CSEM's
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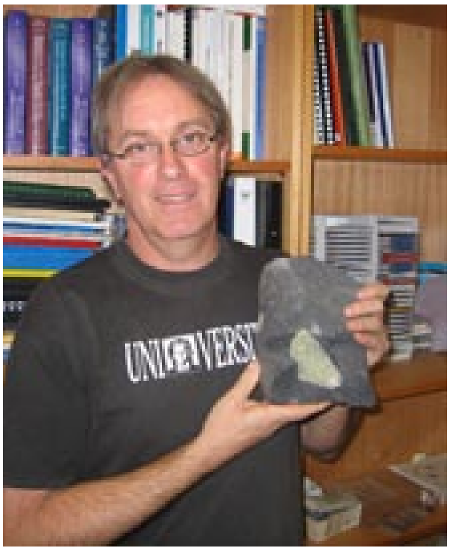
Rocking the world of materials

Reading diamond indicators



Dr Greg Yaxley with a sample of mantle rock encased in magma. Rock fragments like this, known as xenoliths, record in them the conditions of the deep Earth. This understanding is the foundation on which we can read minerals to indicate whether diamonds might be near by.

Inside this MM

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Wherever you find diamonds you'll also find a range of other minerals. Indeed, you're much more likely to find these other minerals than you are to find diamonds. When prospectors are hunting diamonds they usually look for these other minerals as indicators that a diamond source might be near by. However, interpreting the information contained in diamond-indicator minerals takes a bit of skill and a lot of science.

Work at the Research School of Earth Sciences is providing a rich new understanding on how diamond-indicator minerals (DIMs) can help both in finding diamonds and understanding what's happening deep in Earth's mantle.

The king of gems

Diamonds are the 'king of gems', symbols of purity and strength, and one of the most sought after substances on the planet. Diamond is a mineral, a natural crystalline substance, the transparent form of pure carbon.

Because of their beauty, rarity and a suite of special properties (see box), humans have placed a high value on diamonds since the beginning of recorded history. However, tracking them down has never been easy. That's because diamonds form deep in the Earth's mantle, usually at depths of 140 km or more, and are brought to the surface by an uncommon type of magma called kimberlite, that emanates from very deep inside the earth. Kimberlite magmas tend to be erupted extremely violently, forming small, pipe-like rock bodies in the crust. They are mostly only found in ancient landscapes where they are usually covered in weathered, younger rock material. Consequently, they are usually difficult to locate, and not all of them carry diamonds.

When hunting for diamonds the best indicator of a rich deposit containing diamonds is, unsurprisingly, the discovery of diamonds themselves. However, given their rarity, it's more likely you'll come across a range of other, much more common minerals such as garnets and spinels that also formed in the Earth's mantle, including in and around the zone where diamonds form. These minerals were also brought to the surface by the kimberlite magma.

So, given the fact that these associated minerals are relatively easy to find, can they be analysed in some way that will predict the likelihood of diamonds being present?

"Over the years the Research School of Earth Sciences (RSES) has developed a rich capacity in both the science and technology of analysing minerals," says Dr Greg Yaxley, a research scientist based at PRISE, a research group within the school that conducts commercially-oriented research. "And this understanding is now playing a valuable role in using minerals as indicators of where diamonds are most likely to be found.

"Diamond-indicator minerals, or DIMs, can tell you a lot about the likelihood of diamonds being present but they also hold a lot of other precious information about the area of the mantle in which they formed. Besides making a valuable contribution to our basic earth science, this information can also shed light on the possible quality of the diamonds that might be found and the extent to which the kimberlite magma has crossed through the diamond stability field."

The diamond stability field is the

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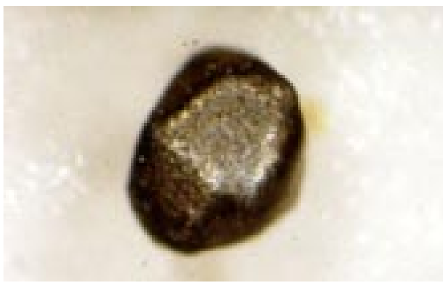


Know what to look for in this black mineral (known as a chrome spinel) and it can be used as an indicator of potentially diamond-bearing rock.

Reading diamond indicators (continued)

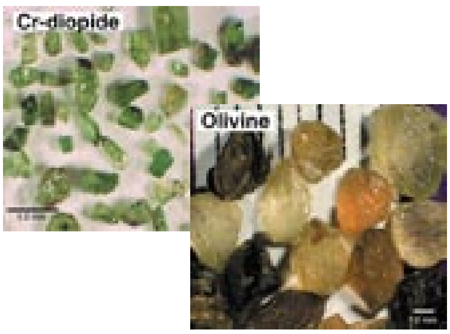
area deep beneath the most ancient parts of our continents where conditions for diamond formation are best.

Provenance indicators

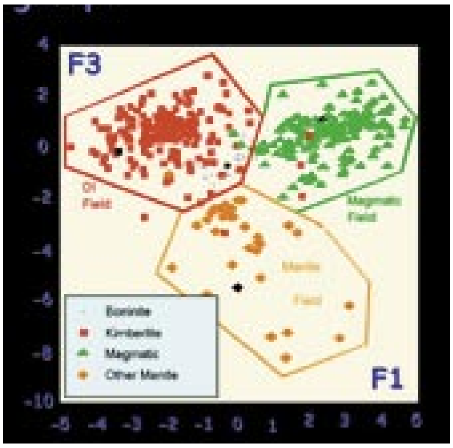
In the first instance, and probably of most direct interest to diamond companies, is the question of how mineral grains can indicate whether diamond-bearing rock such as kimberlite might be close by.

"In the past it's been thought that by knowing the ratios of the major elements making up some minerals it was possible to predict the nearby presence of associated rock types that are most likely to contain diamonds," says Dr Yaxley. "For example, chrome spinels are a class of mineral with major components of aluminium, magnesium, oxygen and chromium. By analysing chrome spinels from various rocks for chrome oxide plotted against magnesium oxide it was believed it was possible to spot minerals that indicated that the rock kimberlite was near by.

"Kimberlite is a volcanic rock type in which diamonds are known to sometimes occur. The diamonds don't actually form in kimberlite, but crystallize from carbon-rich fluids deep in the earth's mantle.. Passing kimberlite magma, on its way to eruption at the surface, can accidentally pick up the diamonds and other mantle rocks including so-called diamond-indicator minerals, and bring them rapidly to the Earth's surface. From there, these mantle minerals, including diamonds, are dispersed about the landscape over time by normal processes of weathering and erosion.



Chrome diopside and olivine are two other minerals often associated with diamond fields. Olivine is usually the most abundant heavy mineral in kimberlites. (Images from Natural Resources Canada)



By analysing spinel minerals for a suite of minor and trace elements it was found it was possible to separate the spinels associated with kimberlite, a rock type associated with diamonds. Above is an example of the type of results that were generated.

"In any event, it was believed that by analysing chrome spinels for the major elements that it was possible to identify the rock type that it came from. However, that belief is somewhat misplaced as it doesn't provide a sufficiently unique signature that allows you to differentiate spinels from diamond-bearing rocks from spinels from non-diamond bearing rocks.

Multi-element analysis

"Several years ago one of our Research Fellows, Dr Wayne Taylor, began looking for other ways to differentiate chrome spinels that held promise as an indicator of diamonds," says Dr Yaxley. "Rather than just look at the major elements, he also looked at the minor elements and trace elements in spinels from a range of different rocks groups, including spinels collected near known diamond-bearing rocks."

The minor elements were analysed using the school's electron microprobe while the trace elements were measured using inductively-coupled mass spectrometry on minerals that had been microsampled using laser ablation (LA – ICPMS, see the July 2003 issue of Materials Monthly for details).

"Wayne measured and compared a number of elements including concentrations of aluminium, vanadium, scandium, chromium, niobium and tantalum. Depending on which combination of elements you compared it was possible to discern patterns emerging in which spinels from diamond-bearing rocks carried different signatures from spinels from other rock types.

"However, the breakthrough came when you combined the data from a suite of 14 elements together using a multi-discriminant analysis. This allowed the spinels from the diamond-bearing rock to clearly stand apart.

"Of course, we knew this analysis worked because we began with spinels of known origins. To be useful, however, we needed to apply this analysis to spinels where the origins were unknown so we could test whether they could be used to spot the potentially diamond-bearing rock.

"When we carried out the analysis on unknown grains of spinel the technique proved to be a winner giving us a clear indication of which

Under pressure

If it's possible to synthesise diamond indicator minerals, why don't we simply synthesise our own diamonds?

Diamond was discovered to be carbon in 1796, and it took more than 150 years from that time until a method of diamond synthesis was invented. The secret was pursued by many scientists but not unlocked until the 1950s, when diamond was synthesized almost simultaneously by Swedish and American researchers. Pressures of over 55,000 atmospheres and 1400°C were applied, plus molten iron was used to facilitate the change from graphite to diamond. Now some 80 tons of synthetic diamonds are produced annually by General Electric, De Beers, and many others for industrial firms.

"It is possible to synthesise tiny diamonds in the lab for industrial purposes," says Dr Yaxley whose background is in the area of high pressure petrology. "However, it's still not possible to generate gem stone quality diamonds in this manner. It's not just a question of temperature and pressure because these can be simulated, albeit at significant cost. However, even if you can simulate the right conditions it would still takes a huge amount of time to grow the diamonds to a gem size."

Greg Yaxley with the RSES high pressure rock presses used to synthesise olivine and garnet.

spinels came from diamond-bearing kimberlite or lamproite and which came from other rocks which have nothing to do with diamonds."

PRISE has applied this method extensively on a commercial basis, to spinel grains collected during diamond exploration programs being undertaken by a number of major companies exploring for diamonds in India, southern Africa and Australia.

Reading the pressure and temperature of the mantle

By carrying out multi-element analysis of diamond-indicator minerals it is possible to improve your chances of spotting a potential diamond field however there's a lot more these DIMs can tell us both about conditions in the deep mantle and about the expected quality of a diamond field.

"To spot kimberlite or lamproite is valuable but, unless you were to chance upon diamonds, you still wouldn't know if the volcano that had produced these rock types had originated from deep enough in the planet to sample the diamond field," explains Dr Yaxley. "To figure this out you need to be able to interpret the elemental composition of your diamond-indicator minerals so you can determine at what temperature and pressure they originally formed. This information will also tell you how deep they were before the kimberlite magma carried them to the surface."

The science of determining temperature and pressure from mineral composition is called thermobarometry and it's one of the foundations of petrology (the study of rocks and the conditions by which they form).

"Given a sample of the major rock-type from the mantle (a green rock called peridotite) it's a relatively straightforward task to determine the pressure at which it formed by measuring the amount of aluminium in the component mineral orthopyroxene," says Dr Yaxley. "This method assumes that the aluminium is in chemical equilibrium with other components of the rock, specifically garnet, which can be verified by measuring the aluminium in grains of garnet contained in the same rock sample."

"To measure temperature there are a couple of commonly applied methods. One involves the partitioning of iron and magnesium between the minerals olivine and garnet which varies according to temperature."

This volcano goes down how far?

So, the idea is that a magma carries with it fragments of the mantle it passes through (often referred to as 'having sampled'). These rock fragments or xenoliths are brought to the surface where they are collected and taken back to the lab. Thin polished sections are made from the xenoliths, their constituent mineral components are identified, and these minerals are then analysed for the key elements indicative of temperature and pressure (usually with an electron microprobe). From this information you can plot the various depths at which the xenoliths originally formed giving you an idea of how deeply the magma sampled. If none of your rock fragments came from deeper than 140 km then it's unlikely you're going to find diamonds.

While these methods of

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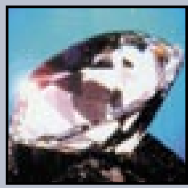


Diamonds are forever

In our modern world of wonder materials, there's something undeniably special about diamond. A natural diamond is likely the oldest thing you will ever own, possibly 3 billion years in age, fully two thirds the age of the Earth. Diamond, however, is also a high-tech super material for our technological age.

Its hallmark property is hardness. Hardness is the measure of a substance's resistance to being scratched, and only a diamond can scratch another diamond. Diamond is the hardest substance known.

But diamonds hold a variety of other properties that make them quite unique:

Diamonds repel water, an unusual property for a mineral. Diamond's strong bonding and carbon composition cause its surface to repel water but to readily accept wax and grease.

A diamond's brilliance and lustre are two of its most valued attributes. Diamond displays the maximum amount of reflectance for a transparent substance, displaying what is called an 'adamantine' lustre.

Diamonds are called 'ice' with good reason. Its high thermal conductivity means that when you touch a diamond to your lips, it feels ice-cold because it robs your lips of their heat. The capacity of diamond to conduct heat distinguishes it readily from other gems and exceeds that of copper by about 4 times at room temperature. This exceptional property of diamond is increasingly being used for extracting heat from electronic devices to make them smaller and more powerful.

Diamonds are good conductors of heat but poor conductors of electricity though some rare forms, particularly the gray-to-blue ones called type IIB, are semiconductors, and are somewhat conductive. These electrical properties also make diamond a valuable material in electronics.

Eighty percent of the diamonds mined annually are used in industry; 4 times that production is grown synthetically for industry - that's a total of over 500 million carats or 100 metric tons. Diamond is a fundamental industrial material that is used to cut, grind, and polish most hard substances.

More recently, diamonds are also finding valuable roles in radiation detectors, light emitters in electronic displays, and coatings to make surfaces unwettable. Diamonds will be showing up in more and more products in the future, probably in your home electronics, appliances, and automobiles.

Africa is the richest continent for diamond mining, accounting for roughly half of world production. However, the Argyle mine, located in Australia's far north Kimberley region, is the world's largest single producer of diamonds. Every year the Argyle diamond mine is responsible for producing more than a third of the world's total annual supply. The average annual production now totals over 35 million carats.

The Argyle diamond mine yields approximately 45 per cent near gem quality, and 50 per cent industrial quality diamonds. The remaining 5 per cent is made up of gem quality diamonds and yields the rare and highly valued pink diamonds, as well as the range of sparkling champagne and rich cognac diamonds.

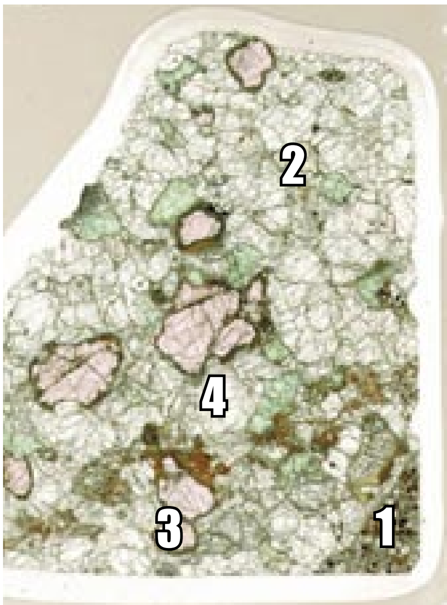
Reading diamond indicators (continued)

thermobarometry are well accepted they are contingent on being able to simultaneously measure several different mineral grains in one rock fragment. Unfortunately, what the prospecting geologist is more likely to find are disaggregated mineral grains.

"These deep-seated volcanoes are particularly violent beasts," explains Dr Yaxley. "Their very strength tends to shatter any rocks it carries from the mantle. In addition to that, any surviving fragments tend to weather down to their constituent parts once they've reached the surface. Consequently, we need a technique that works for isolated grains."

Grow your own

"In recent years a number of efforts have been made to estimate temperature from the concentrations of nickel, cobalt, manganese and zinc found in isolated grains of garnet, olivine and spinel. This has been done



A polished thin section of a peridotite xenolith; or in plain speak: a sliver of a piece of rock from the Earth's mantle brought up to the surface by a volcano. You can see a remant of the kimberlite in which it was encased in the lower right hand corner (1). By studying mineral crystals contained in the xenolith researchers can estimate at what temperature, pressure and depth the rock came from. Pressure can be determined by measuring the amount of aluminium in the mineral orthopyroxene (2) and garnet (3). Temperature can be determined by measuring the iron and magnesium in the minerals olivine (4) and garnet. Olivine is the main mineral in peridotite comprising around 50-60% of its mass.

by analysis of mineral grains still in rock aggregates from a number of samples and by growing synthetic samples of garnet and olivine under a range of pressure and temperature conditions that simulate conditions over a variety of mantle depths.

"The original studies came up with guides for predicting temperature from the nickel content of isolated garnets and these results are widely used today however the range over which they sampled was somewhat limited and was based on a number of assumptions."

Dr Yaxley is now in the process of refining these studies by growing his own set of synthetic mixes of garnet and olivine minerals using the school's high pressure rock presses and measuring how added quantities of a variety of elements partition themselves between the two mineral types.

"It's a study I'm undertaking in collaboration with De Beers. We're growing mineral samples at pressures and temperatures that simulate a range of lithospheric conditions. We then accurately measure how nickel and cobalt divide themselves between garnet, olivine and spinel. This generates valuable data that allows us to

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Working with RSES

As this story on diamond mineral indicators illustrates, the Research School of Earth Sciences possesses a wide range of facilities and expertise on rock and mineral characterisation.

Part of the school's success lies in the fact that it was the institution that developed the SHRIMP (Sensitive High Resolution Ion Micro Probe; see the April 2005 issue of Materials Monthly for a history of the SHRIMP), a technology that allows for the accurate determination of different elements in microscopic samples of rock. So successful is the SHRIMP that there is a high demand for its services, leading to development of several more advanced versions of the machine.

Because demand from outside the university is so high for the SHRIMP (and other forms of analysis available at the school), a unit called PRISE manages commercial and collaborative scientific interactions between RSES and external clients. Much of PRISE's work involves the analysis of radiogenic isotopes, although more recently PRISE has become involved in work more diverse than this, as the story on diamond indicators suggests.

PRISE provides access to any of the 'state of the art' facilities available at the RSES including the SHRIMP, thermal ionisation mass spectrometry, EPMA and LA-ICP-MS. There are few organisations world-wide that have under one roof the range of equipment and expertise available to PRISE. All equipment used is run and maintained at the highest possible standard. PRISE has a wide range of projects in progress on every continent (and is even working on samples from the Moon!). These arise from contracts and collaborations with a variety of people and organisations including universities, geological surveys, other government bodies and industry.

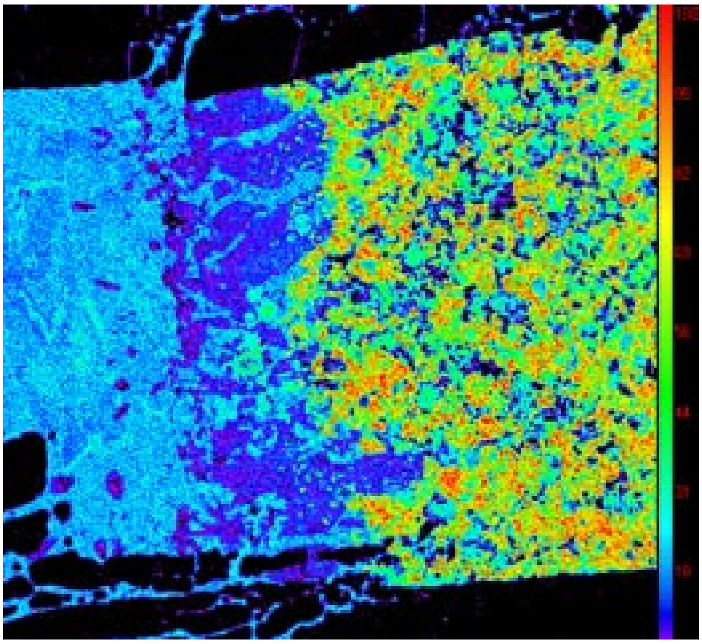
PRISE provides a full confidential report of analyses performed and results obtained with all commercial work undertaken. In addition, where collaborative work is involved, PRISE will prepare any necessary results, photos and diagrams for publication in journals or presentation at conferences.

Here are a few examples of the many geochemical studies currently being carried out by PRISE:
- SHRIMP U-Pb dating of minerals such as zircon, titanite, rutile, baddeleyite, monazite and perovskite, in a large range of geological studies on every continent;
- Direct dating of metalliferous mineralisation using the Re-Os system in sulfide minerals;
- Dating of kimberlite using Rb-Sr geochronology by Thermal Ionisation Mass Spectroscopy (TIMS);
- Provenance and correlation of sediments using zircon U-Pb geochronology, trace elements and Hf isotope measurements;
- High pressure experimental studies of the melting behaviour of the upper mantle

More info: http://rses.anu.edu.au/prise/

The art of EPMA

Introducing the Cameca SX100



A map produced by the SX100 of calcium concentrations in a thin section of rock. The colours in the sidebar provide a guide to the x-ray intensity being measured. Roughly speaking, the greater the intensity the higher the level of calcium. Maps like this assist in identifying different minerals present in the rock.

The principle of electron probe micro analysis (EPMA) is quite simple: fire a beam of electrons at a micrometre-sized polished section of your sample and measure the x-rays given off. The spectra of wavelengths of the emitted x-rays provide information on what elements are there while the intensity of the x-rays tells you how much of any particular element is present.

EPMA has been a basic analytical tool in geoscience since the 1960s but a modern instrument like the Cameca SX100 electron microprobe at the Research School of Earth Sciences makes the technique both easy and convenient to apply.

"The electron microprobe is really just a specialised scanning electron microscope," says Ashley Norris, the officer in charge of the electron probe. "Like an SEM it's based on a focused beam of electrons, though our beam is much brighter, stable and more powerful, running up to 50 keV.

"However, where an SEM is all about recording a visual image of the subject based on the electrons emitted from the sample surface, the electron microprobe is about exciting x-rays from the sample being tested and then measuring those x-rays.

"The Cameca SX100 electron microprobe acquired by RSES represents the best technology available in this field. It has the capacity to carry out multi-element analyses in a matter of minutes, and the ability to detect most elements down to a concentration of only 100 parts per million."

The SX100 comes with 4 spectrometers, an EDS detector and full electron, optical and x-ray imaging capability. The controls are easy to use and samples can even be setup in such a way that the analysis can be preprogrammed to take place automatically.

Ashley Norris at the controls of the SX100.

"The SX100 is run and maintained as part of the Experimental Petrology group," explains Mr Norris. "Not surprisingly, it's most common use has been in the elemental analysis of high pressure minerals, however, it's proved valuable across a wide range of disciplines including archaeology, environmental geoscience and a number of areas of materials science.

"For example, it's been used to describe the properties of germanium glass and analyse microdots on silicon wafers. It's also been used in some historical investigations. Recently, archeologists at ANU used it to determine if iron fragments from the gold rush period were produced by a back yard smithy or from a professional smelting operation, you can tell this from the sulfur content and levels of certain trace elements in the metal.

"While the SX100 is very easy to use once you know its basic operation, because it is used for so many different purposes, with each analysis having its own specific characteristics and challenges, it's not simply about pushing a button and getting an answer. There are many ways you can use the SX100. You have to know your sample and how to use the machine to extract the appropriate kind of information.

"If you need to use the SX100 for a one-off job we're happy to operate the machine for you. However, if you want more than one analysis carried out then we'll train you on how to operate the machine yourself.

"It's not just a superb facility for the analysis of major, minor and trace elements in a sample. It's also that this facility operates in an environment we're there's an enormous amount of expertise available to assist with any of the problems that might confront you."

The SX 100 is available for use by anyone at ANU and any research institution in Australia. ANU users enjoy a research rate while external users are charged at a commercial rate.

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Ashley with the specimen holder for the SX100. Six samples can be loaded up for each run and samples must be coated in carbon to prevent charging from the electron beam.

Reading diamond indicators (continued from page 4)

calibrate the results we obtain when analysing single garnet or spinel grains from the field," says Dr Yaxley. "In other words, this will help us obtain better information on temperature and depth when we only have single mineral grains available for analysis, which is more often than not all we have."

Oxygen fugacity

Diamond mineral indicators can therefore tell us a lot about whether kimberlites or lamproites are close by, plus it's possible to get an idea from them as to how deep the magma sampled. However, there's another vital piece of information that they can provide as well.

"To form diamonds you need carbon being subjected to the right pressure and temperature," says Dr Yaxley. "However to preserve the diamond you need an appropriate chemical environment. If, for example, a diamond finds itself in a highly oxidising environment the carbon will transform over time into carbonate. Diamonds need a relatively reducing environment in order to be preserved. This is referred to as oxygen fugacity and diamonds need a low oxygen fugacity in order to remain stable.

"Oxygen fugacity can be determined by measuring the ratios of different iron cations in garnets and spinels, specifically the ratio of iron (III) (Fe^{3+}) to iron (II) and iron (III) (Fe^{2+} + Fe^{3+}).

"Unfortunately, the low levels of iron oxide in garnets means there's no easy way of precisely measuring this ratio so in addition to our other work on diamond-indicator minerals I'm now working on a new method that uses synchrotron radiation to accurately measure Fe^{2+} and Fe^{3+} in garnets."

Greg Yaxley and Andrew Berry at the Photon Factory in Japan.

As with the temperature work, Dr Yaxley has been using synthetic garnets, this time grown by Professor Alan Woodland and co-workers in Germany with known levels of the different forms of iron, for measurement in a synchrotron. The work is being done with Dr Andrew Berry, who has recently left RSES to work at Imperial College, London, and Dr Hugh O'Neill at RSES. Dr Berry has extensive experience measuring the oxidation state of metal cations in minerals and glasses using synchrotron radiation (see the January 2002 issue of Materials Monthly).

"The particular technique we're exploring is known as XANES or X-ray Absorption Near-Edge Structure spectroscopy," says Dr Yaxley. "It involves measuring the degree to which the garnets fluoresce at different wavelengths of incident synchrotron x-rays.

"We've already carried out tests on the Australian National Beamline Facility at the Photon Factory in Japan. The hope is that we can develop this into a rapid and reliable technique that will be suitable for use at the Australian Synchrotron in Melbourne when it comes on line in a couple of years."

Reading diamond indicator minerals is an art that has come a long way in recent years. At one stage they simply gave mild encouragement to continue searching for diamonds in an area. Now, thanks to work at the Research School of Earth Sciences, they can provide you with a good idea on whether that search is likely to turn up the goods.

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