Headlines

Catalysis

Observing the earth from space

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Editorial

The two research domains highlighted in the present issue are both emblematic of our university. Indeed, let us first remind ourselves that our university was named after the world famous chemist Paul Sabatier, who was awarded the Nobel Prize in 1912 in recognition for his outstanding work on heterogeneous hydrogenation catalysts. With the need to reduce chemical production energy costs worldwide in the context of sustainable growth, homogeneous catalysis is now more specifically the focus of our university since it allows the development of more selective processes that offer better compatibility with the environment. With such a goal in mind the research groups involved in catalysis research at our university work closely with industry to allow fast transfer of knowledge and technology for future industrial applications.

Keeping in mind that we are going to celebrate the international year of Planet Earth we decided to select an equally important subject: observing the Earth from space. Toulouse is often praised as one of the prominent European capitals of space, and, while reading the relevant articles in this issue, you will realize that the local university laboratories involved in this research domain are leaders in the field at an international level -- particularly in using spatial data for analyzing the Earth, from the internal structure of its fluidic envelopes to its surface.

The development of scientific satellites has allowed a number of important breakthroughs in the observation of our natural environment and in predictions of how it will evolve. Such data can not only be exploited for agriculture and weather forecasting, but can also provide valuable information on the oceans and the evaluation of natural risks, and are of particular interest for land management.

Gilles FORTANIER
President of Paul Sabatier University

Currently used abbreviations

UPS: University Paul Sabatier (Toulouse, France)
CNRS: French National Center for Scientific Research
INSERM: French National Institute for Health and Medical Research
INSA: National Institute of Applied Science
INRA: National Institute for Agricultural Research
INPT: National Polytechnic Institute of Toulouse
IRD: Institute of Research for Development
CNES: French National Space Agency
Catalysts, mediators in chemistry

Chemistry in Toulouse is renowned for its expertise in catalysis, a process that allows for faster chemical reaction rates. Producing reaction products using less energy than through direct heating of reactants, that is the promise offered by catalysis according to its classical definition. More interestingly today, small amounts of catalysts are introduced into the reaction medium, not only to facilitate a reaction, but also to favour a given pathway. Homogeneous catalysis involves transition-metal complexes in which a metal atom is surrounded by ancillary ligands and the reactants. Usually, noble metals, like rhodium, ruthenium, palladium, iridium or platinum, are involved in what is called coordination catalysis. In the homogeneous process, coordination chemistry is a powerful tool for understanding the subtle interactions that occur between the metal centre and the reactants at each step. It thus allows researchers to introduce appropriate modifications in the catalytic system, so that the selectivity required by modern chemistry can be reached.

Expertise at Toulouse

More than a century ago, Paul Sabatier discovered heterogeneous catalysis and provided the first rational explanations. His work, which was awarded the Nobel Prize in 1912, made Toulouse famous in this field, although our university is now also renowned for homogeneous catalysis as well as enzyme catalysis carried out by our colleagues at INSA. Within Paul Sabatier University, and in association with the Institut National Polytechnique, the Toulouse Molecular Chemistry Federation has developed a very active policy for cooperative research in various areas, among them catalysis.

Several teams are directly involved in catalysis and in collaborations with industry to design novel outstanding systems. These teams include the CNRS Coordination Chemistry Laboratory and the Fundamental and Applied Heterochemistry Laboratory. More than 70 researchers are involved in this field and contribute to Toulouse’s outstanding reputation in homogeneous catalysis.

Sustainable development

The following six articles illustrate several methodologies that Toulouse has recently developed. They represent our research in this field and also show that highly efficient reactions can be designed. They allow a sophisticated level of selectivity so that only the desired product – be it for pharmaceutical, material or chemical intermediates – is obtained at the lowest energy cost with no loss of starting material. Thus, chemistry can be used for sustainable development - an important issue today.

The word catalysis has largely exceeded the concept originally outlined by Paul Sabatier because it has also entered our everyday language. For example, a diplomatic person may sometimes be called a “catalyst”. According to the classic definition he should remain unchanged after his interventions but no doubt he may also improve and even be acknowledged for his talent.

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Note: All photos in the catalysis section are courtesy of Cyril Frésillon
The Chemistry Federation

The Toulouse Molecular Chemistry Federation is organized thus:

> Coordination Chemistry
  (LCC, CNRS lab associated with UPS, director Bruno Chaudret).

> Molecular Chemistry and Nanoscience at the Centre for Material Elaboration and Structural Studies
  (CEMES, CNRS lab associated with UPS, team leader: André Gourdon)

> Synthesis and Physical Chemistry of Molecules with Biological Interest
  (SPCMIB, joint UPS/CNRS lab, director: Michel Baltas).

> Fundamental and Applied Heterochemistry
  (HFA, joint UPS/CNRS lab, director: Antoine Baceiredo)

> Molecular Interactions and Chemical and Photochemical Reactivity
  (IMRCP, joint UPS/CNRS lab, director: Monique Mauzac).

> Pharmacochemistry of Natural Substances and Redox Pharmacophores
  (Joint UPS/IRD lab, director: Françoise Nepveu).

The federation consists of a scientific and technical platform that regroups 20 joint departments that work together for the scientific community as whole. It regroups 300 permanent staff and 200 temporary staff (PhD students, post-doctorats, short-term contracts and interns).

The director is Philippe Kalck and deputy director is Antoine Baceiredo.
When a catalyst is too “lazy”, adding another one can help

Making acetic acid, a basic chemical compound, is an energy-intensive process, but thanks to a remarkable collaboration between academy and industry, this is not true anymore.

How do we assure the annual world production of 9M t/y of acetic acid needed to manufacture artificial fibres or for use as a solvent? An industrial process that satisfies the criteria of easy accessibility to raw materials at a cheap price, and that presents a high selectivity, was discovered and developed in the early 1970s by the American Monsanto company. It is based on rhodium homogeneous catalysis in the presence of an iodide promoter and uses two cheap (300 €/t) building blocks, carbon monoxide and methanol, to produce acetic acid. The reaction selectivity is very high since it reaches 99.5% with respect to methanol, but the selectivity regarding CO is only 90% since part of the CO reacts with water present in the medium to give hydrogen and carbon dioxide through the water-gas-shift reaction. However, to prevent catalyst deactivation, a water content of 14% in the medium must be maintained during catalysis. But, using such large quantities of water introduces a costly distillation step to remove water from the acid, since the latter needs to be sold as anhydrous.

Pilot micro-unit

Very early on, researchers from Monsanto noticed that iridium gave similar results to rhodium. However, if the water content was reduced to 5%, the kinetics of the reaction were very slow.

Thanks to a detailed spectroscopic study of the catalytic cycle, based on high-pressure NMR experiments in the presence of labelled compounds (13CO, 13CH3I), and to infrared observations under pressure, we were able to obtain a realistic view of the rate determining step of the reaction, and realised that adding a second metal, platinum, could help "unlock" the system. This discovery was patented in 1998 as part of a collaboration with Acetex, a company that owns a large capacity plant near Lacq, close to Pau. This patent has now been extended to many countries. A technological research team worked on this subject from 1999-2002, and we built a pilot micro-unit to study the pre-development phase of the [Ir-Pt] catalytic system. For long-term runs, the kinetics of the reaction is 20% higher than that obtained with rhodium, the selectivity with respect to methanol and acetic acid reaches 99% and the water content can be as low as 5%. Globally, the high rate and the easier removal of water from acetic acid by distillation allows us to save 30% in energy costs!

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Pilot micro-unit of methanol carbonylation to acetic acid.
Asymmetric Catalysts

Without being aware of it, snails are chiral...

You would think that there would be equal numbers of right-handed helicoidal snail shells as left-handed ones but in fact, this is not the case: only one snail in 1000 has a left-handed shell. Both kinds of helices are symmetrical but not superimposable and are therefore chiral, like most bioactive molecules found in nature.

Chiral molecules often possess an asymmetrical carbon, leading to two spatial configurations, called right and left-handed. These two molecules, almost identical but chiral, are called enantiomers. Very often, only one of the two enantiomers has pharmacological activity while the other enantiomer is toxic or, at best, inactive. This is because the spatial geometry of the four substituents around the asymmetrical carbon leads to only one configuration being recognized by the active site of a target biological macromolecule.

Chiral molecules are synthesized to make drugs, but also for food additives, agrochemicals or fragrances. In the drug industry, for instance, 80% of molecules now in clinical or preclinical development, are chiral. A major challenge for organic synthesis is to develop efficient processes to produce chiral molecules with good yields and selectivities. Furthermore, these processes have to be economically viable and environment-friendly. In this context, the concept of “atom economy” is crucial, and asymmetric or enantioselective catalysis is a major challenge for “green chemistry”. Asymmetric catalysis allows a small amount of catalyst bearing a chiral auxiliary to produce a large amount of product as a single enantiomer (only the right-handed shells for the example of snails) starting from non-chiral materials. This type of process is more productive and consumes less reagent, often making it superior to other techniques.

Asymmetric catalysis has been relevant for industry since 1975 to prepare (L)-dopa (an amino acid used for treating Parkinson disease) via a hydrogenation reaction developed by Nobel Prize winner William S. Knowles of Monsanto Company.

Another important example is (-)-menthol, which possesses 3 asymmetric carbons, which means 8 stereoisomers. Only one of these stereoisomers has the refreshing taste and special flavour of mint. Half the world’s production (1500t/year) of this chemical is obtained by an asymmetric isomerization reaction designed by the Nobel Prize winner Ryoji Noyori and developed by the Japanese company Takasago. It is up to 99% pure.

Through a collaboration with Holis Technologies, a start-up company at Toulouse, we are interested in the asymmetric hydrogenation of enamines and imines to synthesize chiral amines, which are important chemical intermediates in the drugs industry.

We are also studying asymmetric carbonylation reactions catalyzed by transition metals because they are excellent for obtaining enantiomerically pure intermediates to synthesize drugs or agrochemicals. Carbonylation reactions allow us to introduce one additional carbon using the cheap (300 euros per ton) and easily obtained synthon CO. We have chosen to functionalize monoterpenes which are natural products obtained from plants. However, existing catalysts do not produce expected reaction rates and selectivities. In the field of asymmetric catalysis, the role of the chiral auxiliary (1) is important because it is rather like an orchestra conductor, giving instructions (“to the right or to the left”) during chemical transformations. This is why we are involved in the design and synthesis of new chiral auxiliaries for specific catalytic transformations like other teams at LCC.

(1) Chiral auxiliary : chiral molecule used in asymmetric synthesis to control the construction of a new chiral unit.

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“Sigma” complexes: New tools for catalysis

Step-by-step catalysis with low energy cost, this is the promise of “sigma complexes”

A reaction catalyzed by a complex with a metal M yields new products via a series of simple chemical reactions. These catalysts are often organometallic complexes made of a central metal stabilized by different organic or inorganic building blocks, called ligands. Our research team is interested in a particular type of organometallic complex, the ruthenium “sigma” complex and its applications in homogeneous catalysis that respect “green chemistry”.

Coordination without disconnection

Three families of “sigma” complexes are now known. They result from the coordination of either a dihydrogen molecule H2, a silane (HSiR3), or a borane (HBR2) with a metallic centre. The key to this type of coordination is that it occurs without H-H, H-Si, or H-B bond breaking. The hydrogenation reaction, which allows the synthesis of many products that we use on a daily basis, is without a doubt one of the most important industrialized chemical process. During catalysis, the organometallic precursor undergoes a series of transformations, one of which is “oxidative addition”. This key step consists of breaking the H-H bond of the dihydrogen in order to form two M-H bonds. It is at this specific stage of the process that the “sigma” complexes play a crucial role.

Because the intermediates are stable, it is possible to go from one species to another (the dihydride complex) by very gradually tuning the stability of the bonding modes during the reaction. When we face more complex functionalizations, such as in the case of silanes and boranes, it is possible to go through the same type of catalytic process via the formation of a series of “sigma” complexes that lower the energy cost. This is the “sigma-CAM” mechanism that is being developed in our group. Of course, optimizing such catalytic systems requires a better understanding of the mechanistic pathways involved.

Applications in biology

Our research team has obtained exciting results for two types of catalysis: first, hydrogenation and isotopic exchanges (hydrogen/deuterium) can be used to label molecules for biological applications or for analyzing the surface of porous materials. Secondly, the hydrofunctionalization of silicon or boron-containing products can be used to form vinylsilanes or vinylboranes. Vinylsilanes are very important building blocks for applications in organic chemistry and in the domain of silicones, while the vinylboranes are involved in the elaboration of more complex organic building blocks, such as polymers, therapeutic molecules, or sugar receptors. One of the main problems with this type of chemistry is that the sigma complexes are sensitive to oxygen. It is therefore essential to work under an inert atmosphere (argon), which requires specific equipment like a glove box. Reactions under high gas pressure are performed in reactors and the organometallic complexes are characterized by techniques such as NMR (Nuclear Magnetic Resonance), X-ray crystallography or neutron diffraction and gas chromatography.

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>>> Mary GRELLIER, assistant professor, UPS, Gilles ALCAREZ, CNRS scientist and Sylviane SABO-ETIENNE, CNRS senior scientist, researchers in AOC group (Organometallic and Catalysis Architecture group) at the Coordination Chemistry Laboratory (CNRS lab associated to UPS).
Organocatalytic polymerization is environmentally friendly and opens up various perspectives for life sciences.

Polymer applications are varied, from commodity to specialty materials. Polymers are macromolecules resulting from the covalent linking of “repetitive units” called monomers and polymerization is the process of progressively reacting the monomer molecules together. The structure of the resulting polymers must be precisely controlled to obtain the desired properties. In this context, polymerization must involve highly efficient and selective transformations to avoid harsh reaction conditions, long reaction times and thus the formation of complex mixtures of macromolecules.

Resorbable sutures
Among the various types of polymers, our group has been particularly interested in biodegradable materials over the last decade, and especially in linear polyesters. Thanks to their ability to be assimilated by the human body, these biomaterials are crucial in surgery (resorbable stitches, for example) and pharmacology (drug delivery systems with controlled and prolonged release profiles). In this field, the organocatalytic systems are especially important for avoiding potentially toxic metal residues within the materials. In collaboration with several industrial firms (including Ipsen Pharma, Isochem and Arkema), we have demonstrated that polyesters can be efficiently prepared using very simple organocatalytic systems.

Furthermore, by replacing the standard monomers by activated equivalents, the efficiency of the catalytic polymerisation can be significantly improved. For example, the polymer derived from lactid acid, PLA, usually prepared with a tin catalyst at temperatures as high as 140°C, can be obtained within a few hours at room temperature by polymerizing an “activated” monomer in the presence of a weak organic base as a catalyst. In addition, organocatalytic polymerization can allow functional groups to be introduced along the entire polymer chain, thus allowing the physico-chemical properties of the polymer to be modulated.

With most of these organic systems, the catalytic process involves several weak interactions, and results in the simultaneous activation of both the monomer and growing chain. Such a mode of action is similar to that of enzymes. With activated monomers, the organocatalyst can be replaced by a lipase, so that the biodegradable polymers are produced thanks to a biocatalyst.

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Nanoparticles form the base for nanoscience and nanotechnology and have gone from strength to strength in the last two decades. Nanoparticles, and in particular metallic nanoparticles (metallic aggregates 1-10 nm in size), are also important for making catalysts and the goal is to obtain highly active and selective transition metal nanocatalysts. These new catalysts have a high surface/volume ratio, which means they have a significant number of active sites. For instance, nanoparticles 1.5 nm across possess around 80% of active atoms. Furthermore, nanoparticles display different properties to those observed both for molecular complexes of Angstrom size and for bulk materials. Nanoparticles therefore lie at the border between homogeneous and heterogeneous “classic” catalysts.

To guarantee reproducibility, we need to be able to synthesize nanoparticles whose composition and size can be perfectly controlled. However nanoparticles are not thermodynamically stable and can evolve into bulk metals by agglomeration or molecular complexes by atom loss. Protective agents, like polymers, ligands, surfactants or dendrimers, are therefore crucial for making sure the nanoparticles remain stable.

Perfect size, shape and composition
We are interested in preparing nanocatalysts in solution from organometallic precursors, which are usually decomposed under an atmosphere of hydrogen and mild temperatures and pressures in the presence of a ligand. In addition to its stabilising role, the ligand can also "tune" the nanocatalyst surface state and therefore its chemical properties and reactivity. The potential poison effect of the ligand must be taken into account too to avoid catalyst deactivation and to obtain the desired reactivity. Adding well-adapted ligands to the nanocatalyst surface (via anchoring centres and flexible structures) bearing appropriate functional groups compatible with the target catalytic reactions represents one of our main research areas. Our aim is to design nanoparticles of controlled size, shape and composition that show original catalytic properties, mainly in terms of selectivity.

The catalytic efficiency of these nanocatalysts is evaluated in a number of reactions (including hydrogenation, carbon-carbon coupling and hydroformylation). Their activity and selectivity are compared to those obtained using analogous homogeneous catalytic systems. Thanks to the collaboration between our two laboratories (LCC and LHFA), we have already obtained interesting and promising results. For example, we have demonstrated that ligands commonly used in coordination chemistry, like oxazolines, aminoalcohols and phosphines, are also capable of stabilizing nanoclusters. Specifically, excellent kinetic resolution has been achieved for the allylic alkylation catalyzed by palladium nanoparticles when compared to the corresponding molecular system. An extension of our research concerns preparing nanocatalysts in non-contaminating solvents (ionic liquids and water, for instance) for applications in sustainable chemistry. In particular, ionic liquids can also stabilize nanoparticles, which avoids the use of expensive ligands and volatile organic solvents in some cases. Moreover, immobilizing metallic catalysts in ionic liquids allows for easier recycling than for common solvents.

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Catalysis without metals: what a challenge!

Organocatalysis offers many advantages. Excluding metallic contaminants is environmentally friendly and makes the systems biocompatible. However, we need to overcome the lack of efficiency compared to organometallic catalysts... The answer: carbene catalysts!

Organocatalysis is one of the most promising approaches to green chemistry. However, the catalytic activity of these catalysts is often inferior to that of organometallic complexes. But, carbenes are the exception.

Carbenes, which comprise a divalent carbon atom with a pair of electrons (singlet carbene), are extremely reactive and, for a long time, were considered to be only short-lived reactive intermediates. However, in 1987, our research group succeeded in synthesizing the first stable carbene. Since then, the chemistry of stable carbenes has developed tremendously.

Bathroom sealants and breast implants
We are now able to synthesize variable stable carbenes with different properties and tune them to explore their unique reactivity as organocatalysts, particularly in the polymerization of silicones. Carbenes have remarkable physical properties (including high thermal stability) and are biocompatible too. Applications range from bathroom sealants and breast implant material to coatings for rockets such as Ariane V.

In collaboration with international industry (Rhodia, Bluestar and MAP), we have demonstrated that the N-heterocyclic carbenes (NHCs) are very efficient catalysts for silicone synthesis. Indeed, they are active catalysts for the ring-opening polymerization (ROP) of cyclic monomers such as D4 (the carbene acts as nucleophile), and the polycondensation of dihydroxyoligosiloxane with the elimination of water (the carbene behaves as an organic base).

High purity
In contrast to classical synthetic methods using ionic strong bases and high temperatures, our polymerization system is neutral and efficient at relatively low temperatures. The catalytic system can be deactivated simply by heating the resulting polymers, which avoids the complicated neutralization-filtration step. Moreover the silicone polymers obtained are remarkably clean.

In addition, silicone derivatives are an efficient protective medium for moisture-sensitive N-heterocyclic carbenes. The weak carbene-silicon interaction stabilizes these highly reactive species and allows us to handle them in air without any special precautions. The NHCs in silicone also behave as free reactive carbene in organic solvents, which can be thought of as a new type of encapsulation of carbene in silicone matrices that does not affect the high reactivity of these materials. The discovery that carbenes are compatible with water could also expand the scope of carbene organocatalysts for new catalytic reactions.

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Toward eternal grafts...

In order to stop graft rejection once and for all, Joost van Meerwijk’s team has just developed a new therapy. Does this mean the end of immunosuppressive treatments?

What was the starting point of your discovery?

“Immunological tolerance” is an ensemble of mechanisms that protect our bodies from attacks by our own immune systems. If it is deficient, autoimmune diseases such as multiple sclerosis, juvenile diabetes or rheumatic arthritis will develop. Researchers select lymphocyte precursors with a view to eliminating cells capable of attacking our own bodies. However, such a selection always misses some lymphocytes that regard the body as a target. It is then the role of “Treg lymphocytes” to remove this autoimmune response. This “immunosuppressive” activity was discovered in the 1970s but we only realized afterwards that these cells play a central role in maintaining the immune system.

What is the link with graft rejections?

If scientists know that Treg lymphocytes protect our body against immune system attacks, then why do we not exploit them to protect against foreign bodies such as grafts? If we want Treg lymphocytes to protect grafts, we need to “educate” them. One way of doing this is to put cells of the donated organ in contact with the patient’s Treg lymphocytes. Given that the body produces every sort of Treg conceivable, some of these will be able to recognize the graft and, unlike the others, will activate and proliferate. These “specific” Tregs will then prevent immune system attacks against the graft.

Is it sufficient then to inject specific organ Tregs to prevent rejection?

No. Four years ago, we noticed positive results by injecting some Treg lymphocytes into a mouse to protect a bone-marrow graft. However, we observed rapid rejection for other types of graft (such as heart or skin). We wondered why the bone-marrow graft was protected against rejection while the other types of graft were not. We discovered that, contrary to the skin or heart, the bone marrow contains cells that allow the injected Treg cells to survive. Therefore, no rejection occurs if we associate bone marrow graft and injected “educated” Treg cells at the grafted organ. In our protocol, the bone marrow allows the Treg cells to survive, leading to a “educated” Treg population! In turn, the cells infer tolerance to the graft. The conclusion is that both Treg and bone marrow are essential to control immune system response.

What are the advantages of your techniques compared to other currently employed methods?

Even if immunosuppressive drugs prevent immediate rejection of the grafted organ, they do not work against long-term rejection. These drugs may also have serious side effects: by weakening the immune system, they make it easier for diseases like cancer to develop and also expose the body to infection. Moreover, they are toxic to organs, such as the kidneys. The new therapy not only prevents both immediate and long-term rejection, but has no harmful side effects. It also allows patients to receive organs from donors that are genetically different from themselves, so considerably increasing the number of compatible grafts possible. This could help overcome the problem of the lack of organs available.

Comments obtained by G.Esteve
Translation by I.Ahrioui

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Why do electronic devices age?

By studying an aluminium-silicon alloy at high temperature, Marc Legros at CEMES, together with an international research team, has shown that some crystalline defects considerably speed up atomic transfer. This is the first step in understanding how electronic components age.

Could you describe your experiments?

We succeeded in heating up a thin section of an aluminium-silicon-copper film deposited on a silicon substrate inside an electron transmission microscope. This method, also called in-situ microscopy, allowed us to directly and dynamically observe changes occurring in solid matter, at micro- or nanometre scales.

Why did you decide to study an aluminium-silicon alloy?

From a materials science point of view, an aluminium layer on a silicon wafer can be considered as a model microprocessor. In microelectronics, the silicon acts as the transistor, while the connexions between these transistors are made up of metallic lines, consisting of either pure copper or aluminium alloys, with smaller and smaller dimensions. We do not know how these interconnections behave mechanically when the device is exposed to high temperatures. Adding silicon to the copper or aluminium alloy both strengthen the interconnects and limits the diffusion of silicon from the substrate into the metallic lines.

You measured very fast atomic diffusion rates in this alloy. What does this imply?

Because silicon dissolves poorly in aluminium, it precipitates out and can easily be observed with an electron microscope. Moreover, when heated, the aluminium-silicon film tends to expand more than the silicon wafer it is attached to. Above a certain temperature (typically 200°C), the aluminium film permanently deforms, and this so-called “plastic” deformation occurs by the displacement of "dislocations". These dislocations are atom-sized linear defects and are found in large numbers in all metals and alloys. When one of these dislocations hooks up to two precipitates, it creates a diffusion short-circuit for the silicon atoms. Atoms are then transported between 500 and 800 times faster than in the absence of the dislocation, from the smaller silicon precipitates to the larger ones. This process, also known as “pipe-diffusion” leads to a reduction of the surface energy of the precipitates.

Can this mechanism help explain electronic device ageing?

Yes, it can explain the ageing of metal interconnects. Metal lines are the weakest parts of a microprocessor as regards deformation and temperature. Because pipe diffusion makes the silicon precipitates grow abnormally fast, it may be that one of these precipitates clogs the whole section of an aluminium line. This has two consequences: the electrical conductivity of the line locally drops and it heats up considerably. Also, since the alloy becomes much less homogeneous, the thermal stress can lead to an abrupt failure at the points where large silicon precipitates, which are naturally brittle, are located.

Comments obtained by F. Mompiou

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Progress not only concerns solid Earth but also its fluid envelopes (atmosphere and oceans) as well as land surfaces. Two factors have played an important role here: observations of continuously improved quality, and modelling tools developed for simulating Earth's past, present and future structure.

Satellites

Observations from space have played a crucial role. The importance of satellites for observing planet Earth is well known: satellites offer global coverage, high resolution and continuous or frequent measurements. Their data are well calibrated and, in general, easily accessible. Not to mention that observations from space have also helped improve model performance.

The technical center of the French National Space Agency (CNES) has been located in Toulouse since the mid-1970s. The centre has strongly contributed in enhancing regional development of space research, in particular in geosciences.

In the Toulouse region, Earth observation research using space techniques is mainly conducted at the Midi-Pyrénées Observatory (OMP), which is part of Paul Sabatier University. Five OMP laboratories are involved in space research to study the solid Earth, land surfaces, atmosphere, oceans and ice bodies. Two of them, CESBIO (Centre for Space Studies of the Biosphere) and LEGOS (Geophysics and Spatial Oceanography Study Laboratory) are partially sponsored by CNES. The other three (DTP – Terrestrial and Planetary Dynamics-, LMTG –Mechanism and Transfers in Geology Laboratory- and the Aerology Laboratory) also routinely use satellite observations. Let us also mention the pioneering role of the Groupe de Recherches en Géodésie Spatiale –GRGS-, a national institution created in 1971 for developing space geodesy in France, which includes several OMP teams.

High-precision oceanography

Although OMP is not the only French institution developing Earth-oriented space research, its teams are clearly world leaders in several areas. These include space oceanography, thanks to the development of a French program in satellite altimetry (Topex/Poseidon and Jason missions) by CNES. During the past 15 years, LEGOS, in collaboration with other Toulouse groups (for example, CLS –Collecte Localisation Satellite-, a CNES subsidiary, and MERCATOR) have made important contributions in several areas of space oceanography, such as ocean tides, ocean circulation, ocean-atmosphere interactions related to El Niño and sea level rise. Satellite altimetry data are also now routinely used by MERCATOR for forecasting the state of the ocean one or two weeks in advance, as is currently done in meteorology. Today, such a satellite altimetry applications are well integrated in the ongoing European project GMES (Global Monitoring for Environment and Security).

Land surfaces

CESBIO is also a leader in the domain concerning land surfaces and the terrestrial biosphere. In addition to contributions to fundamental research

Average sea level rise since 1993 from space altimetry measurements (blue dots are raw data, red curve is smoothed data). There is an observed increase of 3mm per year over the last 15 years (Topex-Poseidon and Jason-1 data)
(for example, on the carbon cycle and land hydrology), numerous applications for society as a whole have been developed, such as in agriculture, for instance.

**Crustal deformations**

In the 1990s, scientists from the DTP, together with CNES engineers, were the first to use radar interferometry (a technique derived from “synthetic” aperture radar on satellites such as ERS, JERS and Radarsat) to measure crustal deformation in tectonically active regions, with unprecedented resolution. Such a technique is now routinely used worldwide to monitor co- and post-seismic deformations, volcanic deformations, ground subsidence, land slides and glacier motion. Another example concerns the use of precise positioning from space (for example, GPS, satellite laser ranging and DORIS) to measure large-scale tectonic plate motions.

**Terrestrial waters**

In recent years, several teams from OMP (at LMTG, LEGOS and CESBIO) have developed a new research area, hydrology from space. Space techniques such as satellite altimetry, space gravimetry (the GRACE space mission), radar and visible imagery, radiometry, active and passive microwaves can be used in synergy to measure key variables in land hydrology and their evolution in response to climate variability and anthropogenic forcing. Examples include soil moisture, lake water levels, rivers and floodplains, surface water volumes and total land water storage. This data is very valuable for better understanding the global water cycle. It is also highly useful for applications, such as water management, river navigation, agriculture and land use, flood and drought prediction and hydroelectric power production. The same techniques also yield information about the mass balance of the Greenland and Antarctica ice sheets in response to global warming and their impact on sea levels.

**Atmospheric pollution**

The use of satellite data in meteorology has been around for a long time but it is only recently that satellite observations have been used to study atmospheric pollution. The Aerology Laboratory at OMP is now involved in such a field, providing information about atmospheric pollution on vast scales by combining space data with modelling approaches.

The examples mentioned here highlight the advantages of using space observations to study our planet. Important advances have been made over the last decade by OPM laboratories in studying oceans, solid Earth, terrestrial waters, land surfaces and atmospheric pollution. With existing space missions and those to be launched soon, future research in these areas is very promising. OMP will no doubt continue to play a leading role at both the national and international level.

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The interactions between precipitation and lateral transfer of energy and mass fluxes from the ground or “root zone” are being studied at CESBIO. Instantaneous satellite observations in the visible, infrared and near infrared wavelength have poor spatial resolution and require complex data processing. Soil moisture is estimated indirectly from active (radar) and passive (radiometers) microwave satellite measurements.

CESBIO is in charge of the AMMA/CATCH programme (African Monsoon Atmosphere and Water Cycle Coupling) and for soil moisture in situ and satellite measurements in Mali.

The water cycle

Variations of the gravity field derived from GRACE (Gravity Recovery & Climate Experiment) satellite measurements are used at LEGOS to quantify the spatio-temporal variability of continental water stock (surface and ground water, and snow), ice sheet and glaciers, which cannot be observed by any other means on a global scale.

To estimate surface water levels for large rivers, lakes and enclosed seas, LEGOS and LMTG use radar altimeter satellite data (Topex/Poseidon, ERS, Jason and Envisat) initially designed to measure ocean surface topography. These measurements are used for studying climate and anthropic processes. New results from altimeter estimates of water levels have been obtained by modelling river discharge, and calculating riverbed elevation using theoretical relationships between altimeter-derived water levels and slopes, and discharge. These measurements are used for hydrodynamic modelling. For large river basins, radar altimeters provide measurements of flood plains and estimates of the corresponding water volume used to model the dynamics of flooded regions. These studies are especially important for estimating the carbon cycle dynamics in tropical regions.

Suspended sediment

Recently, LMTG developed new methods to estimate the concentration of surface suspended sediment using visible and near infrared images (300 m resolution) from MERIS (on board the Envisat satellite) and MODIS (on board AQUA and TERRA satellites). The suspended sediments come from the erosion of continental surfaces and are carried away by large rivers. To validate and calibrate the satellite data LMTG uses networks of in situ measurements in the Amazon basin through official collaboration agreements with the different countries in this region.

Since 1979, LEGOS has been monitoring the dynamics of the high latitude snowpack, derived from passive microwave satellite measurements. Since the launch of the ERS-1 satellite in 1992, the surface topography of Antarctica and Greenland has been monitored with unprecedented precision from radar altimeter measurements. The combination of satellite radar altimeters with gravimetry shows that ice mass is decreasing in the western portion of Antarctica and globally over Greenland.

Future satellite missions

A new satellite mission SMOS (Soil Moisture and Ocean Salinity) was proposed by CESBIO in 1998 to estimate soil moisture and ocean salinity on a global scale. This new mission (whose interferometer functions at 1.4 GHz) will be launched in 2009. LEGOS is also the lead for a new satellite mission SWOT (Surface Water Ocean Topography) for continental surface water hydrology and high resolution ocean topography. SWOT is a new wide swath interferometric altimeter (36 GHz) that will provide complete global coverage with 100 m resolution for continental surface water and 1 km resolution for oceanography studies. SWOT is a NASA-CNES collaboration and its launch is scheduled for 2015.

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Several approaches combining field work, remote sensing and terrestrial ecosystems dynamics modelling using conceptual models adapted to different study scales are being used to answer the above questions. Our research focuses on three region: the Sahel zone, the southern part of the Mediterranean sea and southwest France.

Vegetation dynamics (land-cover, leaf-area index and biomass distribution) can be analyzed in the field by sampling protocols. However, the sampling areas are limited and are sometimes difficult to access. On the other hand, large scale observation of vegetation characteristics can be carried out at daily to monthly intervals by remote sensing data through analysis of vegetation indices calculated form surface reflectance in different wavelengths: visible, infrared and radar can be used to obtain information on land use and vegetation biomass, height, leaf area and water status (figure 1). However, such remote sensing requires field calibrations and validation campaigns.

Water vapour (evaporation and transpiration) and CO₂ (photosynthesis and/or respiration) exchanges between vegetation and the atmosphere can be studied in detail in the field by infrared gas analyzers that can be either connected to small gas exchange cuvettes for leaf photosynthesis or transpiration measurements, or combined to 3D sonic anemometers analyzing eddies transporting H₂O and CO₂ for ecosystem net flux measurement at larger scales. Finally, the analyzer can be transported by tethered balloons to measure changes in vertical CO₂ or water concentration profiles at the frontier with the atmosphere. Such experiments have shown that wheat and rapeseed crops have a good ability to store carbon and that it is important to encourage intercropping to improving crop carbon budgets.

Since field campaigns are restricted in time and space, remote sensing is a good way to extend the zone studied and increase the frequency of operations. Remote sensing data can then be used as input data or to constrain vegetation models. These models use simplified descriptions of the processes driving vegetation dynamics. They are therefore used for monitoring yield estimates or for ecosystem management (including irrigation). In parallel, mechanistic models, some of which are being developed at CESBIO, are used to analyze sensitive ecosystem processes. They may be used at smaller scales to study how agrosystems respond to climatic and anthropic constraints in a global climate change perspective.

More generally, the tools developed at CESBIO can be used to analyze the relationships between carbon and water cycles, and to assess terrestrial ecosystems’ response to climate changes.

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Remote sensing of Earth’s Interior

Dynamics, such as tectonic movements, affect the surface of our planet and can thus be observed by satellites from space. Surface phenomena, like volcanic eruptions and seismic events, can be spectacular but “hidden” phenomena like the gravity field and how it changes with time, can also be seen.

At the Midi-Pyrénées Observatory, two laboratories, the DTP and LMTG, are working with other French researchers to develop and exploit space technologies to observe Earth’s surface so that processes occurring in the interior of the planet can be characterized.

The space gravimetry decade

Techniques to model Earth’s gravity field advanced rapidly in the first half of this decade, essentially thanks to new space gravimetry missions, including CHAMP in 2000, GRACE in 2002, and GOCE (to be launched in 2008-2009). Using EIGEN models, these missions have improved our knowledge of the total gravity field by a factor of 100 to 1000. Moreover, the micron precision of GRACE measurements allowed scientists to measure how gravity varies on monthly time scales for the first time, at spatial resolutions of around 500 km. GOCE, a European Space Agency satellite, should extend this resolution to 100 km by the end of the decade.

The GRACE mission’s main achievement was to produce temporal models showing that great mass variations could be detected from space, and that these variations are related to the hydrological cycle, to ice shrinking or to major tectonic events. In a few orbits, GRACE was effectively able to detect the consequences of the great Sumatran earthquake, which occurred in December 2004 and which generated a 8 mm depression of the geoid as well as a land rise in the east of Sumatra.

Continental deformation: small and great

Since the beginning of the 1990s, remote sensing has made significant progress in precisely measuring continental deformation and plate tectonics. The first geodetic measurements were carried out at the beginning of the last decade using the American GPS (Global Positioning System) composed of 24 satellites. Positioning on Earth’s surface is now accurate to a resolution of centimetres in absolute terms and millimetres in relative terms. The resolution depends on the number of the measured points.

The European Space Agency, for its part, launched two aperture radar (SAR) satellites, which made it possible to quantify the deformation field at continental surfaces with millimetre precision using interferometry. This radar technique, the first images from which were the fruit of a collaboration between the CNES and DTP, opened up the possibility of observing geophysical phenomena with a hitherto unseen hectometric resolution without having to go on-site. Nevertheless, optical imagery is still useful because satellite sensors have increased in resolution (50 to 70 cm) and the correlation technique also allows deformation at the surface to be mapped with a good resolution.

The research undertaken in our laboratories mainly concentrates on the Mediterranean region and South America and makes use of these techniques, combined with other geological and geophysical observations. Thanks to developments in digital techniques, we are improving the precision for observing deformations to the millimetre scale to better characterize the dynamics of seismic and volcanic zones, and to quantify the associated risks.

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The oceans play a key role in moderating our climate and maintaining its equilibrium, by absorbing and damping out climate perturbations. The ocean responds to atmospheric forcing (wind, heat flux and precipitation changes) at scales of tens to thousands of kilometres. Oceanic time scales range from seconds to hours for surface waves and extreme events such as hurricanes or tsunamis, from days to months for large current systems and their eddies and meanders, and up to years and even centuries for deep ocean currents. Atmospheric perturbations can therefore invoke changes to the ocean circulation at both local and global scales, with significant repercussions on the climate. An example is El Nino, which is a strong ocean-atmosphere perturbation centred on the tropical Pacific, but which induces climate perturbations on regional and global scales.

Monitoring ocean changes over these wide range of space and time scales is now crucial for understanding and predicting climate change. Up until the 1980s, most oceanographic measurements were made “in situ”, either from ship-born observations or from moored instruments and analyzed every few months. In the 1980s and 1990s, the advent of satellites revolutionized oceanographic observations, allowing regular monitoring of the ocean surface, including sea surface temperature and sea level. For the first time, the wide range of ocean movements could be observed for all of the ocean basins over time periods of many decades.

Since electromagnetic radiation cannot penetrate water, satellites are restricted to observing surface parameters. Satellite altimetry, measuring sea level variations, is the only instrument which detects deeper ocean currents. A warm deep current will induce a thermal expansion at depth, which in turn raises sea level. Wind can push water up against the coast, raising sea level by mass convergence. Local precipitation, river flow and polar ice melting can also raise sea levels and can be observed by satellite altimetry. Since 1992, a series of altimeters have provided global maps of sea level variations every 10 days.

At LEGOS, a number of different research groups use satellite altimetry to unveil the rich structure of oceanic dynamics, in collaboration with the CTOH, an observational service dedicated to altimetry observations. Among the new discoveries, the GOHS research group at LEGOS has used altimetry to determine increases in sea level, which have risen by 2-3 mm/yr over the last 15 years (figure 1), and to better understand the different factors contributing to this sea level rise (Lombard et al. 2007). The OLVAC group has observed how the ocean responds to El Nino and La Nina events in the tropical Pacific with altimetry, helping researchers develop new theories to explain these events and their global impact on climate (Bosc and Delcroix, 2008). The CTOH has developed new surface current products based on different satellite captors, and other products specifically adapted to monitoring coastal currents. For the first time we have been able to track ocean eddies, which move systematically across the ocean over many years, and which are an important mechanism for oceanic heat transport (Morrow et al., 2004).

In addition to the physics, LEGOS scientists use ocean-colour satellites to detect changes in the surface chlorophyll concentration, which is important for understanding the distribution of ocean biomass. Future satellite missions will provide new observations, such as sea surface salinity (for example, SMOS will be launched in 2009). Today, we use different satellite measurements, in combination with realistic numerical models, to better understand and predict the changing ocean and its affect on the climate.
Research at Paul Sabatier University

Research at Paul Sabatier University is developed in 74 laboratories organised in research units, supported both by the University and by at least one of the following research institutions: CNRS, INSERM, IRD, INRA, CNES...

The research staff includes about 2350 scientists whereas the administrative and technical staff consists of 1400 people. The number of graduate students is around 1500 in six doctoral schools.

The main research themes developed on our campus site are:

> **Mathematics**: 1 laboratory.
> **Physics and nanophysics**: 5 laboratories.
> **Chemistry and Materials Sciences**: 6 laboratories.
> **Engineering Sciences**: 6 laboratories.
> **Computer sciences and information systems**: 2 laboratories.
> **Sciences of Earth, Space and Universe**: 7 laboratories.
> **Life and Health Sciences and Biotechnologies**: 14 laboratories.
> **Biology and Life Sciences**: 11 laboratories.
> **Health Sciences**: 4 laboratories.
> **The Humanities and Social Sciences**: 4 laboratories.