

800,000 years' climate history read in the ice

Polar ices provide the only archive that, for the same samples, allows information to be accessed both as regards alterations in the planet's climate, and the composition of the atmosphere. Analysis of ice cores consequently plays a crucial part in gaining an understanding of the various mechanisms involved in natural climate evolution, during the last major cycles of glacial and interglacial periods. Three kilometers of ice cores were extracted from the Dome C site, in Antarctica, allowing research workers to unravel the secrets of the Earth's climate over the past 800,000 years, this being the oldest climate reconstruction obtained to date.

The **EPICA** consortium (see Box 1), coordinating the endeavors of ten European countries, has just completed two deep core drilling campaigns in the Antarctic icecap (see Figure 1). The Dome Concordia (Dome C) site, located on the central plateau of East Antarctica, at an altitude of 3,230 m, is extremely cold, with an annual average temperature of -54.5°C , and very dry. The amount of snow accumulating, on average, each year, corresponds to a depth of water of 2.5 cm. The aim of the Dome C drilling is thus to take advantage of this modest yearly accumulation of snow, to obtain the oldest possible climate records.



CEA-IPEV

Ice core extracted from the Dome C site, in Antarctica. Ice sheet drillings allow climate archives, built up over millennia, to be accessed.

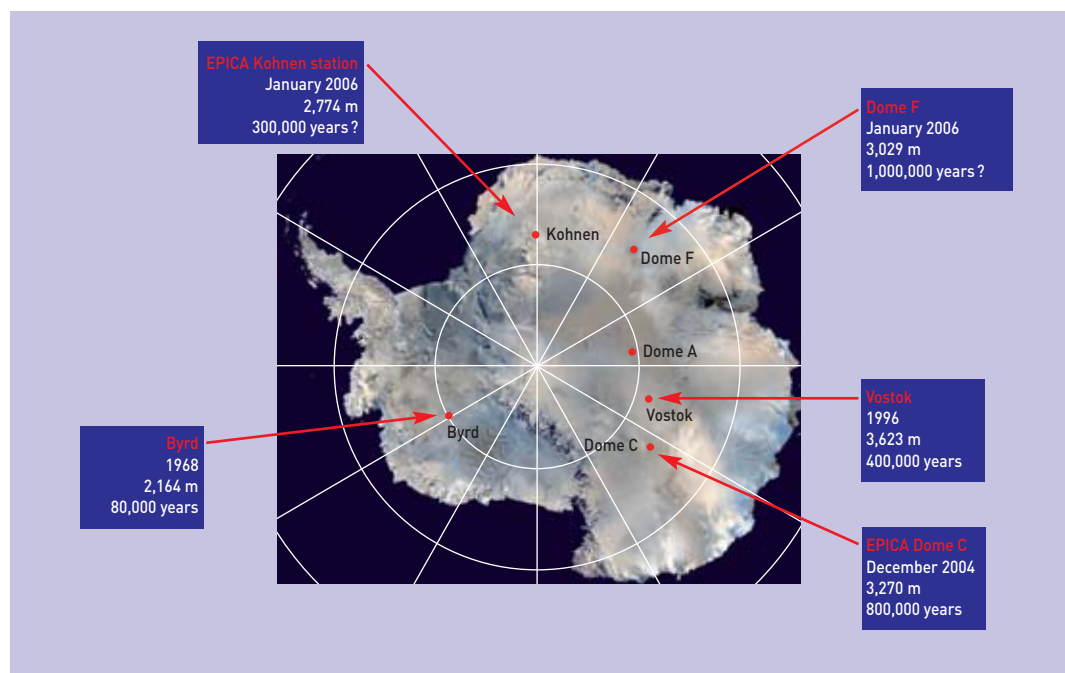
The EPICA consortium: a strong French participation

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The **EPICA** (European Project for Ice Coring in Antarctica) consortium, bringing together ten countries – Belgium, Denmark, France, Germany, Italy, the Netherlands, Norway, Sweden, Switzerland, and the United Kingdom – has been supported by the European Science Foundation (ESF), and the **European Commission's** 5th and 6th **Framework Programs** (FP5 and FP6). The French contribution to this consortium is very strong, both in terms of logistics, and of scientific participation. The French Paul-Émile Victor Polar Institute (IPEV: Institut polaire Paul-Émile Victor), in particular, mounted the heavy expeditions across land, to transport equipment to the Dome C site. The technical team from the Glaciology and Geophysics of the Environment Laboratory (**CNRS**–Université Joseph-Fourier/**LGGE**), based near Grenoble,

played an essential part in developing the core barrels. In scientific terms, the French teams are involved in all aspects related to capitalizing on a deep core drilling. LGGE is involved in activities concerning analysis of trace gases and chemistry, investigation of ice mechanical and physical properties, and ice sheet **modeling**. The Nuclear Spectrometry and Mass Spectrometry Center (**IN2P3/CNRS/CSNSM**), at Orsay, near Paris, has concentrated on measurement of **cosmogenic isotopes**, while the Climate and Environmental Sciences Laboratory (CEA–CNRS–Université de Versailles – Saint-Quentin-en-Yvelines [UVSQ]/Institut Pierre-Simon Laplace [IPSL]/**LSCE**) is involved in reconstruction of climate parameters, mainly on the basis of isotopic measurement of the ice, and the air bubbles held in it.

Figure 1.
Map of deep drillings
made in Antarctica.
For each drilling,
the label shows date
of completion, depth,
and the period of climate
history it covers,
or may cover.



This Dome C EPICA drilling began in 1995, terminating in 2004 at a depth of 3,270 m, close to the bedrock, notwithstanding arduous logistical and technical difficulties. To complement the Dome C drilling, the EPICA consortium decided to drill a second ice core, this time however in the Atlantic sector of Antarctica, in the Queen Maud Land area (Norwegian: Dronning Maud Land). At this second site, at the Kohnen station, temperatures are milder, with an annual average standing at a mere -44.5°C , and the snowfalls more abundant (6.4 cm of water annually). This second drilling has just yielded, in January 2006, 2,774 m of ice core, providing the most detailed Antarctic record of the rapid climate changes experienced in the last ice age.

Unique climate archives

The very deep ice cores yielded by the Dome C drilling were no match for the depth record set at the Vostok

site (over 3,600 m!), however they did prove to be the oldest climate archives retrieved to date from the polar ice sheet. These climate archives are particularly rich. On the one hand, analysis of the water from that ice allows past variations in local temperature to be quantified. And, on the other, its chemical composition, and investigation of the particles enclosed in the ice reflect the variation in **aerosols** present in the **atmosphere**, coming from the continents or oceans surrounding Antarctica. Finally, the composition of the air trapped in the ice yields global information.

Unraveling past variations in temperature

Measuring the abundance of the various **isotopic** forms of water **molecules** provides the means to quantify past variations in temperature (see Box 2). The experimental know-how of the Climate and Environmental Sciences Laboratory (CEA-CNRS-UVSQ/LSCE) draws on a large number of analyses,

Concordia permanent
scientific station is sited
on top of Dome C,
one of the three major
domes of East
Antarctica's central
plateau, above an ice
thickness of over 3 km.
View showing the various
installations at Camp
EPICA Dome C.



effected to a high precision using **mass spectrometers**, in conjunction with measurements carried out concurrently by laboratories at the Universities of Trieste (Italy) and Copenhagen (Denmark), crates of EPICA samples shuttling between these laboratories on a regular basis. An initial set of investigations gave an idea of temperature variations, hence of the successive glaciations, detected as “cold” periods in ice samples particularly depleted in **heavy isotopes**, separated by interglacial eras, such as that we have been experiencing for over 11,000 years. In 2006, examination of the ice samples, taken every 55 cm (bag samples), was finalized for the entire EPICA Dome C drilling, and analyses of even more finely detailed series were initiated, to provide a high-**resolution** reading of climate variations, at the scale of a few tens of years, under the aegis of the PICC (intégration des contraintes Paléoclimatiques pour réduire les Incertitudes sur l'évolution du Climat pendant les périodes Chaudes: Integration of Paleoclimatic Constraints to Reduce Uncertainties on Climate Evolution during Warm Periods) program, supported by **ANR**. Tens of thousands of ice samples yet remain to be examined, before the riches of these new Antarctic cores can be fully exploited.

Detecting subtle variations in composition for atmospheric oxygen

Scientists measure isotopic composition not solely for water, but also for air trapped in the ice. Specifically, the abundance is determined with respect to oxygen-18 and -16 **atoms**, present in the air trapped in Dome C ice. This parameter makes it possible to relate climate changes recorded in polar regions to global variations in sea levels, as reconstructed from marine sediments, and equally to detect changes in productivity on the continents; this impacts the isotopic makeup of atmospheric oxygen, by way of the respiration and **photosynthesis** mechanisms. Some of the Earth's orbital parameters control monsoon intensity, and the continents' productivity. It is then possible to use the oxygen isotopic measurement to identify the signature of these orbital parameters, and improve ice datation. Such analyses use up a relatively large amount of ice, and are a heavy undertaking, as the methodology calls for a delicate stage, for the extraction of air trapped in the ice, involving the melting, and gradual refreezing of the samples in a vacuum chamber.

The ice from the EPICA Dome C drilling has yielded its first secrets

Initial analyses, carried out on the EPICA Dome C drilling, have yielded essential information.

Datation methods for very ancient ice samples

There is currently no method available for the absolute datation of such very ancient ice samples. For some sites, where the abundance of snow deposits makes this feasible, annual layers may be counted, and a highly accurate, year-by-year datation may thus be built up for the ice. For Antarctic central plateau sites, **modeling** methods needs must be employed. The approach involves, first of all, modeling the relationship between snow isotopic composition and

The isotopic thermometer

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Water is not solely made up of “normal” **hydrogen** (of atomic mass 1) and “normal” oxygen (of mass 16). Both of these **atoms** have **isotopes**, **deuterium** (D: hydrogen of mass 2) and oxygen 18, in particular. Existence of these isotopes results in “isotopic” forms of the water **molecule**, HDO and H₂¹⁸O, which are present alongside H₂¹⁶O in every tank where water is held. The physical properties exhibited by these three molecules are slightly different. Heavy molecules – as may be grasped intuitively – preferentially tend to the condensed phase (rain, snow), rather than water vapor. Thus, at every phase change in water, the condensed phase shows a richer **heavy isotope** content than the vapor phase giving rise to it. There is thus a gradual depletion in terms of the relevant isotopic content in water vapor and rainfall, as the air mass gets cooler. This takes the form, in polar regions, of a linear relationship between a site's annual average temperature and isotopic abundance, whether of deuterium or of oxygen 18. This linear character is well accounted for by an isotopic **model**, into which this simplified description of the life of an air mass is transcribed. This forms the basis for what physicists term the *isotopic thermometer*. The colder the weather, the lower the isotopic abundance, and vice versa. Applied to a given site, this correspondence allows climate variations to be reconstructed from records of variations in either deuterium or oxygen 18 content.



Concordia station is the outcome of a French–Italian collaboration, bringing together the Paul-Émile Victor Polar Institute (IPEV: Institut polaire Paul-Émile Victor) and the National Antarctic Research Program (PNRA–Italy), as witnessed by these signposts.

local temperature, then working out the relationship between local temperature and the amount of snow accumulation, drawing on the thermodynamics of humid air, and, finally, modeling the settling of snow layers as they sank into the polar ice sheet. These modeling efforts are partly updated by reference to present-day observations (satellite observations), and making use of datum points obtained through synchronization of the various drillings, by means of certain reference horizons (peaks in **cosmogenic** isotope fluxes, detected volcanic eruptions, common signals of variations in the concentration

Equipment and provisions are brought in by convoy from the coast to Concordia scientific station, located over 1,000 km inland in the Antarctic continent.



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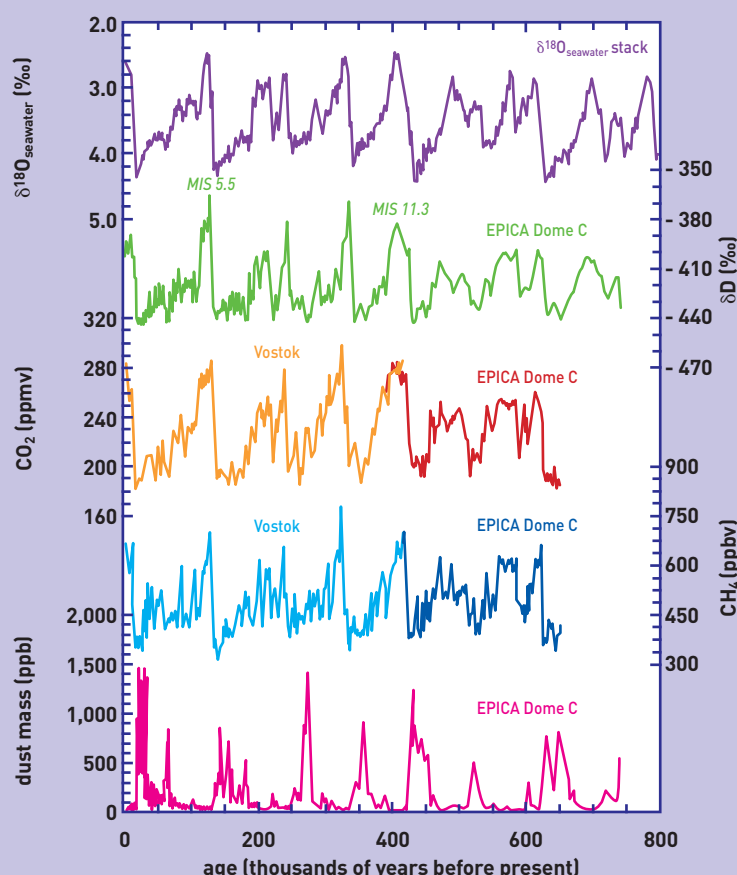


Figure 2. Variations in sea levels (purple curve, on the basis of marine sediment analysis), Antarctic temperatures (green curve, from measurement of Dome C ice isotopic composition), atmospheric carbon dioxide (CO_2) concentration (orange and red curves, based on analysis of air from Vostok and Dome C ices) and methane (CH_4) concentration (blue curves), and dust mass, as measured in Dome C ice (pink curve). The timescale extends back from the present time (0) to 800,000 years ago. (MIS stands for "marine isotope stage.")

of **greenhouse gases**, well-mixed on a global scale, such as **carbon dioxide** [CO_2] or **methane** [CH_4]. The initial datation, published in 2004 by members of the EPICA community,⁽¹⁾ was challenged, for the older periods, by comparing it with datation of sea level variations, as yielded by analyses of marine sediments, and with respect to age discrepancies between air and ice for these selfsame older periods. An inverse glaciological datation method, turning these constraints to advantage, has been developed by Frédéric Parrenin, a former PhD research fellow at LSCE, currently a research worker at the Glaciology and Geophysics of the Environment Laboratory (**LGGE**), based in the Grenoble (France) area. A new datation for the EPICA Dome C drilling is being finalized. The history of temperature variations at the Dome C site, as derived from ice isotopic composition, as a function of time, extending back from 2004 to 740,000 years ago, is shown in Figure 2. The latest measurements carried out on the Dome C drilling show that the drilling as a whole covers 800,000 years, reliable climate records ending about 60 m before the bottom of the drilling. The latter portion corresponds to ice which may have undergone complex flow conditions close to the bedrock, analyses suggesting a mix of ice layers of different ages.

Glaciations and interglacial eras

The Dome C climate record has already yielded crucial information as regards climate evolution. First of all, it corroborates the elements available to scientists, for the history of Antarctic temperatures, from two other sites: Vostok for 400,000 years or so, and Dome Fuji for some 300,000 years. Typically, the amplitude of temperature changes between the last glaciation, about 20,000 years ago, and the present

■ (1) *Nature*, p. 2981, 2004.

day stands at $9^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Such temperature reconstructions are essential, if the realism of climate **models** is to be tested, these being also used to predict future evolution. Presently, it would seem that climate models do tend to underestimate past changes in temperature, in polar regions.

The Dome C drilling covers 800,000 years, this allowing investigation of several glaciations. These periods follow each other at a rate of one every 100,000 years or so, as previously shown by marine sediment investigations. Considering climate was predominantly subject to glacial conditions over that timespan, a long record allows detailed characterization of the subtle differences prevailing with the “warm” interglacial periods, occurring between two glaciations. Dome C ice samples thus show that the warmest of these warm periods reached temperatures some 5°C higher, at most, than today. They further show that warm periods exhibit a great diversity, in terms of duration and intensity.

The longest-lasting warm period occurred some 400,000 years ago (MIS 11), extending over close to 28,000 years. This extended warm period contrasts with the more recent interglacial periods, which were relatively short, lasting around 10,000 years. Understanding the mechanisms bringing about the end of a warm period is essential, with respect to current climate evolution, and the ability for climatologists to predict when the next glaciation is to set in.

The influence of the Earth's orbital parameters on climate dynamics

Large climate variations are driven by the distribution of insolation, as a function of latitude, and of the seasons. The theory put forward in 1941 by Serbian geophysicist Milutin Milankovitch attributes climate change to quasi-periodical variations in the parameters of the orbit the Earth follows around the Sun. Orbital *eccentricity*, determining the Earth–Sun distance, varies over a 100,000–400,000-year period; the *obliquity*, or *tilt* of the Earth's axis of rotation with respect to its orbital plane varies over 40,000 years or so; and the position of the seasons along the Earth's orbit over 19,000–23,000 years, owing to the process of the *precession of the equinoxes*.⁽²⁾ These parameters result in variations in insolation, depending on latitude and season. As regards the current state of knowledge, scientists do identify the signature of orbital frequencies in climate records, and climate models enable the relationships to be tested, that pre-



Once ice cores are extracted, samples are cut and prepared for subsequent analysis, in Europe. Many analyses are also effected on an ongoing basis, on the ground.

vail between these orbital parameters and climate dynamics. Milutin Milankovitch's theory links the occurrence of a Summer insolation minimum in the Northern hemisphere to persistence of the snow cover, leading to gradual accumulation of that snow, building up the icecaps that covered Northern Europe and Northern America during ice ages.

It is an established fact that amplification processes within the climate machine play a key role. Among such processes may be counted variation in albedo,⁽³⁾ this being related to the presence of snow or ice, or changes in vegetation, and alterations in the carbon cycle. Taking climate to be a system subject to thresholds, on the basis of the input in terms of past glaciations, the insolation thresholds may be determined that would be required, to tip climate over from an interglacial to a glacial era. Thus, variation in the position of the equinoxes along the Earth's orbit is especially attenuated when orbital eccentricity is low. Such is the case currently, as indeed it was some 400,000 years ago. Data from the EPICA drilling thus suggest that the present and future configuration of the Earth's orbit, fairly similar to that prevailing during the very long warm period that occur-

(2) Equinoxes: times of the year characterized by an equal length of day and night, for all points on the Earth's surface, heralding the beginning of Spring and Autumn.

The precession of the equinoxes corresponds to a slow drift in the direction of the Earth's axis of rotation, caused by the torque generated by the tidal forces exerted by the Moon and Sun on the Earth's equatorial bulge. These forces tend to draw the excess mass, present on the equator, to the ecliptic (i.e. the geometric plane in which the Earth's orbit is held). Since the Earth is rotating, these forces cannot alter the angle between equator and ecliptic, causing however a motion of the Earth's axis of rotation in a direction perpendicular to that axis, and to the torque. This motion, known as *precession*, results in the Earth's axis of rotation describing a cone.

(3) Albedo: the reflective power of a surface or medium (soils in this case), measured as the ratio of reflected solar energy, over incoming solar energy.



P. Bazoge/CEA

Freezer hall, where polar ice samples from various campaigns are stored. Their analysis is yielding essential information on past climate evolution, and on the workings of the climate machine.

red 400,000 years ago, should involve no glaciation for the next few tens of thousand years. We are thus placed at a very particular point in time, with regard to “natural” climate evolution, where orbital parameters may not be counted on to compensate for the increment in **greenhouse effect** of anthropic origin.

A strong correlation between climate changes and greenhouse gases

This increment in greenhouse effect may be characterized by referring it to the natural variability of greenhouse gas concentrations in the atmosphere, as derived from the analysis of gases trapped in Dome C ice. Carried out at the University of Bern (Switzerland) and at LGGE, these measurements have

just been published, covering the past 650,000 years. The findings corroborate the analysis of air from the Vostok ice, and show that current levels of carbon dioxide and methane in the atmosphere, presently standing at 380 **ppm** and 1,700 **ppbv** respectively, are unprecedented in terms of levels reached and rate of increase, over that entire timespan.

Publication of the greenhouse gas records from the ice further made climatologists confident, with respect to using isotopic measurements from Dome C ice. Indeed, these are wholly independent parameters, undergoing separate record-forming processes, in the water and air phases of the ice. The mechanisms resulting in variations in greenhouse compounds are to be found, for carbon dioxide, in the marine and continental carbon cycle, and, for methane, mainly in humid regions on the continents, hence in the Northern hemisphere. These data show that the history of Antarctic climate does have relevance for the entire planet, on a glacial–interglacial scale, this being corroborated by climate models, these showing that temperature change, at the heart of Antarctica, stays proportional to that affecting global mean temperature.

Now, Antarctic temperature records, just as greenhouse gas records, show likewise a very major alteration in the intensity of climate changes as regards the older period, over 400,000 years ago. For these more ancient times, paleoclimatologists find “mild” interglacial periods, exhibiting much lower intensities than the more recent interglacials. They are presently drawing up hypotheses, to account for this deep-running alteration in warm period intensity. It would appear that small, long-term variations in the maximum and minimum amplitudes of the Earth’s obliquity may result in such major changes, affecting climate and carbon-cycle rhythms. Should this



Ice samples being cut in a cold chamber (– 20 °C) prior to carrying out analysis of the air bubbles trapped in them.

F. Vigouroux/CEA

hypothesis prove correct, this would imply that global climate is far more sensitive to small variations in its radiation balance than scientists had believed so far.

Finally, the close correlation between past Antarctic temperature changes and atmospheric carbon dioxide and methane concentrations shows there is strong coupling between climate evolution, driven as it is by the Earth's orbital parameters, and the feedback processes between climate and carbon cycle. In other words, as climate changes, natural carbon sinks and sources undergo reorganization, which may amplify climate changes. These very processes are at work currently. Massive use of fossil fuels,⁽⁴⁾ deforestation and intensive agriculture are releasing greenhouse compounds, that are altering the Earth's radiation balance, and causing global warming. Climate changes bring about a reorganization of carbon sinks and sources, through changed ocean circulation, and increased rainfall, conducive to vegetation growth. Modeling investigations carried out at LSCE suggest that the impact of future climate change on carbon sinks and sources could significantly increase the buildup of greenhouse gases in the atmosphere, thus amplifying climate upheavals.

Five times faster warming predicted by models

Finally, the analysis, on the basis of the history of Antarctic temperatures, of the "natural" rhythm of temperature changes at Dome C has been carried out. The steepest warming detected occurred during the last thaw, about 14,000 years ago, at a rate of 0.4 °C per century. Should greenhouse gas releases continue at the rate of a rise in carbon dioxide concentrations of 1% annually, climate models predict that warming at Dome C would range from 2.6 °C (in the event of a doubling of carbon dioxide concentration) to 5.7 °C (in the event of a fourfold increase), for an average warming rate of 1.5–2.4 °C per century, which is 4–5 times faster than the fastest "natural" changes. This is an abrupt change, on the scale of past climate variations.

New deep drilling projects, on the Antarctic and Greenland shores (see Box 3), being developed under the aegis of the IPICS (International Partnership for Ice Core Science) program, will allow previously gathered data to be complemented, and enable further advances in our understanding of climate change.

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Analysis of an ice core, using a mass spectrometer. Measurements of ice deuterium and oxygen 18 content allow past temperature variations to be reconstructed.

A. Gomin/CEA

What prospects for deep polar drillings?

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The IPICS (International Partnership for Ice Core Science) program, supported by SCAR (Scientific Committee on Antarctic Research) and IGBP/PAGES (International Geosphere-Biosphere Program/Past Global change), seeks to coordinate efforts, internationally, along four main directions, to promote advances in our understanding of past climate changes. The first goal is that of obtaining the oldest possible Antarctic core drilling, reaching back further than the past million years, to investigate the interactions between climate and carbon cycle at the time of the major transition from 40,000-year to 100,000-year climate cycles. This project requires intensive efforts, to determine potential drilling sites in Antarctica, in particular through expeditions on the ground, to be mounted during International Polar Year (March 2007–March 2009). The second direction consists in achieving a deep core drilling in North-West Greenland, covering the entire warm period leading up to the penultimate glaciation, to characterize the intensity of the warming experienced, climate stability, and the stability of the Greenland ice sheet. The third direction is aimed at establishing the spatial and temporal structures for the sequence of abrupt climate changes that occurred over the past 40,000 years, on the basis of high-resolution drilling arrays at both poles. The new Franco-Italian drilling at Talos Dome comes under this direction. The fourth goal is to characterize climate and climate forcing history, on the basis of very-high-resolution drilling arrays, to cover, in polar regions and mountain glaciers, the past 2,000 years.

(4) Fossil fuels: fuels extracted from the Earth, such as coal, petroleum, and natural gas.

D Spectroscopy and spectrometry

Spectrometric methods are subdivided, as a whole, into two main categories, radiation spectrometry – itself comprising absorption spectrometry, emission spectrometry, Raman scattering spectrometry, and nuclear magnetic resonance spectrometry – and mass spectrometry.

Radiation spectroscopy and **spectrometry**⁽¹⁾ cover an ensemble of analytical methods allowing the composition and structure of matter to be ascertained, based on investigation of the spectra yielded by the interaction between **atoms** and **molecules**, and various types of **electromagnetic radiation**, emitted, **absorbed**, or **scattered** by the former.

Depending on their energy, **photons** interact selectively with the various electron shells, or levels, making up the electronic structure of the atom, or molecule. The electrons involved are **core electrons** (close to the atom's nucleus), for X-rays,⁽²⁾ **peripheral electrons** (furthest from the nucleus, and involved in chemical bonds) for light absorbed, or emitted, in the **near ultraviolet** and **visible** region. In the **infrared** radiation region, it is the leap from one **molecular vibration** level to another that is involved, the switch from one molecular **rotation** level to another for microwave radiation, and **atomic nucleus spin** for NMR.

Absorption spectrometry

Those spectroscopy methods that rely on absorption make use of the Beer–Lambert law, setting out the proportional relation between the intensity of light absorbed, and the amount of absorbing matter:

$$A = \log(I_0/I) = \epsilon \cdot l \cdot C,$$

where *A* stands for the **absorbance** of the medium traversed, *I*₀ for incident light intensity, *I* for transmitted light intensity, ϵ is the characteristic **molar** extinction coefficient, for a given wavelength, for the substance investigated – expressed in

$\text{L mol}^{-1} \text{cm}^{-1}$ – while *l* stands for the thickness passed through, expressed in centimeters, and *C* is the concentration, in moles per liter.

By measuring the medium's absorbance, for a given wavelength, the concentration of a substance, in a sample, may thus be determined.

In an **absorption spectrum**, as recorded by means of a **spectrometer**, **absorption peaks** correspond to the wavelengths the medium is able to absorb. Just as the spectrum from the Sun's light is obtained by making it pass through a prism, which breaks it up, spectrometers analyze the spectral distribution of the whole range of electromagnetic radiations, separating them out according to wavelength, by means of a reflection diffraction grating. Spectra exhibit peaks, each one corresponding to a specific wavelength.

Depending of the type of sample to be analyzed, and the performance level being sought, in the laboratory, **absorption spectrometry** is used either on molecules in liquid or gaseous phase, or on atomic vapor, obtained through thermal breakdown of liquid or solid samples.

Molecular absorption spectroscopy, in the UV–visible region, affords simplicity of use, however it is only applicable to samples of moderate complexity, since, owing to the width of **molecular absorption bands**, absorption spectra, as a rule, do not allow specific discrimination of every constituent, in a complex mixture.

In **infrared (IR) spectrometry**, absorption is the outcome of molecular vibration and rotation processes. Infrared absorption spectra thus allow the nature of chemical bonds to be determined, that make up a molecule, by ascertaining the bond's elasticity constant (influencing vibration frequency, as for a spring), thus confirming structural hypotheses.

As the number of atoms increases, the spectrum rapidly exhibits growing complexity, and interpretation becomes highly problematical, especially for organic compounds.

Atomic absorption spectrometry, in this respect, brings higher performance, since absorption by atoms yields very narrow **absorption lines**. Very precise measurements are thus feasible, even when the sample consists in a complex assembly of chemical elements. Atomic absorption is a reference technique for the ana-

lysis of trace elements in a wide variety of samples, in particular for biological samples.

Emission spectrometry

Atoms or molecules brought to an excited state may deexcite by emitting radiation, known as **emission radiation**. When the excitation is caused by selective absorption, by the atoms or molecules to be analyzed, of electromagnetic radiation, this represents a **fluorescence** emission (or a **phosphorescence** emission, depending on the electron excitation state involved).

As with absorption, fluorescence may be applied, in the UV–visible radiation region, to molecules, or atoms. **X-ray fluorescence spectrometry**, on the other hand, refers to the **X radiation** emitted by atoms excited by absorption of X-radiation. Fluorescence techniques are more complex to implement than is the case for absorption techniques, since they entail that the particle subjected to analysis be selectively excited by a monochromatic radiation. On the other hand, since the radiation emitted is likewise specific to the particle, fluorescence spectrometry involves a double selectivity, resulting in very low background noise, thus making it peculiarly well suited for the measurement of very low concentrations.

Emission of radiation may also occur when atoms are thermally excited, in an environment brought to high temperatures. Emission spectroscopy is based on the fact that atoms, or molecules excited to high energy levels deexcite to lower levels, by emitting radiation (emission, or luminescence). This differs from fluorescence spectrometry in that excitation is not applied selectively, rather it involves indiscriminately all of the particles making up the medium. **Emission lines** thus correspond to radiation directly emitted by a body brought to a high temperature, and the **emission spectrum** allows the detection, and quantification, of all atoms present in the emission source.

Raman spectrometry

Interactions between matter and electromagnetic radiation also give rise to scattering processes, such as **elastic scattering**, and **inelastic scattering**. Scattering may occur when the interface between

(1) The term “spectrometry,” initially used only to refer to recording and measurement techniques, has tended to become synonymous with “spectroscopy,” as the eye was supplanted, for observation purposes, by other receptors and instruments, while the visible region now only formed one special region, in analytical terms.

(2) It should be noted, at the same time, that X-ray crystallography is not deemed to be a spectroscopy method, in the strict sense of the term.

two media is encountered, or as a medium is passed through. This process, in most cases, is an “elastic” one, in other words it takes place with no change in frequency for the radiation forming the beam involved. Elastic scattering of solar radiation by the atmosphere is, for instance, responsible for the blueness of the sky, observed when the eye is not directed towards the Sun (*Tyndall effect*). Indeed, scattered intensity is all the greater, the shorter the radiation wavelength, which, in the case of the solar spectrum, corresponds to the color blue.

As regards spectrometry, the main use of scattering concerns *Raman spectrometry*. This involves the inelastic scattering of incident radiation by the molecules making up the sample. The difference between scattered radiation frequency, and incident radiation frequency allows the identification of the chemical bonds involved. Raman spectrometry is a technique that is widely used for structural analysis, to complement infrared spectrometry, and mass spectrometry.

Nuclear magnetic resonance spectrometry

The principle of **nuclear magnetic resonance (NMR)** is based on the fact that an atom has a *magnetic moment*, just like a spinning charge acting as a tiny magnet, governed by quantum mechanics, aligning in a magnetic field as the needle of a compass in the Earth's magnetic field. The principle of NMR consists in inducing, and detecting, the transition, for the nuclear magnetic moment, from the lowest energy level to the highest energy level, through absorption of electromagnetic radiation of a wavelength lying in the radiofrequency region: when the energy of the photon precisely matches the energy difference between the two levels, absorption occurs. Nuclei having numbers of **protons**, and **neutrons** that are both even exhibit zero spin. Carbon 12 and oxygen 16 atoms, which are very widespread in nature, thus have zero spin. On the other hand, hydrogen only has one single proton, and its nuclear magnetic moment equals 1/2: it may thus take on two possible energy states, corresponding to the two orientation states of its spin, relative to the magnetic field. Measuring the resonance frequency in the electromagnetic field allowing transition from one of these energy states to the other enables the molecu-



Spectromètre de masse d'ions secondaires utilisé au CEA pour réaliser des mesures isotopiques rapides sur un échantillon par exemple prélevé sur une installation aux activités nucléaires suspectes.

les to be analyzed. This frequency is fixed, however the various nuclei in a molecule do not all resonate at the same frequency, since their magnetic environment is modified by their chemical (electronic) environment.

Many NMR spectra exhibit more peaks than there are protons in the nucleus, owing to the interactions between protons and their neighbors. Two nuclei may interact within the molecule, though they are separated by several chemical bonds: this is known as interatomic coupling. This interaction endows the NMR spectrum with a fine structure.

Mass spectrometry

Mass spectrometry is a highly sensitive *detection and identification* technique, allowing determination of molecular structures, and thus of a sample's composition. This is not, strictly speaking, a form of spectrometry, since it is not concerned with discrete energy levels. What is its principle? A compound introduced into the device is vaporized, and subsequently **ionized** by an electron bombardment source (at 70 eV). The ion thus obtained, termed a molecular ion, allows the compound's molar mass to be determined. Breaking chemical bonds within the compound may yield charac-

teristic fragment ions. These are then sorted according to their mass/charge ratio in an *analyzer*, through application of a magnetic and/or electric field, then collected by a *detector*, which amplifies the signal associated to the ions, which arrive with varying delays. A data processing system converts the information from the detector into a **mass spectrum**, readout of which, by comparing it with reference spectra, allows the identity details of the molecule to be drawn up. Through use of a high-resolution mass spectrometer, the exact mass of the compound may be determined, together with isotope percentages for each constituent atom.

Choice of ionization method is directly related to the nature of the sample, and the type of analysis. If mass spectrometry has gradually adapted to meet the growing demands from chemists, and biologists (separation of increasingly complex, highly polarized mixtures, determination of ever higher molecular masses on samples of ever more constricted sizes), this is essentially due to advances in *ionization techniques*, these including secondary ion mass spectrometry (SIMS), chemical ionization, thermospray ionization, and fast atom bombardment (FAB) sources, further comprising, from the 1980s, matrix-assisted laser desorption ionization (MALDI), and electrospray ionization (ESI), together with advances in *detection techniques*, from time-of-flight (TOF) measurement to “ion traps” (ITs), through quadrupoles (MS or Q).

In proteomics, for instance, only MALDI, ESI and SELDI (surface-enhanced laser desorption ionization) are employed.

Ion **mobility spectrometry (IMS)** is a chemical analysis technique in the gaseous phase, which consists in subjecting a gas to an electric field. Ionized molecules acquire a velocity that is characteristic for the ion, since this depends on mass, and charge. Arrival of the ions on one of the plates generating the field results in a current, which is recorded. The length of time after which a peak occurs can be related to the nature of the ion causing it. Scientists often make use of a coupling of devices each belonging to one of the two main families of analytical techniques (see Box E, *What is chromatography?*), e.g. of a chromatograph with a mass spectrometer (or an electron-capture detector [ECD]), particularly for the investigation of trace complex mixtures.

B Fundamental interactions and elementary particles

The **standard model** of particle physics is the reference theoretical framework describing all known **elementary particles** (see Table 1) and the fundamental **interactions** these particles are involved in (see Table 2). The basic constituents of matter, known as **fermions**, are partitioned into two main categories, as determined by their participation in the fundamental interactions, or forces (the **gravitational**, **electromagnetic**, **weak**, and **strong** forces), which are mediated by **vector bosons**, the fundamental particles which carry out the transmission of the forces of nature⁽¹⁾ (see Table 2). Whether a particle belongs to the category of fermions, or to that of bosons depends on its **spin** (i.e. its intrinsic angular momentum, or internal rotation moment), depending on whether it exhibits half-integer spin (fermions) or integer spin (**bosons**).

At the same time, to every constituent of matter is associated its **antiparticle**, a particle having the same *mass*, but the opposite *charge*. The **positron** is thus the positively charged antiparticle of the **electron**, which exhibits a negative charge.

Leptons and quarks

Fermions include, on the one hand, **leptons**, which may travel freely and do not participate in the *strong interaction*, which ensures the cohesion of atomic **nuclei** (it is consequently termed a *nuclear interaction*), and, on the other hand, **quarks**, which participate in all interactions but are not individually observed, enmeshed and confined as they are within **hadrons**, the particles susceptible to strong interaction, of which they are the constituents.⁽²⁾

In the lepton category, **charged leptons** participate in the *electromagnetic interaction* (which ensures the cohesion of **atoms** and **molecules**, and in the *weak interaction* (which underlies **decay** processes, in particular **β radioactivity**). Neutral leptons, or neutrinos, for their part, participate in the weak interaction only. Exhibiting very low mass, there is one type of neutrino for each type of charged lepton.

Independently from their involvement in interactions, the basic constituents of matter are classified into three *gene-*

rations, or *families*, of particles. From one family to the next, quarks and leptons having the same charges only differ by their mass, each family being heavier than the preceding one.

The **electron**, up quark (symbolized *u*) and down quark (symbol *d*), which belong to the first generation, are the lightest massive particles, and are stable. These are the sole constituents of **normal matter**, so-called **baryonic** matter (a baryon is an assembly of quarks), which is made up of **protons** and **neutrons**, this however only accounting for 4% of the Universe's energy content! Particles in the other two families are heavier, and are unstable, except for neutrinos, which on the other hand exhibit non-zero mass, but are stable.

These latter particles may only be observed or detected in the final states resulting from collisions effected in **accelerators**, or in **cosmic radiation**, and rapidly decay into stable first-generation particles. This is why all the stable matter in the Universe is made up from constituents from the first family. According to **quantum mechanics**, for an interaction to take place between particles of normal matter, at least one elementary particle, a boson, must be emitted, absorbed, or exchanged. The **photon** is the **intermediate** (or **vector**) boson for the electromagnetic interaction, the **W⁺**, **W⁻** and **Z** are the intermediate bosons for the weak interaction, and **gluons** are those of the strong interaction, acting at quark level.

As to the **graviton**, the putative vector for the gravitational interaction, it has not so far been empirically discovered. The **gravitational force**, which acts on all fermions in proportion to their mass, is not included in the standard model, due in particular to the fact that quantum field theory, when applied to gravitation, does not yield a viable scheme, as it stands. While gravitational effects are negligible in particle physics measurements, they become predominant on astronomical scales.

Interaction ranges

Quarks and charged leptons exchange photons. The photon having no electric charge, these particles conserve their electric charge after the exchange. Since

the photon's mass is zero, the electromagnetic interaction has an infinite range. Having no electric charge, neutrinos are the only elementary fermions that are not subject to electromagnetic interaction.

In the electroweak theory (a unification of the weak and electromagnetic interactions), the weak interaction has two aspects: **charged-current weak interaction**, for which the interaction vectors are the **W⁺** and **W⁻**; and **neutral-current weak interaction**, for which the mediator is **Z⁰**. These two forms of weak interaction are active between all elementary fermions (quarks, charged leptons and neutrinos). The mass of these bosons being very large (about 80 GeV/c² for **W[±]**, 91 GeV/c² for **Z⁰**), the range of the weak interaction is tiny – of the order of 10⁻¹⁸ m. Since **W[±]** bosons have a non-zero electric charge, fermions exchanging such bosons undergo a change in electric charge, as of nature (*flavor*). Conversely, since the **Z⁰** boson has no electric charge, fermions exchanging one undergo no change in nature. In effect, neutral-current weak interaction is somewhat akin to exchanging a photon. As a general rule, if two fermions are able to exchange a photon, they can also exchange a **Z⁰**. On the other hand, a neutrino has the ability to exchange a **Z⁰** with another particle, though not a photon.

Only those quarks that have a color charge⁽¹⁾ exchange gluons, these in turn being bearers of a color charge. Thus,

(1) The participation of basic constituents in fundamental interactions is governed by their *interaction charges* (electric charge, color charge), or “conserved quantum numbers.” *Color charge*, a quantum number that determines participation in strong interactions, may take one of three values: “red,” “green,” or “blue” (these colors bearing no relation to visible colors). Every quark bears one of these color charges, every antiquark one of the three anticolor charges. Gluons are endowed with double color-anticolor charges (eight combinations being possible).

(2) To take e.g. **nucleons**: the proton holds two up quarks and one down quark, the neutron two down quarks and one up quark. A **meson** is made up of just two quarks (one quark and one antiquark).

B (cont'd)

when a gluon exchange takes place between quarks, the latter exchange their respective colors. Gluons have zero mass, however, since they do bear a color charge, they are able to interact

together, which greatly complicates theoretical treatment of this interaction. The range of the strong interaction is consequently very restricted – of the order of 10^{-15} m.

The quest for unification

The theoretical framework for the standard model is quantum field theory, which allows a quantitative description to be made of the fundamental interactions.

<div><div><div>atom</div><div>nucleus</div><div>electron</div><div>proton charge + 1 mass : 938.272 MeV/c²</div><div>neutron zero charge mass : 939.565 MeV/c²</div><div>nucleon</div><div>quarks</div></div></div>						
<div><div>Fermions</div><div>Normal matter is made up of particles from this group.</div><div>Most of these particles were around just after the Big Bang. Presently only to be found in cosmic rays, and around accelerators.</div></div>	leptons able to move freely			quarks assembled into triplets, or quark-antiquark pairs, to form the many subatomic particles		
	First family	<div>electron (e)</div> <div>responsible for electricity and chemical reactions charge: - 1 mass : 0.511 MeV/c²</div>	<div>electron neutrino (ν_e)</div> <div>has no electric charge, and interacts very seldom with the ambient medium.</div>	<div>down (d)</div> <div>electric charge: - 1/3 the proton holds one, the neutron two mass : 4 – 8 MeV/c²</div>	<div>up (u)</div> <div>electric charge: + 2/3 the proton holds two, the neutron one mass : 1.5 – 4 MeV/c²</div>	
		Second family	<div>muon (μ)</div> <div>a more massive companion to the electron. mass : 105.658 MeV/c²</div>	<div>muon neutrino (ν_μ)</div> <div>properties similar to those of the electron neutrino.</div>	<div>strange (s)</div> <div>a heavier companion to “up” mass : 80 – 130 MeV/c²</div>	<div>charmé (c)</div> <div>a heavier companion to “down” mass : 1.15 – 1.35 GeV/c²</div>
		Third family	<div>tau particle (τ)</div> <div>heavier still. masse : 1,776.99 ± 0.29 MeV/c²</div>	<div>tau neutrino (ν_τ)</div> <div>properties similar to those of the electron neutrino.</div>	<div>beauty (b)</div> <div>tau particle. mass : 4.1 – 4.4 GeV/c²</div>	<div>top (t)</div> <div>heaviest in the family (observed in 1995) mass : 171.4 ± 2.1 GeV/c²</div>
	Vector bosons		photon		gluon	
Fundamental particles carrying out transmission of natural forces.		elementary grain of light, vector for the electromagnetic force		bearer of the strong force between quarks		
Higgs boson?		responsible for “electroweak symmetry breaking”		W [±] , Z ⁰		
				bearers of the weak force, responsible for some forms of radioactive decay		

Tableau 1.

Table showing the twelve elementary constituents for which the standard model describes the interactions involved. The three charged leptons (electron e⁻, muon μ^- , tau particle τ^-) are subject to electromagnetic and weak interactions, neutrinos (ν_e , ν_μ , ν_τ) are only affected by weak interaction, and the six quarks (up, charm, top – or u, c, t – bearing a charge of 2/3; and down, strange, bottom – d, s, b – bearing a charge of -1/3) are subject to all three interactions. Every elementary constituent has its antiparticle, having the same mass, and algebraic quantum numbers (such as electric charge) of the opposite sign.

tions between elementary particles, while respecting the principles of *special relativity*, as those of quantum mechanics. According to the latter theory, if one seeks to observe a microscopic structure at high temporal and spatial resolution, this entails transferring to it an amount of energy–momentum, the greater, the higher the resolution being sought. However, according to the theory of relativity, such an energy–momentum transfer is liable to undergo transformation, yielding particles not present in the initial state: fermions may be generated, or annihilated, in particle–antiparticle pairs, while bosons may be so in any arbitrary number.

All processes involving one and the same fundamental interaction are interrelated. The quantum field theory approach, in which properties of **symmetry** play a fundamental part, seeks to describe all of the processes relating to each fundamental interaction, within overarching theoretical constructions.

The strong and electromagnetic interactions are formalized, respectively, in the theories of **quantum chromodynamics**, and **quantum electrodynamics**. The weak interaction, for its part, is not subject to a separate description, being described jointly with the electromagnetic interaction, in the unified formalism of **electroweak theory**. Theories of the *grand unification* of all fundamental interactions do exist, however they remain as yet lacking any experimental validation.

All the predictions of the standard model have been corroborated by experiment, except for just one, to wit, the existence of the **Higgs boson(s)**, which particle (particles?), it is hoped, will be discovered with LHC. The **Higgs mechanism** is thought to be responsible for the mass exhibited by elementary particles, the eponymous boson making it possible for zero-mass fermions interacting with it to be endowed with mass. This would allow the unification, at high energies, of the weak and electromagnetic interactions within the electroweak theory, while effectively accounting for the **breaking** of this **electroweak symmetry** at low energies, taking the form of two interactions, which may be seen as distinct at that energy level [see *The electroweak*

interaction from one accelerator to the next: the LHC roadmap and the yardstick of LEP measurements, p. 23].

Going beyond, or completing the standard model?

The standard model features a set of parameters (such as the masses of elementary particles, or the intensities of fundamental forces) which are “anchored” in experimental findings. It is, in any event, a theory that is liable to be improved, or further elaborated, or even surpassed and left behind. It does not account in any way for the classification of the constituents of matter into three generations of particles, whereas it is precisely the existence of these three generations which makes it possible to account for **CP** (charge–parity) **invariance violation** (meaning that a physical process involving the weak interaction is not equivalent to its own mirror image), a violation that is in all likelihood the source of the matter–**antimatter** imbalance, running in favor of the former, in the primordial Universe. The model neither allows quantum treatment of gravitation, nor does it fully account for the fundamental property of *confinement*, which prevents quarks from propagating freely outside hadrons.

To go beyond, or to complete the standard model, research workers are mainly exploring two avenues:

– **supersymmetry** (widely known as

SUSY) would associate, to every particle (whether a boson or a fermion) in the standard model, a partner from the other series, respectively a fermion or a boson. Supersymmetric partners would, at first blush, be highly massive, the lightest of them being a particle interacting very weakly only. This would be an ideal candidate to account for the **hidden matter** (or **dark matter**) in the Universe, accounting as it does for some 21% of the Universe’s energy content, the remainder (close to 75%) consisting in a **dark energy**, the nature of which likewise remains to be determined. These WIMPs (acronym for “weakly interacting massive particles”) are actively being sought (see *EDELWEISS II, the quest for dark matter particles*);

– the **substructure** path assumes there could be a new level of elementarity, underlying the particles in the standard model (or some of them). This would lead to a veritable blossoming of new, composite particles, analogous to hadrons, but exhibiting masses two to three thousand times heavier.

It should be noted that, whereas supersymmetry theories yield predictions that agree with the precision measurements carried out at LEP, the theories propounding substructures (or their simpler variants, at any rate) fail to do so. As for the more complex variants, these are encountering difficulties at the theoretical level.

fundamental interaction	associated particles (messengers)	actions
gravitation	graviton?	having an infinite range responsible for the mutual attraction of any two masses and for the law of falling bodies
electromagnetic interaction	photon	having an infinite range responsible for the attraction between electrons and atomic nuclei, hence for the cohesion of atoms and molecules
weak interaction	W^+ , W^- , Z^0	responsible for β^- and β^+ radioactivity, reactions involving particles as neutrinos
strong interaction	gluons (there are 8 gluons)	ensures the cohesion of the atomic nucleus

Tableau 2.
Fundamental interactions, their vectors, and effects.

E What is chromatography?

Chromatography, together with the various forms of spectroscopy and spectrometry (see Box D, *Spectroscopy and spectrometry*), represent the two major basic analytical techniques, the former serving for the separation, the latter for the identification of the constituents of a substance.

Chromatography (from the Greek *chrôma*, "color," and *graphein*, "to write"), allows the *separation* of the constituents of a mixture in a homogeneous liquid or gaseous phase, as blotting paper might spread out in concentric rings a liquid poured onto it.

A chromatograph comprises a sample injection device, a *column*, a detector, and a recording and analysis system. Its principle is based on the equilibrium of compound concentrations, between two phases coming into contact: the *stationary phase*, in the column, and the *mobile phase*, which moves across it. Separation relies on the differential displacement of constituents inside the column, passing through in times that are proportional to their size, or depending on their structure, or affinity for the stationary phase (polarity...). As they reach the far end of the column, a *detector* measures, on a continuous basis, the quantities of each constituent.

The most common form of chromatography is **gas chromatography**, carried out on gaseous samples, or samples that may be vaporized without incurring breakdown. The mobile phase is a gas (helium, nitrogen, argon, or hydrogen), constantly sweeping through the column, which is placed in a thermostat oven. Detectors allow the selective analysis and identification of highly complex mixtures.

If the stationary phase is a nonvolatile, or not highly volatile liquid, exhibiting solvent properties for the compounds to be separated, the process is termed **gas-liquid chromatography**, or *partition chroma-*

tography. If the stationary phase is an **adsorbent** solid (silica, alumina, zeolites, or **polymers**), this is **gas-solid chromatography**. Within this same family, of **adsorption** chromatography processes, **liquid-solid chromatography** is characterized by its stationary phase, this being a polar solid.

In **high-performance liquid chromatography (HPLC)**, the sample must be wholly soluble in the mobile phase (elution solvent). The latter must be kept at high pressure (hence the alternative name of *high-pressure* liquid chromatography), to ensure a constant flow rate inside the column, and preclude any loss of head. HPLC involves solute-mobile phase-stationary phase exchange mechanisms, based on partition or adsorption coefficients, depending on the nature of the phases in contact.⁽¹⁾

A chromatographic analysis yields a **chromatogram**, this being a graphical representation of the evolution of a parameter (intensity of the detector signal), related to instantaneous solute concentration, as function of time. This exhibits *peaks*, rising above the *baseline*, which obtains in the absence of any compounds (see Figure).

(1) There are two further types of liquid chromatography, *ion chromatography*, and *exclusion chromatography*.

N.B: This Box reproduces a number of excerpts from a presentation by Pascale Richardin, head of the Datation Group at the Research and Restoration Center of the French National Museums Administration (Musées de France), taken from the pages dealing with analytical methods, as posted on the site : <http://www.culture.gouv.fr/culture/conservation/fr/biblioth/biblioth.htm>

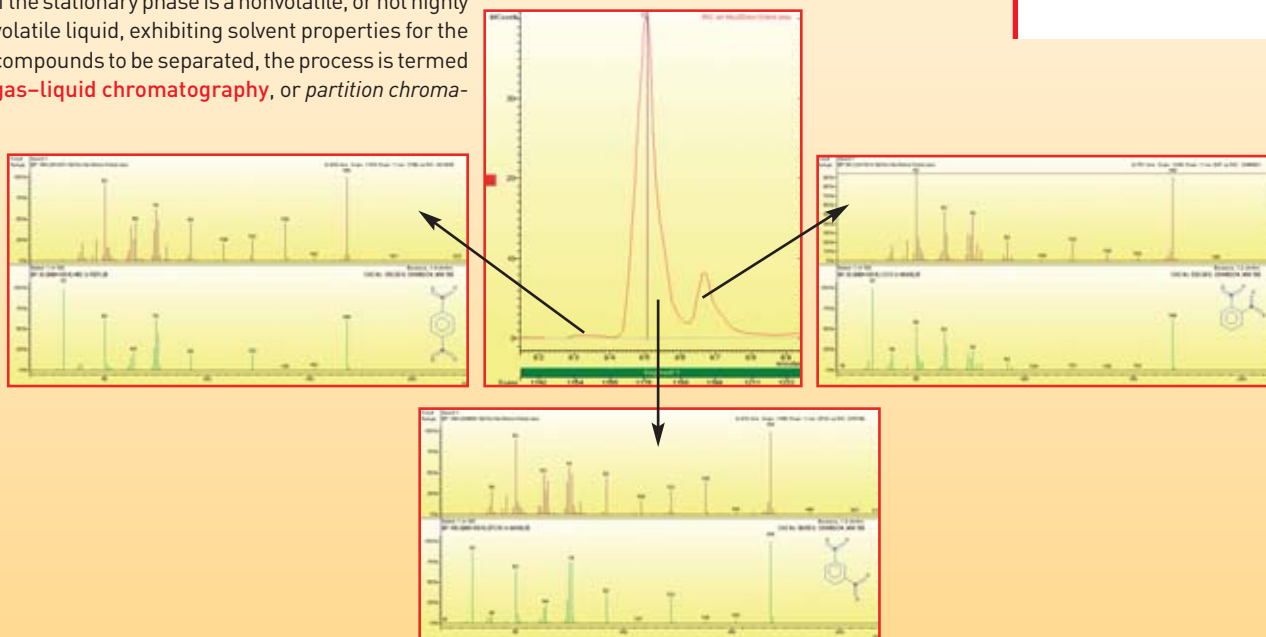


Figure.

An example of the combined use of mass spectrometry and chromatography: the separation of isomers ("sister molecules") of an explosive molecule (dinitrobenzene [DNB]), after solid-phase microextraction sampling, by gas chromatography, and their detection by mass spectrometry (SPME-GC-MS).