Micrometeorites and ion microprobes: silicon isotopic cosmochemistry and the ROSETTA and STARDUST cometary missions.

Les micrométéorites et les microsondes ioniques : cosmochimie du silicium et missions cométagres ROSETTA et STARDUST.

Engrand C., Duprat J., Gounelle M., Slodzian G., Maurette M., Naulin F., Dennebouy R., Bellier J.-D.

Collaborations :
* Laboratoire de Physique et Chimie de l'Environnement (LPCE), Orléans
* Centre de Recherche Pétrographiques et Géochimiques (CRPG), Nancy
* Laboratoire de Structure et Propriétés de l'Etat Solide (LSPES), Université des Sciences et Technologies de Lille
* Institut d'Astrophysique Spatiale (IAS), Orsay
* Department of Mineralogy, The Natural History Museum, London (UK)
* Naturhistorisches Museum, Wien, Autriche
* Dept. of Earth and Planetary Sciences, Kyushu University Hakozaki, Fukuoka, Japan

Résumé : En 2000 et 2002, nous avons pu collecter dans les neiges des régions centrales antarctiques de nouvelles micrométéorites qui n'ont subi qu'une altération terrestre minimale. Nous utiliserons ces échantillons pour une meilleure compréhension des processus de formation et d'évolution de la matière dans le système solaire primitif. Du fait de la complexité et de la petite taille de tels échantillons extraterrestres, l'outil privilégié pour leur caractérisation est la microsonde ionique, capable de réaliser des mesures de compositions chimiques et isotopiques in situ à haute résolution spatiale (de l'ordre du micromètre). Nous disposons depuis fin 2002 au CSNSM d'une microsonde ionique "IMS Orsay" qui a été modifiée par G. Slodzian, concepteur de ce type d'instrument, pour obtenir une plus grande précision sur les mesures isotopiques. Nous avons débuté les études de mesure de composition isotopiques du silicium sur des phases réfractaires de météorites et nous prévoyons de poursuivre et d'étendre ces études en couplant les résultats obtenus pour plusieurs signatures isotopiques (B, O, Mg...). Nous sommes également associés à la qualification scientifique d'un analyseur ionique, COSIMA, de la mission ROSETTA (lancée en Mars 2004), qui effectuera des analyses in situ de grains cométagres lors du rendez-vous avec la comète 67P/Churyumov-Gerasimenko en 2014. A plus court terme, nous participons à la mise en place du consortium national "Poussières Cosmiques" qui vise à préparer la communauté française pour le retour d'échantillons cométagres de la mission STARDUST en janvier 2006.

Introduction

In 2000 and 2002, we developed a new technique for collecting micrometeorites in Antarctica, at Dome C, where the French-Italian CONCORDIA station is under construction. The preservation conditions of micrometeorites in this ultraclean snow combined with our new collection technique yielded a collection of micrometeorites in a
pristine state that was never obtained before [1, and see the contribution of Duprat et al. in this report].

Micrometeorites, along with primitive meteorites (carbonaceous chondrites) are representative of the material that was present in the early stages of the formation of the solar system. They consist of complex assemblages of mineral grains and organic compounds. The ion microprobe is one of the best techniques to investigate the chemical and isotopic signatures of these samples, as it can measure chemical and/or isotopic composition in situ down to a scale of ~ 1 µm.

Many studies of the early solar system processes rely on the measurements of the isotopic compositions of hydrogen and oxygen, in order to give constraints on the distribution of the isotopic reservoirs in the early solar system, and on the conditions of formation and evolution of the dust and of the meteorites in the early solar system [e.g. 2, 3]. Silicon is one of the major rock forming element of meteorites and micrometeorites, but few attempts have been made so far to develop the silicon isotopic cosmochemistry, in particular due to analytical difficulties [e.g. 4, 5]. We have started to develop the measurement of the isotopic composition of silicon ($^{28}\text{Si}$, $^{29}\text{Si}$, $^{30}\text{Si}$) using the CSNSM ion microprobe "IMS Orsay".

In addition, we are associated (as Co-Is, or co-investigators) in the scientific qualification of another type of ion microprobe : "COSIMA". This instrument is a time of flight secondary ion mass spectrometer (TOF-SIMS) which was successfully launched onboard the ROSETTA mission on March 2nd, 2004. COSIMA is designed to analyse grains of the 67P/Churyumov Gerasimenko comet in situ at the time of the rendezvous with the comet in 2014.

The STARDUST mission should also give us the opportunity of getting more insight on the composition of cometary materials when it will return to Earth in 2006 captured samples from the Wild2 comet. The nature of cometary grains is still debated and the ion microprobe will be a well-suited tool to determine their chemical and isotopic compositions. A national "Cosmic Dust Consortium" has been created in France (lead by J. Aleon, CRPG Nancy) to prepare the French cosmic dust community to the analyses of these unique samples.

In the mean time, we pursue our efforts to collect samples from the Temple-Tuttle comet on Earth : the Leonids shooting star storm of 1966 was exceptionally intense. A program to search for such grains the central regions of Antarctica is proposed [6].

**I - Silicon isotopic cosmochemistry**

Meteorites and micrometeorites contain high temperature phases, the refractory inclusions called CAIs (for Ca-Al-rich inclusions) which were among the first solids to condense in the early solar system. Chondrules are submillimeter spheres that crystallised from molten silicate droplets. They are the main constituents of primitive meteorites, the chondrites. Mineralogical and isotopic differences between CAIs and chondrules suggest that they formed in two distinct locals of the protosolar nebula [7, 8], and/or at different epochs.

Studying the isotopic properties of these objects helps to constrain the physical and chemical properties at the time and place of their formation, in terms of temperatures, pressures, gas/dust ratio, etc... In particular, interactions between the silicate and nebular gas at this time could also have played a significant role in the formation and differentiation of the first solids present in the early solar system. Experimental studies have shown that SiO gas incorporated in various proportions in the melted precursor of the chondrules could explain the observed meteoritic chondrule textures [9].

These early solar system processes should have left a signature on the silicon isotopic composition of these mineral phases. The silicon isotopic system is not well characterised in extraterrestrial matter [e.g.4, 5, 10]. At the end of 2003, we started using the CSNSM ion microprobe "IMS Orsay" (figure 1) to measure the silicon isotopic composition in a suite of minerals and phases formed at different temperatures (refractory
This secondary ion mass spectrometer was modified from a Cameca ims4F by G. Slodzian, designer of this analytical technique, in order to get a better precision on the isotopic ratios [11, 12]. In particular, the team of G. Slodzian developed a system of electrostatic peak switching which allows a fast and safe commutation of the masses to analyse. This system, along with the secondary ion detector should be further improved in the next few years (see section IV).

Isotopic measurements with the ion microprobe require careful calibration procedures, in order to compensate for instrumental effects. We have run different sets of terrestrial standards with chemical compositions that match that of the meteoritic minerals. Linear correlations between the instrumental fractionation and the chemical composition were found for two series of minerals (feldspaths and clinopyroxenes, figure 2), which allowed us to correct this effect from the analysis of this kind of unknown meteoritic minerals.

Figure 1: CSNSM ion microprobe "IMS Orsay", designed to measure chemical and isotopic compositions in situ down to a scale of ~ 1 µm.

Figure 2: Well defined linear correlations are found between the instrumental mass fractionation (in permil per atomic mass unit) and the silicon content of the mineral (in red for feldspaths, and in blue for a suite of clinopyroxenes).

The silicon isotopic composition of two different minerals (anorthite and fassaite) from a refractory inclusion from the Leoville meteorite were obtained using these calibrations. Their isotopic compositions significantly differ by a few permils. This preliminary result will have to be confronted to the complementary boron, oxygen, and magnesium isotopic compositions obtained for the same refractory inclusion [13, 14, and personal unpublished data].

II - In situ ion microanalyses of cometary grains by the ROSETTA mission

The ROSETTA cometary mission, successfully launched on March 2nd, 2004, should rendezvous with comet 67P/Churyumov-Gerasimenko in 2014. The analytical capabilities of ROSETTA include a time of flight secondary ion mass spectrometer (TOF-SIMS) "COSIMA", which should analyse the cometary grains in situ at the time of the encounter.

We are involved in the scientific qualification of COSIMA, in close collaboration with the team of R. Thomas at LPCE (Orléans), who has built a laboratory prototype of COSIMA. Our experience with cosmic dust and with the ion microprobe led us to help defining the topics of cometary science which could be addressed by COSIMA. They include: i) the characterisation of the mineralogy of cometary
grains. Mg-rich pyroxenes were only recently discovered in comet Hale-Bopp [15]. They were found in much higher proportion compared to olivine that previously thought. This unique characteristic is only found in a rare class of meteorites (CR2), and in the micrometeorites; ii) the identification (or not) of refractory phases in cometary grains. The discovery among cometary material of refractory inclusions and chondrules, which necessarily formed close to the protosun, would favour models of solar system formation where these phases formed at short heliocentric distances to be later ejected by a "x-wind" in the comet forming regions [7, 8, 16]; iii) the measurement of light elements isotopic composition. Of particular interest is the hydrogen isotopic composition and the associated carbon concentrations, to be related to the previous analyses in cometary water [e.g. 17] and in cosmic dust particles [e.g. 18, 19].

Due to their intrinsic complexity and to their possible cometary origin [e.g. 20], micrometeorites have been proposed as cometary analogues to calibrate COSIMA. As a first step, we used single minerals like olivines and pyroxenes in order to better constrain the capabilities of COSIMA in terms of quantification of the spectra (see figure 3). The main goal is to assess whether we will be able to recognise from the spectra the nature of the individual components present in a mixture of several mineral (and organic) phases, like in the case of a real extraterrestrial sample. The TOF-SIMS technique being very sensitive to surface contamination, the samples are handled and prepared in very clean conditions. The preparation technique consists in crushing the minerals in a clean gold or indium foil.

The results obtained so far on suites of minerals which are common in extraterrestrial matter (olivine, pyroxene, phyllosilicates, carbonates, etc…) have shown the difficulties of identification of the minerals and quantification of their compositions. We have started a statistical treatment of the spectra, which seem promising [21, 22].

III - The STARDUST cometary sample return

The STARDUST mission should return cometary samples to Earth in January 2006. The French community has decided to get organised in a "Cosmic Dust Consortium" in order to be prepared for this unique opportunity. This consortium was recently funded by the French ministry of Research for a duration of 3 years, in the frame of the "Action Concertée Incitative Jeunes Chercheuses et Jeunes Chercheurs 2004", and is lead by J. Aléon (CRPG, Nancy). The study of these sample should also greatly help the interpretation of the data returned from ROSETTA in 2014.
IV - Future prospects
Our first objective will be to finalise the silicon isotopic measurements in meteoritic phases and search for correlations with other signatures of early solar system processes (B, O, Mg isotopic measurements).
We are also planning the measurement of the hydrogen isotopic composition of the new micrometeorites from the 2000-2002 CONCORDIA collection to search for exotic (cometary?) grains [1].
The collaboration with LPCE (Orleans) and with the COSIMA european team will be pursued in order to prepare the scientific return of the COSIMA analyses of Comet 67P/churyumov-Gerasimenko.
In order to achieve our scientific goals, we are also planning instrumental developments on the ion microprobe IMS Orsay. The mass range available by electrostatic switching of the masses should be increased in order to be able to measure the hydrogen and deuterium with this technique. The behaviour of the ions through this system has been modelled by G. Slodzian and F. Naulin and should result in an additional improvement of the mass resolution power of the mass spectrometer. We also started a partnership with the manufacturer of our ion detectors (electron multipliers, by PHOTONIS), which will result in the definition of a new prototype that we will test and validate with the IMS Orsay. Other long term prospects include a complete control on the instrumental isotopic fractionation at the detection stage and the improvement of the detection dynamic range by implementation of a second type of detector (faraday cup).

Acknowledgements :
This research program was supported by IN2P3, CNES (programme "exploration du système solaire") and by the Programme National de Planétologie. The installation of the ion microprobe "IMS Orsay" was made possible by the contribution of "Mission Ressources et Compétences Technologiques" of CNRS. The University of Orsay through the Plan PluriFormation (PPF) led by IAS is also acknowledged.