CSEM's

Materials Monthly

March 2004

Making materials matter

Rock solid resonators

Dr Ulrike Troitzch adjusts a piston cylinder apparatus used to apply pressure to mixes of mineral oxides. Dr Andy Christy looks on. ▼▼

ANU geologists have devised a new way of synthesising low cost, high quality dielectric ceramics – the material that lies at the heart of most wireless communication systems such as mobile phones and GPS systems. And it all started as an unexpected outcome from a basic investigation on mineral chemistry.

Sometimes new materials are produced by design; sometimes novel new materials are stumbled upon in the process of an unrelated investigation. The latter was the case in the ANU Department of Earth and Marine Sciences when Dr Ulrike Troitzsch was working with Prof David Ellis on reactions between minerals containing zirconium and titanium.

Rock thermometers

Ulrike is an earth scientist with an interest in the formation of minerals. By understanding the conditions under which minerals form, it's possible to use the presence or absence of different minerals in a rock, and changes in the chemical composition of the minerals, to understand how that rock formed. The science is known as geothermobarometry, because it uses the minerals in rocks as 'thermometers' and 'barometers'. For example, diamonds form at very high pressures. If you find a diamond in your rock you know immediately that the rock formed at a depth of at least 150 km.

Ulrike's particular interest is zirconium and titanium-bearing minerals such as rutile (TiO_2), baddeleyite (ZrO_2), and titanite ($CaTiSiO_5$) in rocks of the Earth's crust. These are minerals that show variation in chemical composition. For example, rutile can contain traces of Zr replacing the Ti atoms, and baddeleyite can show the reverse substitution. The extent of this replacement depends on the pressure and temperature at which they formed. Through controlled synthesis experiments, we can determine at what pressures and temperatures they form and with what composition. With this information, we can use these minerals as pressure and temperature indicators out in the field.

Knowing which chemical compounds form at what temperatures and pressures is also important if you want to synthesise the materials. Ceramicists and metallurgists, for example, are continually evolving new methods in which raw materials in specific proportions are reacted in furnaces and kilns in order to make, refine or purify specific products.

The experiments that Ulrike has undertaken to create this information involve weighing out different amounts of rutile and baddeleyite to create mixes that cover the entire compositional range from pure TiO_2 to pure ZrO_2, and then 'equilibrating' the samples at different pressures and temperatures. The samples are 'cooked' at a constant temperature until no further reaction occurs. Under some conditions, new compounds may form rather than just titanium oxide with a hint of Zr or vice versa. For example, bake equal quantities of rutile and baddeleyite under the right conditions and zirconium titanate ($ZrTiO_4$) forms. Add two parts rutile to one part baddeleyite and the mineral srilankite ($ZrTi_2O_6$) is produced.

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▲▲ Large crystals of zirconium titanate grown by Ulrike at 800°C. Crystals like this aren't found in nature.

Inside this MM

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Filling in the holes

The end result of such studies is the construction of a phase diagram of the ZrO_2-TiO_2 system that maps out what minerals are present for different temperatures and pressures. However the phase map for this system has a significant gap in it. It's uncertain what happens below 1200°C.

"If you react TiO_2 and ZrO_2 in the oven at any temperature above 1200°C, they form zirconium titanate $(Zr,Ti)_2O_4$, which is the stable compound at these conditions," says Ulrike. "However, if you try the same combination at or below 1100°C, nothing will happen – TiO_2 and ZrO_2 sit side by side without even blinking."

"Normally, your conclusion from this would be that TiO_2 and ZrO_2 are actually the stable phases, and not an intermediate compound. Indeed, this is what I believed for a long time based on my experimental evidence. However, there is some published work suggesting that zirconium titanate should be stable below 1200°C."

"Further to this, when I added some seeds of zirconium titanate into the mix of TiO_2 and ZrO_2 and then heated it, it was the zirconium titanate which grew at the expense of the other two components. If ZrO_2 and TiO_2 were the stable phases, then the $(Zr,Ti)_2O_4$ seeds should have been consumed to form more ZrO_2 and TiO_2."

Ulrike believes there may be two reasons why nothing happens between TiO_2 and ZrO_2 below 1200°C: 1) the reaction is so slow, that we simply can't observe it in the lab (maybe things will react completely over the course of hundreds or thousands of years, but not fast enough to detect on a human timescale)
2) sometimes chemicals don't react even though they should, because they need to overcome an 'activation energy' threshold in order to start the reaction. Natural gas burns (reacts) with the oxygen in air, but only after a flame provides this 'kick start'.

"It's a bit like finishing a manuscript way before the deadline," Ulrike observes. "It simply never happens. To make it happen you need the stress and panic that only exists right before the deadline, and all of a sudden you start writing."

"So, in order to fill in the holes in the phase diagram, we've been trying to figure out ways of making the reaction occur at these lower temperatures," says Ulrike. "My colleague Dr Andy Christy suggested we try using different fluxes to encourage the reaction; and the results have been fantastic."

Cool ceramic

"We introduced small amounts of ammonium carbonate or copper oxide as a flux to encourage the reaction, and then heated them up at a variety of applied pressures. Fluxes are commonly used in the formation of ceramics from mixes of powder. The flux simply works like grease in a machine - makes things run easily and smoothly and a lot faster, which is important for experimentalists."

"We found that the fluxes made all the difference. The TiO_2 and ZrO_2 reacted to form zirconium titanate down to temperatures as low as 800°C. That's up to 400°C cooler than had been previously achieved."

While Ulrike and her colleagues had been able to fill in an important gap in the ZrO_2-TiO_2 system, they soon realised that they had also pioneered a new method for synthesising an important ceramic.

"Zirconium titanate has interesting electrical properties," Ulrike explains. "It acts as an insulator but it can store electrical charge. It's described as a dielectric ceramic, and our ability to synthesise it at lower temperatures has commercial significance."

Dielectric ceramics are widely used as resonators in wireless communication apparatus such as mobile phones, GPS systems and satellites. Their ability to store electrical charge means they are an important material used in capacitors in a

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What is a dielectric material

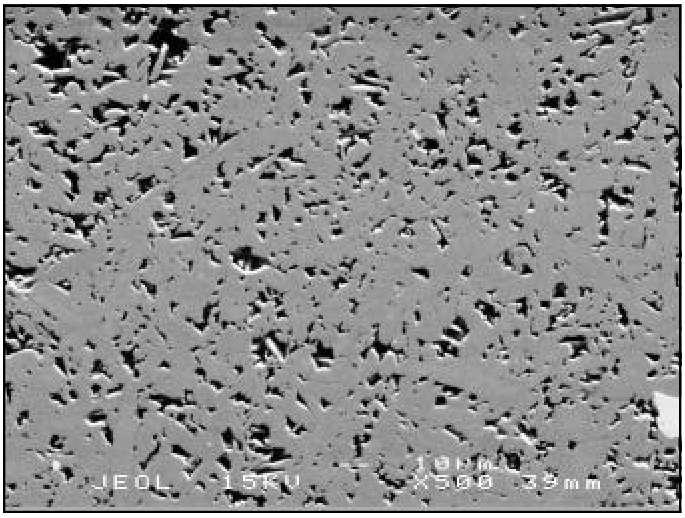
A dielectric material is a substance that is a poor conductor of electricity, but an efficient supporter of electrostatic fields. If the flow of current between opposite electric charge poles is kept to a minimum while the electrostatic lines of flux are not impeded or interrupted, an electrostatic field can store energy. This property is useful in capacitors, especially at radio frequencies. Dielectric materials are also used in the construction of radio-frequency transmission lines.

In practice, most dielectric materials are solid. Examples include porcelain (ceramic), mica, glass, plastics, and the oxides of various metals. Some liquids and gases can serve as good dielectric materials. Dry air is an excellent dielectric, and is used in variable capacitors and some types of transmission lines. Distilled water is a fair dielectric. A vacuum is an exceptionally efficient dielectric.

An important property of a dielectric is its ability to support an electrostatic field while dissipating minimal energy in the form of heat. The lower the dielectric loss (the proportion of energy lost as heat), the more effective is a dielectric material. Another consideration is the dielectric constant, the extent to which a substance concentrates the electrostatic lines of flux. Substances with a low dielectric constant include a perfect vacuum, dry air, and most pure, dry gases such as helium and nitrogen. Materials with moderate dielectric constants include ceramics, distilled water, paper, mica, polyethylene, and glass. Metal oxides, in general, have high dielectric constants.

Source: Whatis.com
<http://whatis.techtarget.com/definition/0,,sid9_gci21194

Many small crystals of ordered zirconia titanate—$(Zr,Ti)_2O_2$—tightly intergrown at 1000°C and 20 kbar pressure. This sample was prepared to be as pure and dense as possible, so that the researchers can measure the dielectric properties on a block composed of many crystals. The black specs are pores and work still needs to be done to work out how to eliminate these. ▼▼



Technology

The spacecraft has landed

ANU's new 800-meghertz NMR Spectrometer is almost open for business

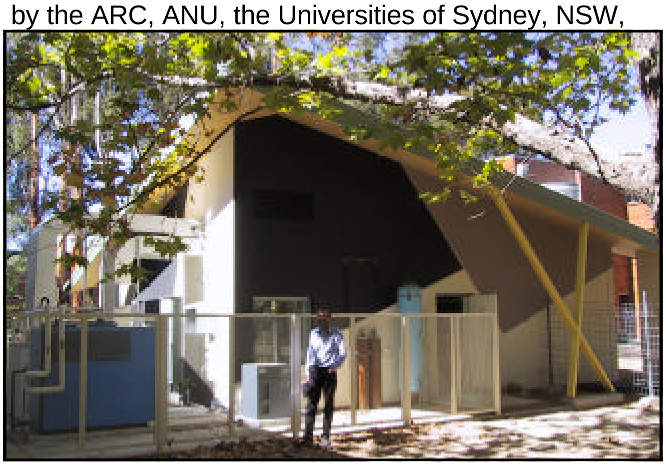
If you've wandered through the leafy space between Chemistry and Engineering in recent months you would have noticed a weird and wonderful building being put together on its western edge. It looks like a spacecraft and when it's operating it could disturb your compass if you're nearby, but this structure is not extra terrestrial in origin. It's the latest piece of research infrastructure at the Research School of Chemistry – an 800 Megahertz Nuclear Magnetic Resonance (NMR) Spectrometer.

NMR spectrometry is a cornerstone of molecular chemistry. It's based on the principle that certain atoms, when placed in an intense magnetic field, will absorb and emit energy at specific frequencies. By measuring this absorption and emission it's possible to map the structure of many molecules.

RSC has been ramping up its already considerable expertise in the area of NMR spectrometry. In 2002, Prof Gottfried Otting, an internationally recognised expert in NMR applications, took up a Federation Fellowship at the School. The new NMR facility has been built for Gottfried and his colleagues from a number of different universities in NSW and ACT to develop new NMR applications to solve problems of protein structure and function, as well as train Australian experts in this highly specialised field.

The heart of the facility is a massive superconducting magnet weighing 4.2 tonnes and standing over 3 m high. It's the most powerful magnet of its type in Australia and operates at a nippy 2.2 Kelvin.

The facility cost $4.2 million to build and was funded by the ARC, ANU, the Universities of Sydney, NSW,



▲▲ Gottfried outside of the facility

Prof Gottfried Otting in front of the superconducting magnet that lies at the heart of the new facility.

Wollongong, Newcastle and ADFA. It will be officially opened in March but won't come on line probably till May. And the facility will be 'on line' in more ways than one. State-of-the-art computer technology will enable it to be operated from anywhere in Australia.

"Of course, our staff will have to load up the samples," says Gottfried. "But, the processing of the samples can be done from anywhere. We'll be aiming for maximum use of the system, 24 hours a day, seven days a week."

How powerful is the magnet? "When it's operating it could rip a steel hammer out of your hands if you're within a couple of metres of it," says Gottfried. "And you wouldn't want anyone standing between you and the magnet if that were to happen. However the field diminishes very quickly as you move away from the magnet."

A ring of boulders has been arranged around the outside of the building marking the line where the magnetic field generated by magnet is approximately equivalent to that of the Earth's magnetic field.

"That's not to keep people away," explains Gottfried. "It's really to stop cars and large machines from getting too close. The magnetic field won't hurt them but the distortion of the magnetic field they're producing would disturb our measurements inside the building."

And as to the wild angles of the building itself? "It's been designed to make windowless walls look a bit more interesting," says Gottfried, "and forms part of a plan to redesign this courtyard."

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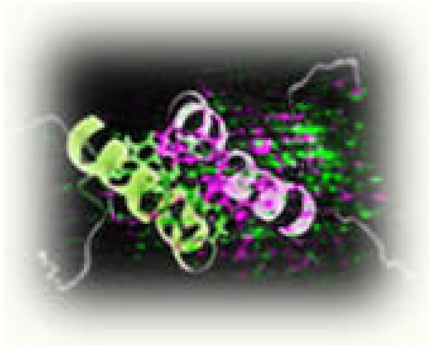
Proteomics & Biological Mass Spectrometry

Workshops 2004



The Bioanalytical Mass Spectrometry Facility (based at the Uni NSW) has had such a fabulous response in the past two years to their Proteomics Workshop and the Mass Spectrometry Workshop, that they're running them again at the end of April 2004.

More info: **http://www.bmsf.unsw.edu.au/training/BioMSCourse/Workshops2004.html**

A helping hand from UNSW

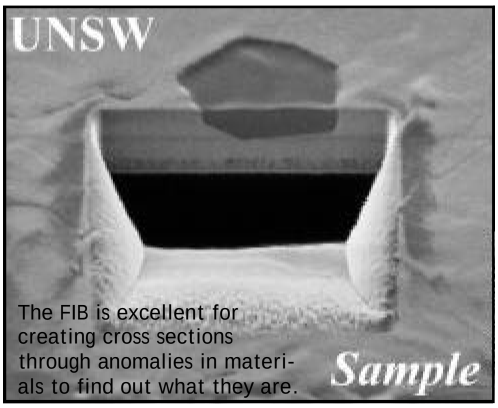
Prof Paul Munroe at the controls of ANU's new FIBSEM

ANU's new FIBSEM (Focused Ion Beam / Scanning Electron Microsope) is up and running but we've still got a steep learning curve ahead of us according to Prof Paul Munroe, Director of the University of NSW Electron Microscope Unit. Paul's Unit has been operating a similar Focussed Ion Beam for the last four years, and he says it took a long time to figure out how to drive the machine to make the most of its potential.

The hope is, however, that ANU will learn from the Uni of NSW's experiences with the machine. Paul visited ANU in March and gave a presentation on what they've learnt about the FIB over the past four years.

The FIB is experiencing growing and widespread application in the characterisation of advanced materials. It uses an energetic gallium beam to cut and section materials with nanoscale precision. It's an exceptionally powerful tool in the preparation and examination of material structure and the preparation of TEM specimens from, often, very challenging materials.

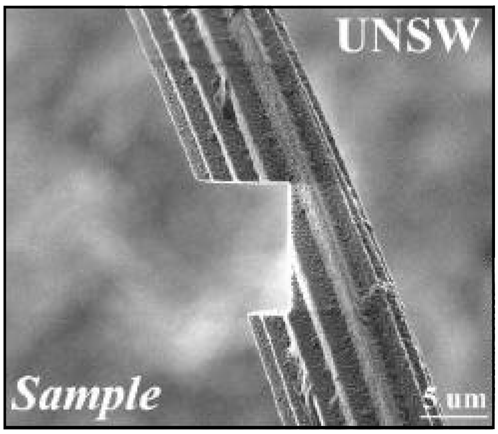
However, the powerful gallium beam needs to be carefully controlled to avoid the introduction of artefacts into the specimen leading to errors in interpretation. These artefacts include the creation of amorphous films, the implantation of gallium, redeposition of milled material, the introduction of crystalline defects and local recrystallized regions. Paul discussed the origin and pervasiveness of such artifacts and suggested strategies to eliminate or reduce them.



The FIB is excellent for creating cross sections through anomalies in materials to find out what they are.

The Uni of NSW was a partner with ANU in purchasing the FIBSEM. The hope is that our shared experience will see both institutions surge ahead in this exciting new field.

More information: Sally Stowe (stowe@rsbs.anu.edu.au)



Particular care needs to be taken when using the FIB to cut into biological materials (such as the insect antenna shown here) as the gallium beam has the potential to substantially modify the material being cut.

Rock solid resonators

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large number of electronic devices. With only a hand full of dielectric ceramic materials to choose from, the electronic industry is constantly searching for new materials with superior performance properties or materials that can be more easily affordable to manufacture.

Cheaper and higher quality

Currently, dielectric ceramics based on zirconium titanate require temperatures of well above 1200°C to synthesise, entailing high costs due to energy consumption and furnace equipment. With this new process, however, there are significant savings in production costs. What's more, the zirconium titanate formed at these lower temperatures potentially has superior qualities compared to the higher-temperature ceramics due to a higher degree of ordering of the crystal structure. The Zr and Ti atoms occur in a regular repeating sequence instead of randomly.

"Before we discovered that we can make this material directly from the oxides at low temperature by adding seeds and flux to the starting mixes, the only way to synthesise it was by first making the high-temperature, disordered version above 1200°C, and then cooling it very slowly to 800°C. During cooling, the structure would order. The problem with this method was that the final product was full of cracks and holes, because ordering increases the density and thus makes the material shrink. For the first time we're able to make this material at high density, a prerequisite for the determination of dielectric properties."

It's still early days in the investigation. Experiments so far have delivered a proof of concept that the fluxes work, but the quantities produced so far are minute. To scope the commercial value of the process Ulrike and colleagues need to refine the process, produce larger samples of high purity and density and then perform a full characterisation on the samples using X-ray diffraction and scanning electron microscope analysis. Most importantly, the exact dielectric properties of the new material will be measured, which will decide its potential usefulness for wireless communication apparatus.

If they're successful with this phase they'll then investigate how the process might be scaled up for commercial production. While there's still a way to go, the project has sparked local interest with the awarding of $30,000 from the ACT Knowledge Fund to carry on with the investigation. Patent applications have been submitted to protect the intellectual property being generated.

"It's nice that a fundamental research problem in earth science has produced a real-world application in materials science," says Ulrike. "This is yet another example of how high-pressure research in earth sciences at ANU has led to a commercial product. Other examples are SYNROC for nuclear waste storage and superabrasive materials."

"The research is continuing and we're also examining ways that these ceramics might be produced at low pressures, even at room pressure. That process involves adding 'seeds' to the starting mix to initiate nucleation – but that's another story for another time."

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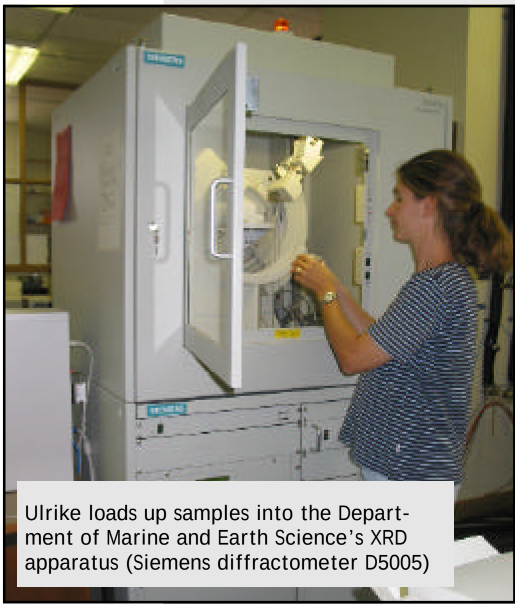
Characterising the sample

The traditional ways to characterise these samples involve X-ray diffraction and scanning electron microscopy (SEM).

"SEM lets you to magnify your sample," says Ulrike. "This allows you to easily see things like pore space (which we try to get rid of in the polygrain samples), or impurities (phases other than ordered $(Zr,Ti)_2O_4$, such as TiO_2 or ZrO_2 left over from the reaction if we didn't put them in at the right proportions). It gives you an idea how large the crystallites are, and an overall impression of the microstructure of your sample.

In addition, with SEM, you can analyse the exact composition of individual grains in your sample - this helps us to refine our starting mix composition. Once we know from SEM that the ordered phase that formed at a certain pressure/temperature is of composition 65% TiO_2 and 35%ZrO_2, then we repeat the experiment using exactly 65% TiO_2 powder and 35%ZrO_2 powder, so that everything in our experiment reacts to form the ordered phase, with no ZrO_2 or TiO_2 left over."



Ulrike loads up samples into the Department of Marine and Earth Science's XRD apparatus (Siemens diffractometer D5005)

X-ray crystallography involves firing X-rays at the samples and recording the diffraction pattern this creates.

"X-ray diffraction (XRD) tells us what types of crystals are in the sample," says Ulrike but not their exact composition. It is used to determine the amounts of the different phases (TiO_2, ZrO_2, ordered or disordered zirconium titanate) or impurities (for example if flux remains in the sample and forms a compound such as $CuZrTiO_5$) in the sample. It also tells us if the structure of the $(Zr,Ti)_2O_4$ is ordered or disordered ."

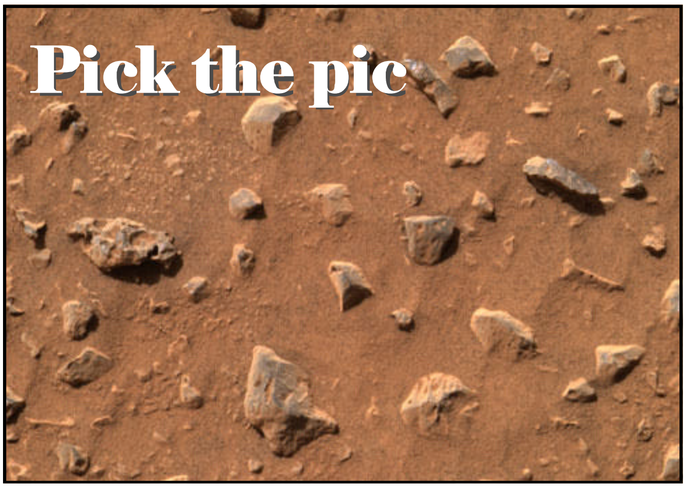
"There are a lot of powerful tools available to interpret the diffraction patterns that are produced. One technique we've been using in the Earth and Marine Sciences Department is the Rietveld crystal structure refinement process. Basically it's a computer program that interprets the diffraction pattern of even finely powdered material to provide detailed information on the crystal structure of the material being examined."

Correction from our February issue

The end of our last feature on 'Stopping Heavy Ions' was cut a couple of lines short when the file was converted to a pdf. Dr Tessica Weijers was discussing the advantages of running the 14UD particle accelerator yourself. The missing lines said: "this imparts a much deeper understanding about the processes you're attempting to study."

More information: tessica.weijers@anu.edu.au

the backpage



Photons@Work, the Australian Synchrotron Summer School, was a brilliant success with all available places filled months before the actual event. Those lucky enough to get in (pictured above in a group photo) were privileged to listen to some of the world's leading lights in synchrotron research and methodology.

"We were delighted with the calibre and range of the students and lecturers that participated in photons@work," says Mark Ridgeway, co-chair of the School. "They came from all over Australia (every state), New Zealand and Korea with a wide spectrum of backgrounds. It augers well for Australia's future in synchrotron science."

The school ran from the 27 January through to the 5 February, and was based at the ANU.CSEM is proud to have been one of the sponsors of the event.

More information: Mark Ridgway mcr109@rsphy1.anu.edu.au

The sands of Mars

Pictured is a patch of Martian dirt in the Gusey Crater close to where the Spirit Rover touched down several weeks ago. Located on the Rover's arm is a palm-sized alpha particle X-ray spectrometer which uses alpha particles and X-rays to determine the chemical make up of Martian rocks and soils (it has the capacity to measure the presence and abundance of all major rock-forming elements except hydrogen). This type of information helps scientists understand how the planet's crust was weathered and formed.

In agreement with past missions to Mars, iron and silicon make up the majority of the Martian soil. Sulfur and chlorine were also observed as expected. Trace elements detected for the first time include zinc and nickel.

Another instrument on the Rover's arm is the Mössbauer spectrometer. It uses two pieces of radioactive cobalt-57, each about the size of pencil erasers, to determine with a high degree of accuracy the composition and abundance of iron-bearing minerals in Martian soil. It detected the presence of three different iron-bearing minerals. One of these is olivine, a shiny green rock commonly found in lava on Earth. The other two have yet to be pinned down. Scientists were puzzled by the discovery of olivine because it implies the soil consists at least partially of ground up rocks that have not been weathered or chemically altered.

Picture by NASA/JPL. More info: http://marsrovers.jpl.nasa.gov/gallery/press/spirit/20040120a.html


Full house


'Is this fun or what'

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