CSEM's
Materials Monthly

August 2006 Making materials matter

Fingerprinting dust

What's in a pinch of airborne dirt

Researchers are discovering that there's a lot more to dust than meets the eye. These days it's possible to characterise dust in numerous ways that allows us to pin point where it has come from and what it carries with it. Fingerprinting dust is not your standard materials science but earth scientists are demonstrating it's not a science to be sneezed at.

"We estimated that the storm deposited around 6 grams of dust per square metre. That's a phenomenal amount of material," says Patrick De Deckker.

A dark presence flowed over Canberra on the night of Tuesday, 22 October, 2002. A fast moving cold front had brought with it not rain but a tremendous plume of dust. A ghostly brown fog enveloped the city coating cars, building and plants in a layer of fine dirt.

Light rain did eventually fall but little reached the ground. Instead it was sucked up by the dry dust forming globules of mud. Like a biblical plague, it rained mud that night. And, because of water restrictions (the region was six months into a severe drought), no-one was permitted to wash down their homes or cars. This veneer of dirt we had to wear for many weeks.

"It was an amazing event," says Professor Patrick De Deckker from the Department of Earth and Marine Sciences (DEMS). "We estimated that it deposited around 6 grams of dust per square metre. That's a phenomenal amount of material when you think about it."

Phenomenal indeed. Calculations based on satellite imagery and meteorological data suggest that the dust storm carried one of the largest dust loads recorded in Australia. The dust plume was 2400 km long, up to 400 km wide and between 1.5 to 2.5 km high. It covered an area of around 840,000 square kilometres and carried an estimated load of between 3-5 million tons of dust.

While it was a memorable event for most people it proved to be pivotal for Professor De Deckker.

Global interest in dust

"My interest in dust and dust storms had been kindled several years earlier," he says. "But it was this event that galvanised my studies.

"My initial interest arose from attending a conference where North American researchers presented data on African dust blown over the Caribbean. It was quite amazing what was in that African dust and how it had such an impact on an area thousands of kilometres away from where it originated. They found that the dust contained bacteria, fungi and viruses, that many forms were pathogenic and that some were believed directly connected to coral disease in the Caribbean.

"I began to look into dust and microbes and discovered that this field, known as aerobiology, was a very popular topic in the 1980's. The World Health Organisation and various big international bodies were very interested, but then the interest seemed to die off.

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(Above) A car parked at ANU displays the evidence of the 'mud fall' of 22 October. (Left) A window shows how the dust became splots of mud following a light rain.

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Fingerprinting dust

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"I suspect this was partly because they didn't have the equipment we have today. These days we can work with extremely small samples, which is often all that's available when you're working with dust, and analyse for DNA, organic chemistry, mineralogy and a range of isotopes allowing us to accurately characterise specific samples of dust. We also have techniques for tracking air movements that are extremely sophisticated such as the HYSPLIT program.

"In any event, I began taking a greater interest in understanding and working with dust when out of the blue Canberra was hit by this storm that dropped a huge amount of material to work with."

Professor De Deckker, along with a number of other researchers from ANU, around Australia and across the world carried out a range of analyses on the dust. And what did they find?

"The most common grain size of the dust particles was around 26 microns," says Professor De Deckker. "The grains were mostly angular and there were many fibres in the dust, some of them up to 200 microns in length. Some people have suggested that fibres may have originated from feacal pellets from rabbits or other organisms.

"The dust was also found to contain 4.5 parts per billion of the organic chemical DDE, a breakdown product of the pesticide DDT."

Numerous other tests were done on the dust including an analysis on pollen, organic chemistry and microbes (see the box 'Who found what'). All of this yielded interesting results but, of course, the question that everyone was interested in was where did the dust come from. To answer that question you first need to record some form of physical fingerprint of the dust that relates to the physical characteristics of a source area.

Major dust storms are a frequent occurrence over northwest Africa and the Sahara Desert. This image of a massive dust storm was aquired on February 11, 2001 by the Sea-viewing Wide Field-of-view Sensor (SeaWiFS). SeaWiFS has seen similar storms every year since its launch in August 1997. Of particular interest in this image are the eddies and waves on the lee side of the mountainous Canary Islands (centre).

Each year, several hundred million tons of African dust are transported westward over the Atlantic to the Caribbean, Central America, and South America. Since the 1970s, coral reefs in the Caribbean have been in continual decline with several episodes of mass mortality coinciding with peak dust years (in particular 1973, 1983, and 1987). Many researchers believe the coral decline in the Caribbean is a result of pathogens transported in dust from North Africa.

[Image courtesy of the SeaWiFS Project, NASA/Goddard Space Flight Center, and ORBIMAGE.]

Analysing dust

To develop a profile or a fingerprint of dust many separate measurements are made. These include powder X-ray (powder) diffraction to work out the mineralogy of the dust particles, and ICP Mass Spectrometry to determine the proportions of major, minor and rare earth elements.

"Strontium, neodymium and lead isotopes are the three elements we particularly focus on in developing a physical profile of the dust," explains Professor De Deckker. "This is because these isotopes are not involved in biological cycles, they are not fractionated by organisms. In other words, the provide us with an accurate guide to the local rock type that was originally weathered down to form the dust. The proportions of these elements have not been altered by biological processes subsequent to it being weathered down."

Having established a fingerprint of the dust, now you need to know the path of the storm. These days there are vast arrays of meteorological data to draw on and some increasingly sophisticated programs available to interpret that data. One program called HYSPLIT allows you to track the airmass anywhere on the planet (see the box 'From where does an ill wind blow').

Finally, to establish the source of your dust you need to match your dust fingerprint with the fingerprint of rock and sediment types from areas upwind of where the dust ended up.

"As it happened, we have doing an extensive survey of river clays over the area of the Murray Darling Basin so we could map where sediments found in rivers were coming from," says Professor De Deckker. "We now have a database of fingerprints with which we could compare with the fingerprint of the storm dust.

"Putting all this information together allowed us to conclude that the

What is dust

The dictionary defines it as fine, dry, pulverised particles of earth or other matter. The earth scientist refines this by describing the particles as primarily consisting of minerals from a natural source, although they can be associated with organic materials. The particles may be as big as grains of sand up to 200 microns (one fifth of a millimetre) down to specks only one tenth of a micron across. In terms of airborne (aeolian) dust, most particles are under 6 microns in diameter because anything bigger tends to drop out fairly quickly. Particles under 6 microns, however, can remain in the atmosphere for days, weeks or even months.

dust that rained down on us on in October 2002 originated from very close to Cobar."

Dust impacts

So, where's the value in knowing what's in a dust plume and where it came from?

"Having the capacity to determine the geochemical and microbiological fingerprint of aeolian dust is important for a broad range of reasons," explains Professor De Deckker. "This knowledge has many implications for human health, ecosystems science and global studies.

"In a direct way, the dust itself can pose a threat to human health. For example, we had another smaller dust event in Canberra in 2005. That dust had a huge amount of lead in it and we suspect it came from around Broken Hill. Had that dust come down in the same quantity as in the October 02 event it would have been dangerous.

"Then there's the threat in what might be carried with the dust. For example, dust sampled above the Caribbean in 2001 which originated in Africa has been shown to harbour over 170 colonies of bacteria, around 75 colonies of fungi and many viruses. Around a third of the bacteria in this study were pathogens known to affect plants, animals or humans, and serious outbreaks of coral disease in the Caribbean have coincided with major dust storms.

"There have also been claims of a link between these dust plumes from west Africa, where foot and mouth disease is common, and the foot and mouth outbreak in the United Kingdom in February 2002. This is based on the fact that an arm of the dust plume did cross the UK at about that time.

"Then there are health issues with organic chemicals found with the dust. We found some breakdown products of pesticides in the 2002 dust event but there's little raw data on this topic to draw any conclusions on what impacts this could have.

"We have a growing problem with allergies and asthma. Many people say it's pollen but it might also relate to other chemicals or organisms in the air too. The studies on the dust in the Caribbean show that when dust plumes from west Africa strike the Caribbean there is a higher record of purchases of asthma drugs and more people in

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Who found what?

In the dust that fell in October 2002 in Canberra?

Dr Raeid Abed working with **Dr Dirk de Beer,** both microbiologists at the Max Planck Institute of Marine Microbiology in Bremen, determined that the dust harboured an exceptionally high diversity of viable bacteria.

Professor Kai-Uwe Hinrichs, Professor of Organic Geochemistry at the University of Bremen, used positive ion base-peak chromatograms and density map from HPLC-MS analysis of intact polar membrane lipids found in the dust samples. The lipids he detected he considered to be a mixture of bacterial and eukaryotic signals.

Dr Enno Schefuß, from the Marine Chemistry and Geochemistry Department at the Woods Hole Oceanographic Institution, informed us that the organic geochemical signature of the dust was predominantly determined by molecular markers for lipid contributions from fresh plant biomass and biomass burning.

Dr Jan Berend Stuut, from the University of Bremen, carried out the grain-size analysis of the dust which showed a relatively well-sorted bimodal distribution with a dominant mode around ~26 µm and secondary mode around ~150 µm.

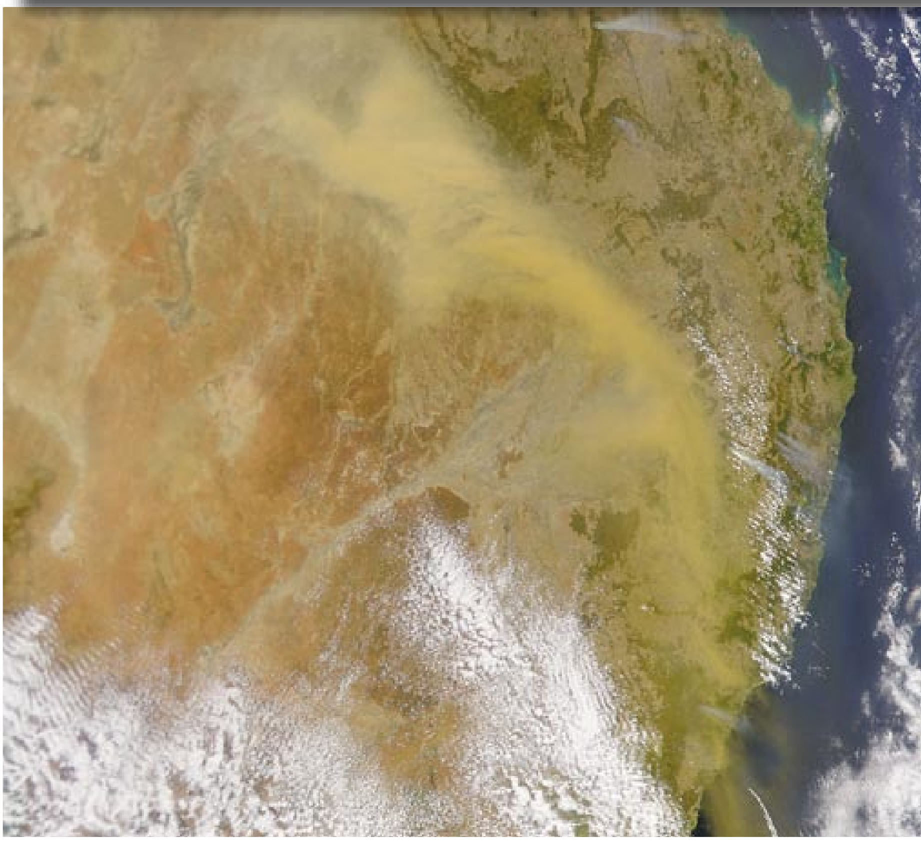
Professor Patrick De Deckker carried out SEM examination of the dust sample and confirmed Stuut's observations but also recognised many long organic fibres thought to have been parts of faecal pellets. He also worked with **Professor Nigel Tapper** from Monash University and they conducted investigations into the meteorological conditions that preceded and were associated with the dust event and also used the HYSPLIT program.

Tadhg O'Loingsigh, meteorology PhD student at Monash put together various datasets corresponding to the dust event, including satellite images, Bureau of Meteorology synoptic charts, friction velocity model readouts and NOAA-Air Resources laboratory model readouts.

Dr Sander van der Kaars from Monash Univeristy is a palynologist who extracted pollen from the dust and reported that this was one of the richest samples he had ever analysed. He was able to reconstruct the vegetation cover for the original site for the dust sample: open *Eucalyptus* woodland with a lower stratum of *Acacia* and *Callitris*; open mixed *Eucalyptus* and *Callitris* woodland with grasses.

Dr Andy Christy from the same department as De Deckker, identified trace and rare earth elements by laser ablation ICP-MS from Li borate discs. Prior to that the discs were used for XRF analyses for major elements. **Dr Uli Troitzch**, also from DEMS, performed the X-ray diffraction analysis of the clays.

Dr Marc Norman of PRISE at RSES carried out the Pb, Nd and Sr isotope analyses of the dust sample that were measured by thermal ionization mass spectrometry, using a ThermoFinnigan Triton TI multicollector mass spectrometer in static mode.



The Sea-viewing Wide Field-of-view Sensor (SeaWiFS), aboard the OrbView-2 satellite, captured this view of Australia's largest recorded dust storm blowing across SE Australia on October 23, 2002. Smoke plumes from wildfires burning in the region are also visible. [Image courtesy of the SeaWiFS Project, NASA/Goddard Space Flight Center, and ORBIMAGE]

Working with free radicals

Australia has a strong reputation in the field of radical chemistry. A new ARC Centre of Excellence has been established to capitalise on this expertise.

What can you do with free radicals? We're not talking about free-spirited revolutionary anarchists, we mean free radicals in the sense of highly reactive chemical entities?

Free radicals are molecules with unpaired electrons that aggressively look for a mate so they are likely to take part in chemical reactions. Oxygen free radicals are particularly interactive because they react readily with many other molecules. (Free radicals drive the process of oxidation, a reaction in which a molecule looses an electron.)

In the popular media you're most likely to read about free radicals in connection with your health. In the human body they can arise from fatty food, smoking, alcohol, environmental pollutants, ozone, toxins and a range of other nasties. They cause damage to our cells, convert good fats to bad fats and attack DNA thereby causing genetic damage. In so doing, free radicals are connected with the process of ageing, cancer and a range of disorders such as diabetes and cardiovascular disease. Our best defence against such processes is the consumption (or topical application) of antioxidants that counteract and minimise free radical damage (indeed, most of the popular press on free radicals is connected to efforts to sell products containing antioxidants).

While all this is true, it doesn't reflect the broader significance of free radical chemistry, because free radicals are everywhere and play central roles in an enormous range of industrial and biological processes. For example, while many people know free radicals as agents of body damage, they also mediate a range of processes that keep us alive. White blood cells use free radicals to destroy bacteria and virus-infected cells. Other free radicals work as enzymes in the liver to detoxify harmful chemicals in the blood. Free radicals are also a normal byproduct of everyday respiration and breathing in which our bodies use oxygen and generate energy.

Dr Phil Barker from Bluescope Steel celebrates the Centre's inaugural symposium (the Free Radical Winter Carnival) held at RSC in June this year. He's sampling a drop of the Centre Beer. Research coming out of the centre in coming years will be improving both beer and steel protection.

And just as free radicals perform many vital functions in the body, so too they play crucial roles in many industrial processes and cause the breakdown of many important materials.

"Free radicals are reactive intermediates, so we're talking about how and why reactions occur because when a chemical process occurs it's via reactive intermediates," says Professor Chris Easton, Deputy Dean of the Research School of Chemistry and Deputy Director of a new ARC Centre of Excellence for Free Radical Chemistry and Biotechnology. "So, if you understand free radical chemistry you can better control a wide range of reactions. Free radical chemistry plays an important part in many processes involved in the manufacturing industry, the environment and human health.

Celebrating the Free Radical Winter Carnival are (from left) Associate Professor Mick Sherburn (ANU), Professor Chris Easton (ANU) and Associate Professor Steve Bottle (QUT), three of the researchers connected with the new ARC Centre of Excellence.

Professor Chris Easton is the Deputy Director of a new ARC Centre of Excellence.

"Australia has a rich history in free radical chemistry with a number of world-leading experts scattered among our universities and research institutions. Australian chemists were intimately involved in determining fundamental kinetic and thermodynamic parameters that revolutionised the field. Our scientists made crucial contributions to the synthetic chemistry of free radicals, as well as developing computational methods to accurately model radical energies. Australian chemists invented the Reversible Addition Fragmentation chain Transfer (RAFT) polymerisation process which has been critical to the development of a wide number of new polymer materials.

"Because of the enormous potential in free radical chemistry an ARC Centre of Excellence has been established to capitalise on Australia's existing strengths in this field. The centre, which kicked off in 2005 and will run for five years, has enabled some of our top free radical chemists to work more closely together in a unique research program that tackles issues that range from quantum chemistry through to chemical synthesis, biochemistry and pharmacology."

The Centre for Free Radical Chemistry and Biotechnology, as it's known, comprises researchers from ANU, the University of Melbourne (which hosts the headquarters of the new centre), the University of Sydney, Monash University and the Queensland University of Technology. Other participants include CSIRO Molecular and Health Technologies, the Howard Florey Institute, Bluescope Steel, Dulux, Fosters Group and the Victorian Institute of Chemical Sciences.

"The diversity of the participants in the centre reflects the wide ranging application of free radical chemistry," says Professor Easton. "So, for example, in polymer chemistry one of the problems in building polymers is that polymers tend to be of random lengths but through recent advances in free radical chemistry it's much easier to control the distribution of chain lengths of the polymer and also build up a lot of block co polymers. Applying this knowledge we can construct a car tyre which has mixture of components in it. In more sophisticated polymers you can chemically bond a polymer that's soft and provides insulation and then add a hard layer that will provide rigidity or you might add another one that allows more air perforation. And you can build these layers up in a stepwise manner, something that was not possible before.

"In the area of protective coatings on steel, free radical chemistry is allowing us to explore the possibility of chemically bonding a paint to the steel surface rather than just layering it on the surface as now occurs, which is the reason why they peel and crack. If you chemically bond the paint to the surface it's never going to peel and crack so the lifetime of the protective coat is going to be considerably extended.

It looks like some radical work of art, and it is in a sense. This is the logo of the ARC Centre for Free Radical Chemistry and Biotechnology and the blobs represent the orbitals of the electrons of a carbon-centred radical.

"In the production of beer radicals cause unwanted degradation. When beer sits for a while you get a beer haze forming, that beer haze is a radical degradation process and so if you can stop that process you can stop the beer haze forming. This is especially important in top end beers because it's also associated with a bitter taste in ageing beer.

"In biotechnology, most diseases are about a biochemical process going out of control, many of which involve a free radical process. If you can stop or intercept those radicals you can do something about it and come up with an essential treatment for a disease state.

"The work of the centre will have applications in all of these areas and many more," says Professor Easton.

"ANU and the University of Melbourne are the two main institutions involved in the centre. It's administered from the Bio21 Molecular Science and Biotechnology Institute at Melbourne Uni.

Two students at RSC involved in the research of the Centre for Free Radical Chemistry and Biochemistry. Roger Coulston is a PhD scholar and Karen Zhang is studying for her Bachelor of Philosophy.

"Here at ANU there are three groups involved in the centre's research: my group, Associate Professor Michael Sherburn's group and Dr Michelle Coote's group.

"Michelle Coote's group is in theoretical and polymer chemistry. She has developed a new RAFT reagent. RAFT is the technique for controlling the length of polymers, and her chemistry is already at a point where it's allowing new types of compounds to undergo radical polymerisation using the RAFT process. This will extend the types of polymers that can be used by this method and is attracting a lot of commercial interest.

"Mick Sherburn's group works in synthetic chemistry. They're basically using radical methods to generate new molecules that are designed to selectively hold specific guest molecules. They may prove useful as molecular sized devices for applications such as improved drug delivery or removal of pesticide residues from the environment.

"My group is working on the biological and radical chemistry interface. What sort of radicals are happening in biological systems or relevant to biological systems, and how can we understand and manipulate it in developing drugs. A particular interest is in peptide hormones.

"About half of the hormones in higher organisms – humans, animals, insects and so forth – are peptide hormones and the final step in their production is a radical process. We're interested in using fundamental free radical chemistry to develop new ways of regulating the production of these hormones."

Australia's fine tradition in radical chemistry looks set to continue.

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www.freeradical.org.au

Fingerprinting dust

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hospital with respiratory complaints. People have put this down to it being dry, hot and dusty. But is it really just the particles, or is it the associated chemicals or maybe it's the microbes? At this point we just don't know.

Global circulation

And tracing the origins of dust also has major implications for our understanding of how our atmosphere is circulating. Possibly the best example of this is new findings on the origins of dust found in ice cores in Antarctica.

"A lot of people postulated that the dust came from Patagonia rather than from Australia," says Professor De Deckker. "The reason being that the French researcher who first made the claim compared the signature of dust from Antarctica with many samples from Patagonia but with only three dust samples from Australia. These three samples came from Broken Hill, South Australia and Western Australia, and he had the idea that these three samples were representative of all of Australia. These sample didn't match very well with the dust from Antarctica which was closer to the Patagonian samples.

"However, when we compared the signatures of the samples we had been collecting for the Murray Darling Basin, it turns out they are very close to the Antarctic samples; indeed, much closer than the Patagonian values. We can confidently say that during warm phases in our planet's recent past that dust in Antarctica originated from around the Darling River in New South Wales.

"These results have major implications because they mean air circulation models need to be revisited because it implies that air masses over Australia can go to Antarctica much more readily than existing models allow for.

"I gave a talk in Italy on this and a lot of people were very skeptical. One modeller said that this can't be right – 'our models are saying differently'. I could only respond by pointing out that he was talking models whereas my stuff is data."

The future of dust studies

"It's really amazing how much we can tell from such small samples of dust," says Professor De Deckker.

"And yet we know so little about aeolian dusts from around Australia. A few years ago it was possible to get away making sweeping generalisations about Australian dusts simply because so little had been collected and intensively analysed."

Professor De Deckker is now working on the establishment of an extensive monitoring system to trap aeolian dust in Australia during future dust storms.

"There is already a national network of dust collecting stations," he says. "But they're not using clean technology, which is necessary if you're to rigorously look for microbes. We'll be seeking to carry out a wide range of analyses on samples collected by our network. We'll characterise the biological, physical and chemical nature of the dust and carry out a range of surveys looking at the effects of the dust on marine life, terrestrial ecosystems and humans.

"The ANU is well placed to take part in these studies. We have an amazing amount of superb analytical equipment and expertise to carry them out. Canberra, being on the fringe of the semi-arid zone, is also ideally located to be one of the dust collection points as it's under the path of many dust storms."

The fact that we're under many dust storms may or may not excite the average citizen of Canberra. However, a greater understanding of what's in that dust is obviously to the benefit of everyone. It might be that the dust sitting on your car is relatively harmless dirt and merely an eyesore. However, if it contained dangerous levels of heavy metals or carried microbes that could impact on your health, wouldn't you want to know about it?

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From where does an ill wind blow?

Have you ever wondered which way the wind was blowing when you were born (maybe after someone has commented: "It was an ill wind blowing the day you were born"). Well, now you can figure it out as long as you were born after 1948. NOAA's Air Resources Laboratory in conjunction with the Australian Bureau of Meteorology runs a web based program called HYSPLIT which allows you to determine which way the wind was blowing at any point on the planet back to 1948. You simply type in the longitude, latitude, altitude, date and time, and HYSPLIT uses archived meteorological data to give you a plot of where the wind was blowing. According to Professor Deckker it's a great tool for researchers attempting to track and backtrack dust storms. It's also quite helpful in challenging slurs made against the wind at the time of your birth.

For more details see www.arl.noaa.gov/ready/hysplit4.html

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