### 10.1 ESA's Cometary Mission Rosetta-Philae

#### A. Context and state of the art

Uwe Meierhenrich, member of the *Institut Convergence*, is involved as Co-Investigator (Co-I) in the COSAC experiment of the Rosetta-Philae mission. He is in particular in charge of the chirality-part of COSAC:

ESA's Rosetta mission [1], successfully launched in March 2004, reached its target comet 67P/Churyumov-Gerasimenko (67P/C-G) in 2014. Contrary to its predecessor missions Giotto and Vega to comet 1P/Halley [2,3], Deep-Space 1 to comet 19P/Borrelly [4], Stardust to comet 81P/Wild 2 [5], and Deep Impact to comet 9P/Tempel 1 [6], Rosetta is the first space mission designed and constructed to follow a cometary nucleus through perihelion passage and to deposit a landing unit on the cometary nucleus. In November 2014 the Philae lander detached from the Rosetta spacecraft and landed on the surface of the cometary nucleus that was of unknown morphology and chemical composition. Philae contains the cometary sampling and composition (COSAC) instrument that is equipped with a chirality module for the in situ identification, separation, and quantification of organic molecules including enantiomers expected to be present in cometary ices. The COSAC analysis was assumed to provide essential information on the Solar System formation and possibly on the origin of organic molecules and molecular asymmetry in biological systems [7].

COSAC is equipped with a multi-column gas chromatograph (GC), a time-of-flight mass spectrometer (TOFMS), and connected to an electronic system that allows remote operation of the suite. The GC system includes a set of eight parallel capillary columns and two types of pyrolysis ovens. The chromatographic columns vary in stationary phase, film thickness, diameter, and length; three of them can provide chiral resolution of organic molecules. COSAC is the first instrument sent to space for the investigation of chirality [8, 9]. The list of Rosetta-relevant chiral molecules includes hydrocarbons, amines, alcohols, diols, carboxylic acids, and amino acids [8–14]. After landing on the cometary nucleus in November 2014 the COSAC instrument analyzed a cometary sample successfully in the sniffing mode [15] and another cometary sample by using its chiral stationary phase in the GC-MS mode.

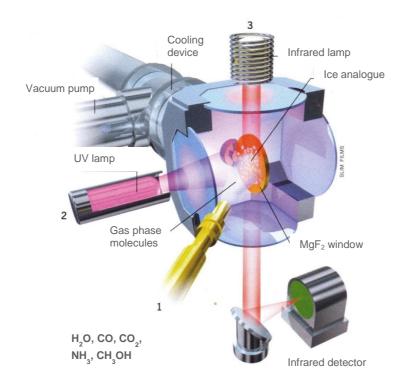


**Figure 1.** Left: COSAC sequences come in at the ESA control center. A gas chromatogram was recorded and successfully transmitted along with 420 mass spectra. Right: Scientific instruments of the Philae lander. This view shows the 'balcony', which is an experiment carrier located in front of the hood that covers the warm compartment and carries the solar generator. The COSAC GC-MS was alimented by a sample taken by the Sample Drilling and Distribution system (SD2).

Meierhenrich was in charge and responsible for the selection, characterization, and testing of COSAC's chiral stationary phases. The COSAC gas chromatograph equipped with a thermo conductivity detector (TCD) and its mass spectrometer that provided 420 mass spectra in chromatographic time intervals of 2 seconds were run on the cometary surface and the data were successfully downlinked via the Rosetta orbiter to the ESA Control Center (Figure 1). This data downlink happened on Friday November 14<sup>th</sup>, 2014, one hour before the primary batteries of the Philae lander run out of power. The here provided COSAC sample of cometary dust and ice was presumably of very low mass but we assume that there is a reasonable possibility of finding therein organic molecules that might show partial enantiomeric excesses (*ees*) in chiral molecules resulting from the exposure of the cometary ices to extraterrestrial chiral fields.

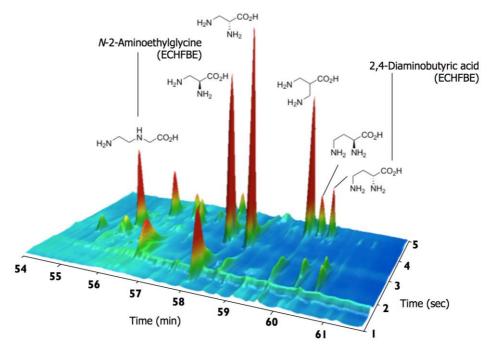
#### B. Current activity

In anticipation of the cometary Rosetta-Philae mission we continue to simulate in the laboratory the formation of organic molecules: We identified amino acids [16] along with aldehydes [17] and ribose [18] in simulated interstellar/circumstellar ices, i.e., organic residues issued from UV irradiation and thermochemistry of ice analogues. We experimentally understand the original formation of pristine organic molecules, including chiral species, via spontaneous photochemical reactions occurring in interstellar molecular clouds. We are able to reproduce such conditions in our laboratory. Figure 2 shows the simulation chamber for pre-cometary ices.



**Figure 2.** Left: Representation of the simulation chamber for interstellar ices. The ice sample typically composed of  $H_2O$ , CO,  $CO_2$ ,  $NH_3$ , and  $CH_3OH$  is deposited **1** in the center on a MgF<sub>2</sub>-window at a temperature of  $-261^{\circ}C$  and irradiated by a lamp producing energetic UV photons **2**. In situ IR-spectra can be taken **3**. We detected amino acids [16], glyceraldehyde [17], and substantial quantities of ribose [18] in room-temperature residues of interstellar ice analogues.

We are chemists and our clean-room laboratory is equipped with modern instruments for the analysis of organic species. Figure 3 represents a multidimensional gas chromatogram depicting a diversity of amino acids including the new family of diamino acids as detected in simulated pre-cometary ices.



**Figure 3.** Multidimensional gas chromatogram depicting amino acids as identified in simulated pre-cometary ices. Each point in this 3D-plot is accompanied by its mass spectrum. The coupling of multidimensional gas chromatography with mass spectrometry allows for the identification of unknown analytes.

#### C. Future steps

Results of the Rosetta-Philae-COSAC instrument accompanied with laboratory simulation experiments will get us one step closer to solving a puzzle of how organic molecules and enantioenriched forms could have originated prior to their delivery to Earth. For the *Institut Convergence* project we propose to further investigate our COSAC data together with partners from the entire international COSAC team to identify organic species including chiral organics in COSAC's above-described GC-MS sample. For this purpose a Ph.D.-student should be recruited, that will work under Meierhenrich's supervision at the University Nice Sophia Antipolis on a GC-MS copying COSAC's instrumental parameters. Data on COSAC's GC-MS sample are not yet published.

We further propose to enlarge the laboratory simulation experiments to a large set of astrophysical conditions, for which we require a GCxGC instrument with high mass resolution.

Expected results are considered important because the excess of L-handed amino acids identical or similar to those observed in meteorites will support the assumption that chiral organic molecules have indeed been delivered onto the early Earth during the Late Heavy Bombardment phase via comets and/or other small interplanetary bodies whose organic content may be of interstellar/presolar origin, out of the molecular cloud from which our Solar System formed.

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### D. International collaborations

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### E. List of people involved in the project

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### F. Most significant publications of the team

[1]Meinert C., Myrgorodska I., de Marcellus P., Buhse T., Nahon L., Hoffmann S., Le Sergeant d'Hendecourt L., Meierhenrich U.J.: Science **351** (2016), in print.

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#### **Short CV of participants**

Uwe J. Meierhenrich studied chemistry at the Philipps University of Marburg. After completing his PhD at the University of Bremen by Prof. Wolfram Thiemann, he identified amino acids in artificial comets at the Max Planck Institute for Solar System Research in Gçttingen and at the CBM in Orléans in preparation for the Rosetta cometary mission. He is now professor 'classe exceptionnelle' at the University of Nice Sophia Antipolis. He was awarded the Horst Pracejus Prize by the GDCh in 2011 for his work on chirality and enantioselective chromatography.

Cornelia Meinert studied chemistry at the Universities of Rostock and Leipzig. After receiving her PhD at the Helmholtz Centre for Environmental Research by Dr. Werner Brack, she became a postdoctoral research fellow at the University Nice Sophia Antipolis, where she studied the asymmetric photolysis of amino acids and used GC\_GC techniques for the enantioselective analysis of cometary and meteoritic matter. In 2013, she became a Chargé de Recherche of the CNRS. Her current research focuses on the origin of the homochirality of biomolecules.