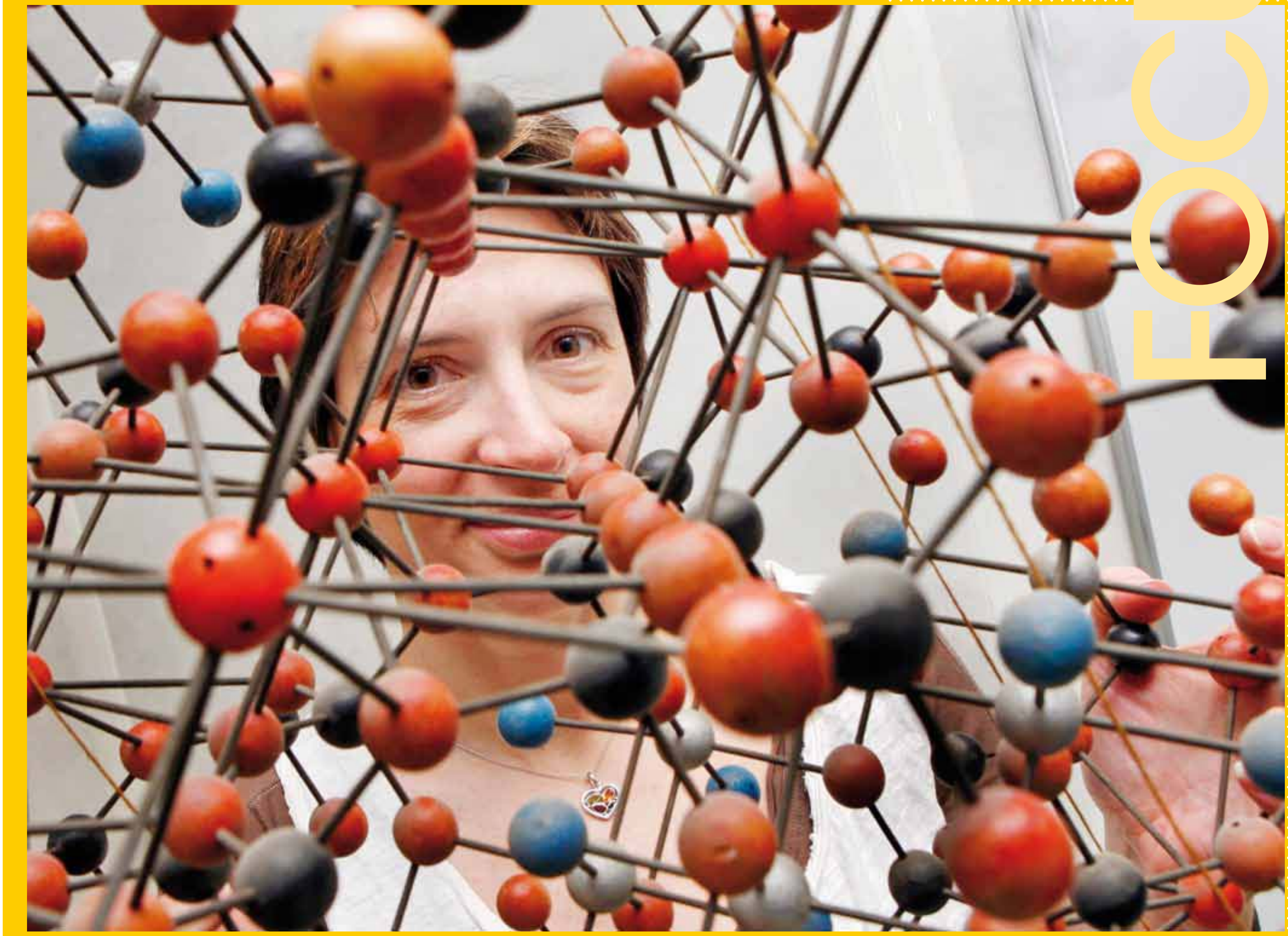
Materials
in SOLEIL's light



Synchrotron radiation is very widely used in materials science, in terms of scientific fields, energy domains and techniques, as well as the number of types of studies undertaken. Whether designing a material or determining its properties, on a microscopic or micro (or nano)-scopic scale, twenty or so beamlines at SOLEIL are or will be available to address this wide range of topics.

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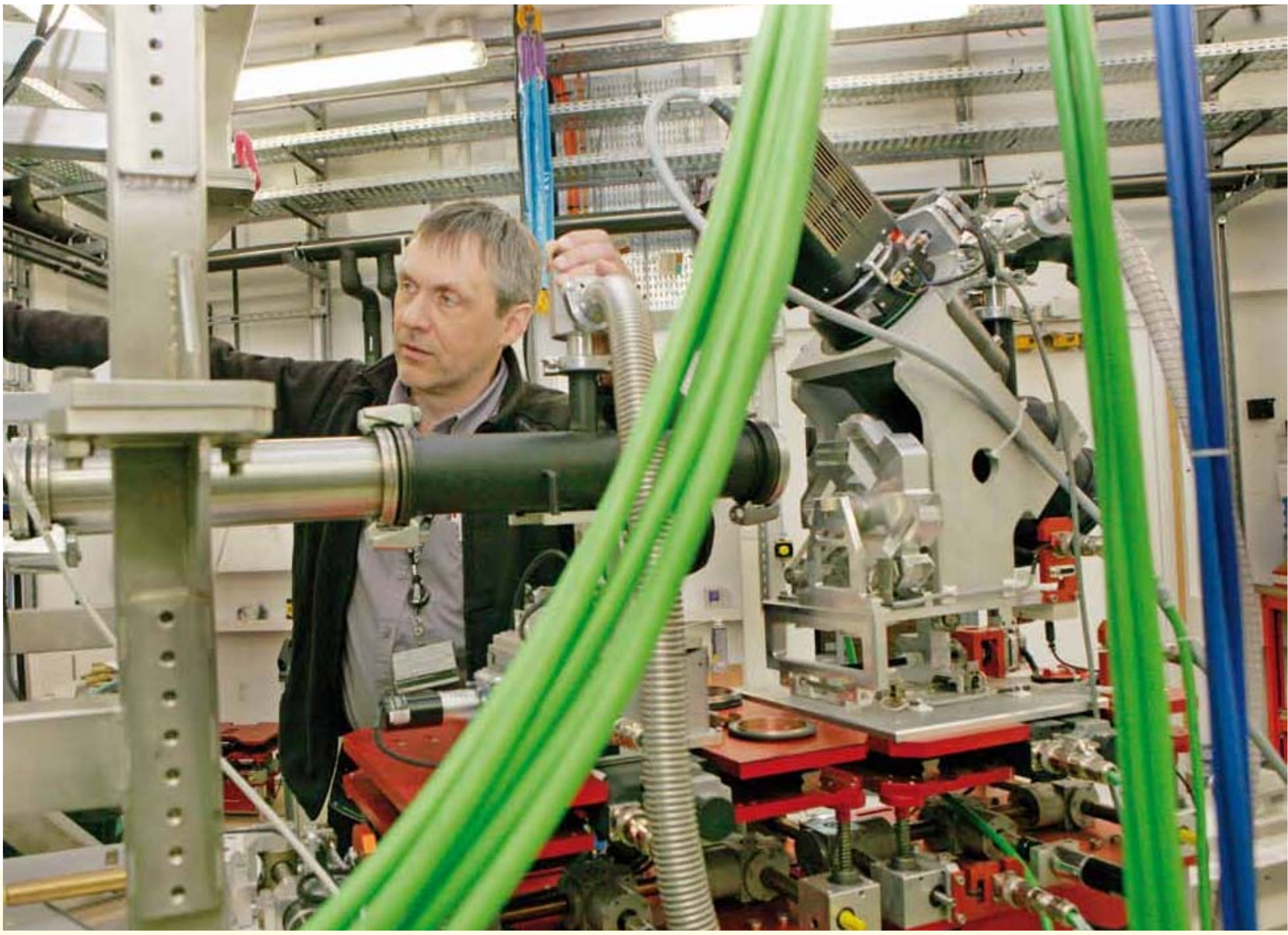


François Baudelet, in charge of ODE beamline, in the experimental hutch of the beamline.

The unique performances offered by the large scale facilities, synchrotron radiation and neutron centers make them "standard" materials investigation tools. Hence, today, in the materials science field, the beam time request is three times more than can be accommodated on some beamlines at SOLEIL.

This document, without trying to be exhaustive, highlights some examples of possible studies, thanks to the unique qualities of synchrotron radiation: brilliance, coherence and tunability.

Properties from the atomic to the macroscopic scale

One often tries to develop materials whose macroscopic properties can be controlled by exterior parameters such as temperature, magnetic or electromagnetic fields, or by effects produced by local confinement. The example proposed in the xxx insert concerns the study of graphene. The very promising properties of this material concern high frequency electronics (THz), due to its very high electron mobility. It still had to be proved that the properties observed on one layer were retained on a multilayer sample, which was shown, under certain conditions, by very high resolution photoemission experiments on the CASSIOPEE beamline. Another example concerns the induction of collective effects (phase transitions) induced by irradiation. This is what is being considered for the CRISTAL beamline, where a pulsed laser will excite a transition in a ferroelectric sample and where the phase transition induced will be followed in real time by time resolved diffraction: this will naturally require perfect synchronization between the pulses from the pump and the probe. The slicing project, which was recently decided at SOLEIL, will produce X-ray pulses less than 100 fs (presently 60ps) to probe ultra-fast dynamics, at the expense of flux, naturally!

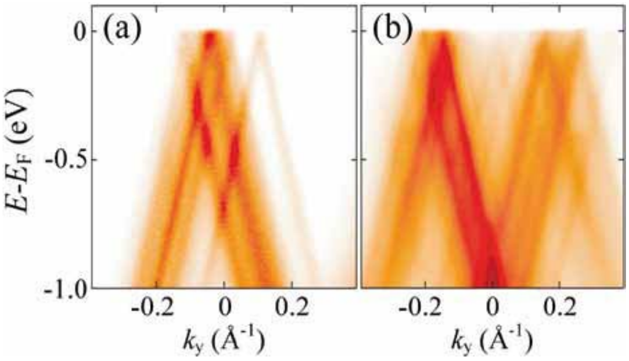
Observation under extreme conditions

A sample's environment and the observation conditions are

CASSIOPEE

Graphene, a promising material

Graphene is a single atomic layer of graphite whose properties – high electronic mobility, strong electrical and thermal conductivity, chemical stability and the possibility of modulating its conductance by means of an electrostatic gate – make it a promising material for high frequency electronics. It has already been shown that multilayer graphene produced on SiC (epitaxial graphene) allows the production of large-scale electronic circuits, but it still had to be proved that this material possessed the electronic properties of a single sheet, conditions required to develop graphene-based electronics.



10-layer graphene band structure, measured by ARPES. A dozen linear Dirac cones are visible.

This is precisely what groups from CNRS (Grenoble), the Georgia Institute of Technology (Atlanta, USA) and the University of Paris Sud have been able to prove, through angle-resolved photoemission spectroscopy (ARPES) experiments carried out on the CASSIOPEE beamline (Ref. 1).

This decoupling between layers results from a particular stacking of the graphene layers. Measurements performed on CASSIOPEE showed that a sample composed of about ten atomic planes of graphene had the same spectral signature as that given by ten individual planes (Figure 1). Moreover, other experiments, aimed at studying defects in the material, proved that a very small proportion of the graphene planes of these samples possessed unwanted electronic properties. Macroscopic single planes of graphene, difficult to obtain by any growth method, are probably no longer necessary since the electronic properties of one layer are still present in multilayer samples (Ref 2). In addition, the "inverted V" spectral signature signals -among other properties- the fact that the graphene electrons can be confined in structures of nanometric size, making it possible to perform electronic engineering with its properties. The advantages of epitaxial graphene, an alternative to carbon nanotubes since on the large-scale production of nanoelectronic circuits on the same support is possible (as is the case with Si), have thus been confirmed.

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Ref 1: M. Sprinkle et al., Phys Rev Lett, 103, 226803 (2009)
Ref 2: M. Sprinkle et al., cond-mat/1001.3869

> « TO UNDERSTAND MATTER, X-RAY PHOTONS AND NEUTRONS ARE VERY COMPLEMENTARY SOURCES AS MUCH BY THE ELEMENTS THAT THEY REVEAL AS THE PROPERTIES IT IS POSSIBLE TO MEASURE WITH THEM. »
>
> CHRISTIANE ALBA-SIMIONESCO,
> DIRECTOR OF THE LABORATOIRE LÉON BRILLOUIN, CEA, SACLAY.

important parameters for targeting the behavior of a material under particular conditions. Thus, the DIFFABS beamline is equipped with a setup optimized for heating the sample at temperatures close to 3000° (with a laser) necessary to observe the phenomena of crystallization in natural and industrial processes, while other tools (diamond anvils) will allow to create pressures greater than 100GPa (e.g. PSICHE). Phase transition diagrams can therefore be obtained over a very large area. The inset on p.17 (DIFFABS beamline), is a good example of the necessity to characterize new materials in a complex environment. The transformation of α–Fe to γ–Fe has been followed by diffraction, as well as the appearance of an amorphous phase depending on the temperature, the metal being confined inside carbon nanotubes. These nanotubes, whose longitudinal growth and transverse assembly were very controlled, formed nanotube carpets and could be used for magnetic information storage. For the study of materials with interesting magnetic properties it could be equally appropriate to combine low temperatures and/or high magnetic fields. The ODE and DEIMOS beamlines are (or will soon be) equipped with high magnetic field coils linked to a cryostat that could reach 7T at around 1.5°K.

Time resolved studies

Absorption spectroscopy is, of course, a method of choice for characterizing materials since it is sensitive to the

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ODE

Redox reactions in vitreous and molten silicates

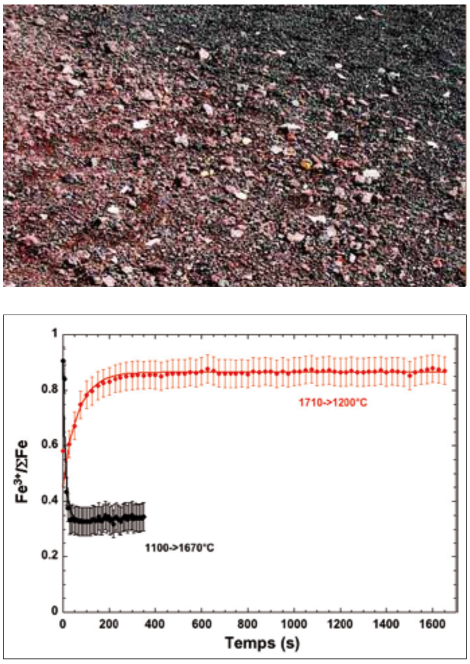

Figure 1 : Redox kinetics of iron in basalt from Lemptegy: oxidation between 1710 and 1200°C, reduction between 1100°C and 1670°C. Photo: Basalt from Lemptegy, the black and red coloring corresponding to reduced and oxidized basalt.

Vitreous and molten silicates are important materials in the earth sciences, notably in volcanology and in mass transfer studies, but also in materials science, where glass, obtained by the rapid cooling of molten silicates, is present everywhere in our daily lives: housing (window panes), communications (fiber optics), conservation (bottle-making), glass ceramics, waste vitrification, etc. These vitreous or molten silicates are formed from oxides and carbonates and especially multivalent oxides such as iron, present in the reduced Fe^{2+} and oxidized Fe^{3+} forms, depending on the chemical composition of the matrix and temperature. The Fe^{2+}/Fe^{3+} ratio can have a significant effect on the properties of molten silicates. Today, changes in the redox state of Fe with temperature, oxygen partial pressure and chemical composition can be determined precisely ex-situ (e.g., ref.1). Yet, although redox kinetics plays an important role in crystallization, viscosity and other processes, in both natural and industrial contexts, the mechanisms are still not fully understood.

To obtain the kinetic information required for a better understanding of this type of mechanism, B. Cochain, D. de Ligny, P. Richet and D. Neuville, from IPGP-CNRS, came to use in-situ temperature-dependent Fe K-edge X-ray absorption spectroscopy (XANES) on the ODE beamline. In this case it was a particularly appropriate technique as it consists of a specific probe capable of determining the redox state of the iron in the material, regardless of the pressure and temperature conditions. By adapting for ODE the mico-furnace that they had designed, the IPGP group was able to obtain the redox kinetics of the Fe in a basaltic lava resulting from an eruption in Puy de Lemptegy (Massif Central) 30,000 years ago, for temperatures between 500 and 1800°C.
Analysis of the XANES spectra at the iron K-edge made it possible to determine changes in the redox state of the iron over time for different temperatures (see fig1 and ref.2).
The heated filament set-up was used to study the structure and certain properties of materials, crystals, liquids or glass at high temperature by X-ray diffraction or absorption.

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Ref 1 : Kress V. C et Carmichael I.S.E. (1991) Contrib. Min. Petrol., 108, 82-92.
Ref 2 : Cochain B. et al. (2009) J. Physics: Conference Series, 190, 012182.
See also: www.synchrotron-soleil.fr/Soleil/ToutesActualites/2009/Silicate

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abundance, local order and chemical environment of the different elements present. Due to the intense photon flux and improved detectors, one can now record the necessary data in very short exposure times and allowing thus true time-resolved studies. Therefore quickEXAFS on SAMBA (recently made available to users) has made it possible to reach kinetics of the order of 10ms, and on the dispersive EXAFS station on ODE, to achieve a few tenths of a micro-second resolution. In the inset above, it is possible to follow the kinetics of the crystallization of molten glass, highlighting, in particular, the role of oxidation-reduction mechanisms.

Materials under stress- defaults- real conditions

For certain types of material, it will be of interest to look at their behavior under various stress conditions, at the presence of defects that could affect both their properties and their development, or on their behavior under real conditions. Therefore advantage can be taken of the coherence of photon beams to visualize the areas of constraint or the presence of defects. On the CRISTAL beamline, it has been possible to visualize a dislocation loop (inset p.19) by selecting just the coherent part of the beam (5x5 μm^2) and mapping the sample by 5 µm steps. Opposite inset is an example of a study in situ. On SWING, the installation rheometer on the beamline has enabled the simultaneous measurement of mechanical properties and organization of a material, which was applied to the study of the flow properties of clay. The link between morphology/organization/flow properties is of interest to many industries such as cosmetics, and civil engineering or the vast field of natural environments.

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DIFFABS

Nanowires and carbon nanotubes at high temperature

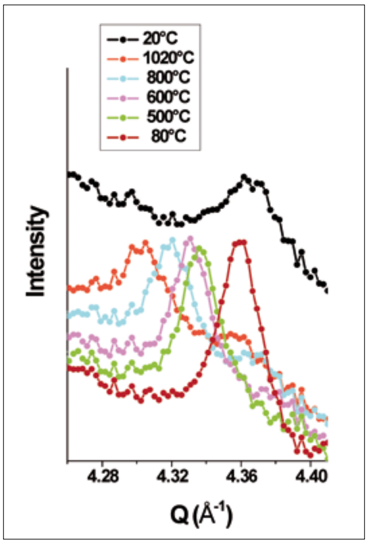

Figure 1 : Change of the intensity of the Bragg α-Fe 200 reflection between ambient temperature (20°C) and 1020°C, then during the drop in temperature (800, 600, 500 and 80°C)

Phase diagrams of materials on the nanoscale can be very different from those of macroscopic materials, even more so if they are confined in one or more dimensions. Their study is of obvious fundamental importance but can also be of applied interest. Modifications of the transition temperatures or even the appearance of new phases can be found that do not exist in macroscopic materials. First results, in the case of nanoparticles and nanowires within carbon nanotubes, were obtained on the DIFFABS beamline. When synthesized by catalytic chemical vapor deposition at 850°C, the nanotubes are partially filled with nanoparticles and nanowires in the α and γ forms, as well as iron oxide nanoparticles near their bases. Post-synthesis experiments, carried out as a function of temperature in an oven working under vacuum on DIFFABS, showed that it was possible to reduce nanoparticles of iron oxide enveloped in carbon using heat and obtain more nanoparticles of α-Fe after heat treatment (Figure 1). In addition, when cooled, there was only partial transformation of γ–Fe, the stable phase at high temperatures, into α–Fe, stable at lower temperatures, which is explained by the confinement since the process is normally accompanied by dilation in two directions. The important point, however, is that this transformation occurs at much lower temperatures than in solid iron (up to 500°C compared to more than 900°C for solid iron, Figure 1), which could be due to the nanometric dimensions. We have also shown the liquefaction of nanowires at lower temperatures than for macroscopic materials.

By pursuing these studies on DIFFABS, our aim is to obtain the complete diagram of the transformations of nanowires confined in nanotubes in relation to temperature. Our first results show that this is very different from that of solid materials. The aim of this work is to understand the transformation mechanisms and to master the formation of α– Fe nanowires and how they can be applied (high density magnetic data storage).

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SWING

Clays under flow, and X-ray scattering

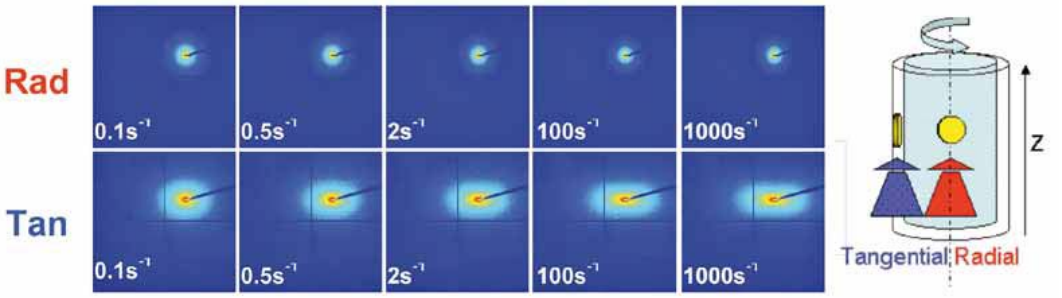

Figure 1 : X-ray scattering images obtained from a natural clay suspension at different shearing rates in tangential and radial positions.

Clays are ubiquitous minerals found in the superficial layers of planet earth, where they play a fundamental role in many environmental processes (pollutant transfer, soil stability, etc.) These minerals are present in the form of thin anisotropic plate-like particles. They usually have a diameter of around a few hundred nanometers, whereas their thickness can vary from a single elementary layer (1 nanometer) up to a stack of several elementary layers (several tens of nanometers). One characteristic of these materials is their ability to form gels when suspended in water at low concentrations of a few percent, but which fluidize easily when made to flow.

The link between the morphology, organization and mechanical properties of these materials remains a major challenge in understanding these natural phenomena and to optimize their use in numerous industrial fields (cosmetics, health, food industry, civil engineering, etc). It is for this reason that a rheometer has been installed on the SOLEIL synchrotron small angle X-ray scattering beamline, SWING (Figure 1). With this tool, it is possible to measure the mechanical properties (in particular, viscosity) of clays at the same time as their organization under flow.

As described in Figure 2, an increase in flow rate radically modifies the scattering images in tangential geometry, which, together with the small changes seen in radial geometry, reveals a more pronounced orientation of the clay layers along the flow plane. Quantitative treatment of the images allows the average orientations of the particles in space to be determined precisely for different solid concentrations and flow rates and provides a better understanding of the links between the microscopic organization of these complex substances and their large-scale physical properties.

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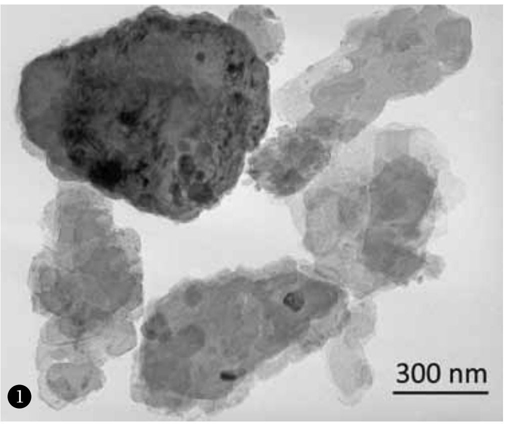
LUCIA

Radioactive waste in clay media



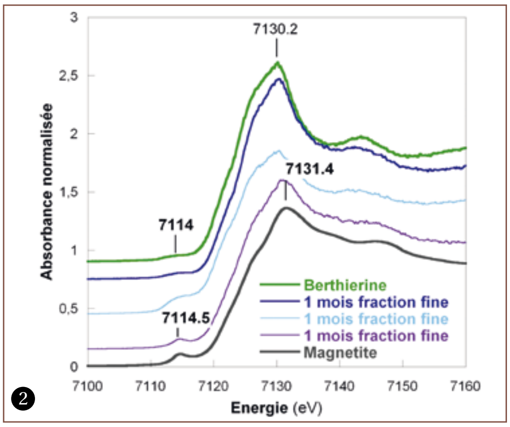


Figure 1: Kaolinite particles after a month of reaction (Transmission Electron microscopy). Before reaction, the particles were hexagonal.

Figure 2: XANES spectra of the fine fraction after one month of reaction, compared to spectra of berthierine and magnetite.

As part of the study on the feasibility of storing radioactive waste in deep geological formations run by ANDRA, work was carried out on the interaction between metallic iron, the main constituent of containers, and the different clay minerals of the host rock. In this study, carried out by scientists from LEM (Laboratoire Environnement et Minéralurgie) KGa2 kaolinite, a 7Å layers aluminosilicate, was put into contact with grains of metallic iron and a solution with low content of sodium and calcium chloride in an anoxic atmosphere. Everything was kept at 90°C for 1 to 9 months. These physico-chemical conditions are close to those expected during storage at depths of 500 meters in the clay formation.

Under these conditions, metallic iron corrodes. X-ray diffraction suggests the formation of a 7Å phyllosilicate and electron microscopy reveals morphological modifications (Figure 1), as well as the clay particles becoming richer in iron.

X-ray absorption micro-spectroscopy analyses at the Fe K-edge were carried out on the LUCIA beamline to determine the localization and status of the Fe in the clay phases and evaluate the heterogeneity of the reaction products. First, the reaction products were separated into two fractions, one coarse-grained (iron grains covered in a thin clay layer) and other fine (free clay particles). These fractions were imbedded in resin then cut into 50 µm thick slices. After mapping (Fe, Si and Al) to localize the clay particles, XANES and EXAFS spectra were recorded at the Fe K-edge under micro-beam conditions (3x3 µm). After 1 or 3 months, the fine and coarse fraction samples show a preponderance of particles bearing Fe^{2+}, close, in terms of the EXAFS signal, to berthierine, a phyllosilicate rich in Fe^{2+} (Figure 2). This new mineral corresponds to the 7 Å phase observed by diffraction. Nevertheless, other zones present different XANES spectra attributed to a mixture of berthierine and magnetite, an iron oxide.

EXAFS spectroscopy confirmed that the Fe-carrying clay phases are essentially berthierine-type phases in which ferrous iron predominates and that these phases are stable over time. In the case of possible storage of radioactive waste, this example of a kaolinite-berthierine transformation shows that interactions between a metal container and a clay environment could lead to the formation of new iron-rich phyllosilicates, to the detriment of the initial minerals.

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Ref 1 : Moëlo Y. et al (2009). Berthiérine hydrothermale de Saint-Aubin-des-Châteaux (Loire-Atlantique). Poster presented at "colloque du Groupe Français des Argiles", Toulouse, April 2009.

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And soon...

Synchrotrons can bring quantitative and qualitative answers to both fundamental and applied questions. As an example, SOLEIL has placed special emphasis on investigating ancient materials, i.e. relating to cultural heritage. A platform to host and develop specific projects will soon be up and running (IPANEMA), equipped with standard tools and a beamline specially optimized for this type of investigation (PUMA) is under study.

In addition, the PSICHE beamline mounted behind a wiggler, will allow X-rays up to 50-60 keV to be used. By taking advantage of the depth of penetration of hard X-rays, the strong point of this energy range, it will allow volume visualization by means of absorption contrast tomography (of great interest in metallurgy, for example); PSICHE will be open to users from 2012.

The effort given to imaging (hard X-ray and soft X-ray with the final beamlines of the first phase at SOLEIL: Nanoscopium and HERMES) aims at linking nanometric and macroscopic properties. Phase contrast, by the visualization of density contours, will also permit non-invasive probing of heterogeneous materials.

SOLEIL's future plans to propose, in the future, reinforced potential for imaging investigations, will be of direct benefit to the material sciences.

CRISTAL

Coherent X-ray diffraction imaging dislocation

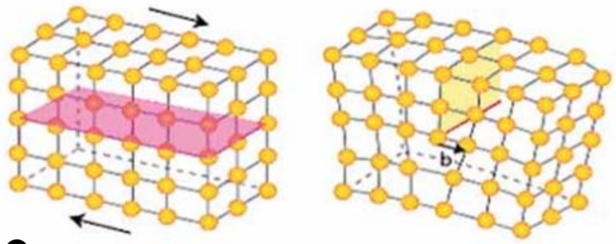

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Figure 1 :
On the left a crystal without faults.
On the right, a crystal with a dislocation line, shown in red (source Wikipedia).

The growth in 3rd generation synchrotrons, as well as progress in X-ray optics, has made it possible to create X-ray beams with high degree of coherence.

Thus new experiments can be designed such as measuring the real diffraction pattern of an object as small as or smaller than one micron.

During a coherent X-ray diffraction (CXD) experiment on a crystalline sample, the intense beams reflected by the atomic planes of the crystal, known as Bragg reflections, are studied.

If the sample is perfectly ordered throughout its illuminated volume, these reflections are peaks whose widths are inversely proportional to beam size.

On the other hand, if the sample contains some disorder or a fault, these peaks split into two or more sub-peaks called speckles, which are the object of CXD studies.

Dislocation is a linear fault in the stacking of the atoms in a crystalline structure (Figure 1).

This fundamental fault in crystals explains why some materials can be bent: the dislocation movements are the cause of plastic distortions in metals.

To study these defects, silicon is often chosen as the model material as it is possible to obtain Si crystals with only a few dislocations in the form of "loops" (obtained when the red line shown on Figure 1 joins up with itself over a diameter of about 100 µm).

The structure of dislocations is generally studied by X-ray topography, with a resolution limited to 1 µm, or by electron microscopy, which can only explore a thin layer of sample.

Experiments carried out on CRISTAL show that it is also possible to study dislocation loops by CXD. Using a beam of a few microns a single dislocation loop in a silicon sample can be mapped by 5 µm steps.

The presence of a single dislocation in the illuminated volume splits the Bragg reflection into two (Figure 2a).

This characteristic has made imaging of the dislocation loop possible in the silicon by combining reflection with topography (overall image of this extended fault: Figure 2e; coherent diffraction: Figure 2c).

These images provide information on the core of the dislocation: it can be seen here that the dislocation loop has broken up, i.e. it is composed of two parallel loops separated by a stacking fault, another classic fault in this material (it gives the tail in the diffraction pattern). Direct analysis of the intensity thus gives an image of the dislocation loop.

Improvements in X-ray sources and optics will soon broaden the possible applications of this technique.

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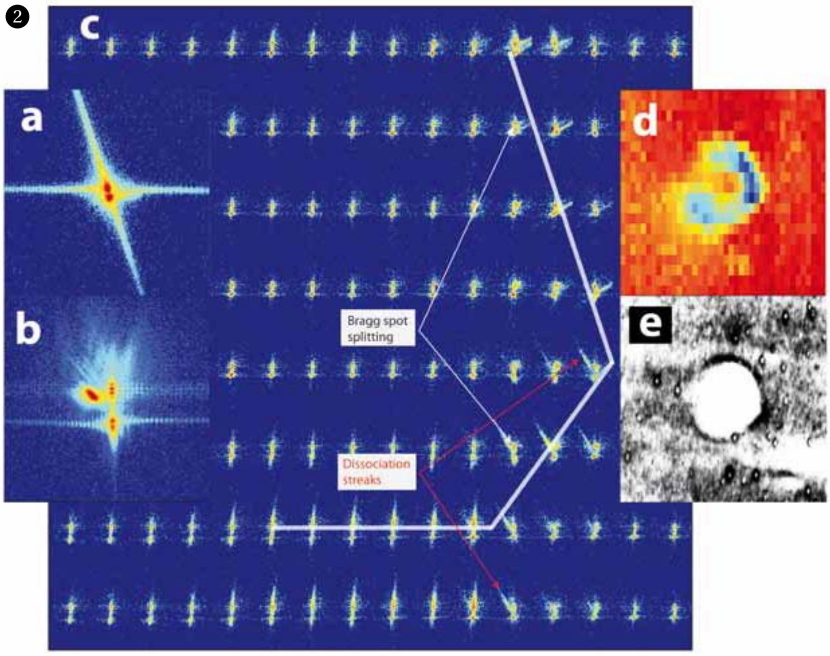

Figure 2 - Diffraction pattern showing the 220 reflection of silicon:
a) Oriented to the angle of reflection
b) Slightly disoriented, when one dislocation line is present in the illuminated volume.
c) Coherent diffraction images on an area containing a dislocation loop, in 5µm steps. Each image taken next to the dissociated line shows the split in the spot and a perpendicular tail at the stacking fault.
d) Dislocation loop by coherent diffraction imaging.
e) Same dislocation loop by reflection topography.

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