the Mt. Carmel area, Israel; (c) relative abundances of different species in C-O-H fluids as a function of fO_2 (after Kadik, 1997). Below the Iron-Wustite buffer the fluids are completely dominated by CH_4 and H_2 . EMOG/D, the buffer reaction Enstatite + magnesite = olivine + graphite/diamond.

of these occurrences provide clues to the nature of those processes?

Here we will give brief descriptions of three such occurrences, in southern Tibet, northern Israel and the Kamchatka volcanoes of NE Russia; by examining their similarities and differences, we can speculate on a common process.

Study Areas

Tibet

In southern Tibet, the Yarlung-Zangbo suture zone (Fig. 3) marks the great continental collision between India and Asia, which began ca 55 million years ago and continues today, pushing up the Himalayan Mountains. Scattered along this suture zone

is a line of peridotite massifs – fragments of Earth’s mantle, up to 1000 cubic kilometers in volume. Some of these contain minable bodies of chromite ore, which formed at shallow depths (5-15 km) ca 325 million years ago, when the peridotites were part of the mantle above a subduction zone. However, structures and relict minerals in the chromite ores and the peridotites indicate that these rocks were later subducted down as far as the Transition Zone (≥ 410 km), where they remained for about 200 million years (McGowan et al., 2015). During their residence in the Transition Zone, the peridotites probably heated up to 1400-1500 °C; this heating, and their composition, would result in them becoming buoyant relative to the surrounding mantle.

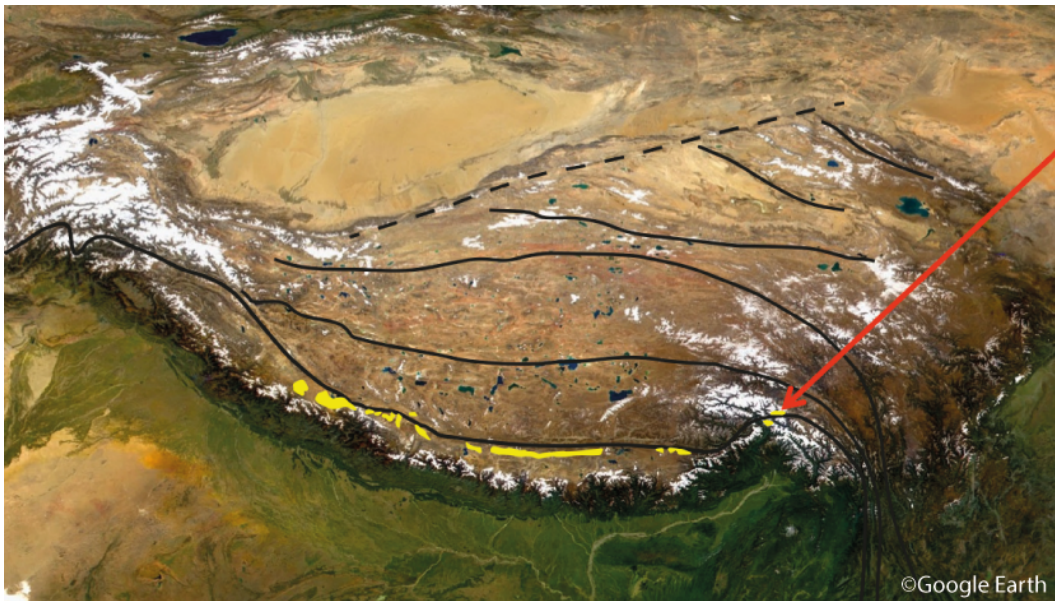


Figure 3. Bird’s-eye view (looking north) of the Tibetan Plateau, bounded in the south by the Himalayas. Black lines show sutures between crustal blocks that have drifted together to form the region. The southernmost line marks the Yarlung-Zangbo suture zone, where numerous bodies of mantle peridotite (yellow) were emplaced 60-70 million years before the collision of the Indian plate with Asia initiated the rise of the Himalayas. Many of these bodies contain diamonds, super-reduced mineral associations and evidence of derivation from the Transition Zone; the red arrow indicates the famous Luobusa peridotite. Map courtesy of Google Earth.

The excavation of these peridotite bodies from the Transition Zone back to the surface can be attributed to the forces exerted by a later slab, subducting during a plate collision event and penetrating into the Transition Zone. As the slab stalled, it began to roll back, causing the mobile asthenospheric mantle (Fig. 1, Fig. 4) to flow in to fill the “gap”. Dynamic modeling (Afonso and Zlotnik, 2011; McGowan et al., 2015) has shown that this can create a broad upwelling in the deep mantle, near the top of the Transition Zone. As slab rollback continues, this broad upwelling rapidly develops into a narrower channel of upward-flowing asthenosphere; this upwelling combined with the compositional buoyancy of the peridotite bodies to bring them rapidly (in 6-8 million years) from the Transition Zone to crustal levels, where at least some became the seafloor in small ocean basins (Liu et al., 2015).

Small diamonds were first recovered from some of the chromite ores in the peridotites more than 40 years ago (Fig. 5; Bai et al., 1993). Since then diamonds have been extracted from both the ores and the peridotites in at least seven tectonically emplaced mantle-derived bodies along the Yarlung-Zangbo suture zone, in peridotites on older sutures in farther north in Tibet (Fig. 3), and in similar bodies in the Polar Ural Mountains of northern Russia (Yang et al., 2014, 2015). These diamonds have created both interest and disbelief, because they differ in many respects from “normal” diamonds with which most geologists are familiar.

“Normal” diamonds come from magmatic bodies of kimberlite (an alkaline igneous rock) that typically occur in the stable cratonic areas of continents. Most diamonds in the kimberlites are fragments from the continental roots, and some may have resided there for billions of years; they usually form

octahedral crystals, which may be rounded by chemical resorption.

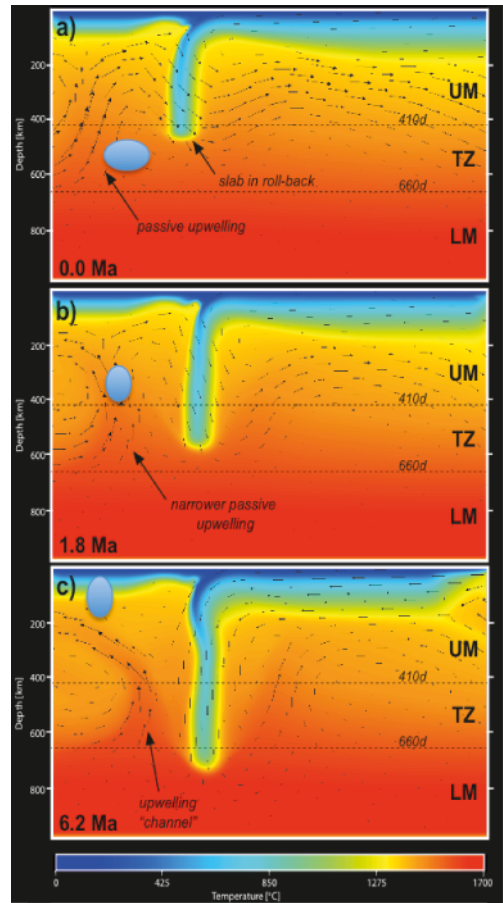


Figure 4. A thermo-mechanical model (Afonso and Zlotnik, 2011) showing how the rollback of a subducting slab sets up forces that lead to rapid upwelling of the mantle from the Transition Zone. The blue marker represents a mass of much older, more depleted peridotite rising from the Transition Zone to the ocean floor. (After McGowan et al., 2015).

The Tibetan diamonds, in contrast, strongly resemble synthetic diamonds that are produced industrially in America, Russia and China. They have smooth cubic faces, which are rarely seen on kimberlitic diamonds (Fig. 5); they contain inclusions of metallic alloys (Ni-Mn-Co); their carbon is isotopically very light; they contain nitrogen as single atoms, whereas nitrogen in kimberlitic diamonds is largely recombined into N-N pairs or N4 tetrahedra. However, several diamonds have been found *in situ* in the chromites (Yang et al., 2007, 2014) where they are surrounded by zones of amorphous carbon. Detailed studies (Howell et al., 2015) strongly suggest that the diamonds in the peridotites and chromite ores are in fact natural and represent a new environment for diamond formation in the mantle – but one that is not well-understood.

Diamonds do not require strongly reducing conditions to form in the mantle (EMOD buffer, Fig. 2). However, the diamonds in the peridotites of Tibet and the Polar Urals are accompanied by a great variety of “super-reduced” minerals (Yang et al., 2007, 2014, 2015). These include moissanite (silicon carbide), native elements (Fe, Ni, Ti, Si, Cr, Al), carbides of titanium and other elements, silicides of iron and titanium, and titanium nitrides. Many of the more unusual minerals occur as inclusions in crystals of corundum (aluminium oxide, Al_2O_3) with unusually high contents of titanium (Xu et al., 2015).

Aside from the very low $f\text{O}_2$ required by many of these minerals, it is difficult to precisely define the conditions of their formation. Many of the minerals imply high temperatures (1200-1500 °C), and the inferred presence of stishovite (a high-pressure form of quartz) around some super-reduced phases suggests depths >300 km (Dobrzhinetskaya et al., 2009).

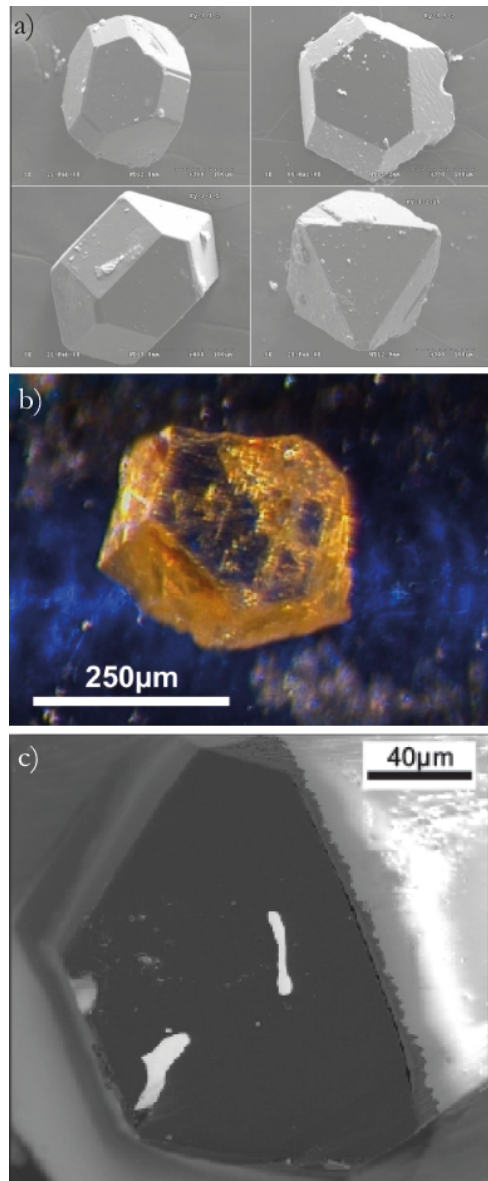


Figure 5. Microdiamonds from Tibetan peridotites (a) SEM images of diamonds, with octahedral and cubic faces; (b) diamond separated in CCFS labs, showing yellow colour and smooth faces; (c) polished section showing melt inclusions of Ni-Mn-Co alloy. Reproduced from Griffin et al. (2016) by permission of Oxford University Press.

Northern Israel

In the Mount Carmel area of northern Israel (Fig. 6), exploration for gemstones by Shefa Yamim Ltd. has discovered a remarkable assemblage of super-reduced minerals, comparable in many ways to the Tibetan assemblage (Table 1). These occur especially in Cretaceous (ca 99-94 million year-old) volcanic rocks on Mount Carmel, and in alluvial deposits derived from them. The volcanism occurs near the Dead Sea Transform Fault, which represents the boundary between the Arabian plate and the

northern (Mediterranean) edge of the African plate.

However, the Cretaceous eruptions predate the first known movements (Miocene) on the fault by about 70 million years (Sass, 1980; Garfunkel, 1989). Gas-rich explosive eruptions produced thick pyroclastic deposits (Fig. 6b) and some flows of frothy, glassy lavas (Sass, 1980). The primary magmas are mildly alkaline basalts. The presence of fragments of dense mantle rocks (garnet pyroxenites and websterites; Mittlefehldt,

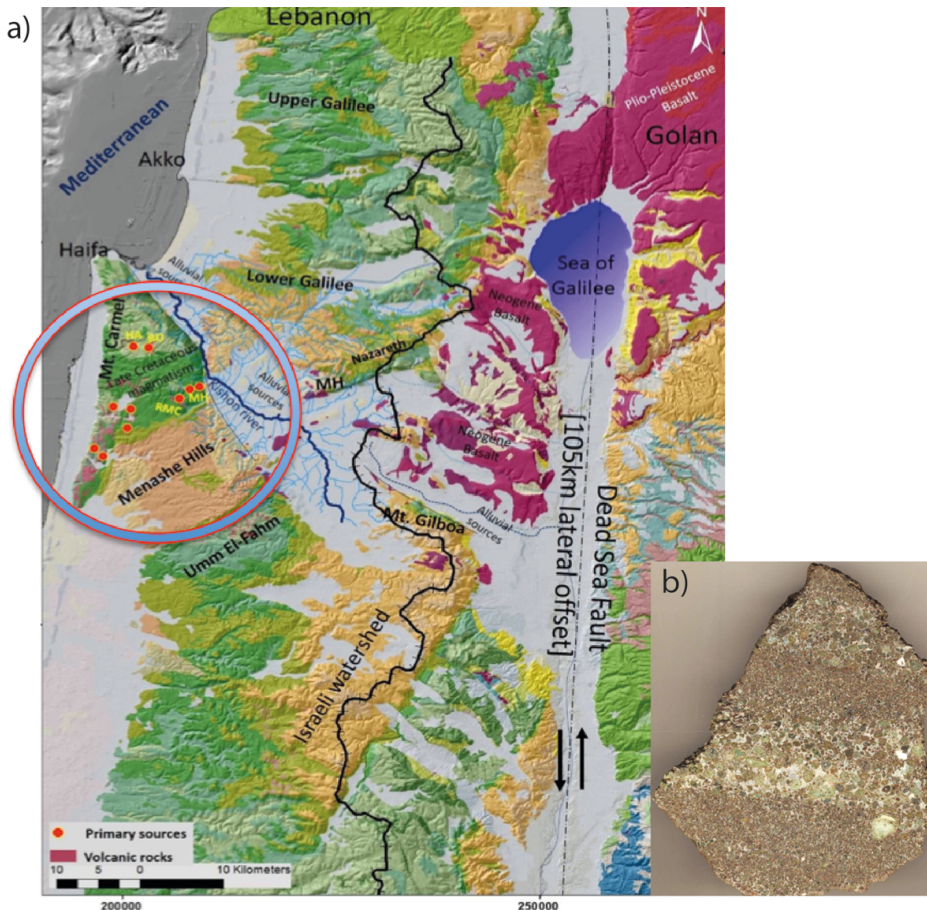


Figure 6. (a) Geological map of northern Israel; Mt Carmel area is circled, and volcanic centres are marked by red dots; (b) sawn section, ca 30 cm high, of volcanic tuff from Mt Carmel.

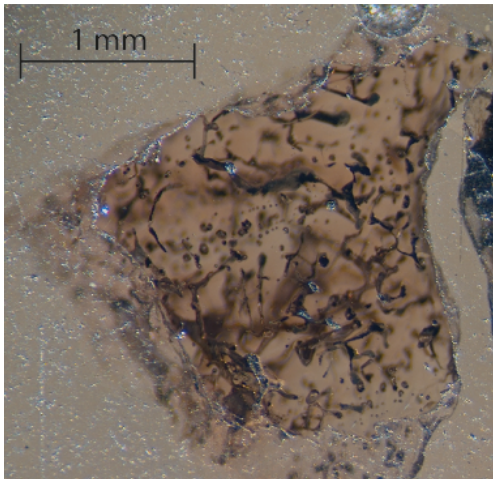


Figure 7. Fragment of non-gem corundum from Mt. Carmel; dark irregular blobs are pockets of melt trapped within and between grains of transparent corundum. (After Griffin et al., 2016b).

1986; Kaminchik, 2014; this work) shows that the magmas erupted very rapidly once they had risen to depths of around 80 km.

In addition to gem-quality sapphires, rubies and “normal” diamonds, the Shefa Yamim exploration program has produced unusually large crystals of moissanite (Fig. 2) and large grains (up to 2.5 cm across) of “non-gem corundum” (Fig.7). The latter has proved to be a *Rosetta Stone* for understanding the development of highly reducing conditions in Earth’s mantle.

Irradiation of the non-gem corundum with electrons produces a bright pink fluorescence (cathodoluminescence, or CL; Fig. 8), which shows remarkable patterns that outline the growth of the crystals. Microchemical analysis shows that variations in the CL response correlate with differences in the Ti content of the corundum – light areas fluoresce brightly, while high Ti contents

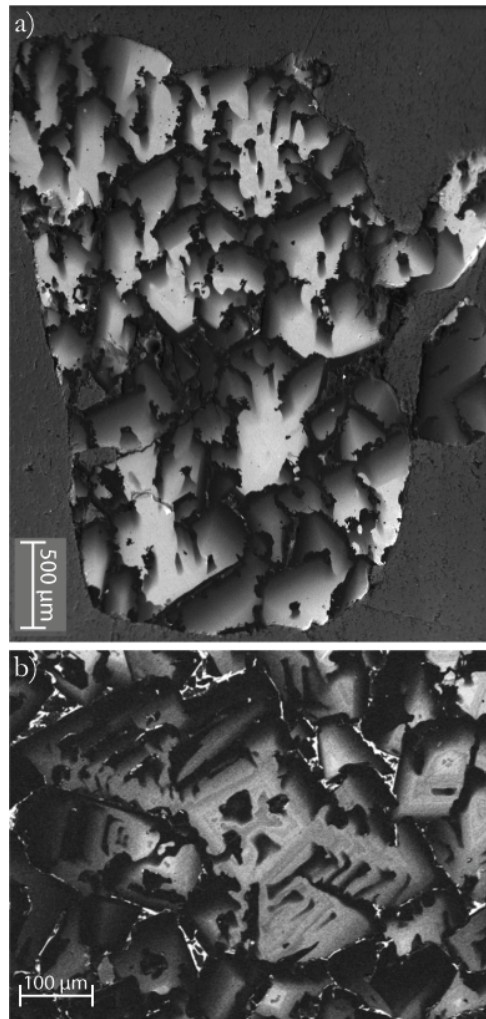


Figure 8. Cathodoluminescence images of polished fragments of non-gem corundum. Real colours range from light to dark pink to nearly black. Light areas have low concentrations of Ti; dark areas are zoned toward melt pockets and have up to 2.6 at.% Ti. (a) multiple “stacked” crystals of corundum outlined by high-Ti zones; (b) detail of crystal showing growth zoning that outlines hollow (“hopper”) faces and internal cavities filled with glass (dark CL; frozen melts). (After Griffin et al., 2016b).

induce darker shades. The patterns show that individual samples of the corundum typically consist of many smaller crystals, with pockets of melt trapped along the grain boundaries and within the crystals (Fig. 7, 8). These melt pockets now consist of calcium-aluminium-

magnesium silicate glass and minerals that crystallized from it before the volcanic eruption carried the corundum fragments to the surface – so these minerals were crystallizing in (or somewhere above) the magmatic plumbing system.

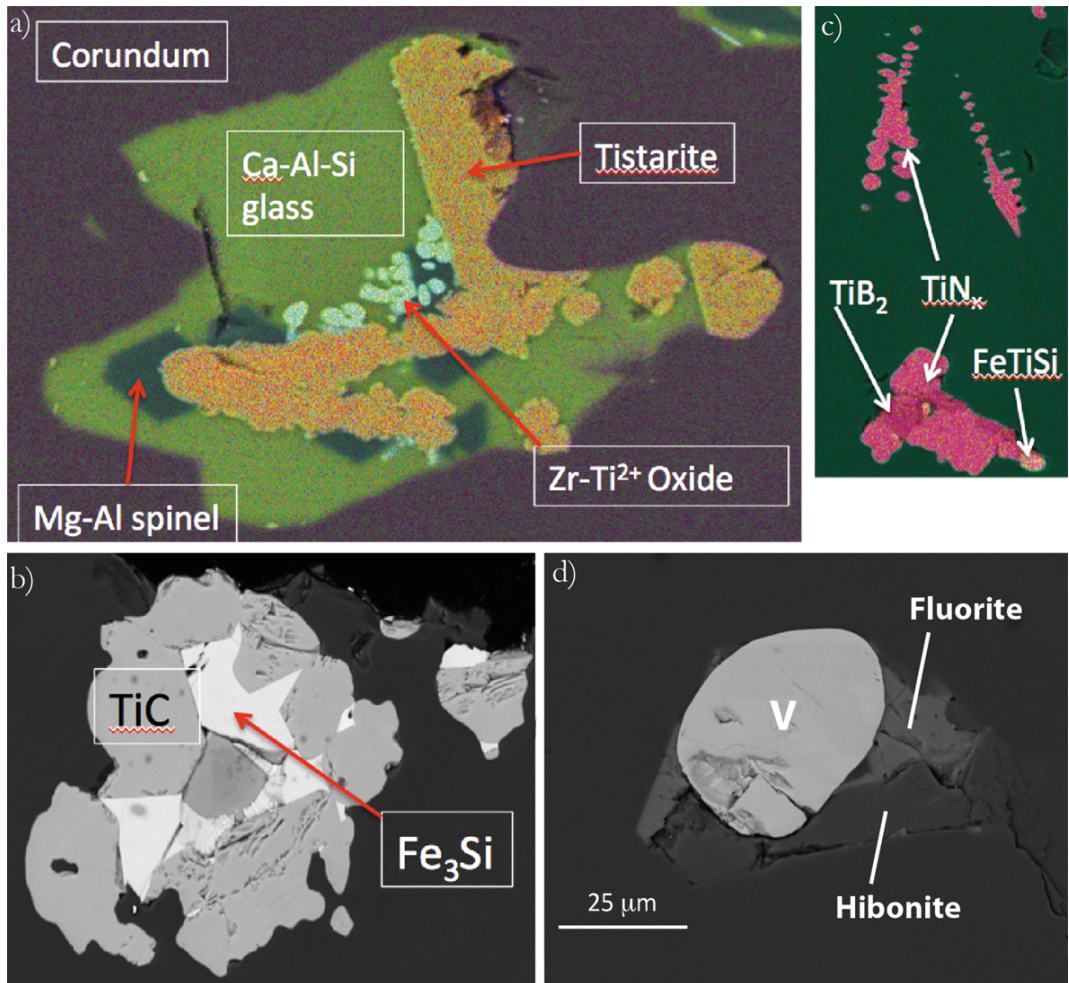


Figure 9. Four types of melt pocket in non-gem corundum from Mt. Carmel, illustrating some of the unusual, highly-reduced mineral associations. (a) SEM false-colour phase map showing minerals and glass in a typical silicate melt pocket in corundum; (b) Ti map showing nitrides, borides and silicides filling internal cavities in hopper crystal of corundum; (c) back-scattered electron (BSE) image of TiC crystallized from an Fe-silicide melt, enclosed in corundum; (d) BSE image of composite pocket of native vanadium, fluorite (CaF₂) and hibonite (a Ca-Al oxide) enclosed in corundum.

The corundum and its trapped minerals record very reducing conditions. Microchemical analysis shows that the Ti substituting in the corundum is the highly reduced form Ti^{3+} (most Ti minerals contain the more oxidized Ti^{4+}), and one of the most common minerals in the melt pockets is *tistarite* (Ti_2O_3 ; Fig. 9a). Reduction of TiO_2 (Ti^{4+}) to Ti_2O_3 (Ti^{3+}) requires fO_2 6-8 orders of magnitude below the IW buffer; these are seriously reducing conditions. However, *even lower* fO_2 is required by the presence of TiO (with Ti^{2+}) as a separate mineral, and as a component in other oxides (Fig. 2). Other low- fO_2 minerals in the melt pockets include kharambaevite (titanium carbide, TiC), iron silicide (Fe_3Si), titanium nitrides, native iron and native vanadium (Fig. 9b-d). The crystallization sequence of minerals in the melt pockets suggests a continuous decrease in fO_2 during their formation.

Moissanite has been found included in the corundum, suggesting that both were part of the same magmatic system. The CL patterns of the corundum show that it grew as “hopper crystals” (Fig. 9), with hollow faces and branching internal cavities. This type of growth is characteristic of rapid crystallization from fluids that are supersaturated in a component, in this case Al_2O_3 . There is no obvious genetic link between the diamonds and the corundum, although exploration has recovered a few microdiamonds similar to those found in Tibet. However, the abundance of carbide minerals, and breccia veins full of amorphous carbon cutting the grains of corundum, imply the presence of fluid(s) very rich in carbon. These two observations may be the key to the origin of this bizarre mineral system (see below).

It is difficult to constrain the temperature and depth of the fluid plumbing system. As in the Tibetan example, some of the minerals present (and the presence of glass) suggest

temperatures in the range 1200-1500 °C. The presence of the feldspar anorthite ($CaAl_2Si_2O_8$) in some melt pockets suggests the reaction corundum + melt \rightarrow anorthite, which would constrain the depth to between 30 and 100 km. Fragments of mantle rocks found in the volcanic ashes suggest that the lithospheric mantle (Fig. 1) beneath the area at the time of eruption was less than 100 km thick.

Kamchatka Peninsula, NE Russia

The Kamchatka peninsula (Fig. 10) hosts many large, active stratovolcanoes, reflecting the ongoing subduction of the Pacific plate beneath NE Asia. From November 2012 - September 2013, fissure eruptions occurred on the flank of the Plosky Tolbachik volcano. The first eruptions, especially at the site known as Proryv Naboko, were voluminous and highly explosive, with gas jets erupting >250 m in the air (Gordeev et al., 2013); later stages produced huge emissions of sulfur dioxide (SO_2), with lava fountains and pyroclastic deposits. Much of the early-erupted material consisted of extremely frothy, glassy lavas and pyroclastic material. The lavas are silica-rich basalts, and can be divided into a low-Fe group and a high-Fe group.

Two samples of the frothy lavas from the first eruptions yielded abundant diamonds (>700 grains); most were of a “yellowish-greenish” colour, and occur in gas cavities in the lava. Individual grains of moissanite, corundum (red, blue and Ti-bearing) and native elements (Fe, Cu, Al) were found in the same samples, also within gas cavities. Similar reduced minerals also have been reported from the lavas of several other volcanos on Kamchatka (Gordeev et al., 2013), and both moissanite and Ti-bearing corundum are common associates of “diamond-bearing ores of unconventional

types” related to explosive volcanism in Russia (Karpov et al., 2014).

The diamonds from Tolbachik (Karpov et al., 2014) are typically 250-700 μm in size, and show many remarkable similarities with those from the peridotites of Tibet and the Polar Urals. They have the same distinctive colour and the same cubo-octahedral habit, with smooth cubic faces (Fig. 10); they contain nitrogen almost entirely as single

nitrogen atoms; they have similar isotopically-light carbon ($\delta^{13}\text{C} = -27$ to -23 , compared to -28 to -24 in the Tibetan diamonds). Some crystals show hollows on the cubic faces, suggestive of hopper growth (“diffusion hunger”; Karpov et al. 2014). Unfortunately, no information is available so far on the nature of inclusions in the Tolbachik diamonds.

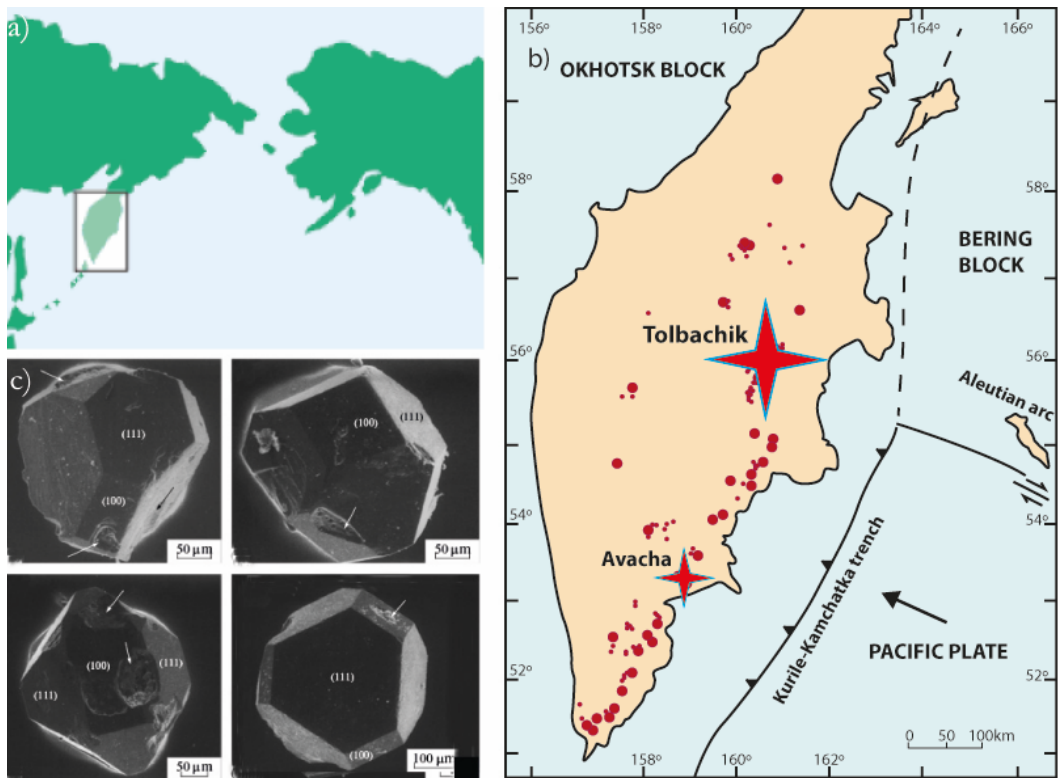


Figure 10. (a) location of the Kamchatka Peninsula (box) in Far Eastern Russia; (b) map of the Kamchatka Peninsula showing lines of volcanoes (red dots) related to subduction of the Pacific Plate beneath the continental margin (Okhotsk Block); red stars mark sites of Avacha volcano, and the 2012-2014 Tolbachik eruption; (c) SEM images of diamonds from lavas of the Tolbachik eruption of 2012, showing mixtures of octahedral (111) and cubic faces (cf. Fig. 5a); arrows point to hollow faces that may indicate either hopper growth or later dissolution (After Karpov et al., 2014).

Discussion

Similarities and Differences

(1) Tectonic environment: The three localities discussed here lie in three distinct tectonic environments, but there may be common factors. The Kamchatka peninsula lies above a major ocean-continent collision, with ongoing subduction and large active volcanoes. The Tibetan peridotites are in a major continental-collision zone (India-Asia), as are the Polar Urals occurrences (Asia-Europe), and there is only limited evidence of volcanism related to their emplacement. However, the continent-continent collisions in both cases were preceded by the subduction of oceanic plates, which may have brought up the peridotite bodies. The Cretaceous volcanism in the Mt Carmel area also lies along a plate boundary, but in this case it is the Dead Sea Transform Fault (Fig. 6), along which the plates grind past one another rather than subducting. In this case the movement on the fault accommodates the opening of the Red Sea to the south, transferring the movement to another major fault in southern Turkey. This plate boundary (1000 km long) thus must extend well down into the mantle, and could provide a conduit for deep-seated magmas and fluids similar to those generated by deep subduction.

(2) Associated magmas: The composition of the lavas that carry the Kamchatka and Mt Carmel low- fO_2 mineral assemblages lie in the broad spectrum of basaltic compositions associated with shallow melting of the mantle below the lithosphere. The Kamchatka lavas are characteristic of the volcanic rocks of magmatic arcs above continental-margin subduction zones. The basalts of northern Israel are more similar to “intraplate” basalts, and have been described as the products of a deep-seated mantle plume, with most of the melting occurring just below the base of the lithosphere (Fig. 1c; Stein and Hofmann, 1992). The only

magmas contemporaneous with the Tibetan peridotites are similar to the basalts erupted at mid-ocean ridges (Liu et al, 2015; Zhang et al., 2015); there is no evidence to link these magmas to the super-reduced mineral suite. These differences suggest that the composition of the magmas is not a critical factor in generating the low- fO_2 assemblages.

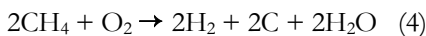
(3) Super-reduced mineral assemblages: The major minerals of the low- fO_2 assemblages are similar in all three occurrences (Table 1). The investigations of the Kamchatka lavas have only begun, so relatively few phases have been identified. The Tibetan minerals, which have been studied by many Chinese scientists for more than 30 years, include more than 80 different species, many known only as single grains (Yang et al., 2014). The assemblage from northern Israel has been under detailed study for only a year or two; it contains >65 identified compounds, many not previously known as naturally occurring minerals, but it also lacks many of those identified in Tibet. This may reflect the vagaries of observation, but may also indicate subtle differences between the conditions of crystallization in different localities. For example, diamonds are relatively abundant in the Tibetan and Siberian localities, but very rare in the Mt. Carmel volcanics (one microdiamond in a 252 kg sample); this might reflect differences in the depth of their respective volcanic systems. It is important to recognize the unique nature of the diamonds found in both Tibet/Polar Urals and Kamchatka, which appears to require processes different from those that generate the “normal” kimberlitic diamonds formed in old continental roots (Howell et al., 2015).

Generating super-reducing conditions – some evidence, some speculation

As noted in the Introduction, there are two problems – how to generate super-reducing

conditions in the upper mantle, and how to stop the products from reacting with the surrounding oxidized mantle. A key to the first question may lie in the mineral tistarite (Ti_2O_3 ; Fig. 9). The N. Israel samples represent the first known terrestrial occurrence of this mineral; its “type locality” (Fig. 11) is a single tiny grain in the Allende meteorite, where it occurs together with TiC and corundum, as in the N. Israel samples. Allende is a carbonaceous chondrite – one of the most primitive types of meteorite, and one of the oldest objects in the Solar System. The tistarite-TiC-corundum association in Allende represents early condensates from the solar nebula, in regions near the Sun; they reflect conditions of low pressure, but high temperature ($>1400\text{ }^\circ\text{C}$) and a very low $f\text{O}_2$ (Fig. 2) related to the streaming of the hydrogen-dominated solar wind through the nebular cloud. How could we generate such “nebular” conditions on Earth?

One possibility is illustrated by Figure 2c; in the deep Earth, at $f\text{O}_2$ below the IW buffer, mantle fluids are dominated by methane (CH_4) and hydrogen (H_2). If we can bring large amounts of such fluids to shallow depths, and keep them from equilibrating with the mantle on the way up, they would have a strongly reducing effect on their environment when they reached the upper mantle, as shown by reactions such as (4):



where C is diamond or graphite, depending on pressure.

In addition, reaction (5) can occur at shallow depths ($<3\text{ km}$), and carbon monoxide is a very powerful reducing agent in its own right:

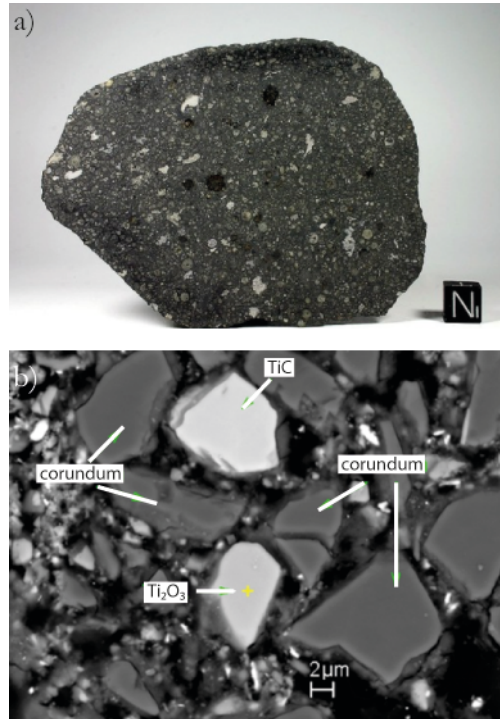
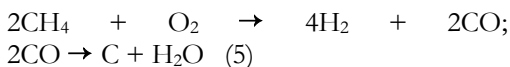


Figure 11. (a) Slice of the Allende meteorite, showing pea-sized chondrules and irregular light-coloured Calcium-Aluminium Inclusions, containing refractory phases condensed from the early Solar nebula; (b) the association of tistarite (Ti_2O_3), khamrabaevite (TiC) and corundum in the Allende meteorite (After Ma and Rossman, 2009). This is the type material of tistarite, and was the only known occurrence before the discovery of this mineral association in the corundum from the Mt Carmel area (cf. Fig.9).

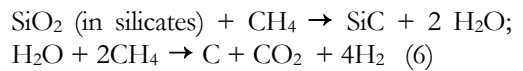
Note that these reactions also can liberate and deposit large proportions of carbon, which is consistent with the abundance of diamonds and/or carbide minerals in these deposits.

Rapid crystallization of corundum, SiC and other minerals

The second problem noted above is in keeping the newly-formed low- f_{O_2} minerals from reacting with the surrounding mantle; the available observations offer a few suggestions. Where the Tibetan moissanite (and diamond) have been seen *in situ*, the grains are surrounded by mantles of amorphous carbon. The nature and origin of this material is not clear from the available research, but it could at least provide a protective coating. Perhaps more important is the presence in all three localities of a Ti-rich corundum; our work suggests that this is itself an indicator of low f_{O_2} . The hopper growth of the corundum in the Mt Carmel localities is an important clue. The rapid growth of a large, porous network of corundum crystals in a magmatic (or hydrothermal) conduit could provide a low- f_{O_2} “sheltered environment” that would be isolated from the surrounding mantle, while reducing fluids could continue to flow through the network. This process could be the key link among the localities.

But what processes can produce a melt or fluid that is so super-saturated in Al that it can rapidly crystallize large volumes of corundum, apparently unaccompanied by any of the minerals common in mafic magmas? One possibility is suggested by the crystallization of anorthite (a feldspar mineral; $CaAl_2Si_2O_8$) in the melt pockets of the Shefa Yamim corundum. Anorthite melts directly to liquid, or crystallizes directly from melts, at low pressure, but at depths of 10 km-30 km, corundum crystallizes first from Al-rich melts (Goldsmith, 1980), and anorthite only begins to crystallize at lower temperatures. Anorthite is unstable deeper than about 30 km, but corundum can crystallize from melts to much greater depths. The simplest way to make a basaltic magma “dump” corundum is to remove silica (SiO_2). If this occurs at 10-30

km depths, this desilication can move the magma into a compositional space rich in Ca and Al (the anorthite component); at depths >30 km, corundum will be the first phase to crystallize, and will continue to be the only crystallizing phase over a wide span of temperature as the magma cools. The reducing processes discussed above provide a way to desilicate the magma, for example by reactions like (3) and (6):



Thus the streaming of CH_4 -rich fluids through the large “plumbing systems” associated with deep-seated volcanism at plate boundaries could be the process that results in the crystallization of both corundum and moissanite, and their associated low- f_{O_2} minerals, within the upper mantle. In the case of the Tibetan peridotites, these plumbing systems have not been recognized; they may have been obscured by the post-emplacement deformation and recrystallization of the peridotites and many of the chromite ores.

Conclusions: Relationships to tectonics

It appears that the common factor in the three localities described here may be the streaming of CH_4 from deep inside Earth’s mantle, related to deep-seated volcanism at plate boundaries. In Tibet, geodynamic models suggest that the peridotites were exhumed from the Transition Zone (>400 km) at rates of 6-8 cm/year (McGowan et al., 2015) – very rapid in geological terms. We expect that this upwelling process also would generate large fluxes of deep-mantle fluids, helping to produce the basaltic magmas. Kamchatka lies above a major subduction zone, and the rollback of this slab would

produce similar upwellings from the deep mantle. In both cases, fluids rich in CH₄ and H₂ might also be supplied by the “dewatering” of carbon-rich marine sediments attached to the subducting slab that triggered the rise of the peridotites.

There was no obvious subduction system active beneath northern Israel in Cretaceous time; the magmatism has been ascribed to the activity of a deep-seated mantle plume, and it seems likely that such plumes also would carry deep-mantle, CH₄-rich fluids. However, seismic tomography shows that the whole Eastern Mediterranean region is underlain by a network of ancient subducted slabs, from which buoyant material could rise, if triggered by tectonic activity or slab rollback, as in the Tibetan situation. In either case, local plume-like upwellings could be focused into the major plate boundary that became the Dead Sea Transform Fault, providing a tectonic environment where both magmas and deep-mantle fluids could rise to shallow levels.

We therefore suggest that such “jets” of CH₄ ± H₂ may commonly accompany certain types of mafic volcanism, especially along plate boundaries, driven by deep tectonics. We expect that in the future, the unusual low-*f*O₂ mineral assemblages described here will be recognised in many types of volcanic settings. However, they will only be discovered when researchers begin to look more carefully at the minute trace minerals in volcanic ejecta; future studies will reveal if our speculations are correct.

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