The Cometary Rosetta Mission:

Analytical Chemistry on the Nucleus of Comet 67P

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Heidelberg Initiative for the Origins of Life – HIFOL

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Interstellar dust particle in diffuse and dense interstellar medium

Fig. IDP with thin ice layer containing molecules such as H_2O, CO_2, CO, CH_3OH, and NH_3.

Fig. IDP with thick ice layer from the dense interstellar medium; in the diffuse medium this ice layer becomes irradiated by energetic UV-irradiation

Fig. In the ice mantle of the IDP photoreactions occur that from radicals and organic molecules.

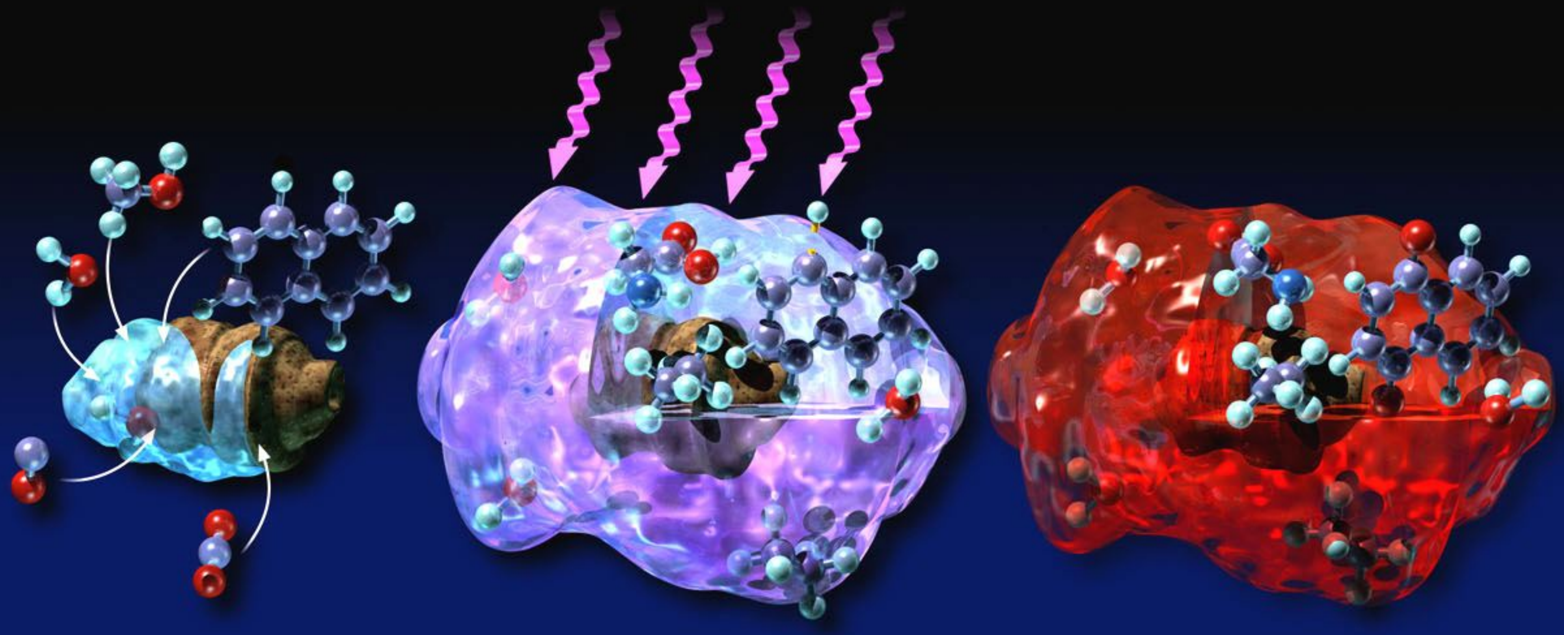


Image courtesy of Andy Christie, Slimfilms.com, Scientific American.

Irradiation set-up for simulating interstellar ices

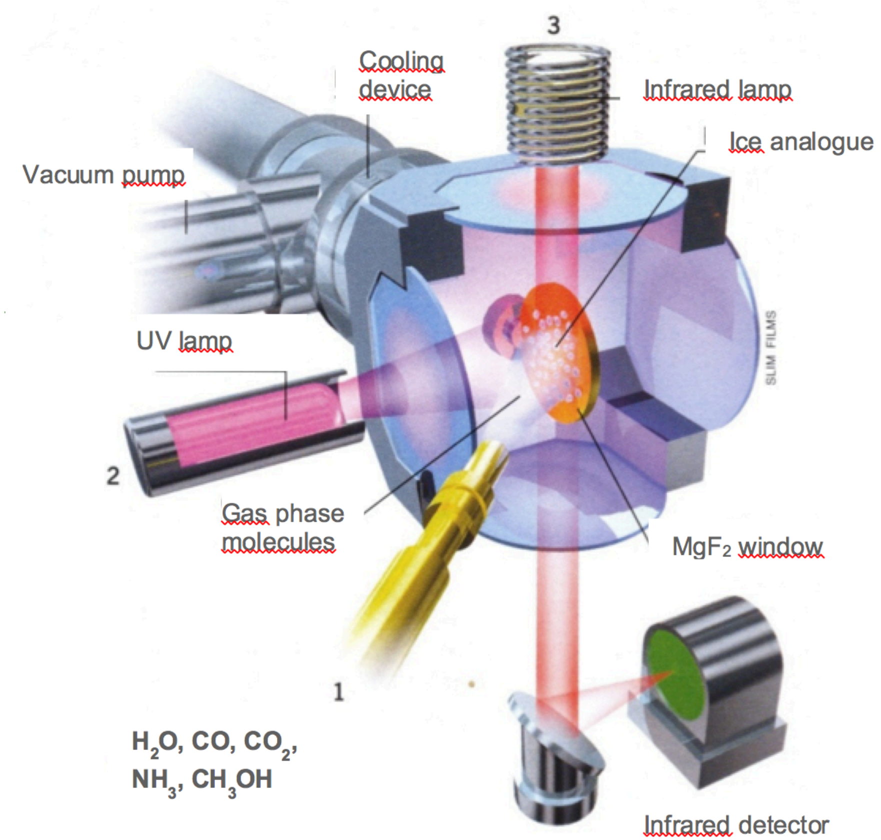


Fig. Simulation chamber for interstellar particles. The ice sample composed of H_2O, CO, CO_2, NH_3, and CH_3OH is deposited **1** in the center on a MgF_2-window at a temperature of –261°C and irradiated by lamp producing energetic UV photons **2**. *n situ* IR-spectra can be taken **3**.

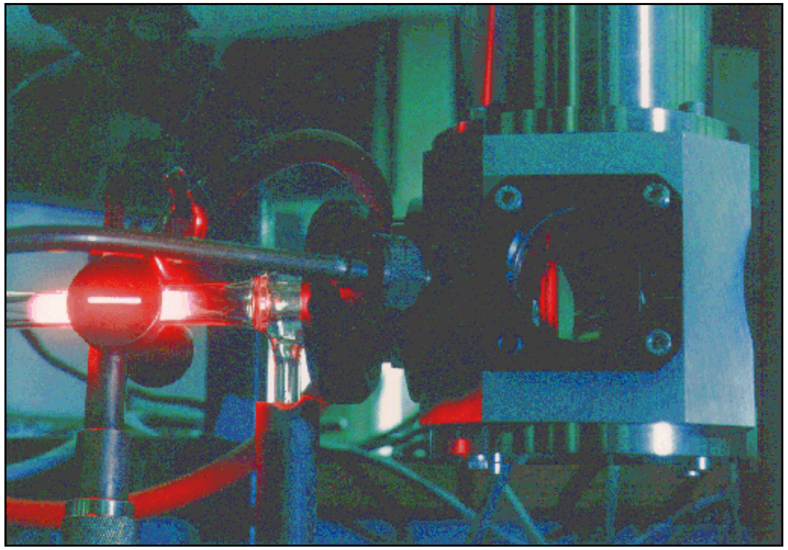


Fig. Space simulation chamber at the Leiden Observatory. The ice sample (inset) is located inside the vacuum chamber at T = – 261°C and irradiated by energetic UV photons, $h\nu$ = 10.2 eV. Matter remains after irradiation.

Amino acids in interstellar ice analogues

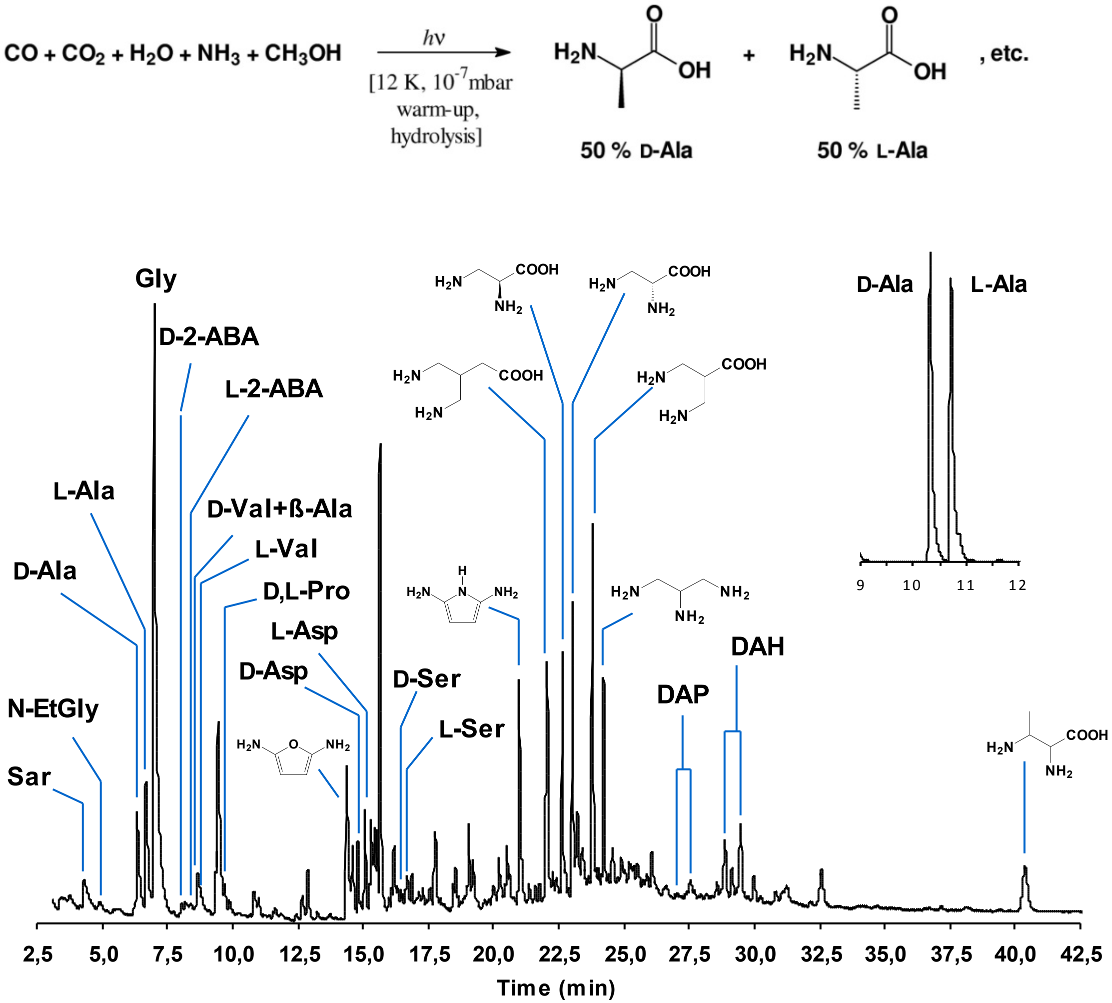
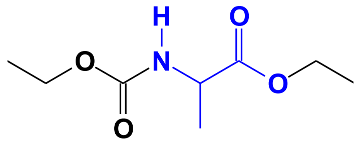


Fig. Gas chromatogram showing the amino acids and other compounds generated under simulated interstellar pre-cometary conditions. Data were obtained from analysis of the room temperature residue of photoprocessed interstellar medium ice analogue taken after 6 M HCl hydrolysis and derivatization (ECEE derivatives, Varian-Chrompack Chirasil-L-Val capillary column 12 m 0.25 mm inner diameter, layer thickness 0.12 μm; splitless injection, 1.5 ml min-1 constant flow of He carrier gas; oven temperature programmed for 3 min at 70 °C, 5 °C min^{-1}, and 17.5 min at 180 °C; detection of total ion current with GC–MSD system Agilent 6890/ 5973). The inset shows the determination of alanine enantiomers in the above sample (Chirasil-L-Val 25 m, single ion monitoring for Ala-ECEE base peak at 116 a.m.u.). DAP, diaminopentanoic acid; DAH, diaminohexanoic acid; a.m.u., atomic mass units.

Mass fragmentation of amino acids in interstellar ice analogues



$^{12}M^{+\cdot}$=189 amu

$^{13}M^{+\cdot}$=192 amu

Table 1 Mass spectroscopic peak Identification for amino acids in simulated interstellar ices

Amino acid	Quantum yield of ISM sample, Φ x 100/Φ(Gly)	MS-fragmentation ^{12}C sample (a.m.u.)	MS-fragmentation ^{13}C sample (a.m.u.)	R_t analyte (min)	Biological occurrence
Glycine	100	175, 130, **102**		6.99	Yes
α-D-alanine	19.29	189, 144, **116**, 88		6.33	No
α-L-alanine	20.00	189, 144, **116**, 88		6.68	Yes
β-alanine	4.29	189, 160, 144, 116, **115**, 102, 98		8.66	No
Sarcosine (N-methylglycine)	5.71	189, 144, **116**, 88		4.29	No
D-2-aminobutyric acid	0.46	130		8.05	No
L-2-aminobutyric acid	0.48	130		8.37	No
N-ethylglycine	1.91	**130**, 84, 58		4.90	No
D-valine	0.61	**144**		8.66	No
L-valine	0.61	**144**		8.80	Yes
D,L-proline	0.06	142		9.59	No, Yes
D-serine	3.29	175 (McLafferty), 160, **132**, 114		16.45	No
L-serine	3.86	204, 187, 175 (McLafferty), 160, **132**, 114		16.67	Yes
D-aspartic acid	1.14	**188**, 142		14.90	No
L-aspartic acid	1.07	**188**, 142		15.05	Yes

For glycine, Φ (Gly) = 3.6 x 10^{-5}. Numbers designated in boldface are the main mass fragments. Rt retention time, ISM interstellar medium, MS mass spectrometry, d.l. detection limit.

Muñoz Caro, Meierhenrich* et al.: *Nature* **416** (2002), 403–406

Public outreach

Washington Post **"Elements of life may have been delivered to Earth from space ..."**

Die Süddeutsche Zeitung **„Kometen sollen als „Biofähren" durchs Universum reisen und bei ihrem Absturz Planeten befruchten ..."**

New Scientist **"Life's building blocks created in space simulator …"**

Der Spiegel **„Das Leben erhielt außerirdische Nachhilfe …"**

Astronomy **"This not only suggests that the seeds of life on Earth might have come from space, but that prebiotic ingredients could be everywhere …"**

Le Monde **„Des briques du vivant dans un cosmos artificiel ..."**

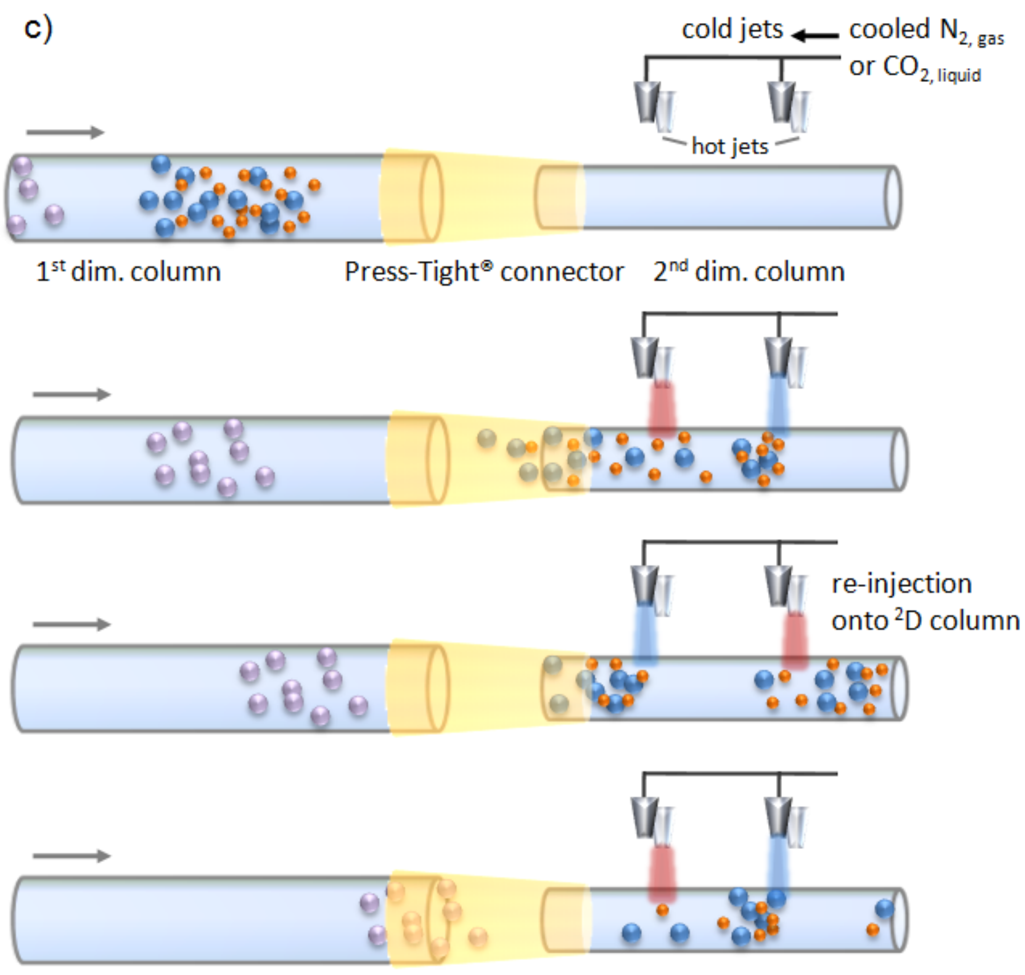
BBC News **"Life's origin among the stars …"**

ZDF **„Mit Bruchstücken von Kometen sind möglicherweise die ersten Lebensbausteine auf die Erde gekommen. Für diese schon recht alte Theorie glauben Bremer Forscher nun Beweise gefunden zu haben..."**

ARD **„Bremer Forscher stießen auf etwas, was eine der meistgestellten Fragen in den Naturwissenschaften beantworten könnte ..."**

etc.

Multidimensional Gas Chromatography



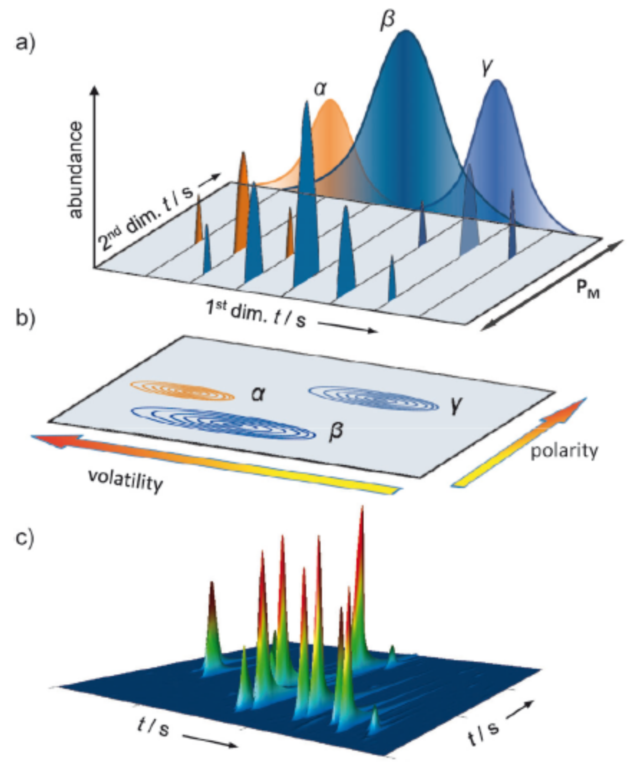


Figure 1. Illustration of a GC×GC chromatogram. a) Chromatographic peaks (α, β, and γ) eluted from a typical apolar ¹D column sequentially sliced into distinct fractions during a defined modulation period (P_M). Non-resolved analytes are often better resolved on a (generally polar) short micro-bore ²D column. b) The data stream from the detector is then plotted based on the modulation in a 2D contour color plot format or c) directly showing signal intensities in 3D presentation as conical peaks.

Multidimensional gas chromatogram (amino acid standard)

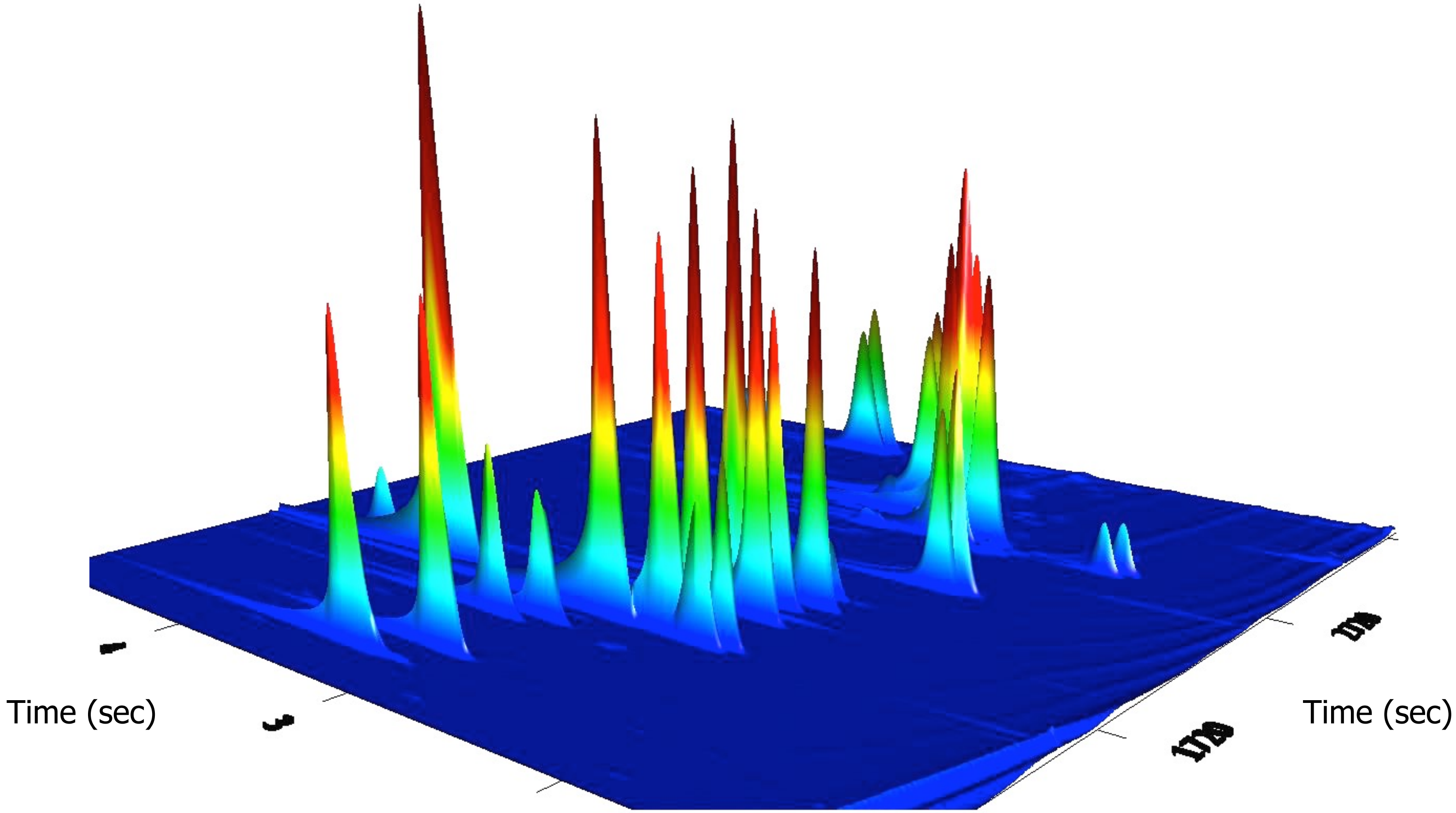
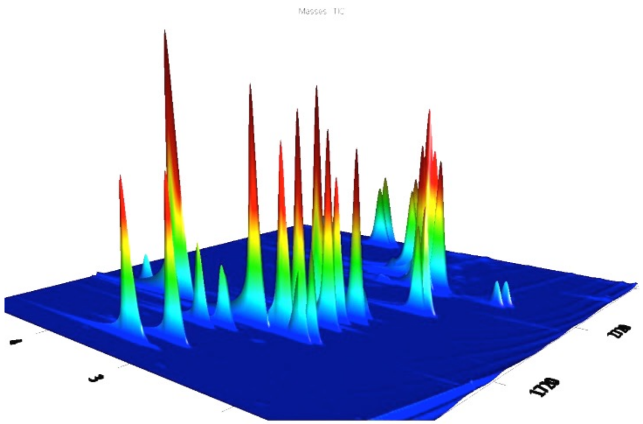


Fig. 30 : Chromatogram representing amino acid N-ethoxycarbonyl heptafluoro-butanol esters (ECHFE). Sarcosine, 2a d-Alanine, 2b l-Alanine, 3a d-Valine, 4 d,l-Proline, 3b l-Valine, 5a d-Iso-leucine, 5b l-Iso-leucine, 6a d-Leucine, 6b l-Leucine, 7a d-Acide aspartique, 7b l-Acide aspartique, 8a d-Threonine,8b l-Threonine, 9a d-Glutamine, 10a d-Methionine, 9b l-Glutamine, 10b l-Methionine, 11a d-Serine, 11b l-Serine, 12a d-Phenyl-alanine, 12b l-Phenylalanine, 13a d-DAP, 13b l-DAP, 14a d-Histidine, 14b l-Histidine.

Diamino acids in simulated interstellar ice



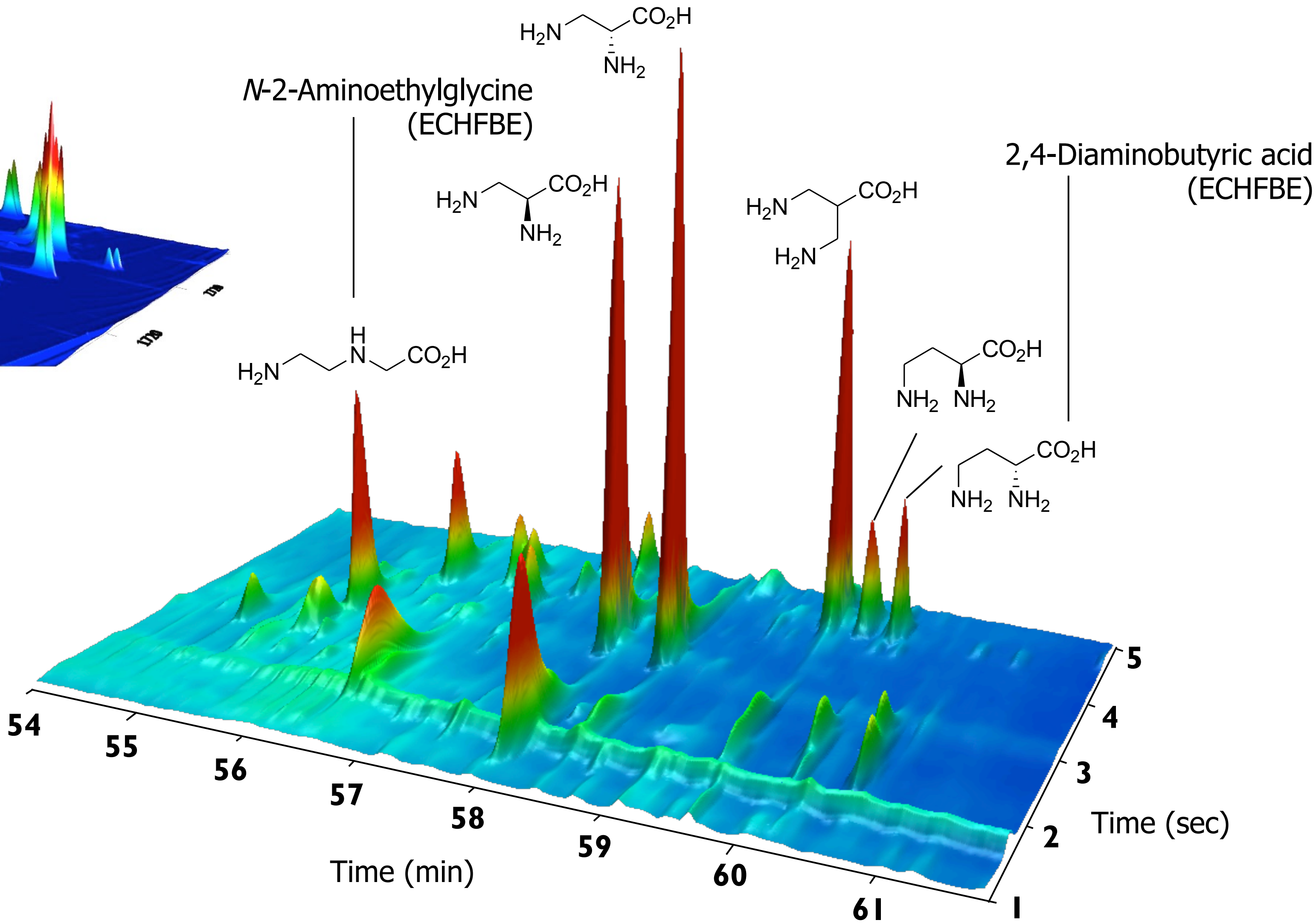
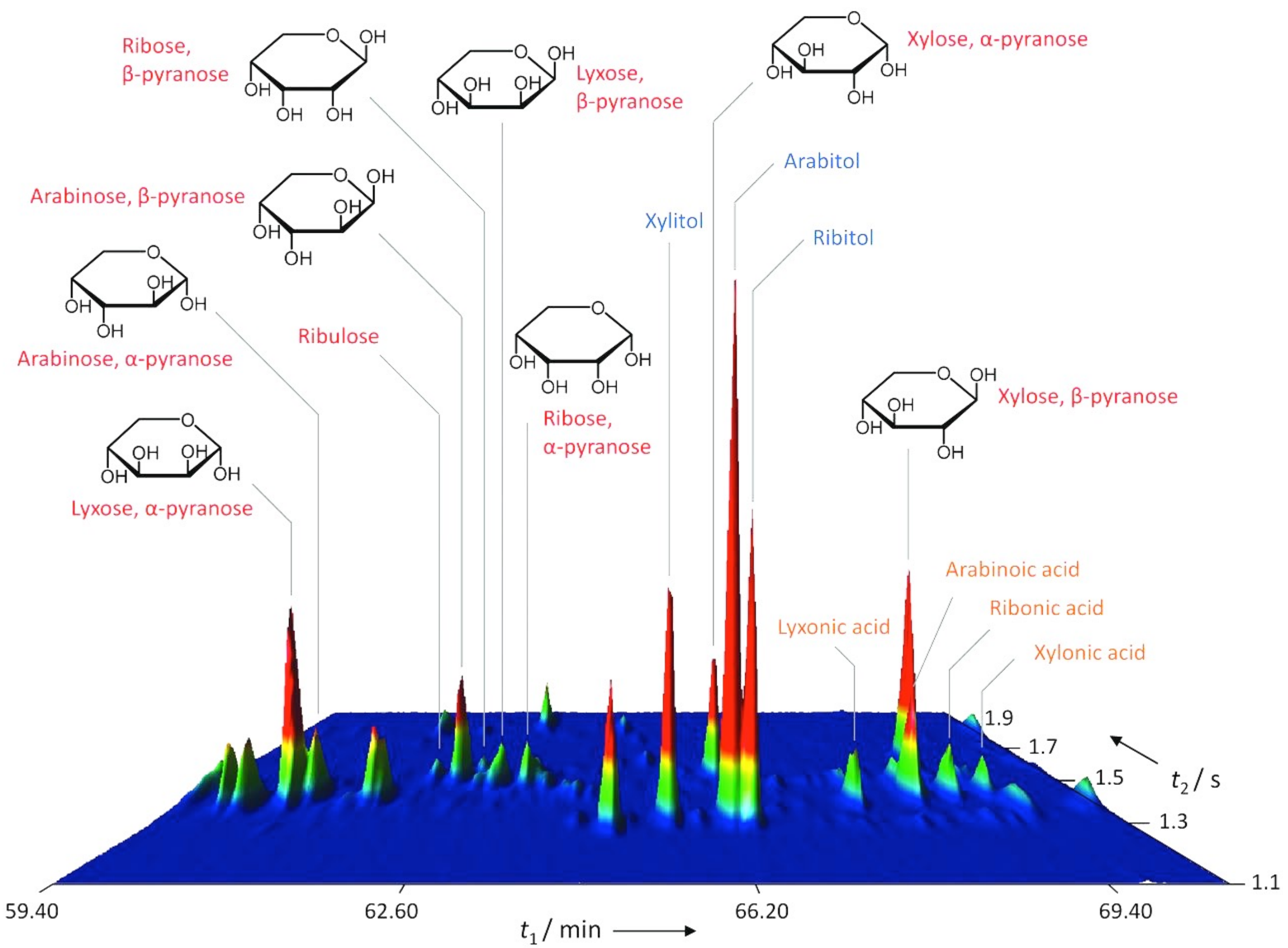
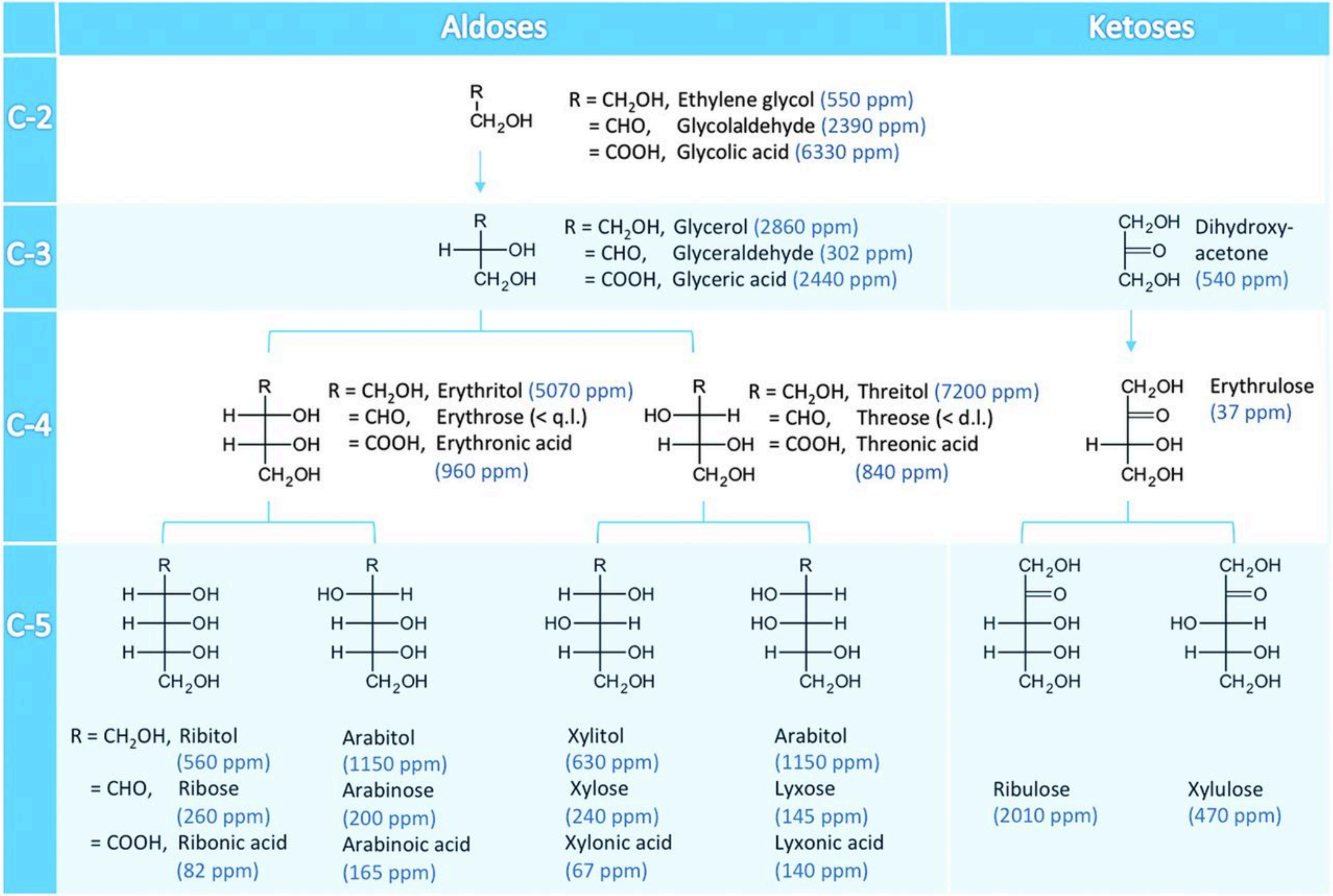


Fig.
Multidimensional gas chromatogram of diamino acids in simulated cometary ices (right). Amino acid Standard (top).

Ribose in simulated pre-cometary ices



Ribose in simulated pre-cometary ices



Development of genetic material during Chemical Evolution

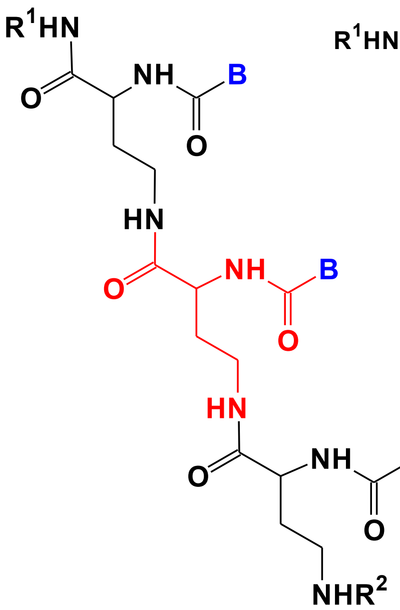


Fig. 11a: Peptide nucleic acid daPNA, Nielsen *et al.*: *Science* **254** (1991), 1497 Polyamid-chain

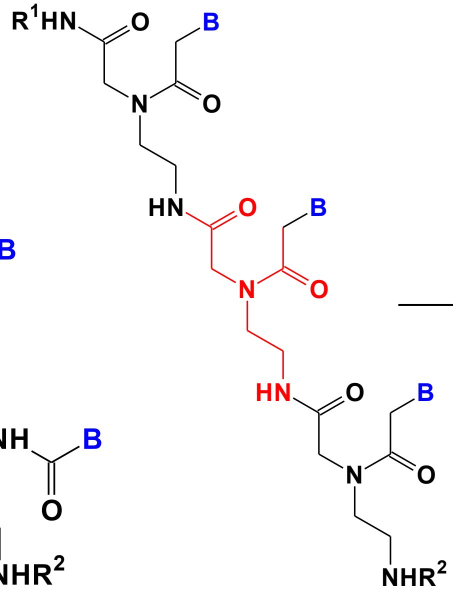
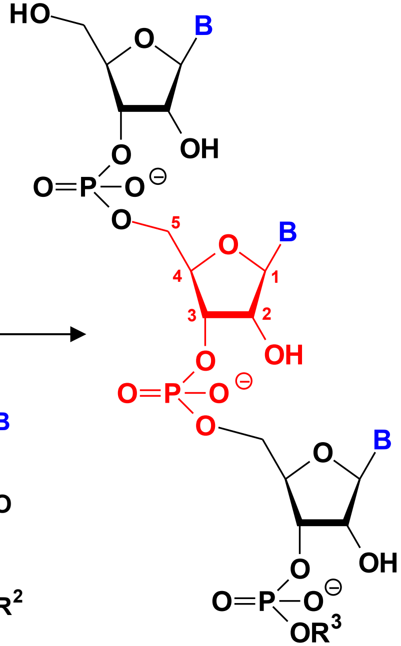
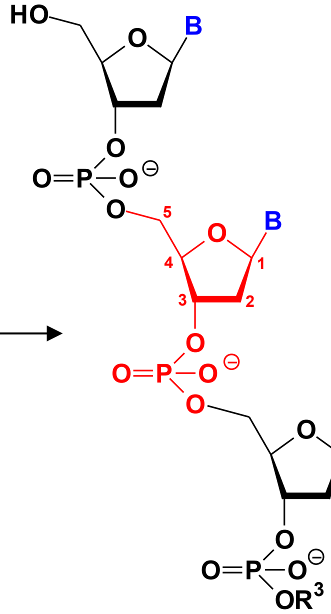


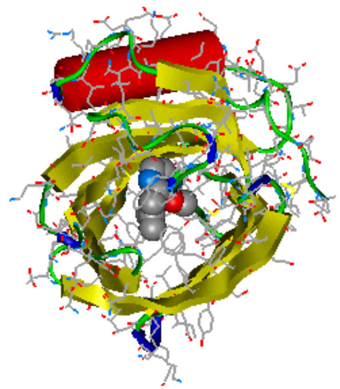
Fig. 11a: Peptide nucleic acid aegPNA, Nielsen *et al.*: *Science* **254** (1991), 1497. Polyamid-chain



Ribonucleic acid RNA **"RNA-World"** Gilbert: *Nature* **319** (1986), 618, D-ribose in furanose form



Desoxyribonucleic acid DNA, today's genetic material; Polyester-chain with D-2-desoxyribose in Furanose form



Odorant binding (OB) protein including α-helix and β-sheet

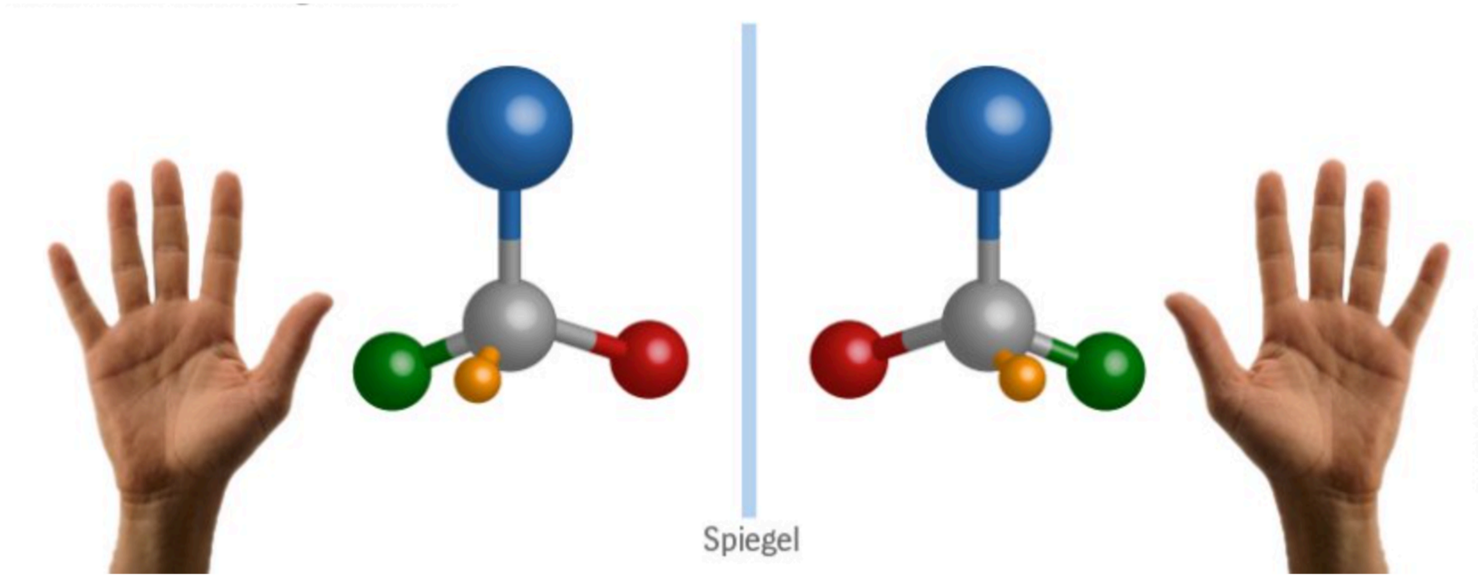


Fig. Chirality. Chiral compounds are ones which exist in two forms (enantiomers) which are non-superimposable mirror images of each other and so are asymmetrical.

CPL in Orion star formation region

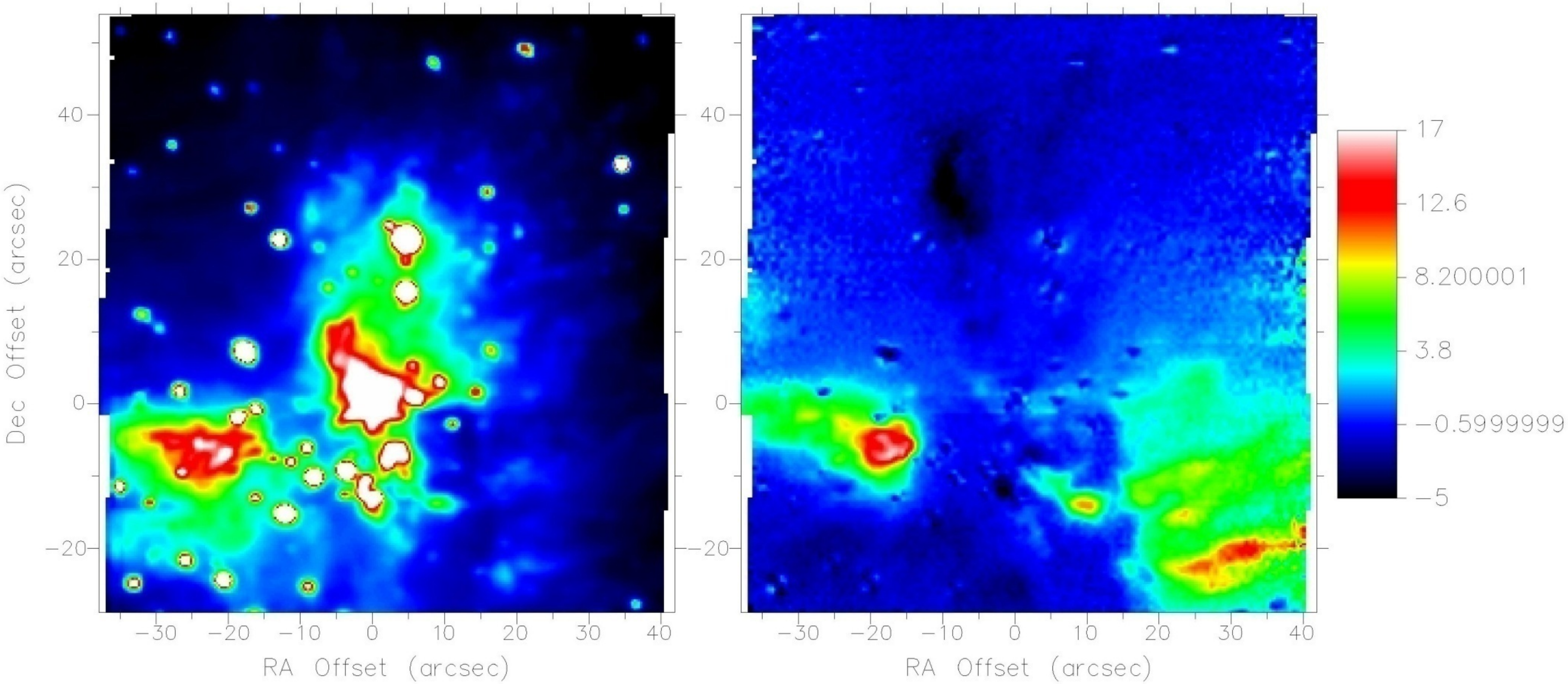


Fig.6: Circular polarization image of the OMC-1 star formation region in Orion at 2.2 µm. (Right) Percentage circular polarization ranging from – 5 % (black) to +17 % (white). Polarization accuracy ranges from about 0.1 % in the brighter regions to 1 % in the fainter regions. The size of a typical protostellar disk (100 astronomical units) is less than 1 arc sec at the 450 pc distance of OMC-1 and therefore much smaller than the observed polarization structure.

Synchrotron SOLEIL, Paris-Saclay, France

Fig.7: Synchrotron SOLEIL with beamline DESIRS and its storage ring.

SOLEIL
SYNCHROTRON

Vacuum ultraviolet CD spectra of alanine enantiomers

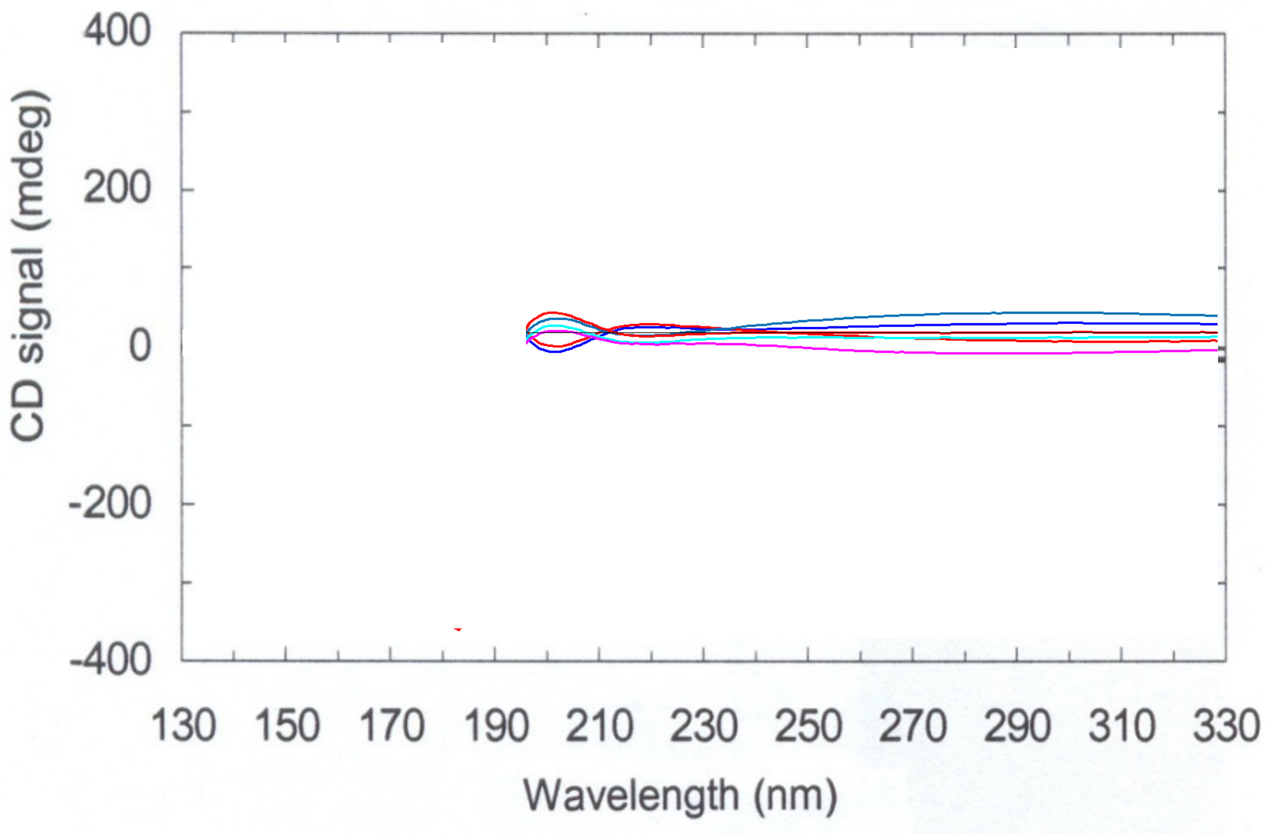


Fig. 8. Vacuum ultra violet circular dichroism spectrum of amorphous solid-state alanine enantiomers. *Blue and red lines*: L-alanine. *Rose, green, turkish and bright red lines*: D-alanine.

Meierhenrich et al.: *Angew. Chem. Int. Ed.,* **49** (2010), 7799-7802.

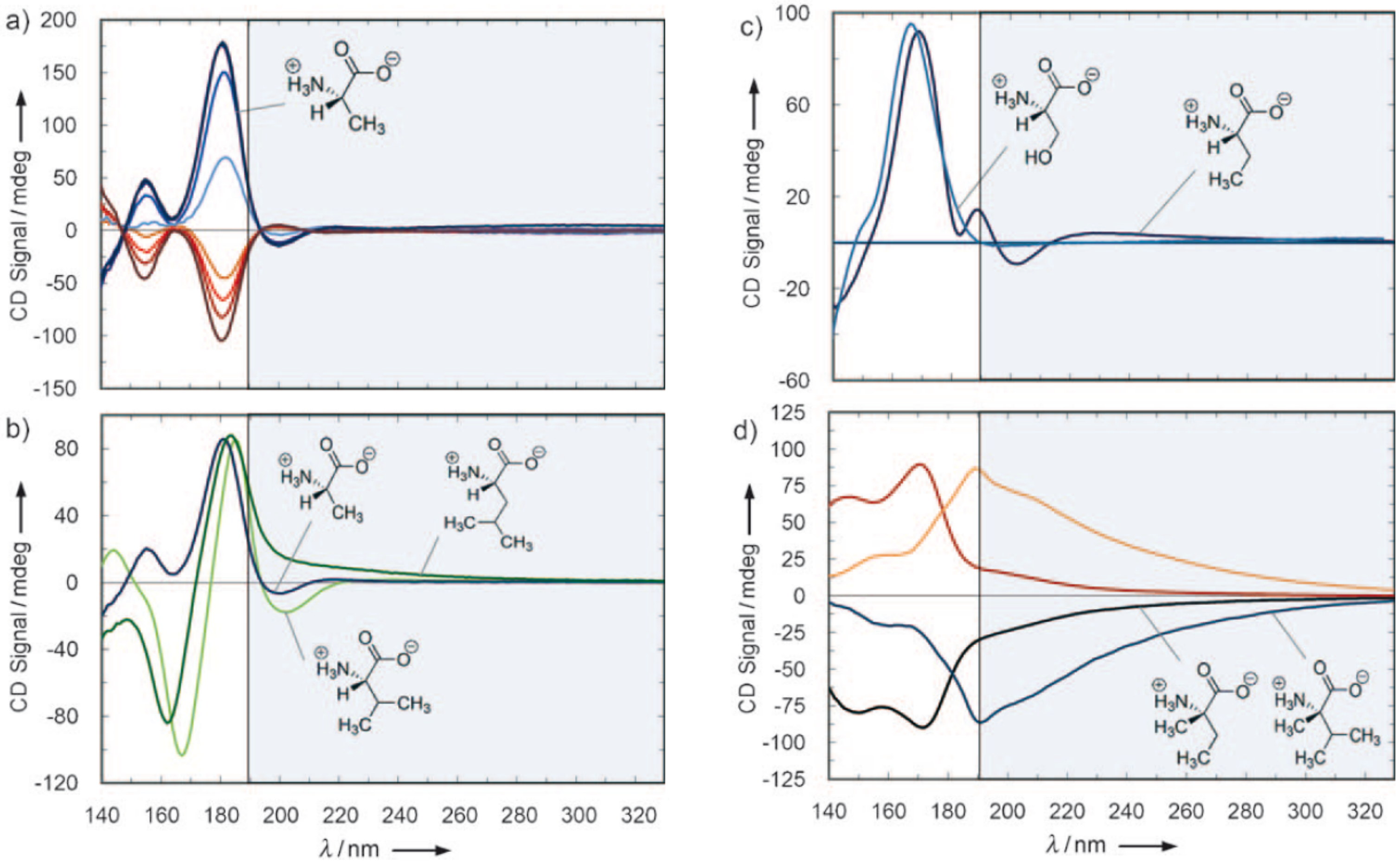


Fig. 9. Vacuum ultra violet CD spectrum of amorphous solid-state amino acid enantiomers. L-Ala, D-Ala and L-Val, L-Leu (left), L-Aba, L-Ser and Iva, methyl-Val enantiomers (right)

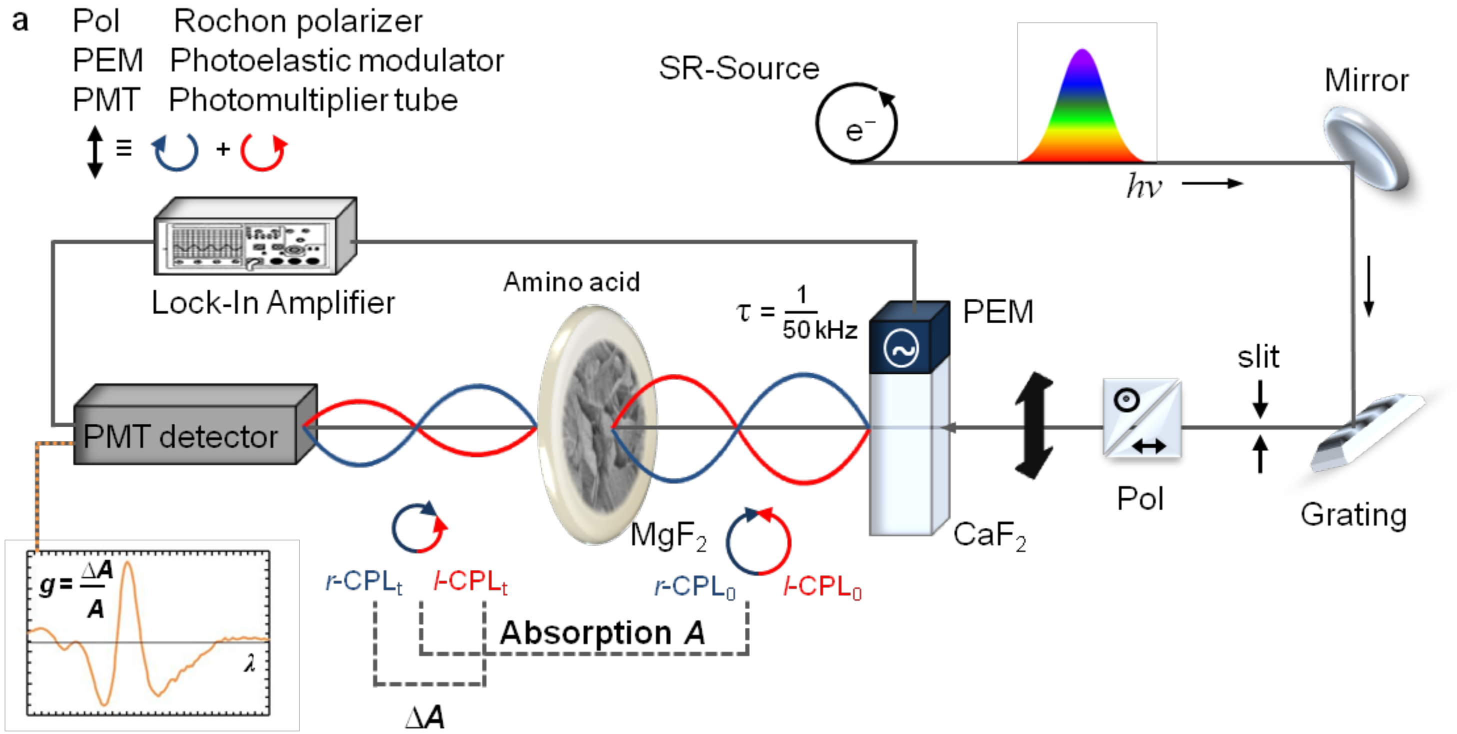


Fig. Experimental set-up for recording anisotropy spectra of amino acid enantiomers condensed in form of isotropic amorphous films on VUV-MgF_2 optical windows in the VUV and UV spectral range using a synchrotron radiation source. The PEM converts monochromatic SR into alternating *l*- and *r*-circularly polarized light (CPL). Both the differential absorption ΔA of alternating *l*- and *r*-CPL by optical active amino acid enantiomers and the sample absorbance *A* is recorded simultaneously to obtain anisotropy spectra $g(\lambda) = \Delta A/A$.

$$ee \geq (1-(1-\xi)^{g/2}) \times 100\,\%$$

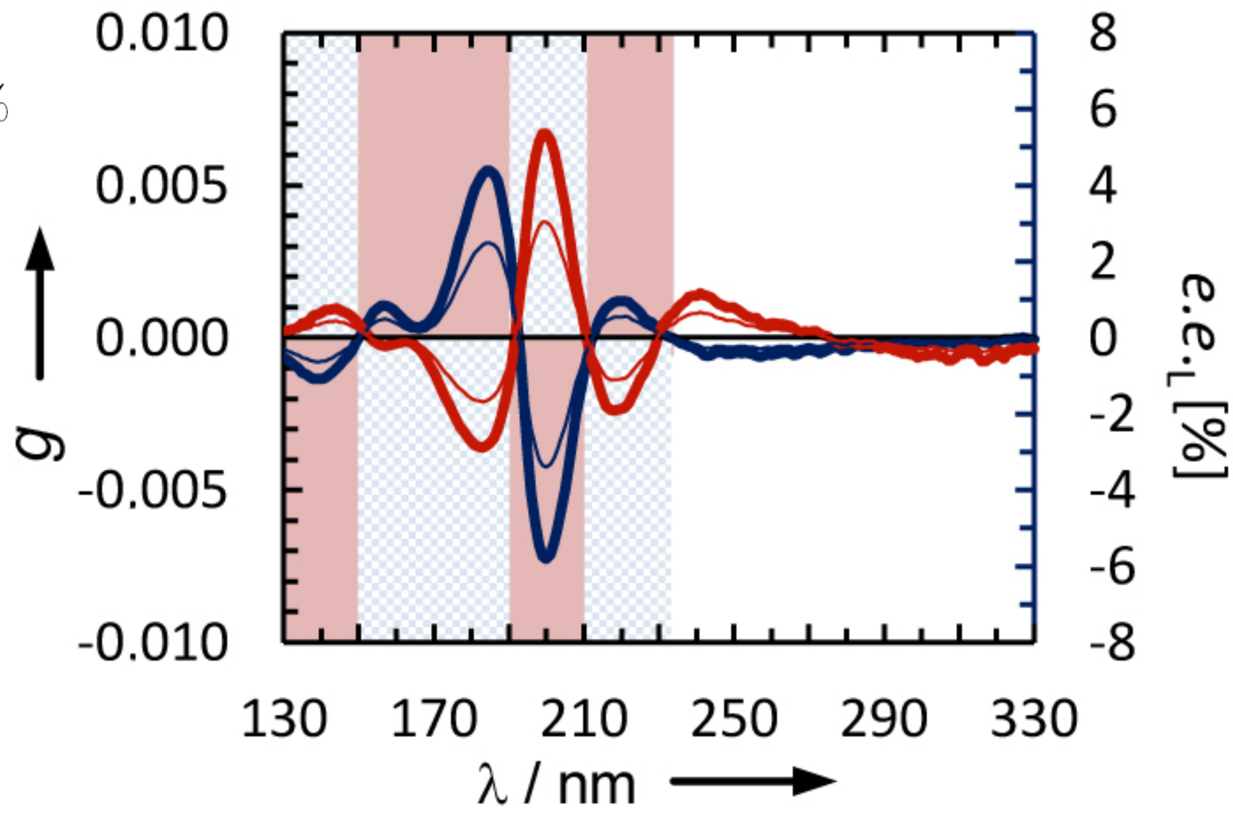
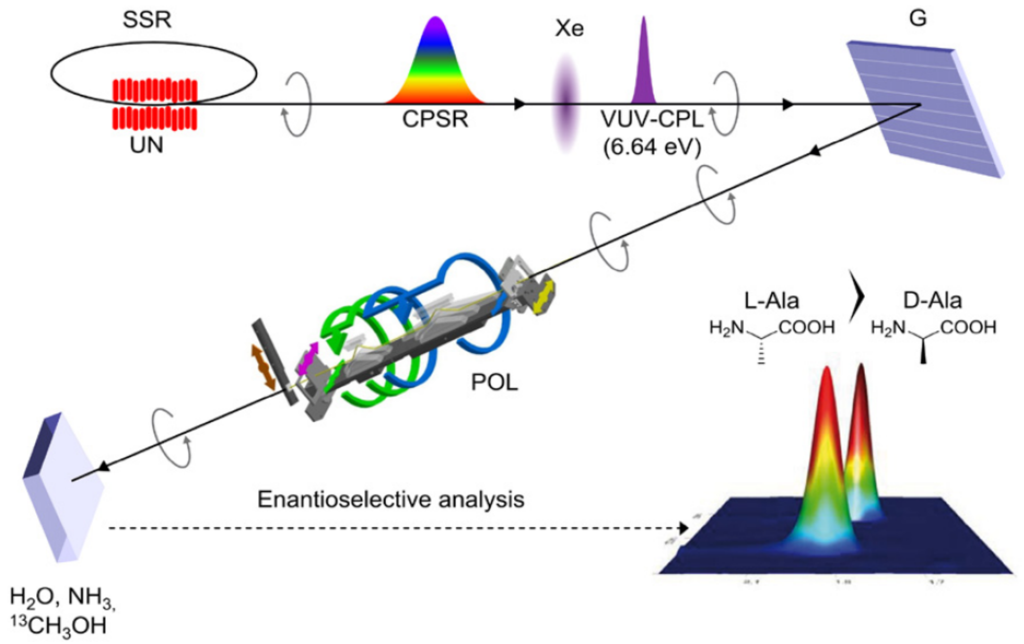


Fig. Anisotropy spectra (thick lines) of amorphous solid-state alanine enantiomers. L-Ala (blue), D-Ala (red). Thin lines represent the corresponding eeL plots inducible by either left or right circularly polarized light at ξ = 0.9999.

Asymmetric VUV photosynthesis of D,L-alanine



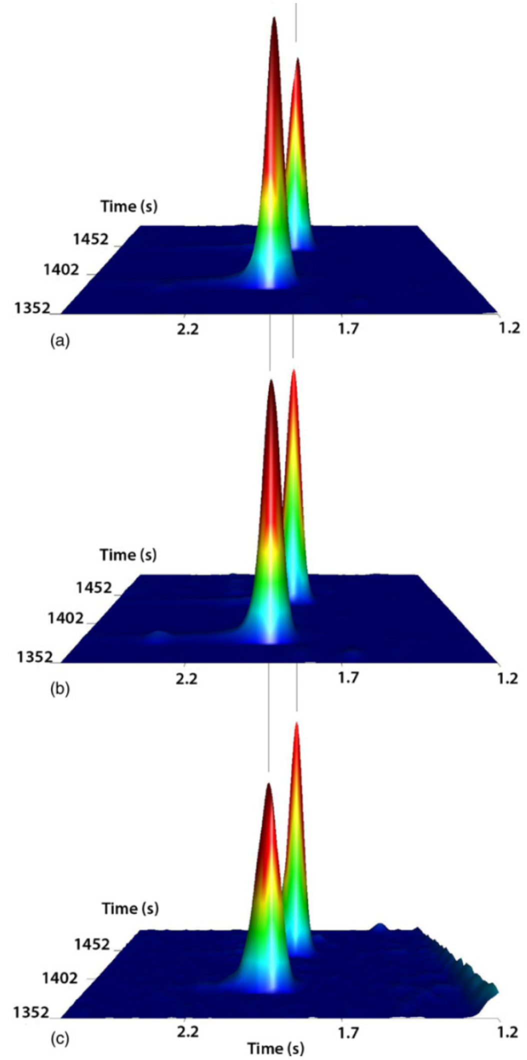


Fig. 29: Full schematic of the experimental setup for the asymmetric photochemical synthesis of amino acids from achiral interstellar precursor molecules (top). Multidimensional gas chromatograms of ^{13}C-alanine enantiomers for the three polarization regimes. Amino acids L-alanine (left signals) and D-alanine (right signals) were produced by the $h\nu$ = 6.64 eV UV photoirradiation with (a) left-handed circularly polarized light (L-CPL), (b) linearly polarized light (LPL), and (c) right-handed circularly polarized light (R-CPL) (right).

Asymmetric VUV photosynthesis of alanine

Le Monde

January 8th, 2011

Fig. 30 : « La lumière a donné un sens à la vie »,

Le Monde, January 8th, 2011.

De Marcellus, Meinert, Meierhenrich et al. *Astrophysical Journal Letters* **727** (2011), L27.

Rosetta – Scientific Payload

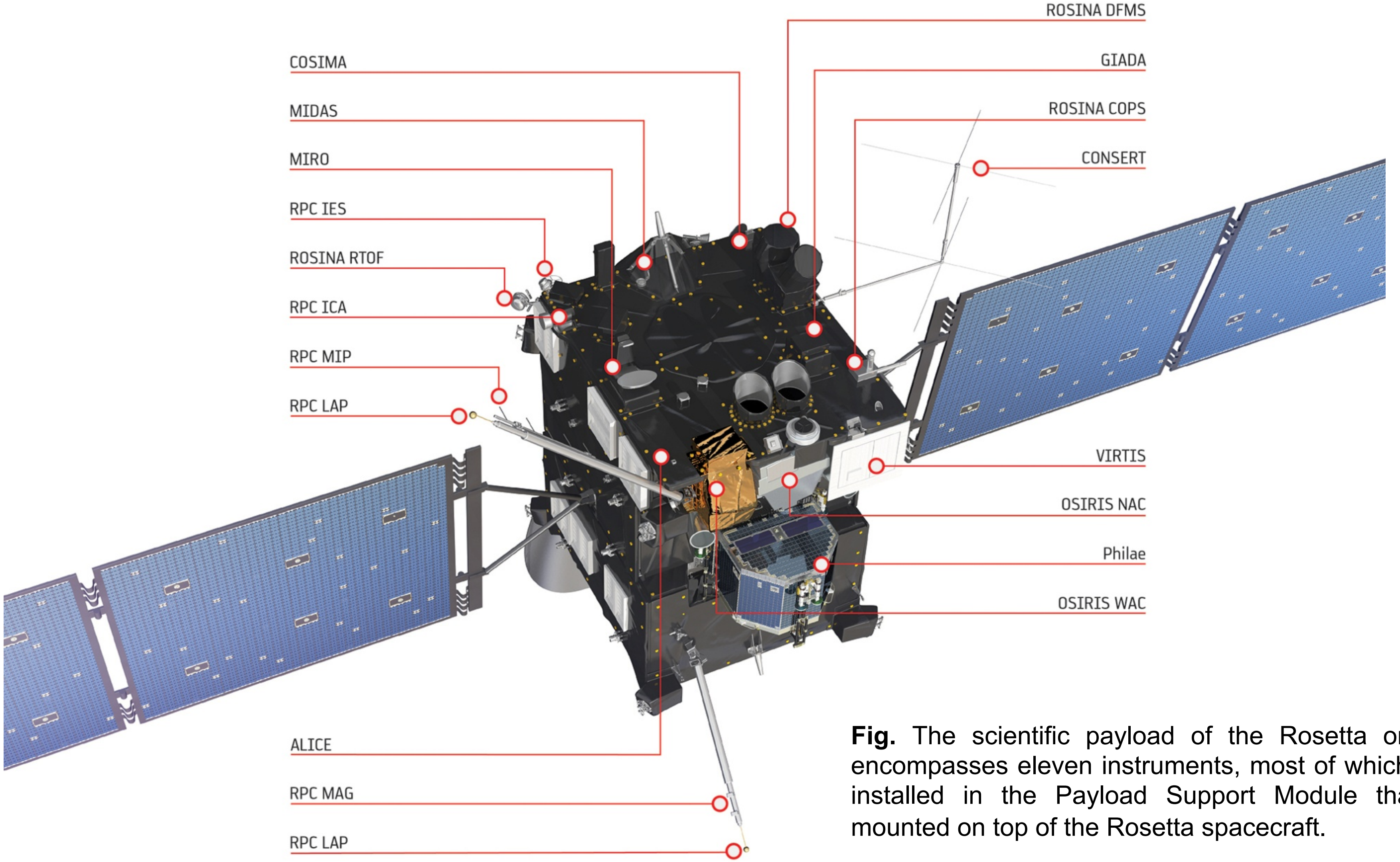
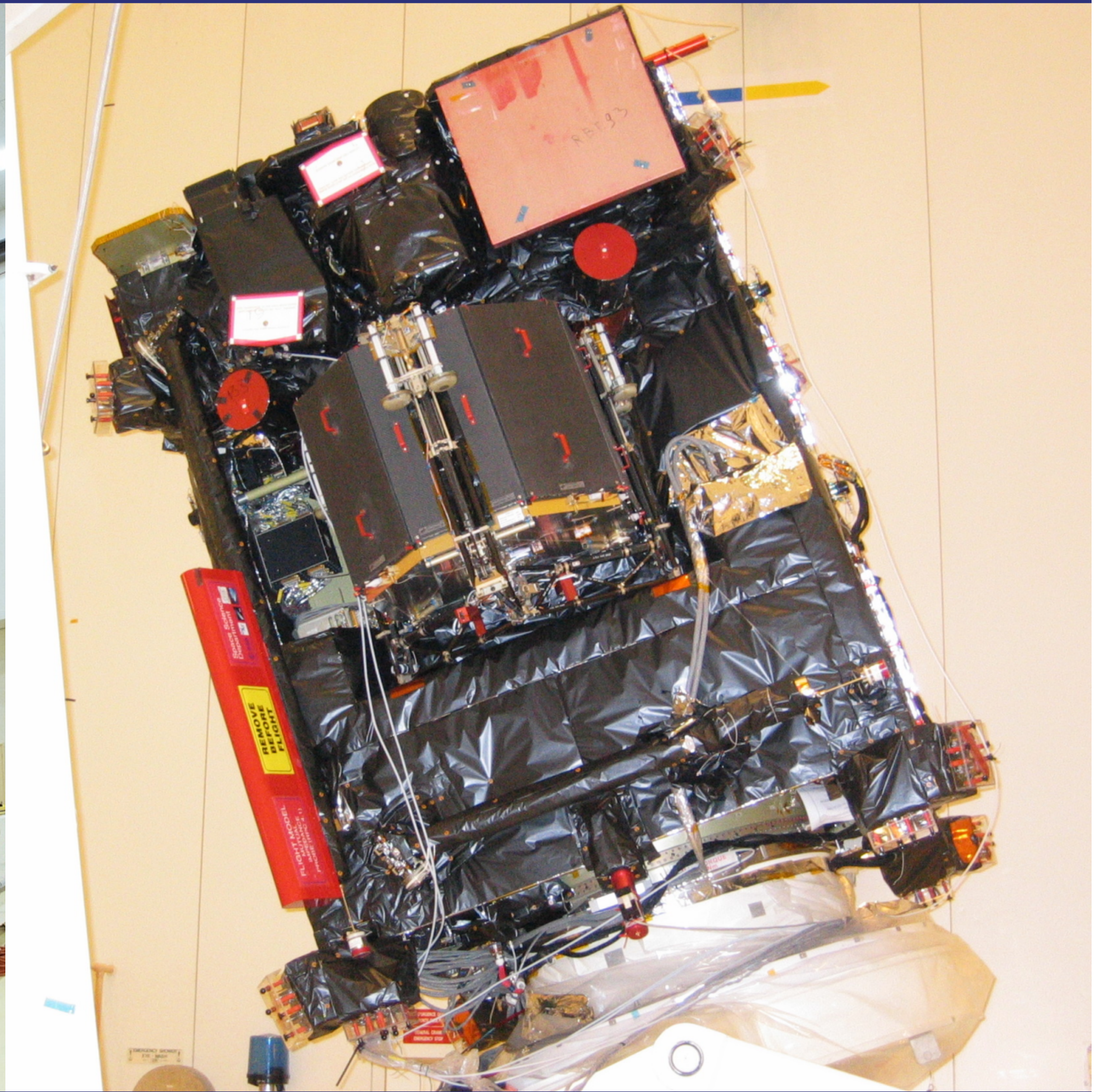
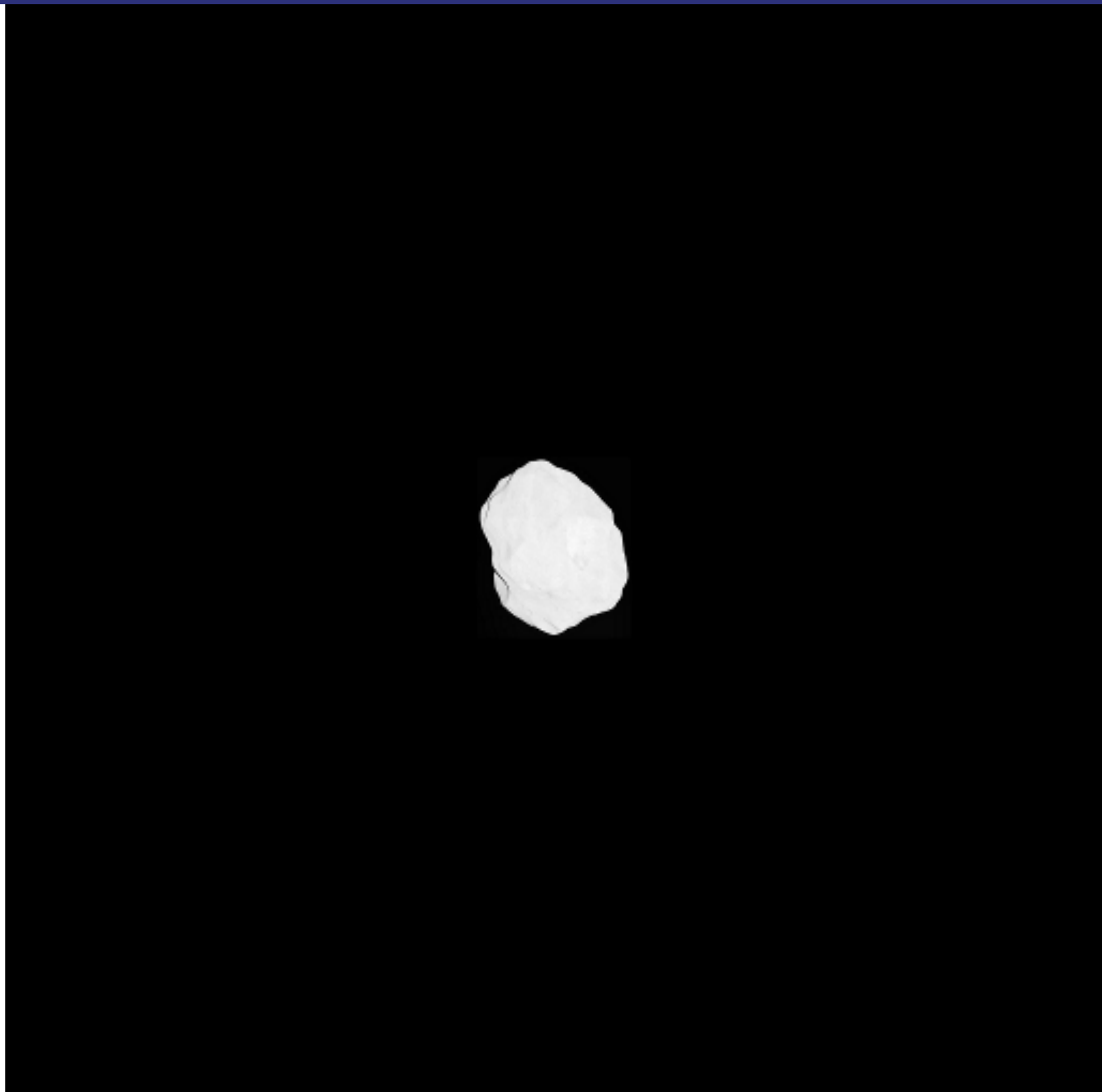


Fig. The scientific payload of the Rosetta orbiter encompasses eleven instruments, most of which are installed in the Payload Support Module that is mounted on top of the Rosetta spacecraft.

Implemantation of the Philae lander

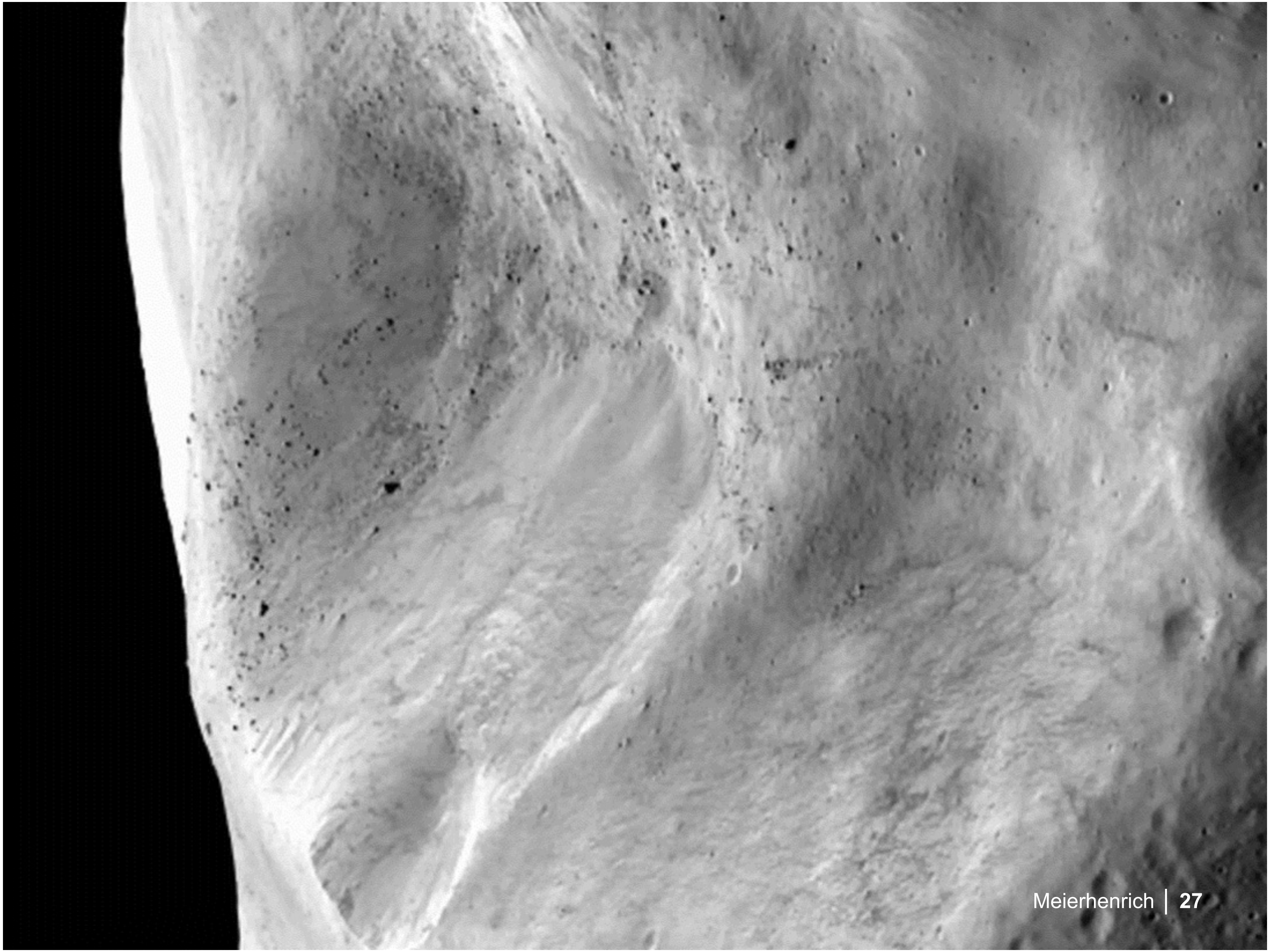


Rosetta : Landing on a cometary nucleus



2004: Décollage !
2005: 1er survol de la Terre
2007: Mars & Phobos !
2007: 2e survol Terre/Lune
2008: (2867) Šteins
2009: 3e survol Terre/Lune
2010: (21) Lutetia

Diamètre 120 km
Peut-être différentié
Morphologie de surface très complexe (linéaments, fractures, cratères, avalanches)



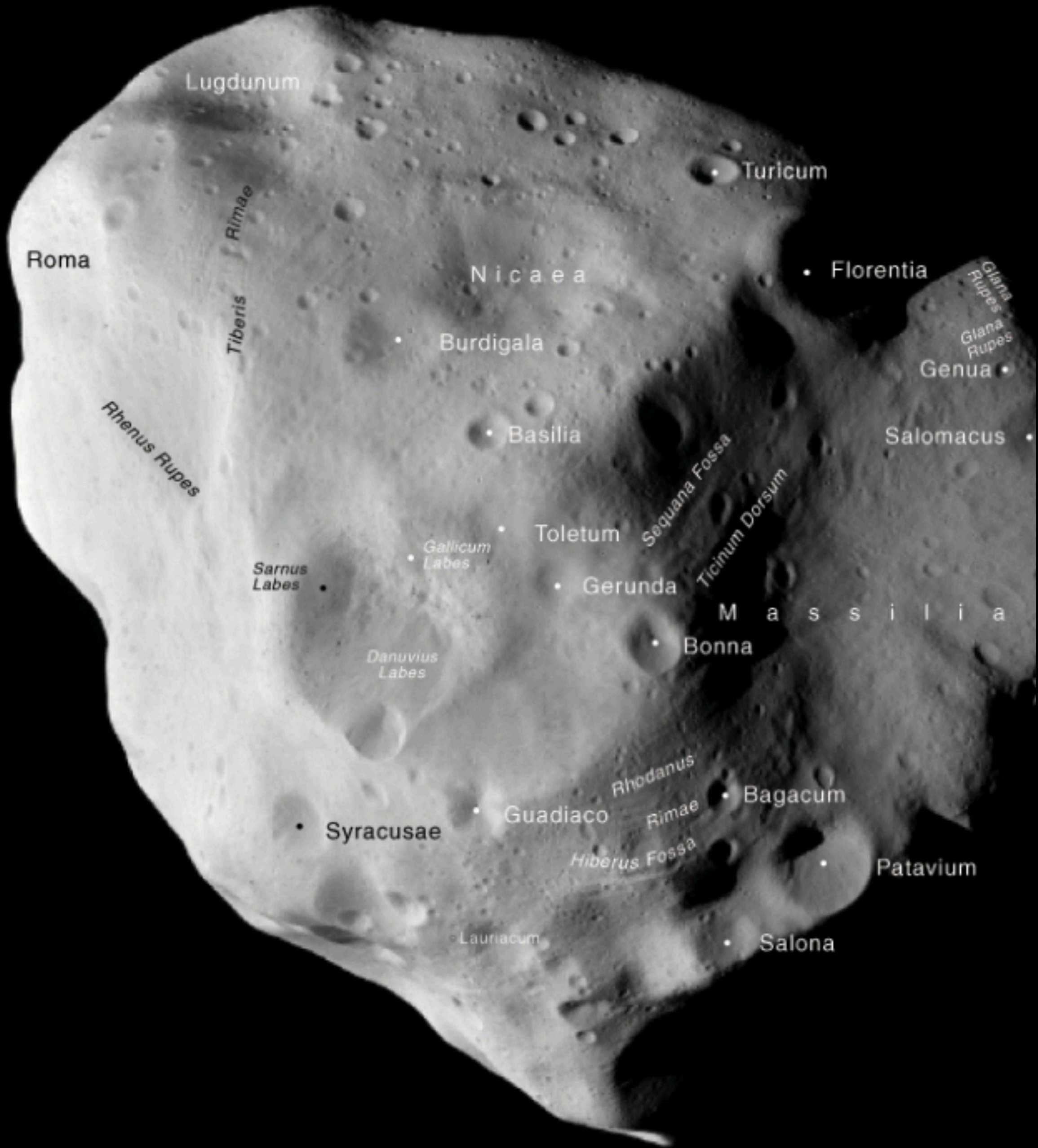
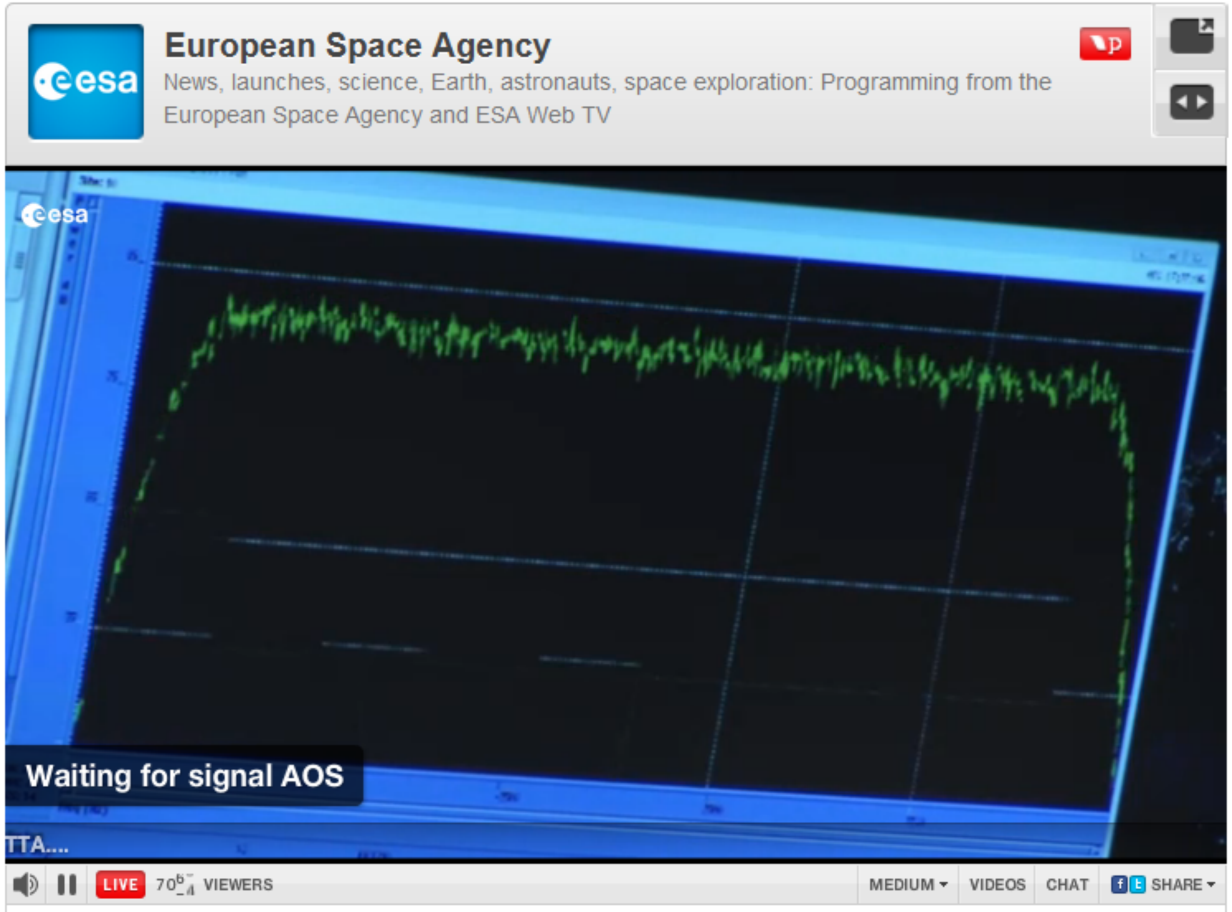


Fig. (21) Lutetia imaged at closest approach by the OSIRIS camera onboard the Rosetta space probe. The OSIRIS team proposed naming the craters according to the names of European cities (Florentia, Genua, Massilia, and Nicaea, for example) at the time when Paris was called Lutetia. (Image credit: ESA and MPS for OSIRIS Team MPS/UPD/LAM/ IAA/RSSD/INTA/ UPM/DASP/IDA.)

Rosetta : Landing on a cometary nucleus



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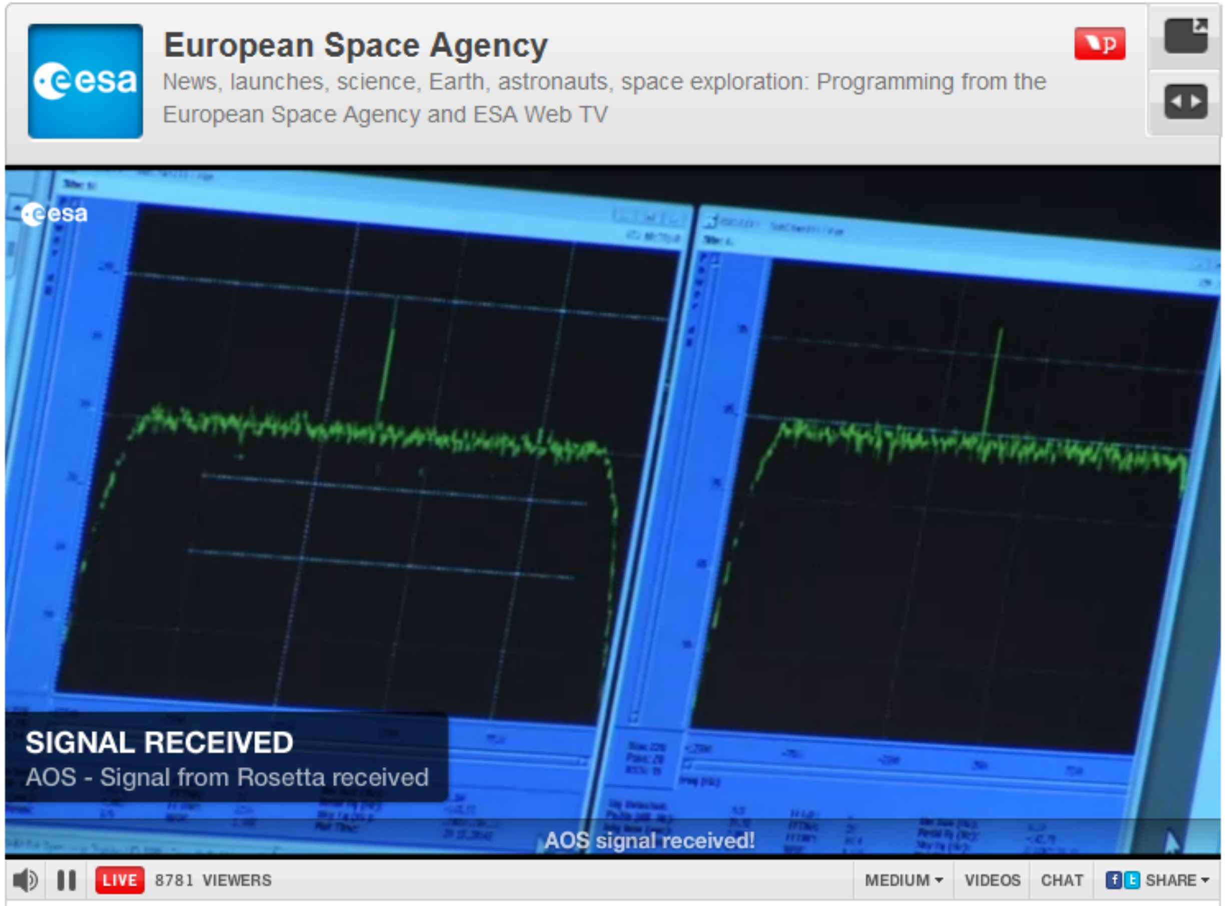
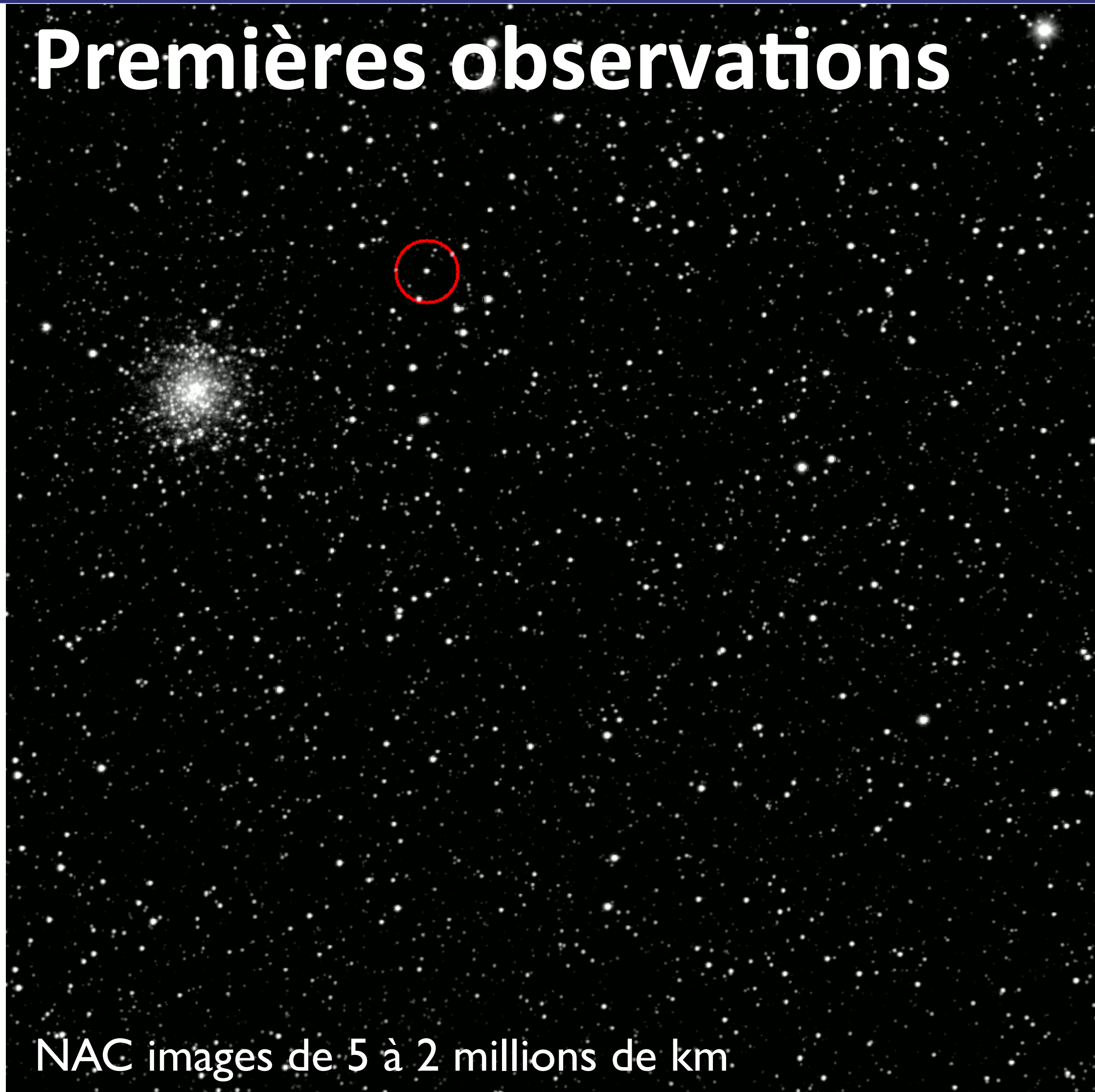
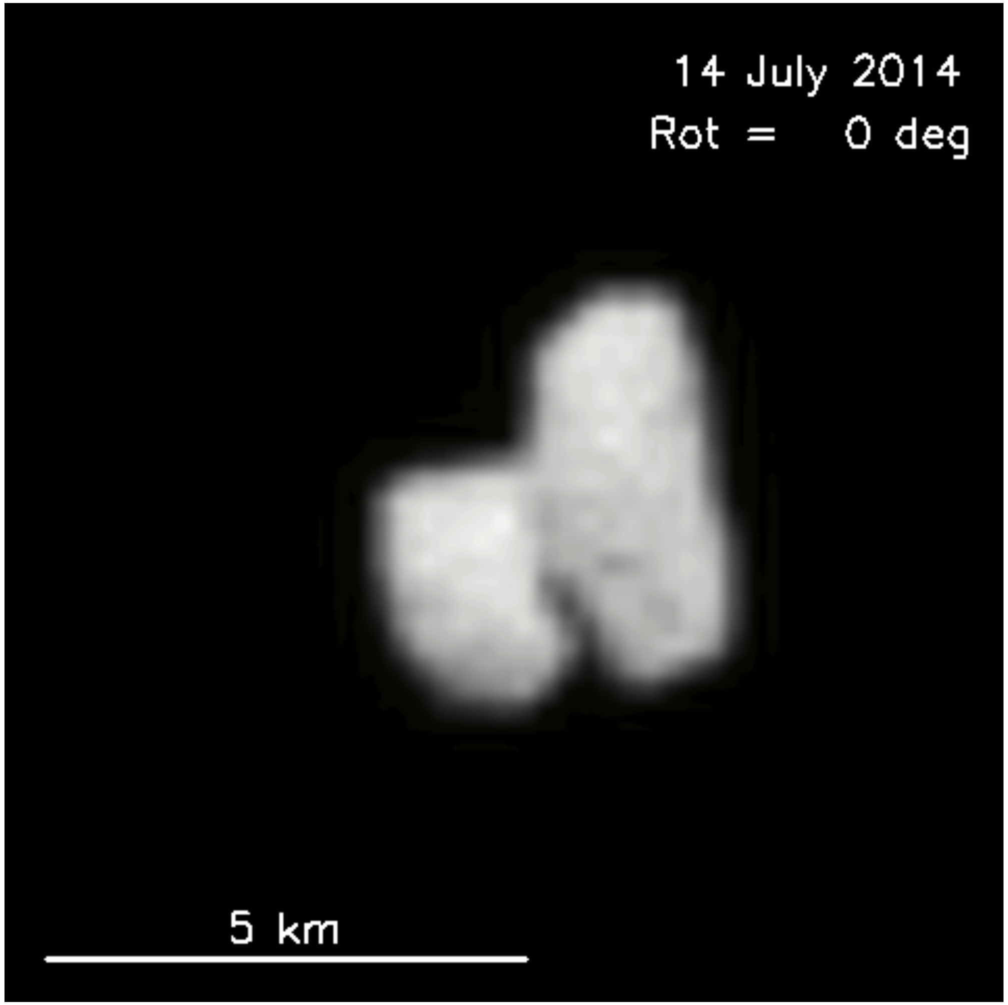
2010: (21) Lutetia
2011: Mise en hibernation

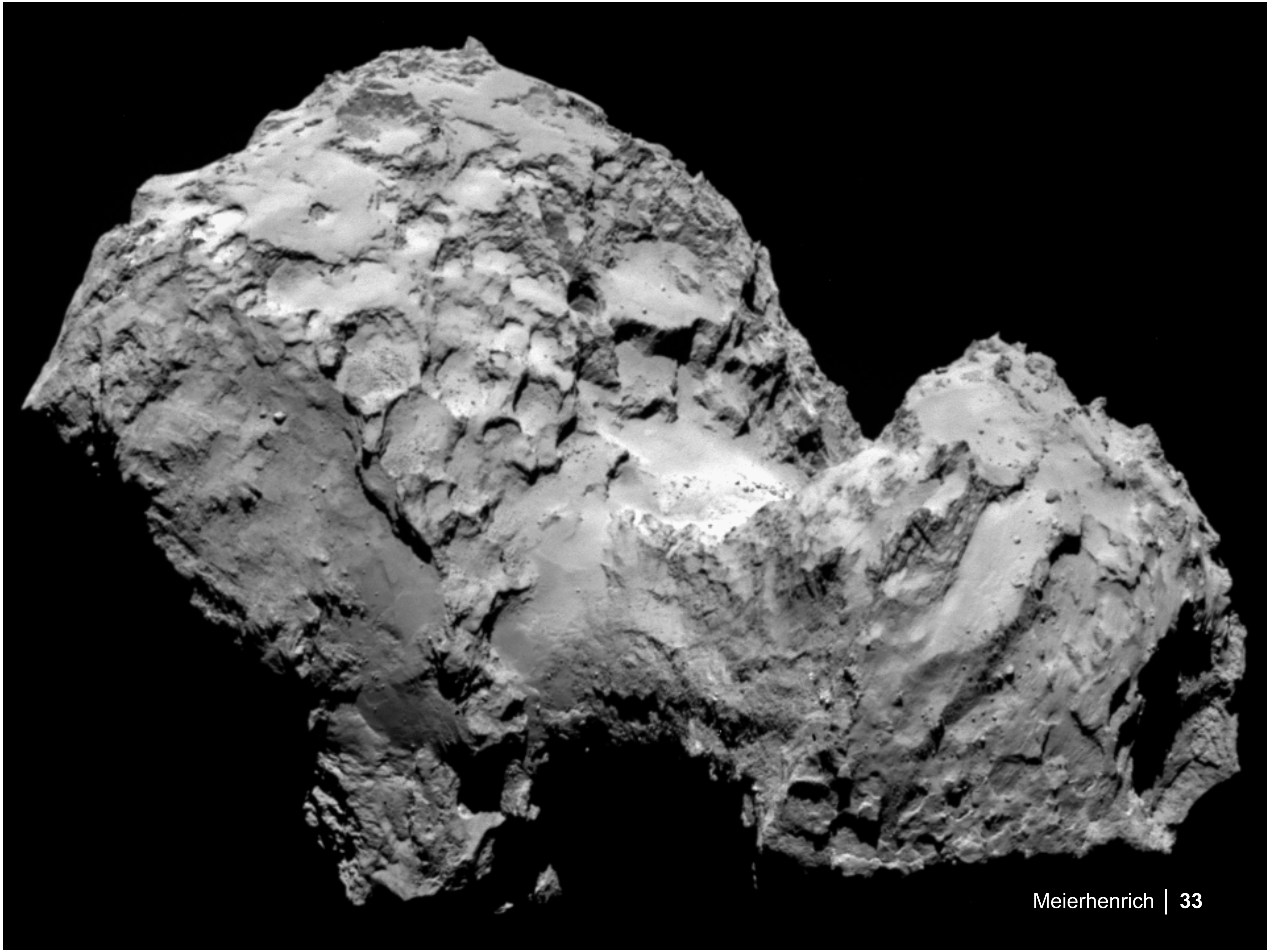


2004: Décollage !
2005: 1[er] survol de la Terre
2007: Mars & Phobos !
2007: 2[e] survol Terre/Lune
2008: (2867) Šteins
2009: 3[e] survol Terre/Lune
2010: (21) Lutetia
2011: Mise en hibernation
2014: Réveil !

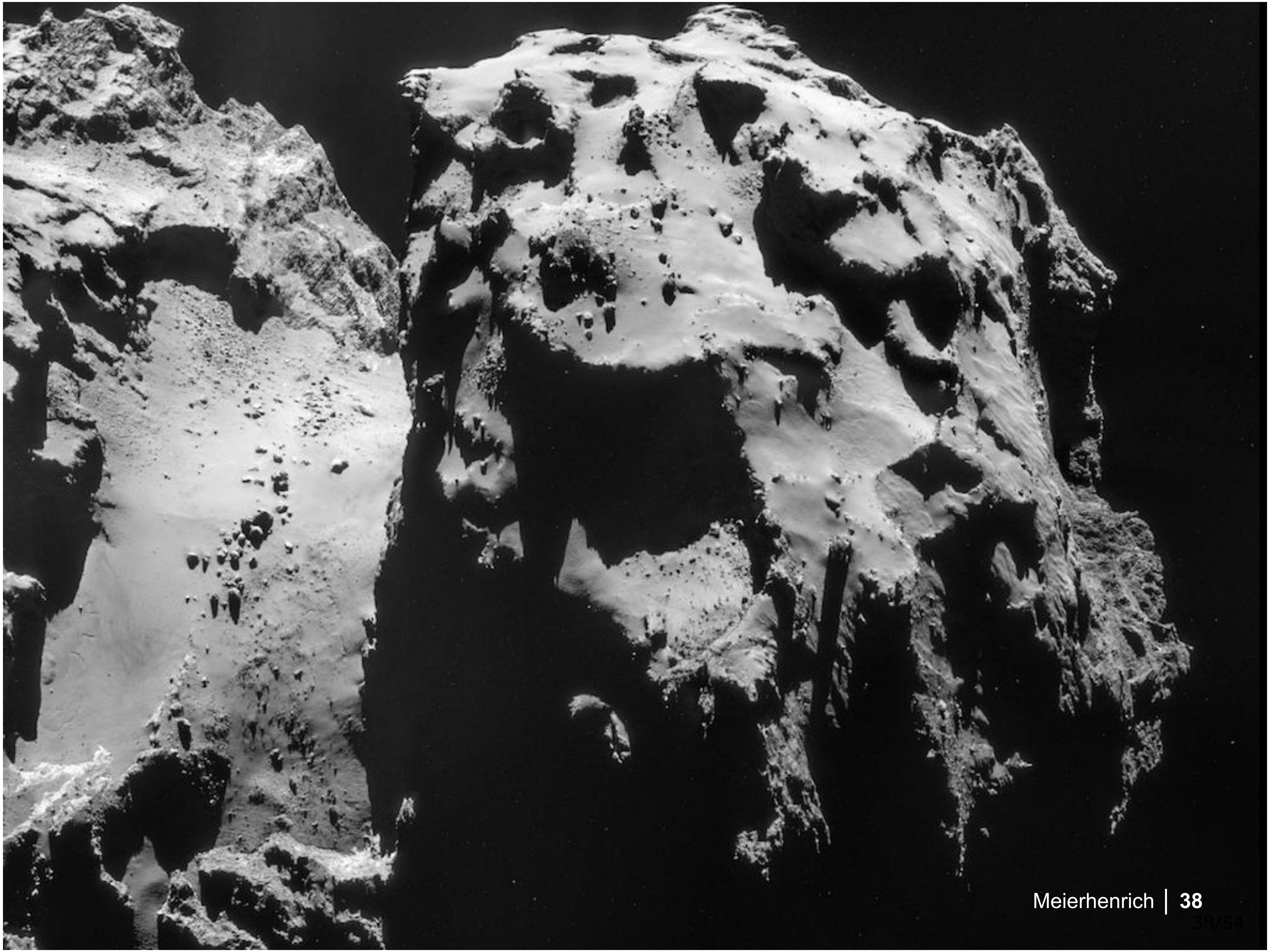

Premières observations
NAC images de 5 à 2 millions de km

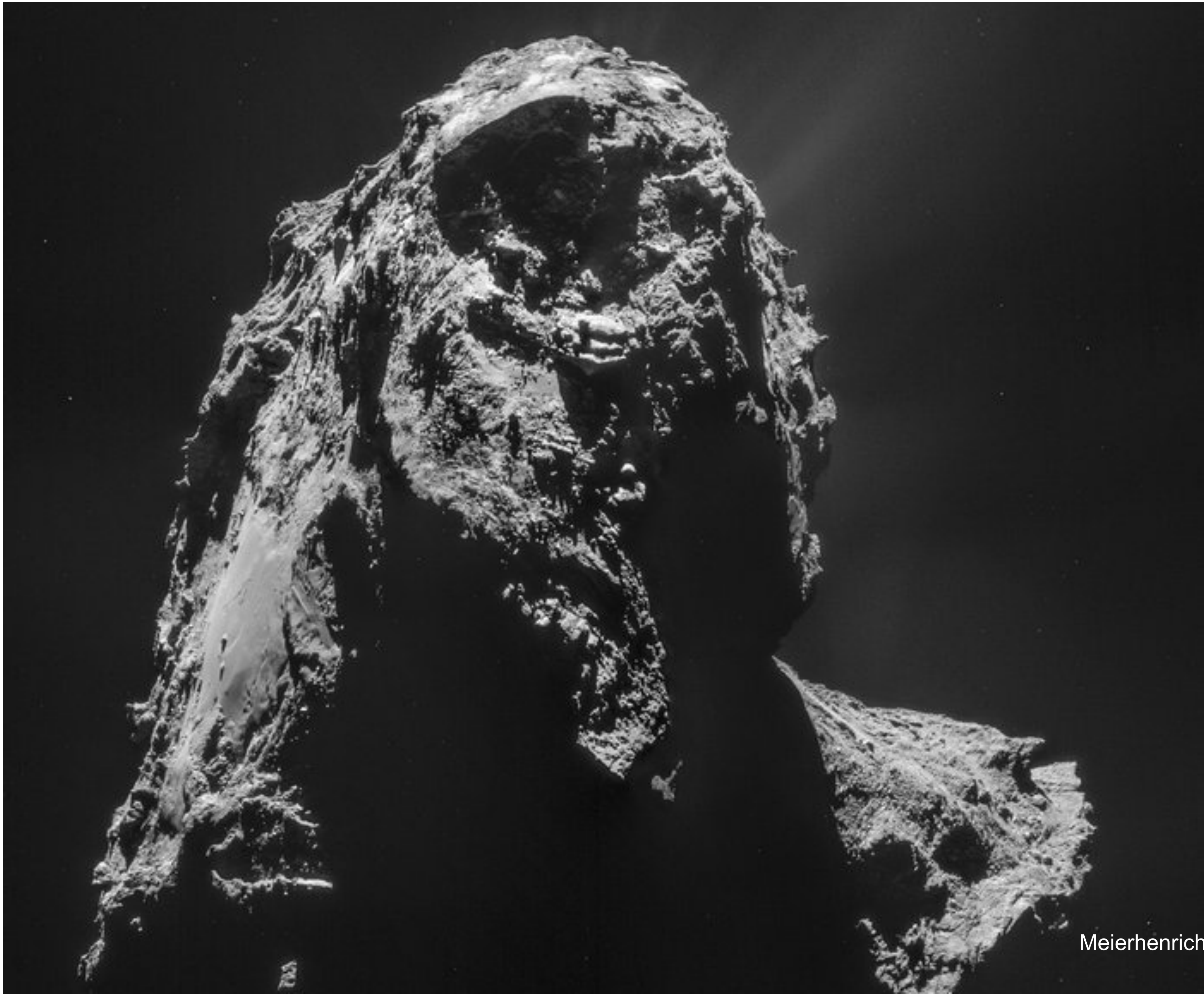
14 Juillet 2014 - 12 000 km

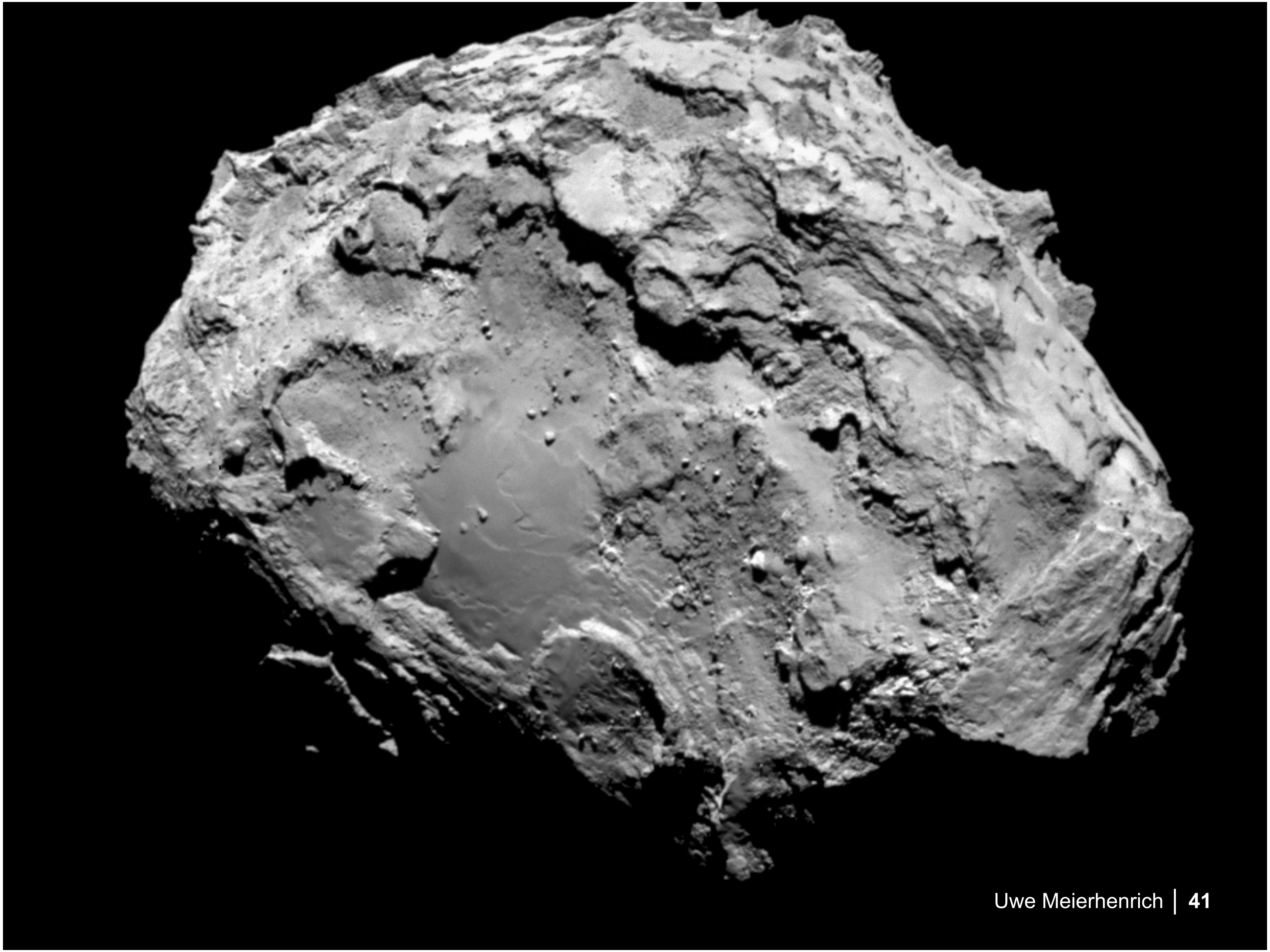


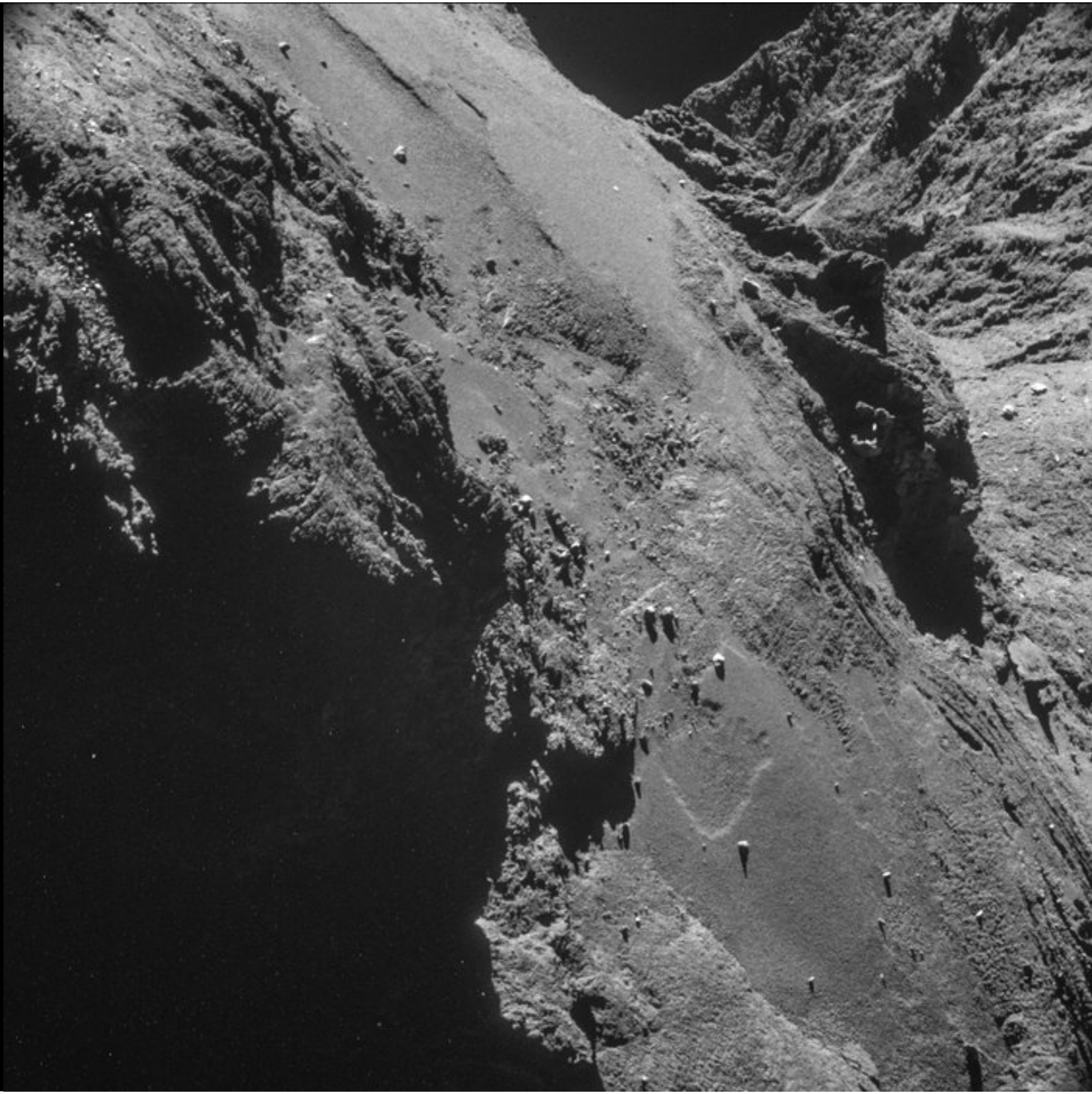


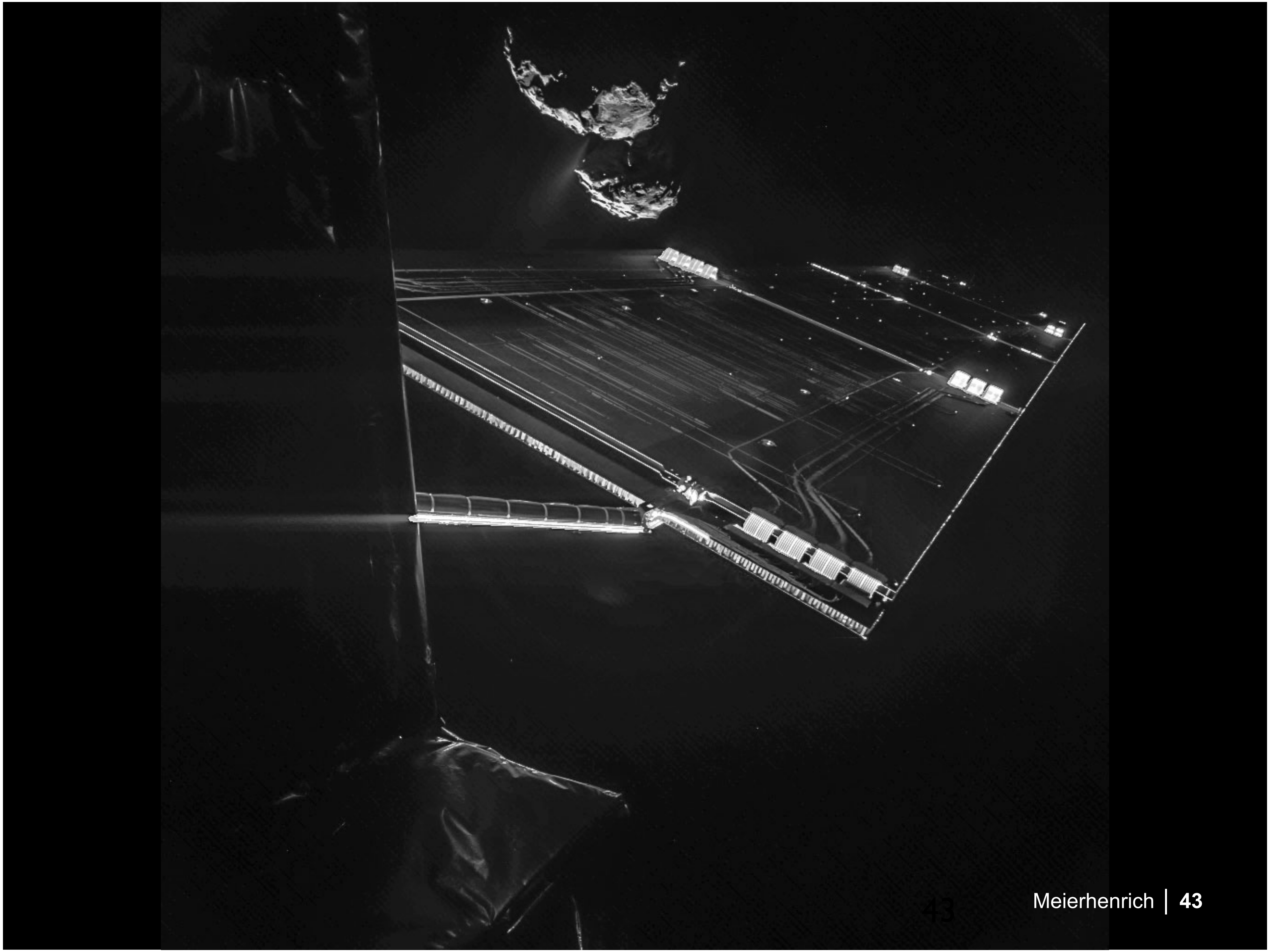
Sierks et al.: *Science* **347** (2015), 1044

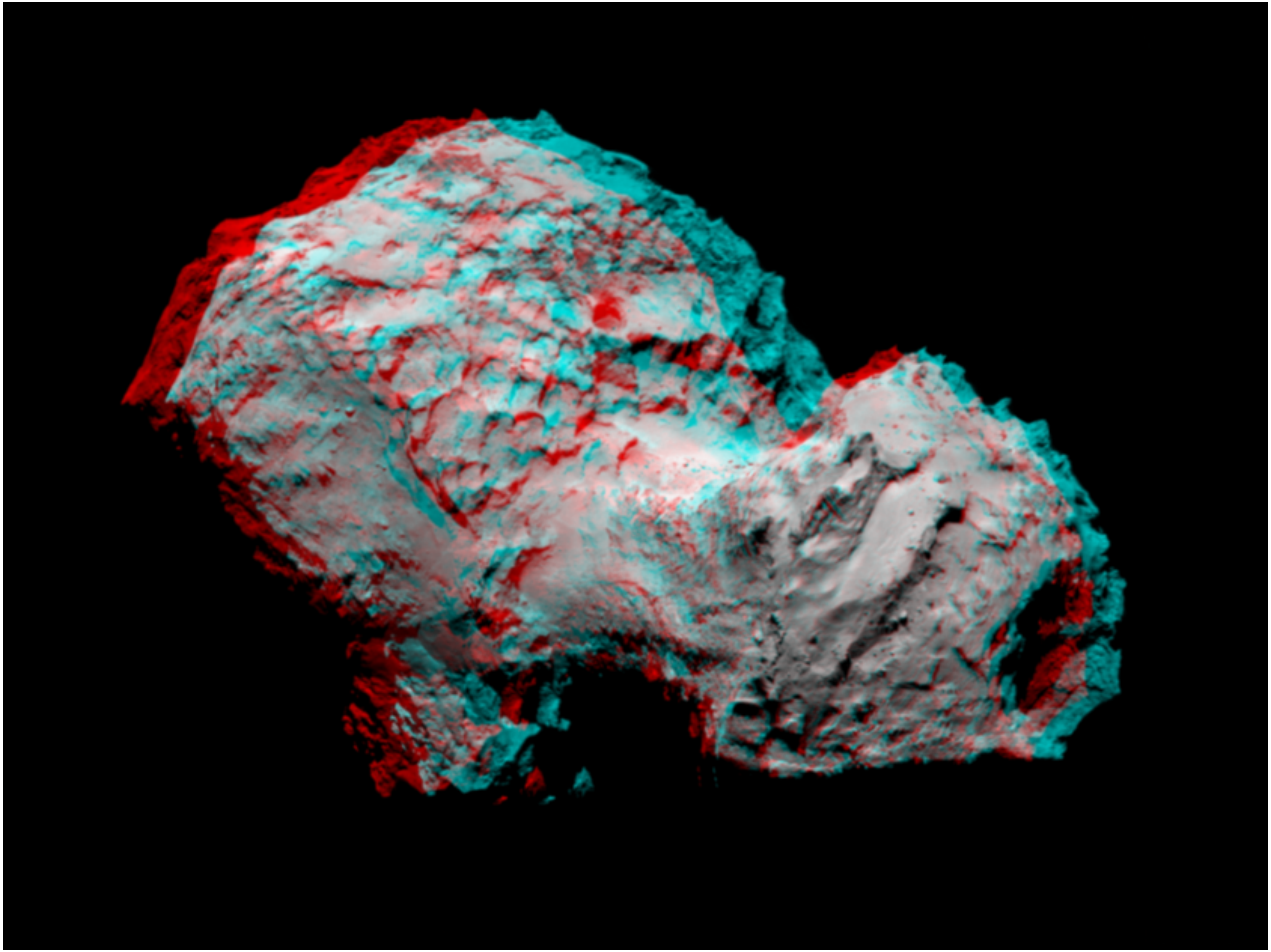


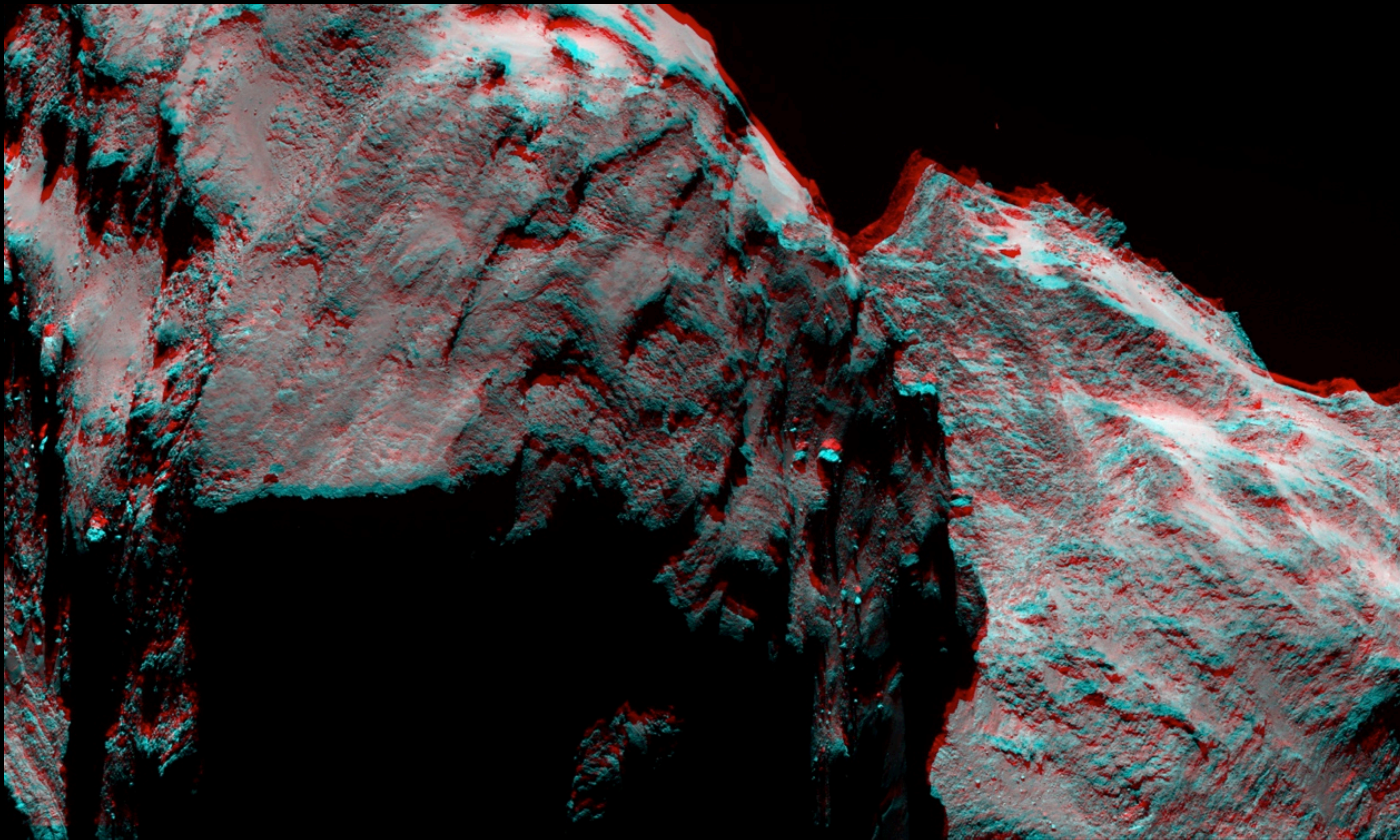


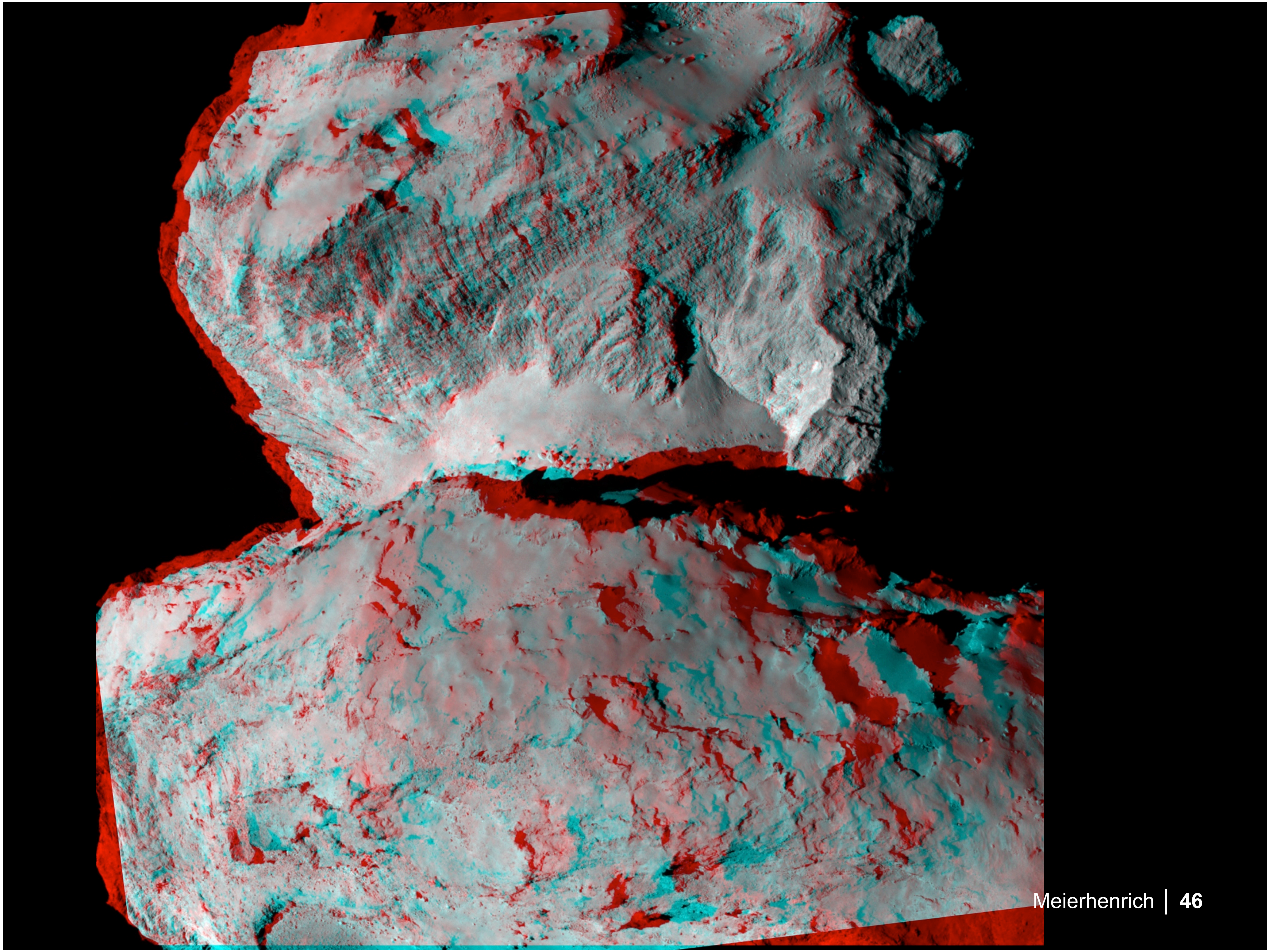


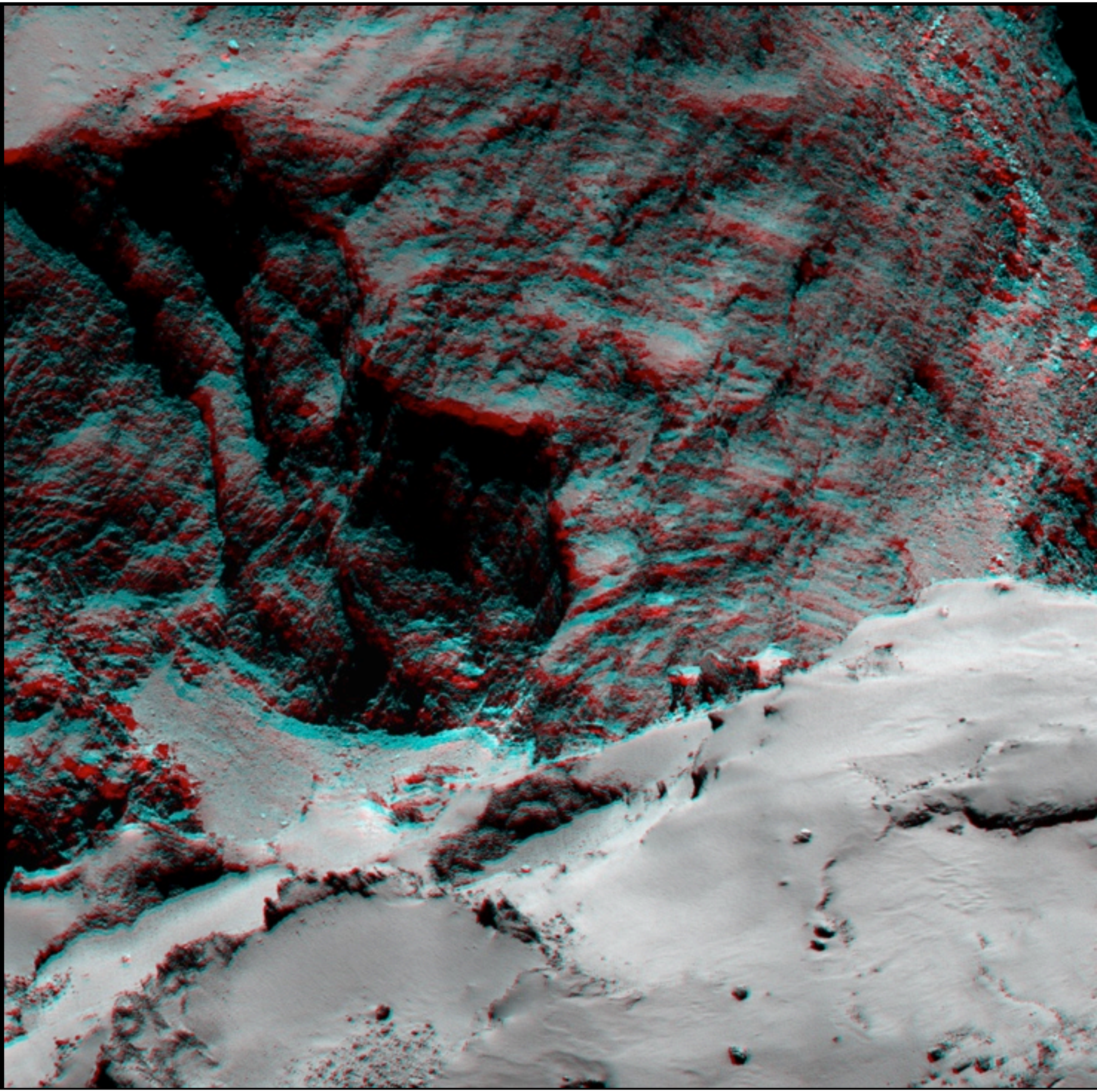


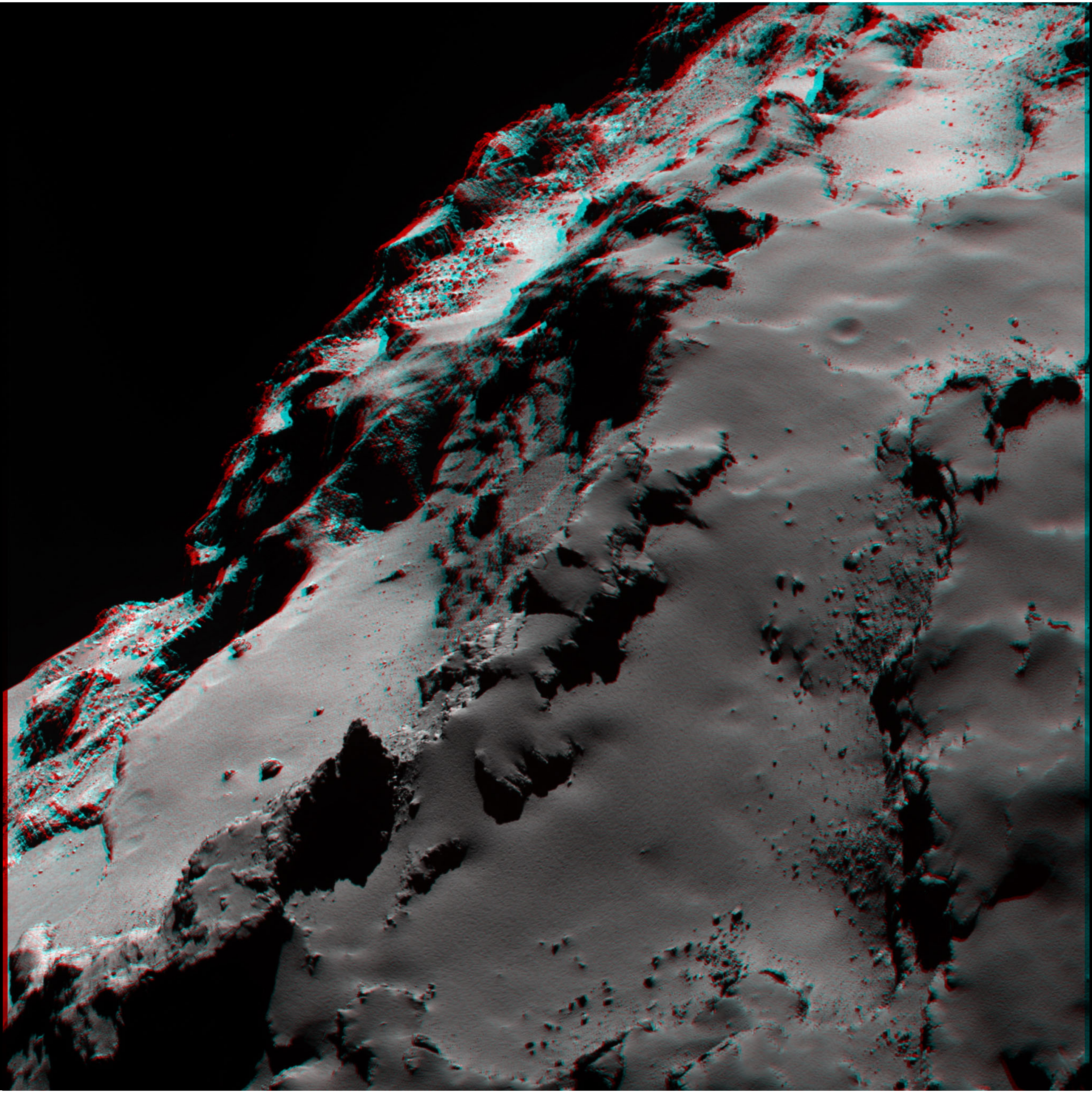


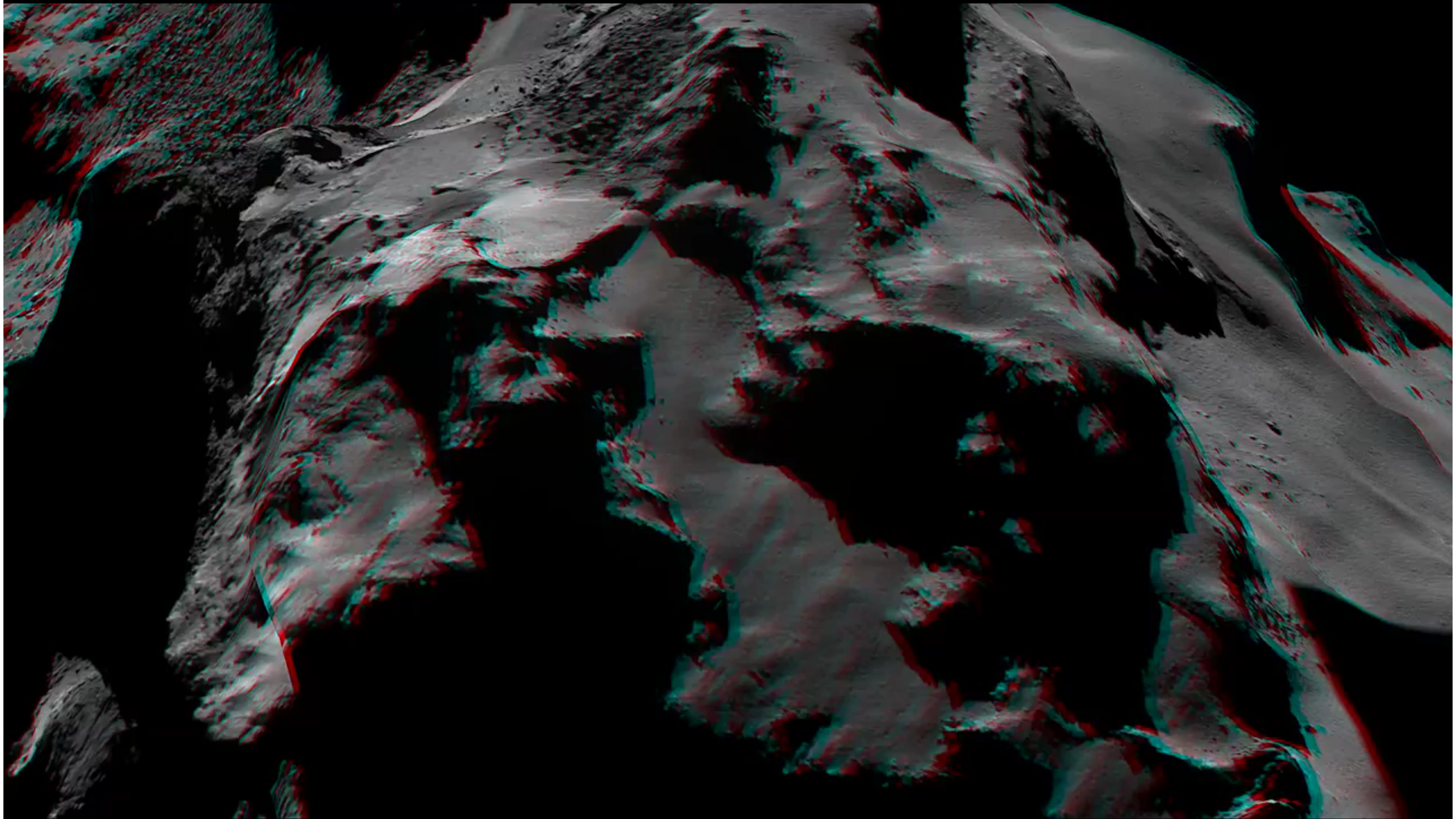


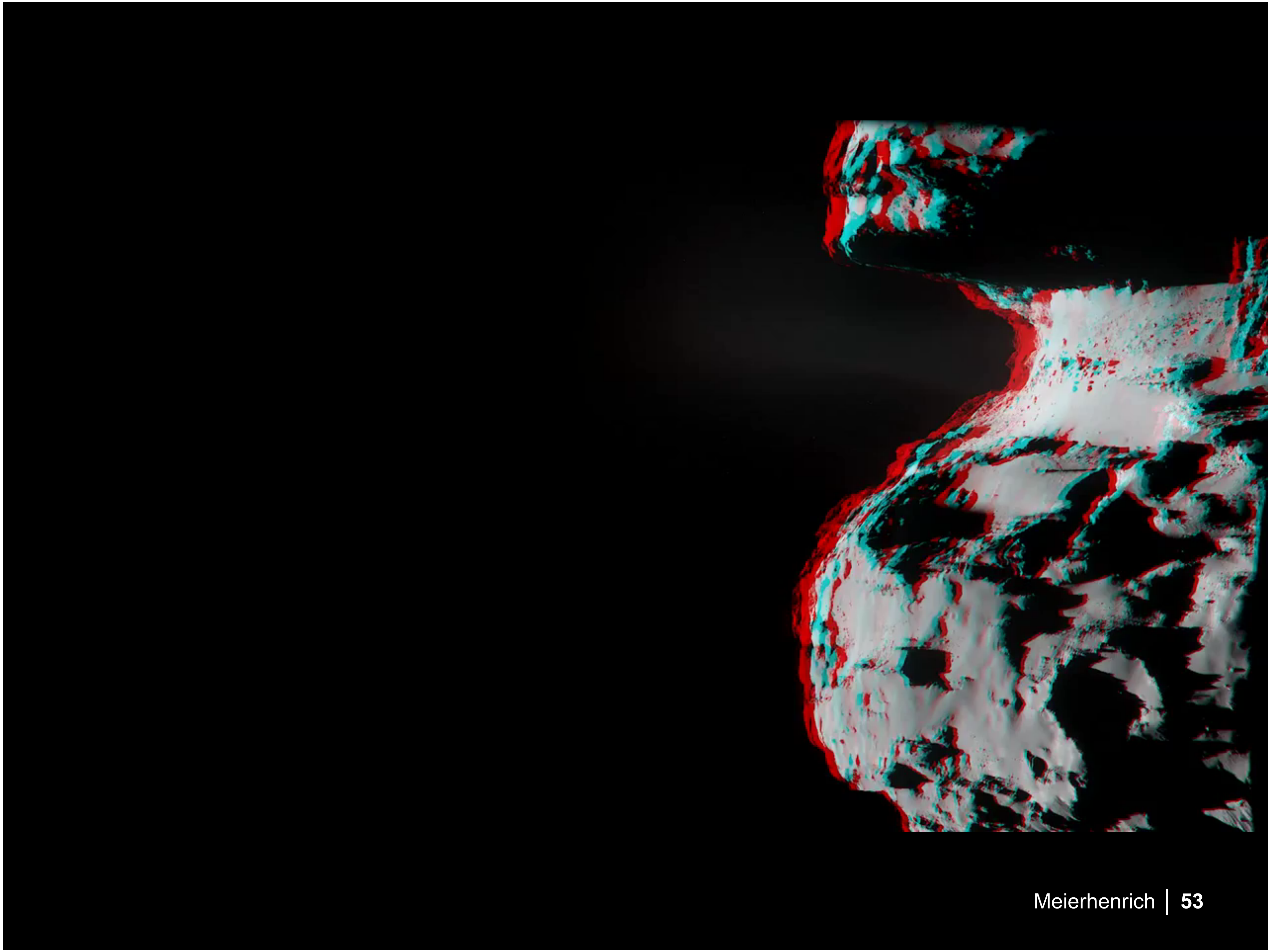


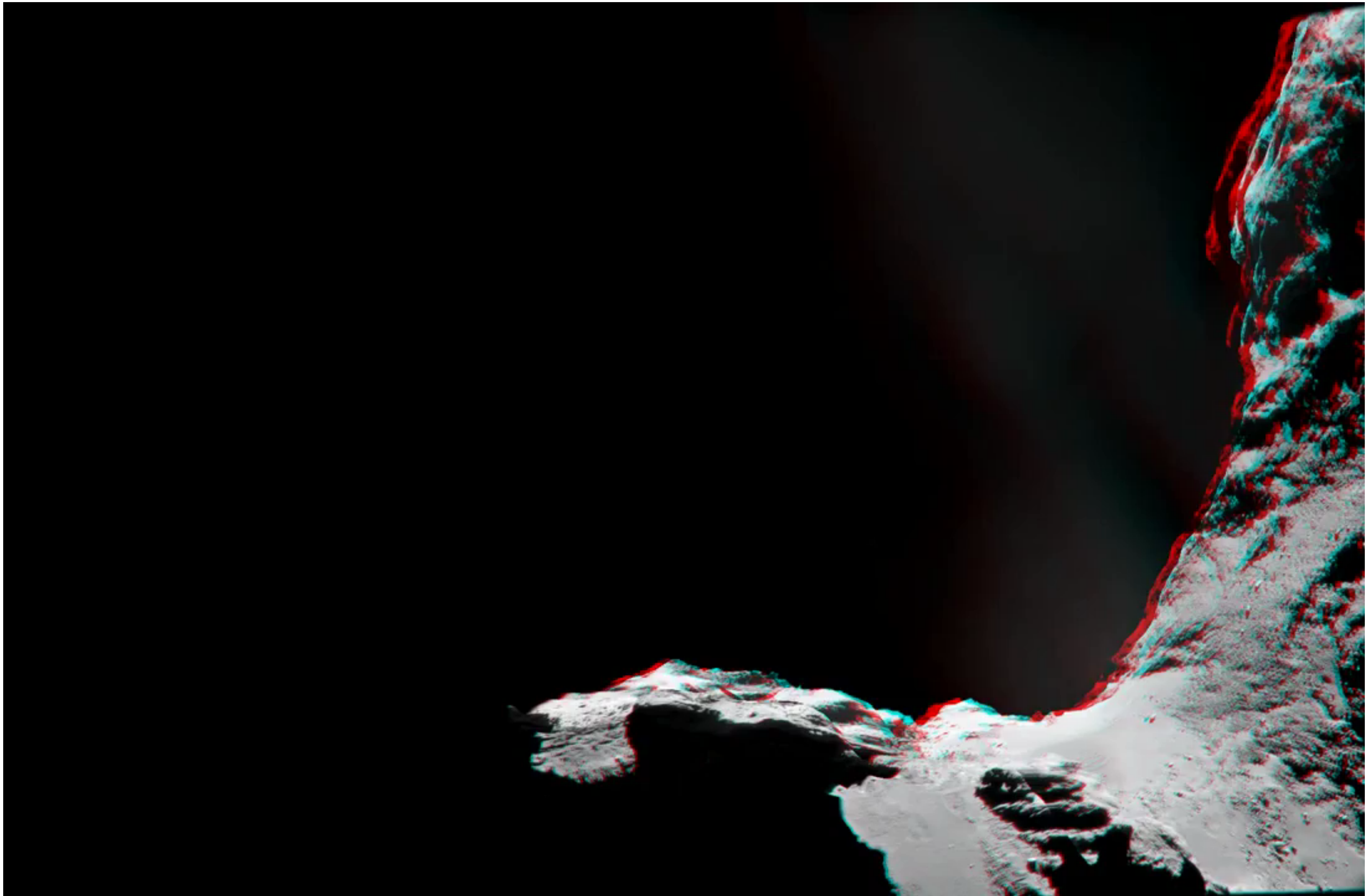


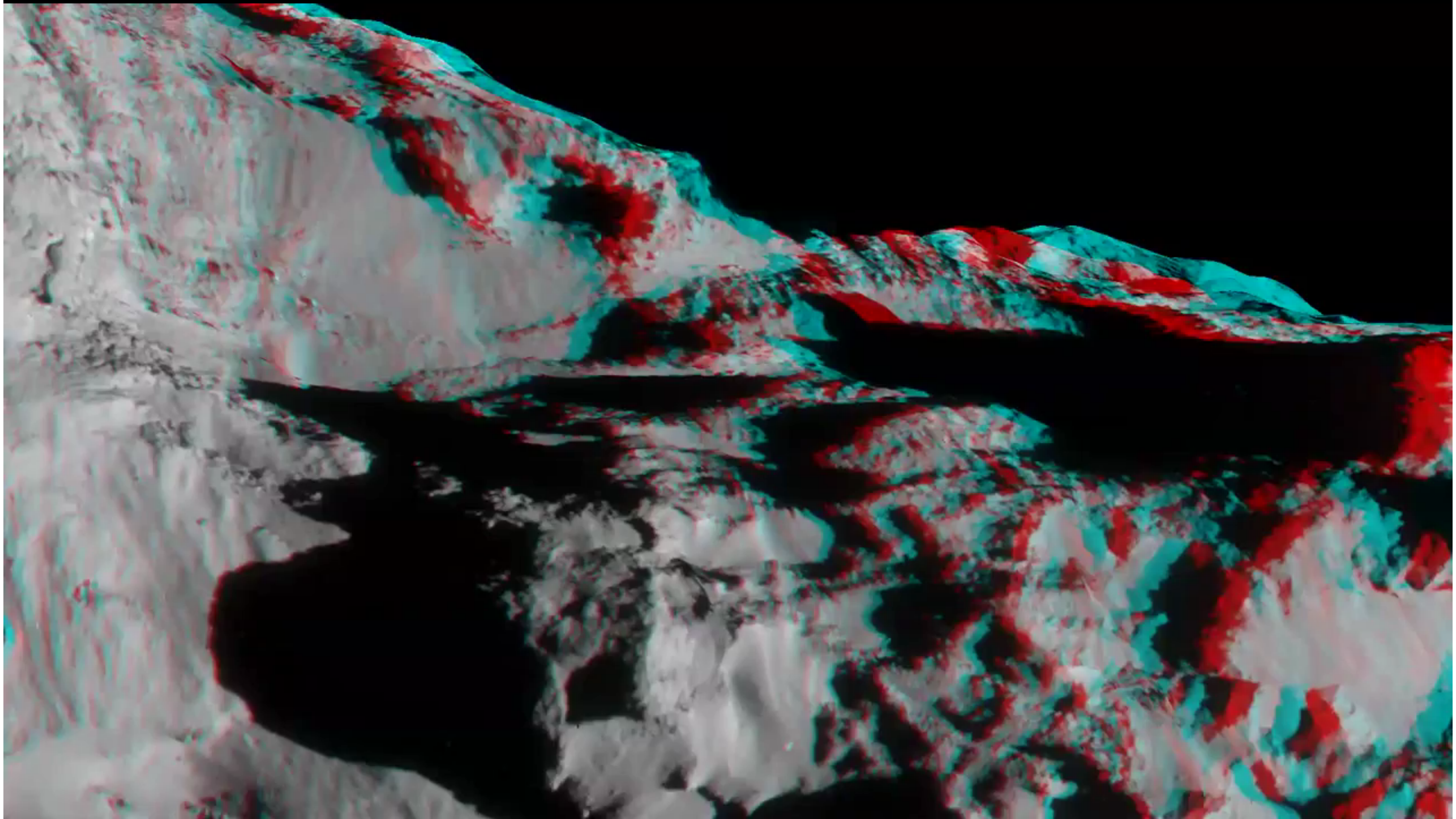










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Counting molecular garbage chutes in intact neurons
Science
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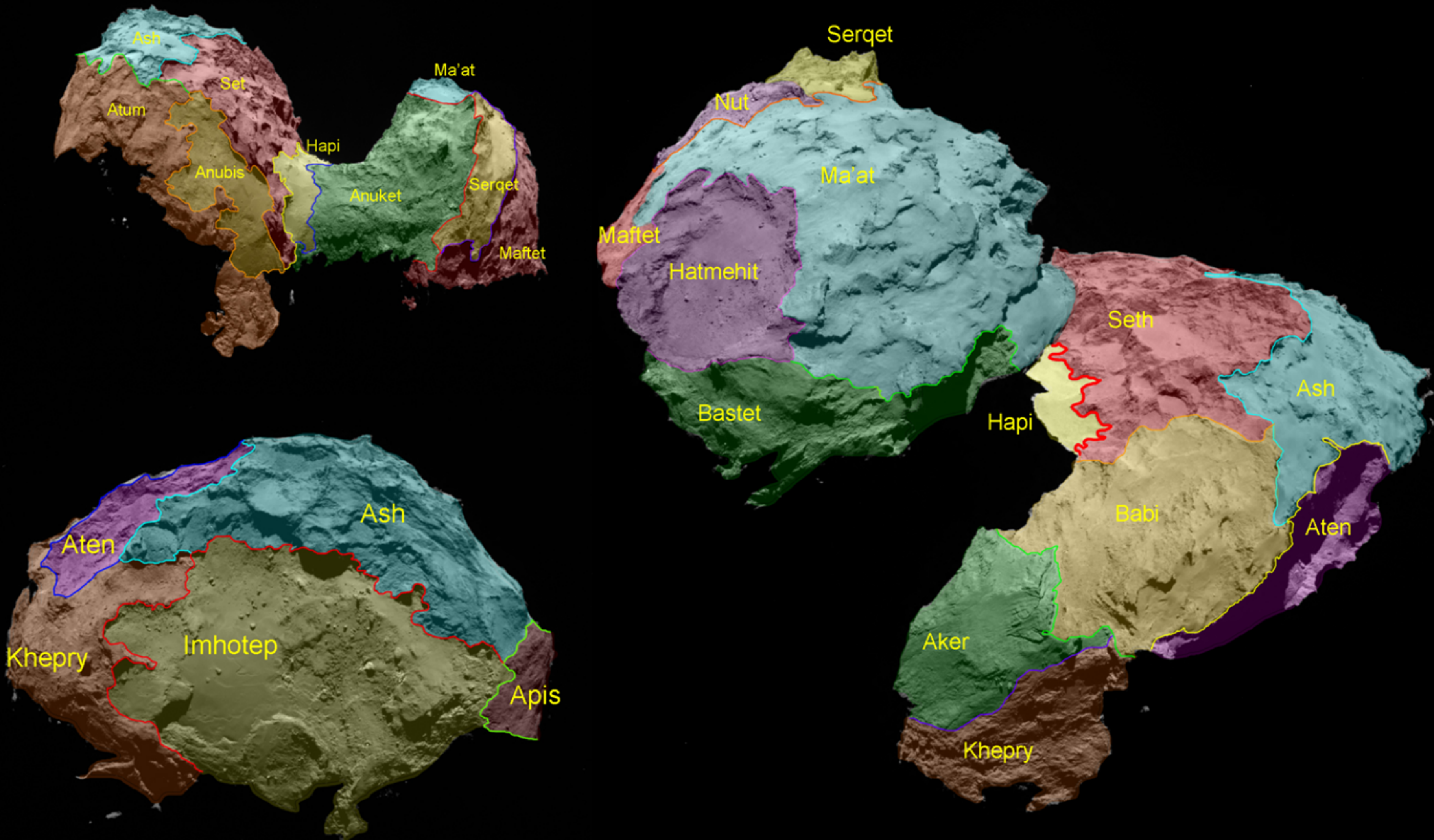
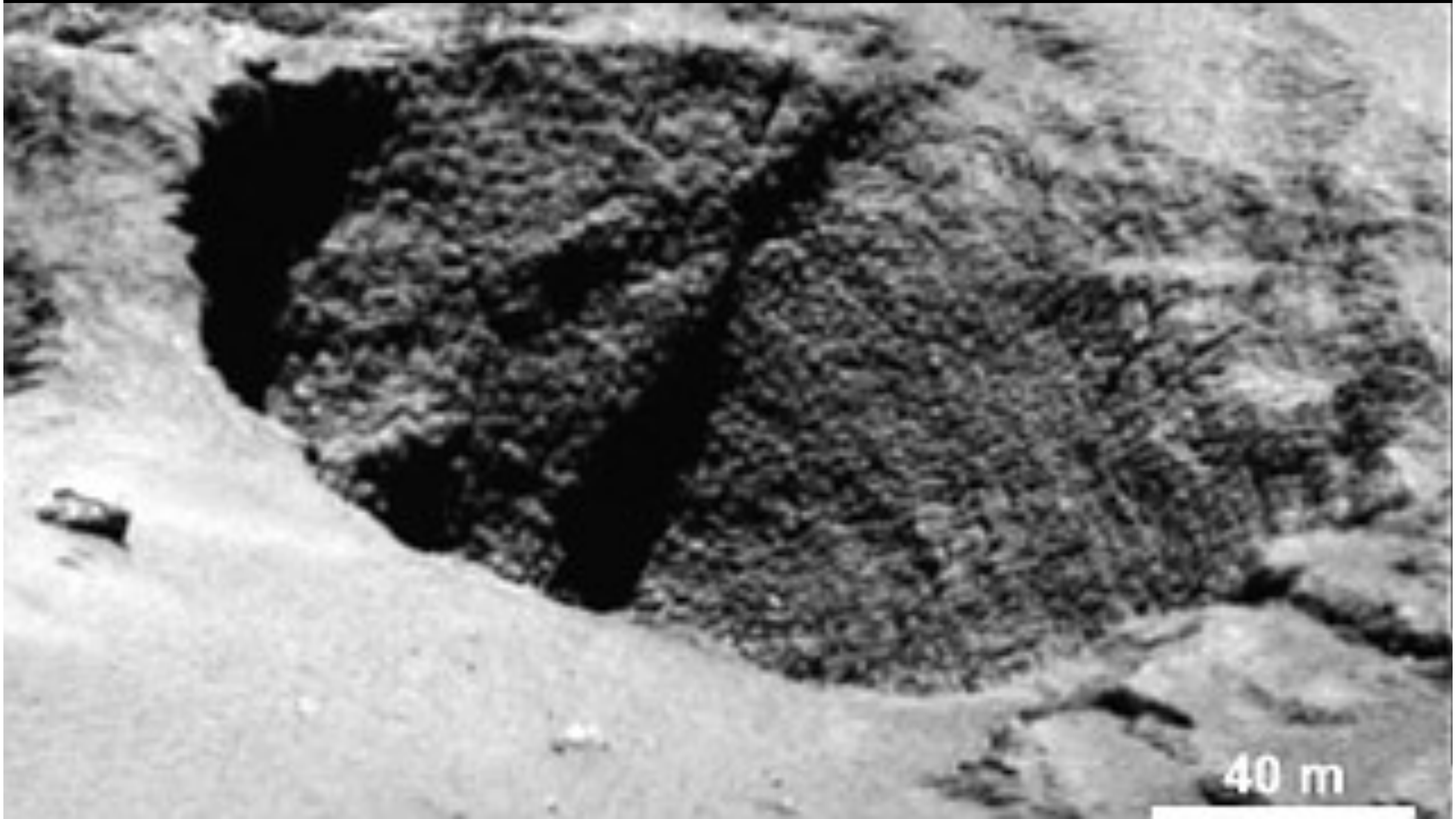
Catching a comet
Rosetta follows a relic of the early solar system toward the Sun
pp. 358 & 387

Geologic mapping

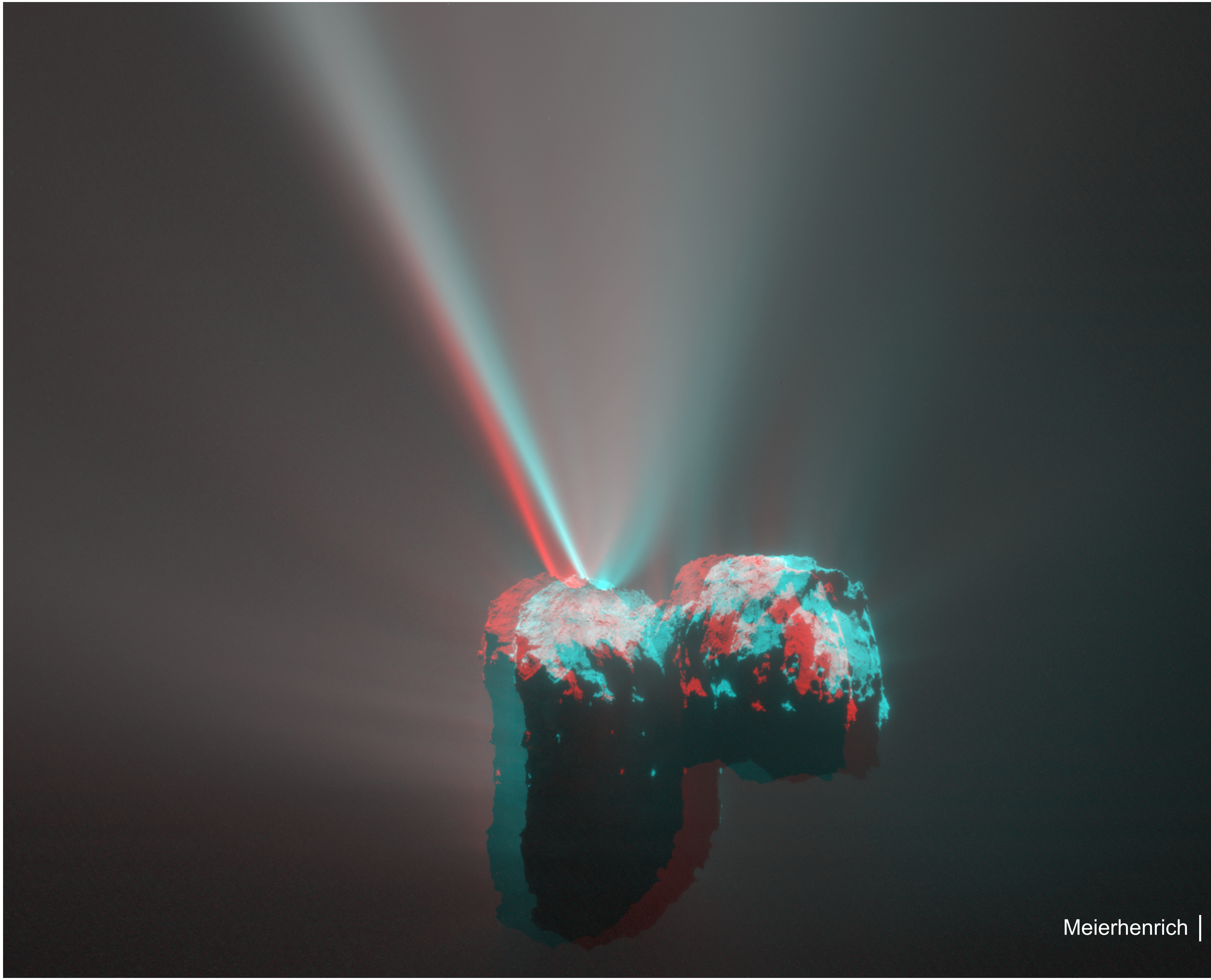


Sierks et al.: *Science* **347** (2015), 1044

Sierks et al.: *Science* **347** (2015), 1044



Sierks et al.: *Science* **347** (2015), 1044



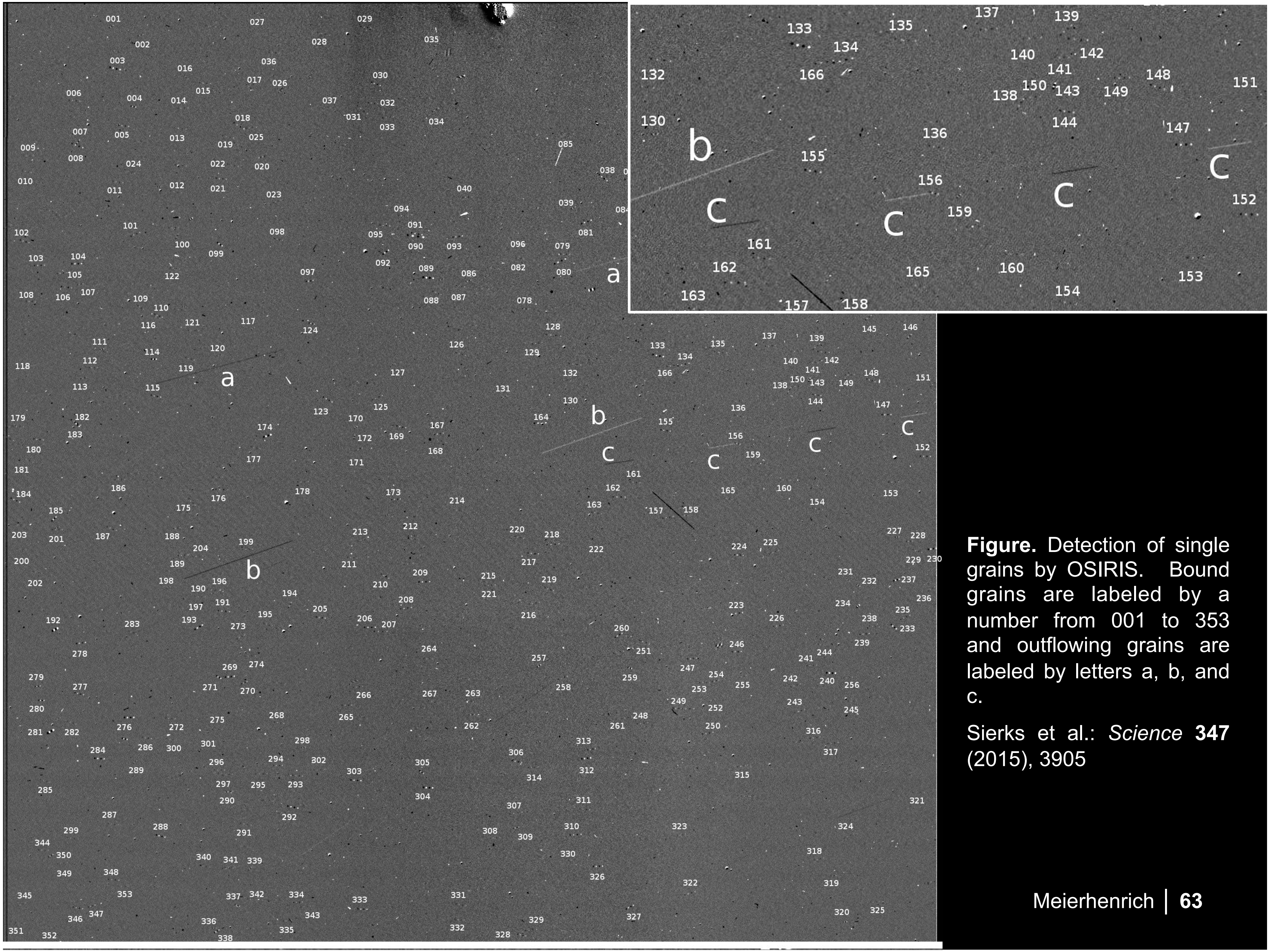
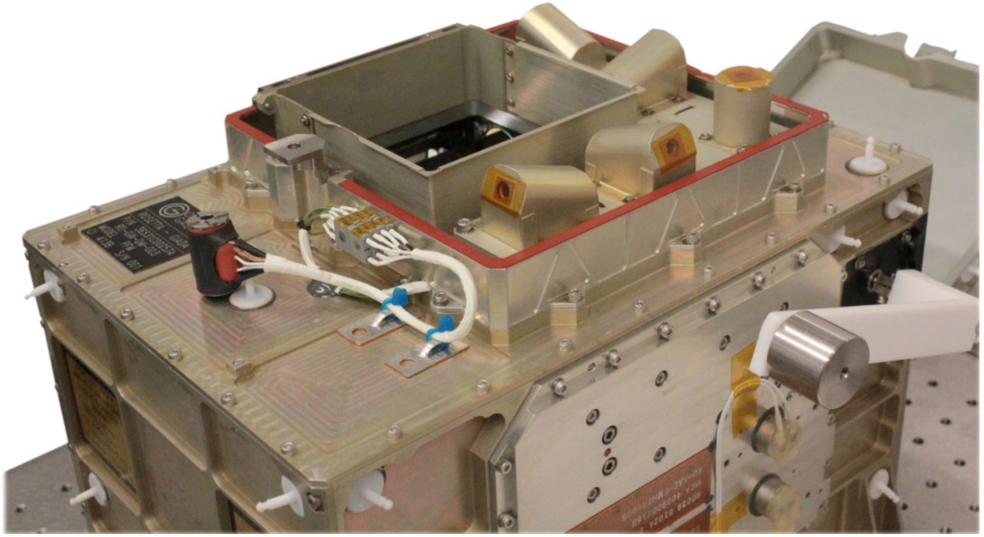


Figure. Detection of single grains by OSIRIS. Bound grains are labeled by a number from 001 to 353 and outflowing grains are labeled by letters a, b, and c.

Sierks et al.: *Science* **347** (2015), 3905

Rosetta's GIADA dust detections along the 30, 20, and 10 km bound orbits



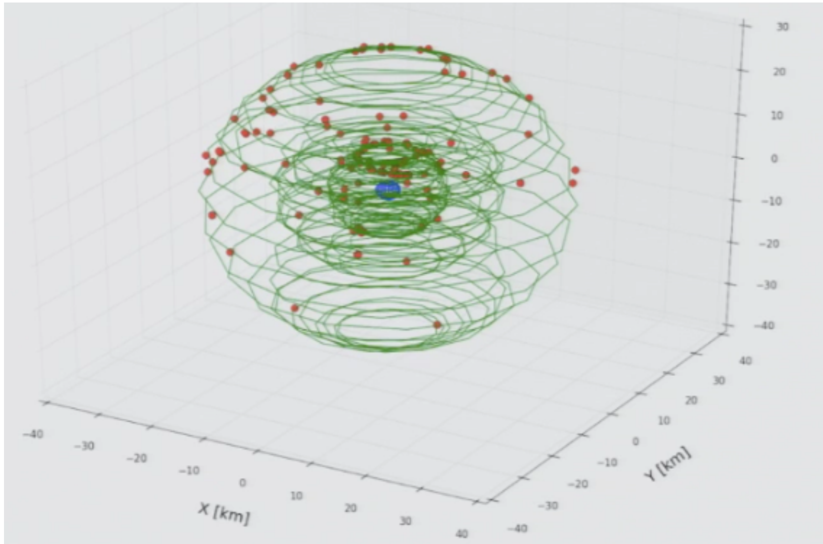
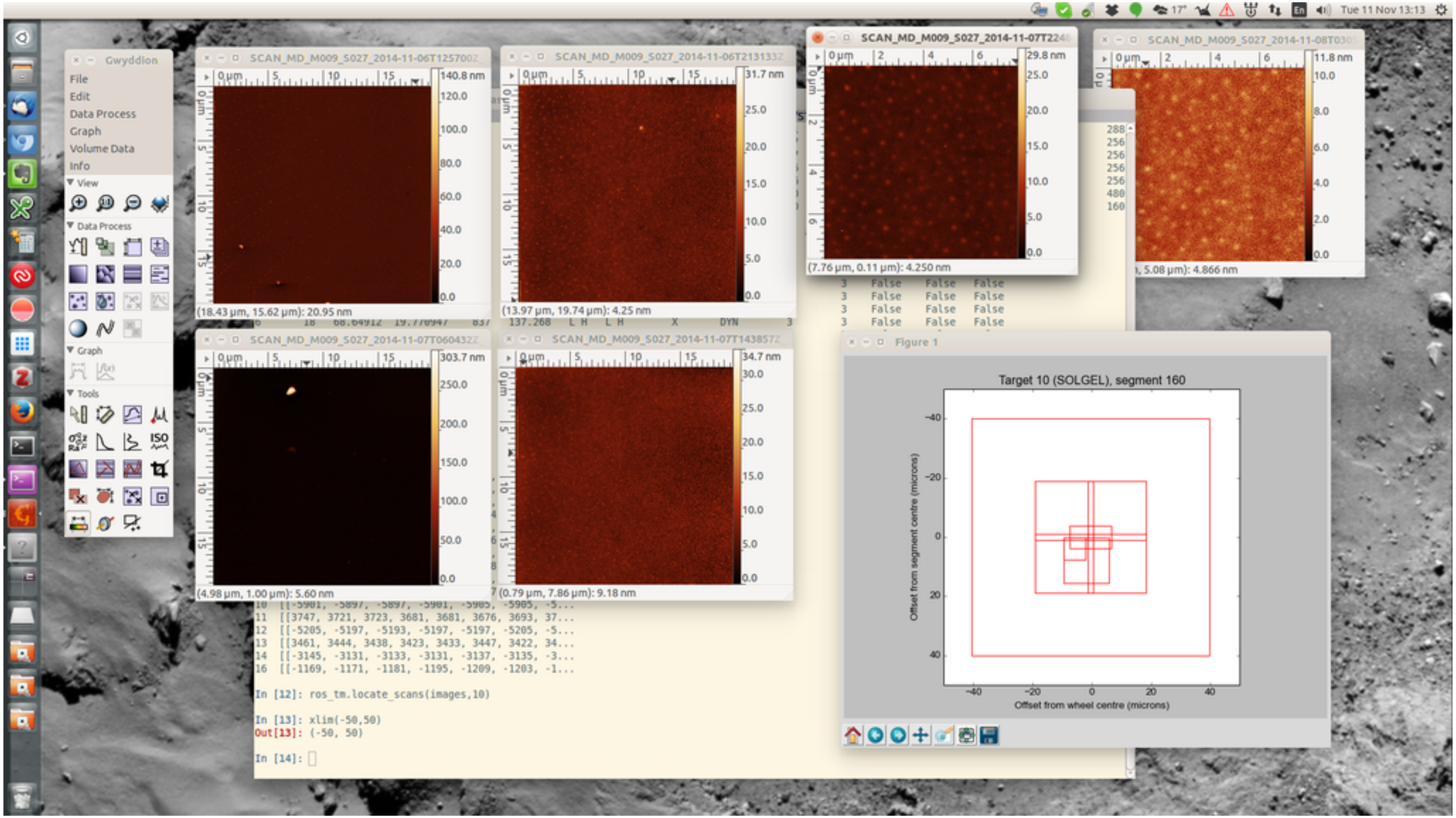


Fig. The GIADA instrument uses five independent quartz crystal micro-balances (QCMs) that are mounted on top of the instrument and point toward different directions in space. The 10 cm x 10 cm frame that is close to the QCM device is the optical grain detection system (GDS), which provides a 3-mm thick laser-light curtain for the detection of single entering grains. Image credit: Alessandra Rotundi and the GIADA Team, Università degli Studi di Napoli, Italy.

Colangeli L. et al.: *Space Sci. Rev.*, **128**, 803–821.

The AFM MIDAS searches for cometary grains



Screenshot of Marc Bentley, Graz, Austria, PI of MIDAS

COSIMA identified > 3000 cometary grains

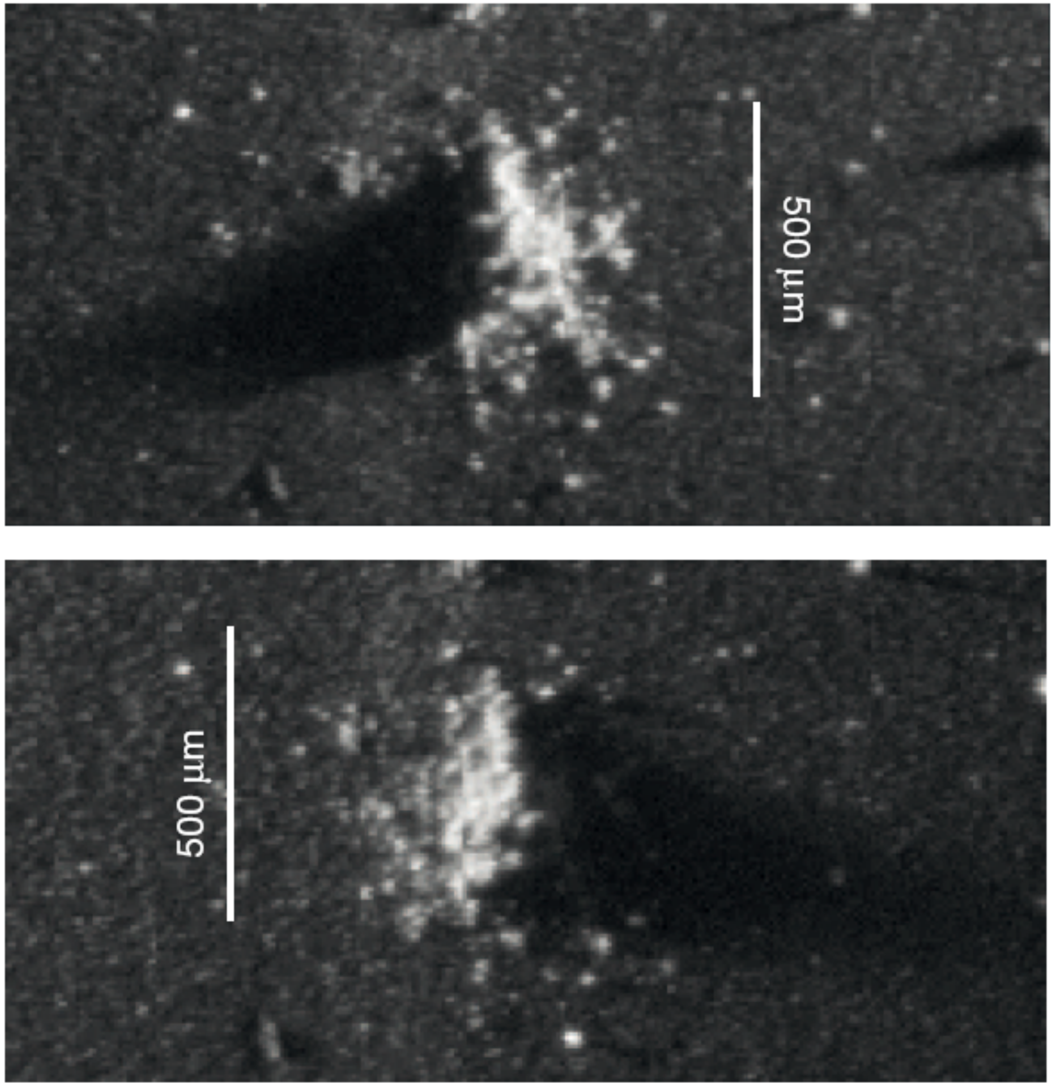


Fig. An example of a dust particle collected by Rosetta-COSIMA that crumbled into a rubble pile when collected. The particle was collected at a nucleus distance of 10–20 km, between 25 and 31 October 2014, with corresponding heliocentric distance range 3.11–3.07 AU. The image was obtained with two different grazing illumination conditions (top image illuminated from the right, bottom image from the left). The brightness is presented in logarithmic scale to emphasize the shadows, which indicate that the altitude above the target reaches about 100 mm. As the particle lies 4.2mm below the centre of the collecting target, the shadows are tilted with regard to the horizontal direction.

Schulz R., Hilchenbach M. et al.: *Nature* **518** (2015), 216-218

Scientific instruments of the Philae lander

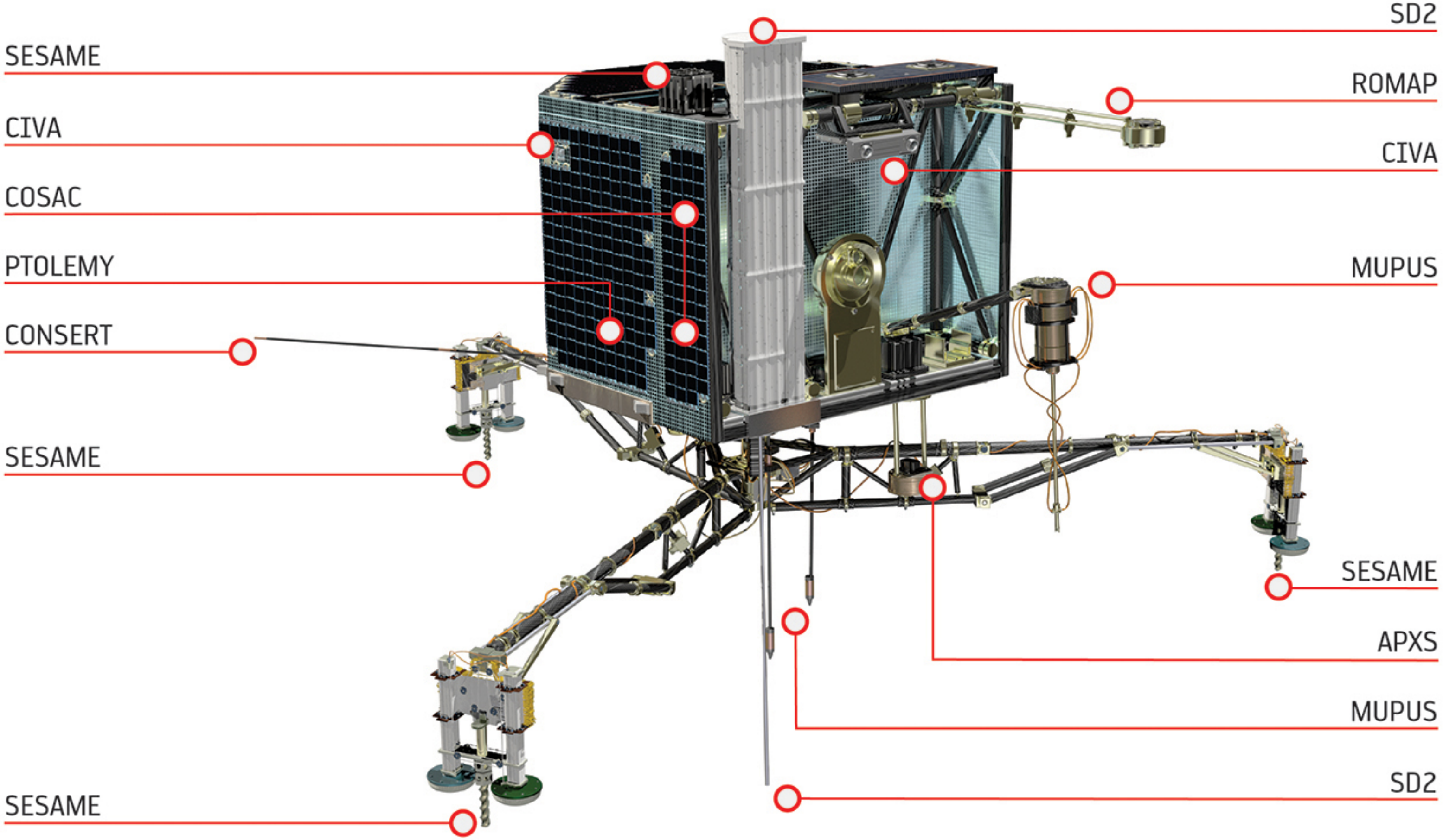
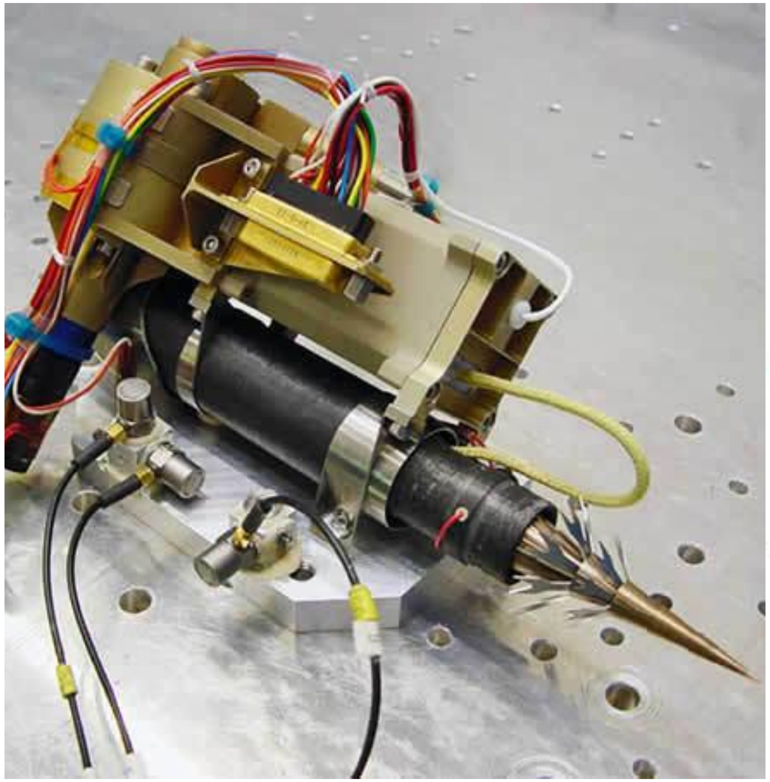
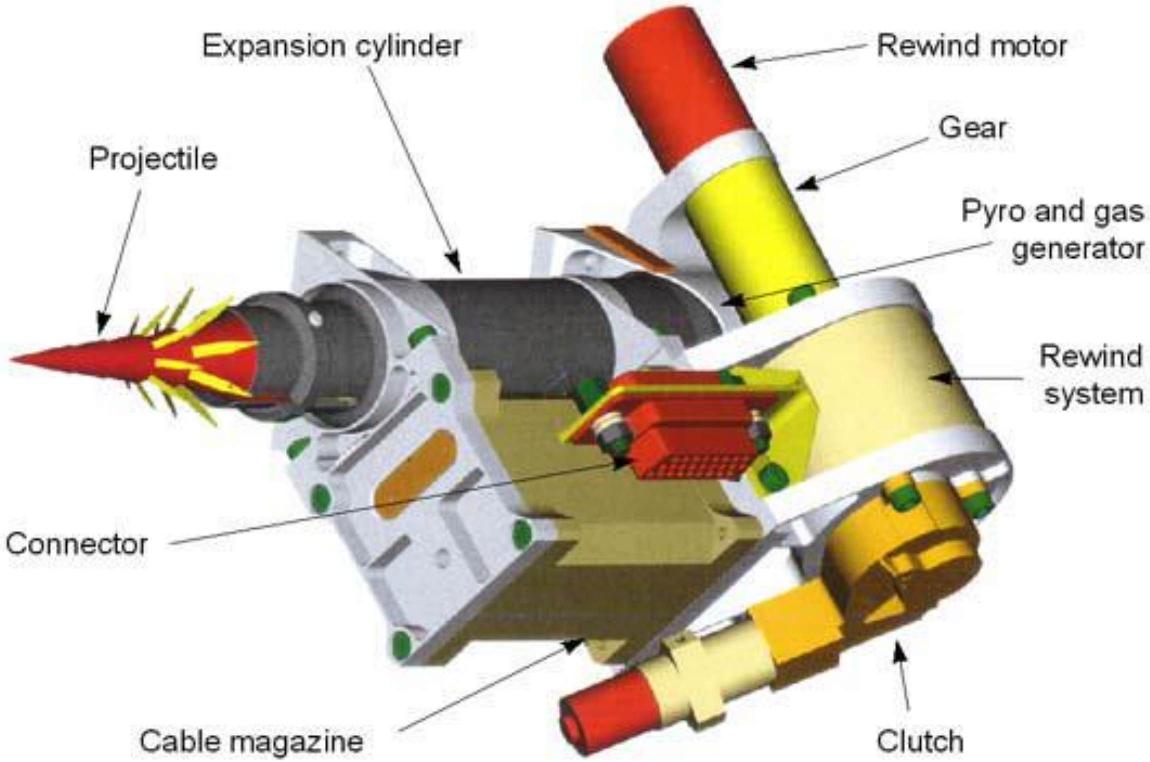


Fig. Scientific instruments of the Philae lander. This view shows the ‘balcony’, which is an experiment carrier located in front of the hood that covers the warm compartment and carries the solar generator

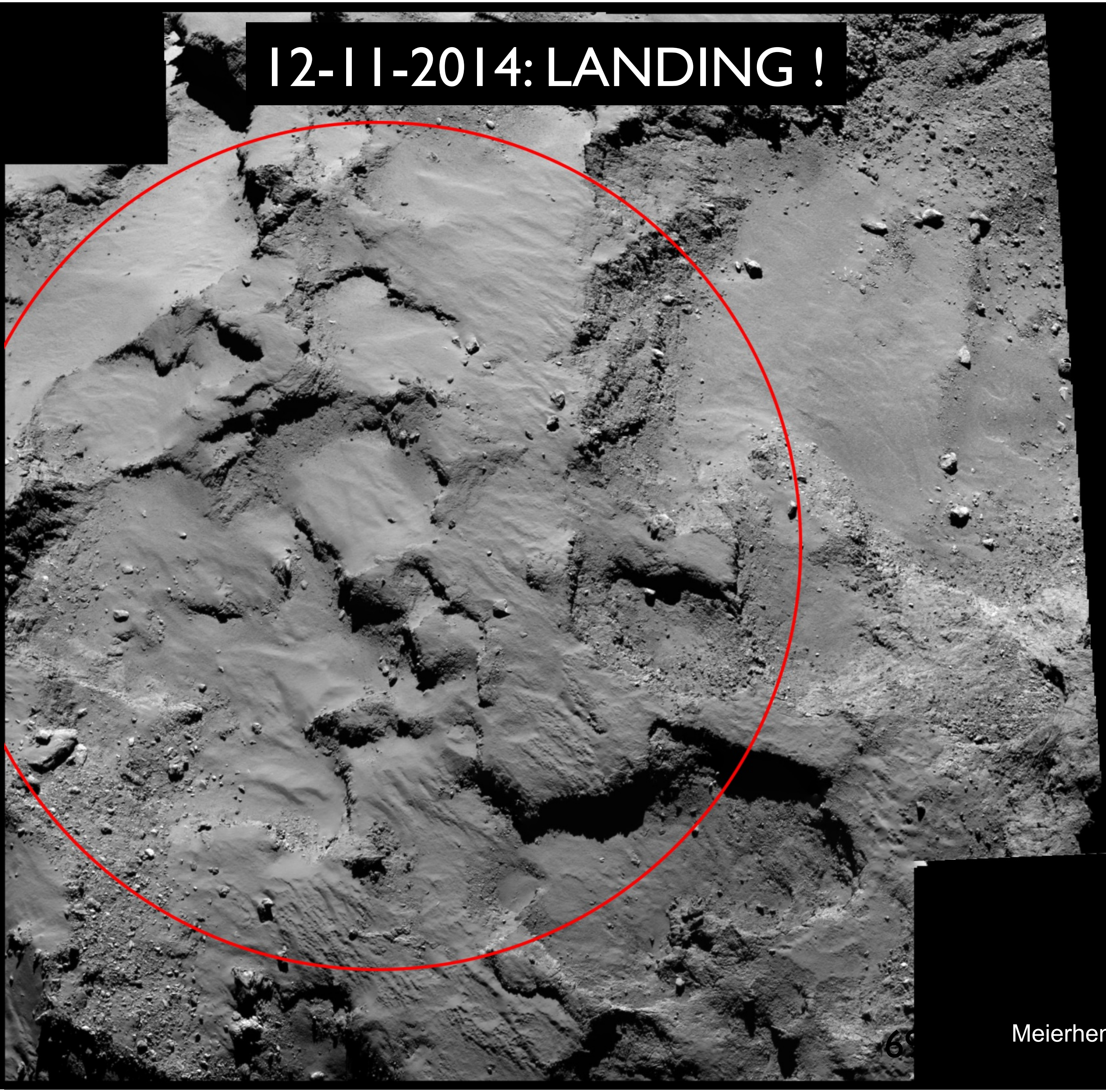
Image and scheme of Philae’s two harpoons





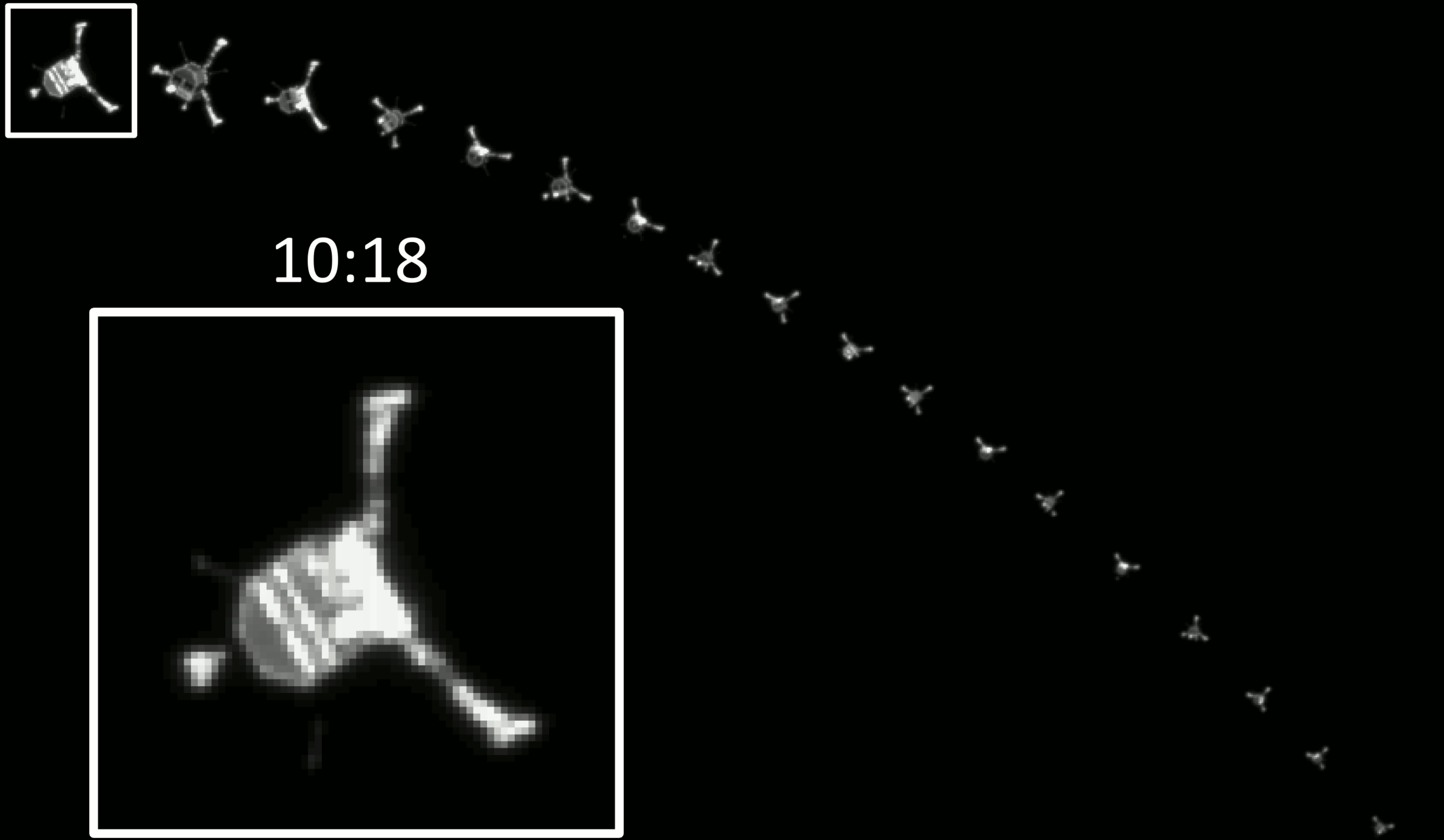
Meierhenrich U.J.: *Comets and Their Origin*. Wiley-VCH (2015)

12-11-2014: LANDING !

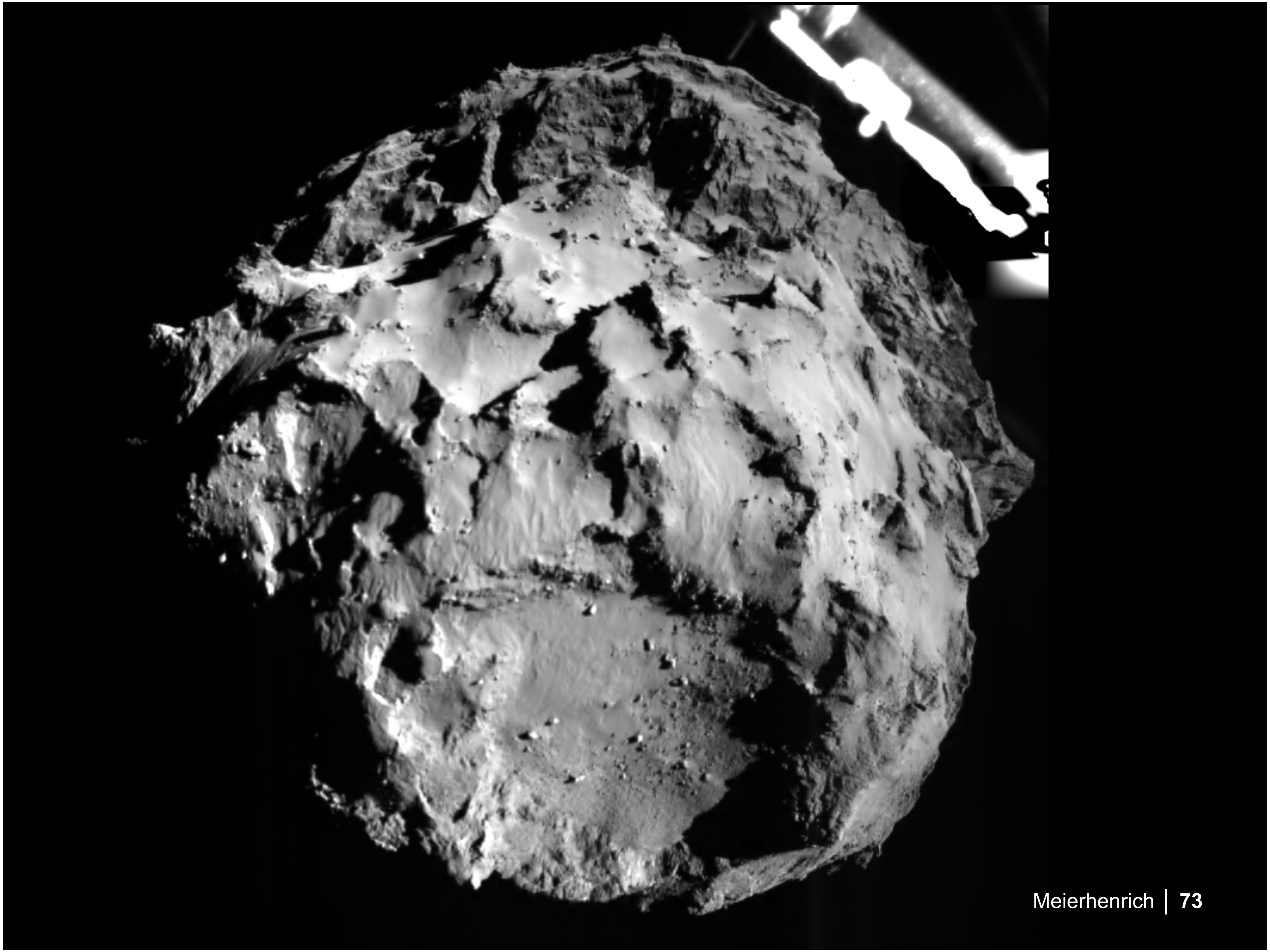


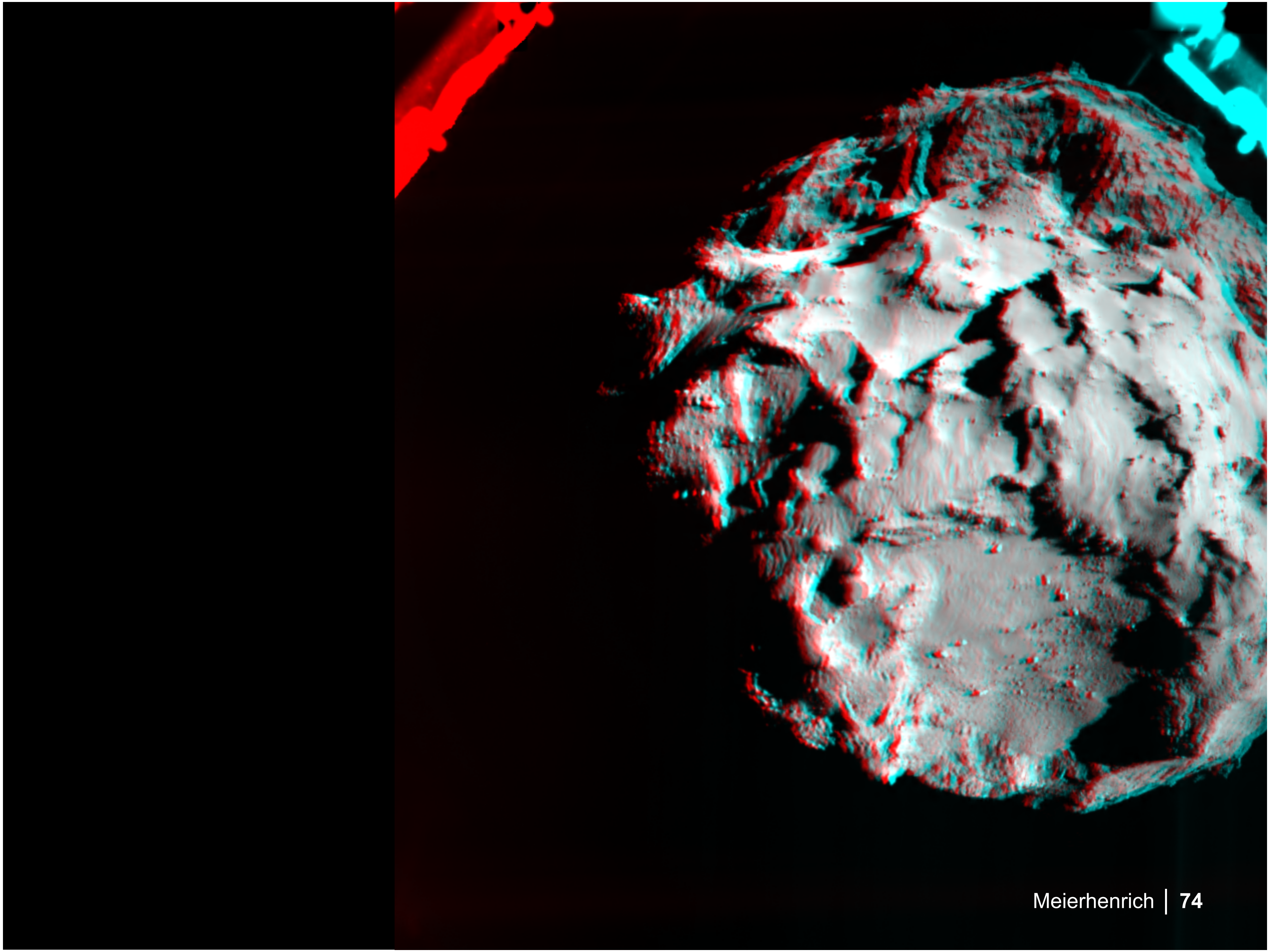
12 Novembre 2014 : Atterrissage !

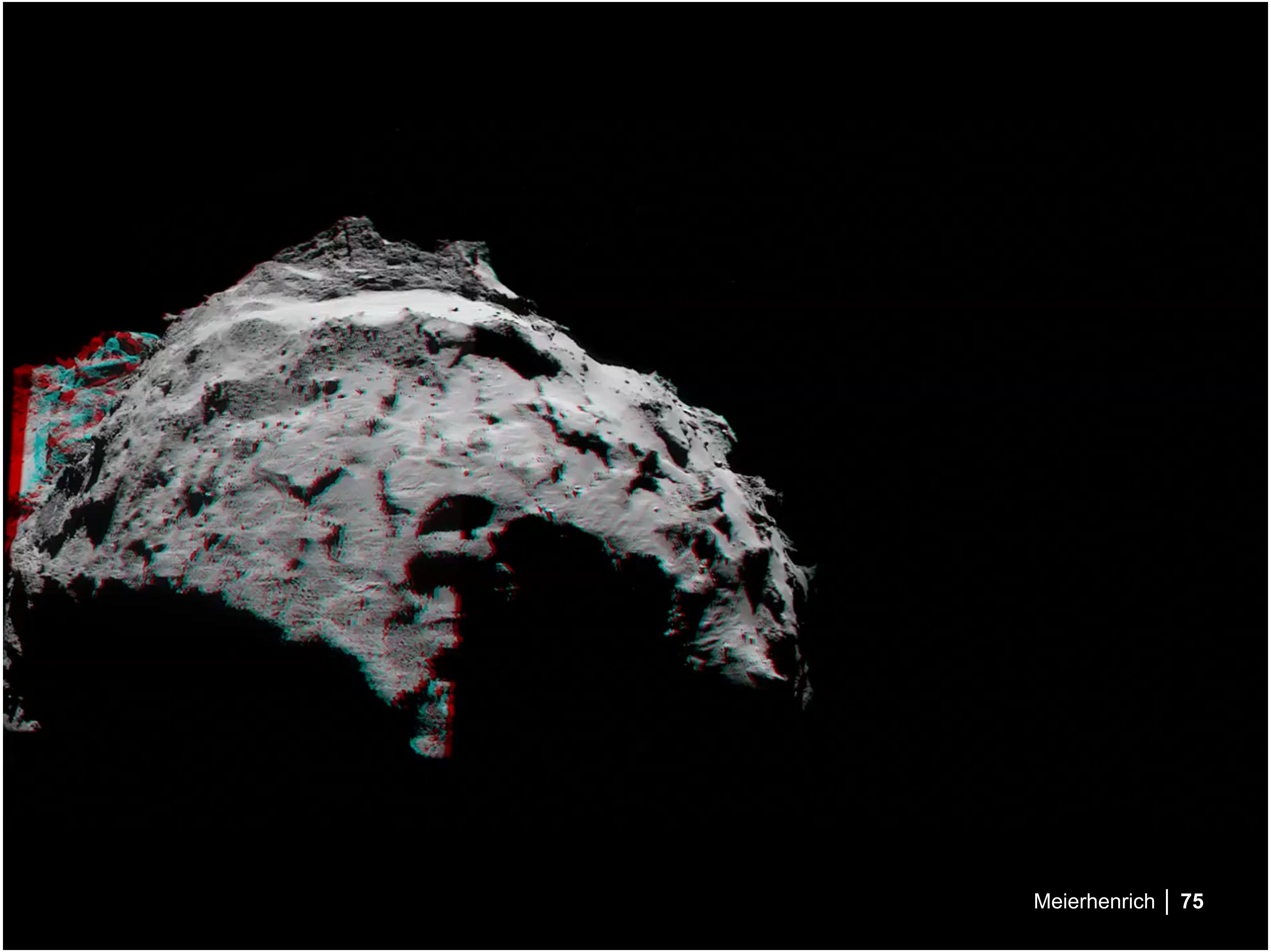
12-11-2014: LANDING !

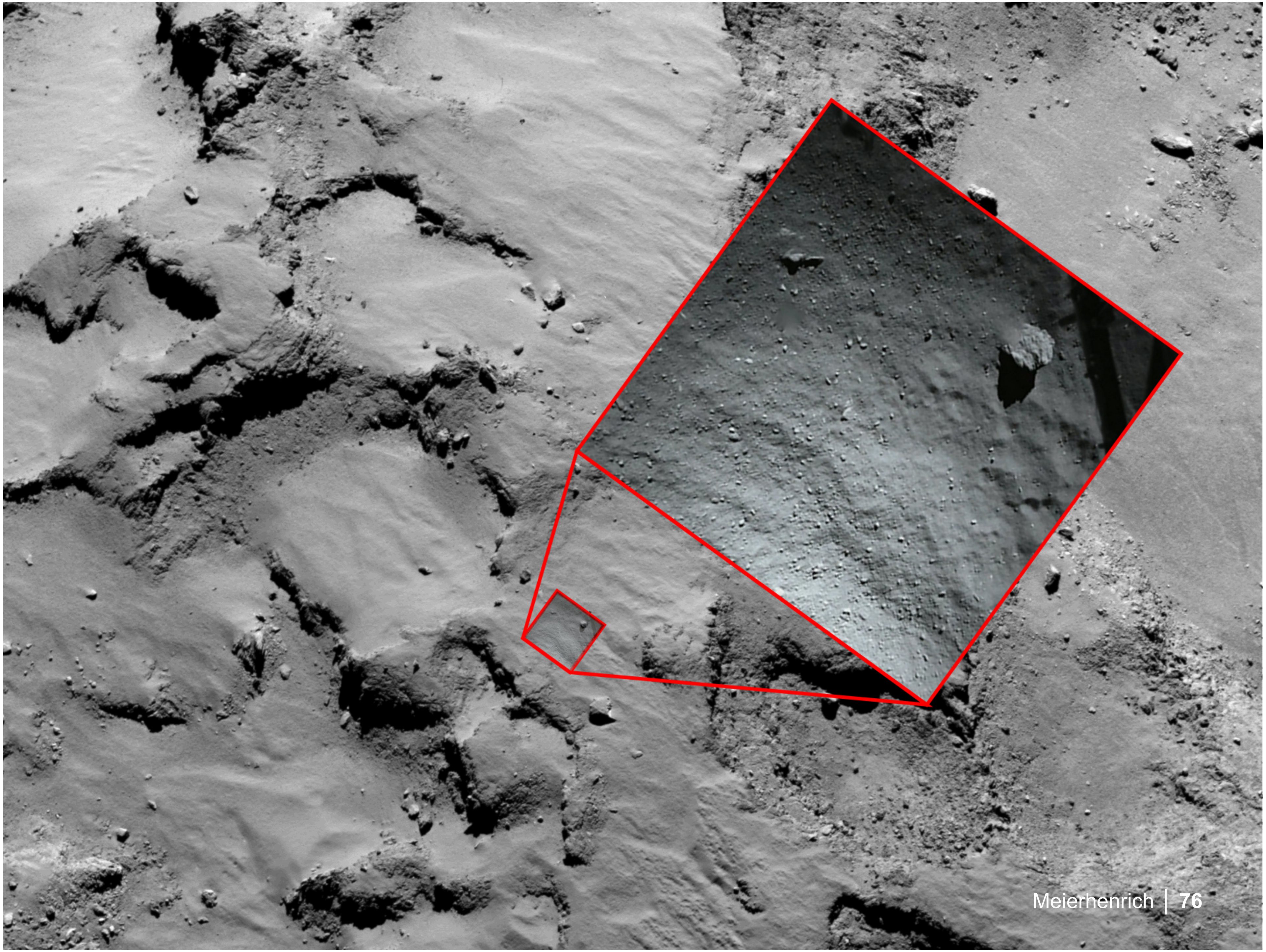


Meierhenrich comments in
Nature 515 (2014), 319-320 on Rosetta landing



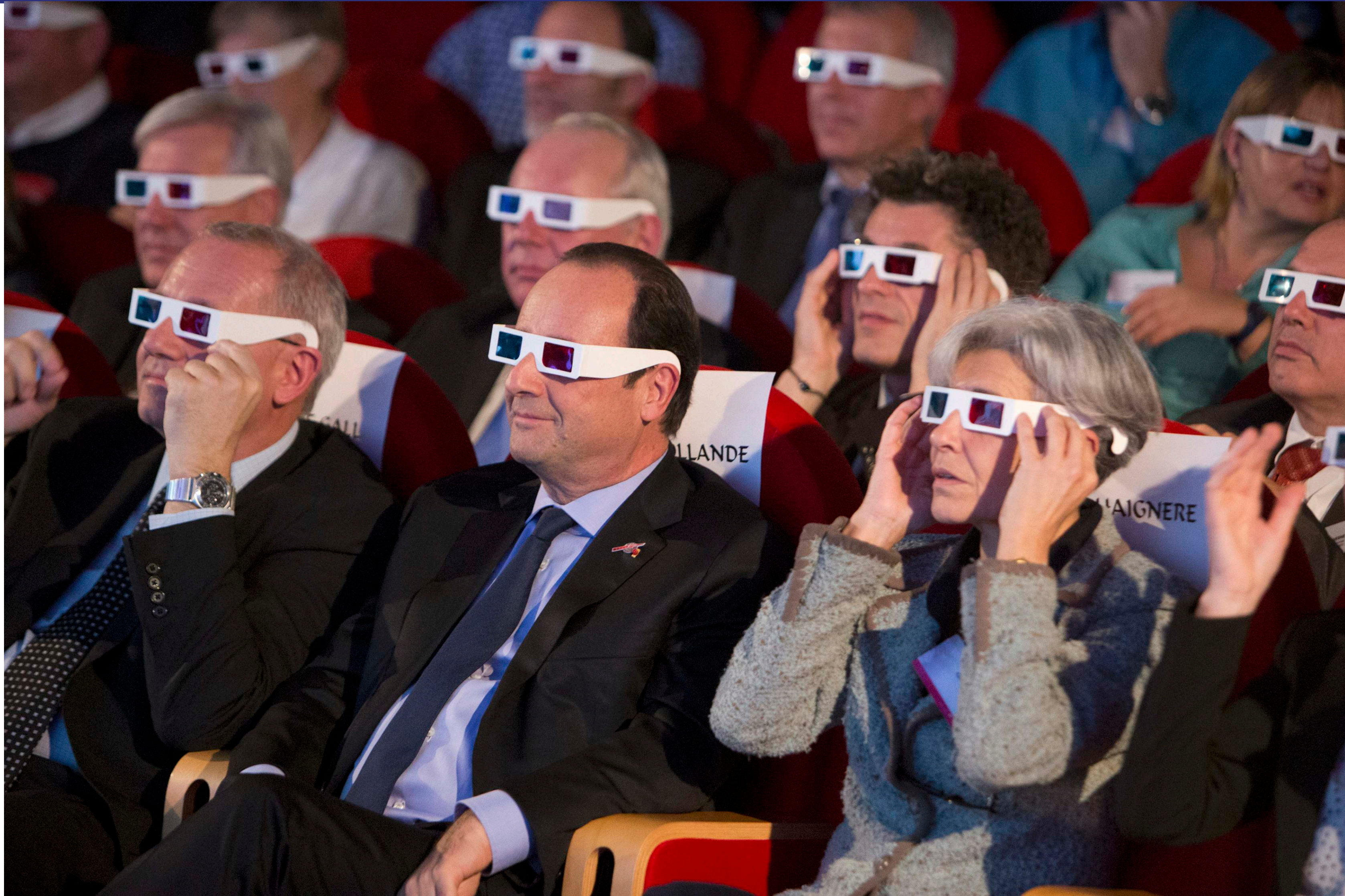






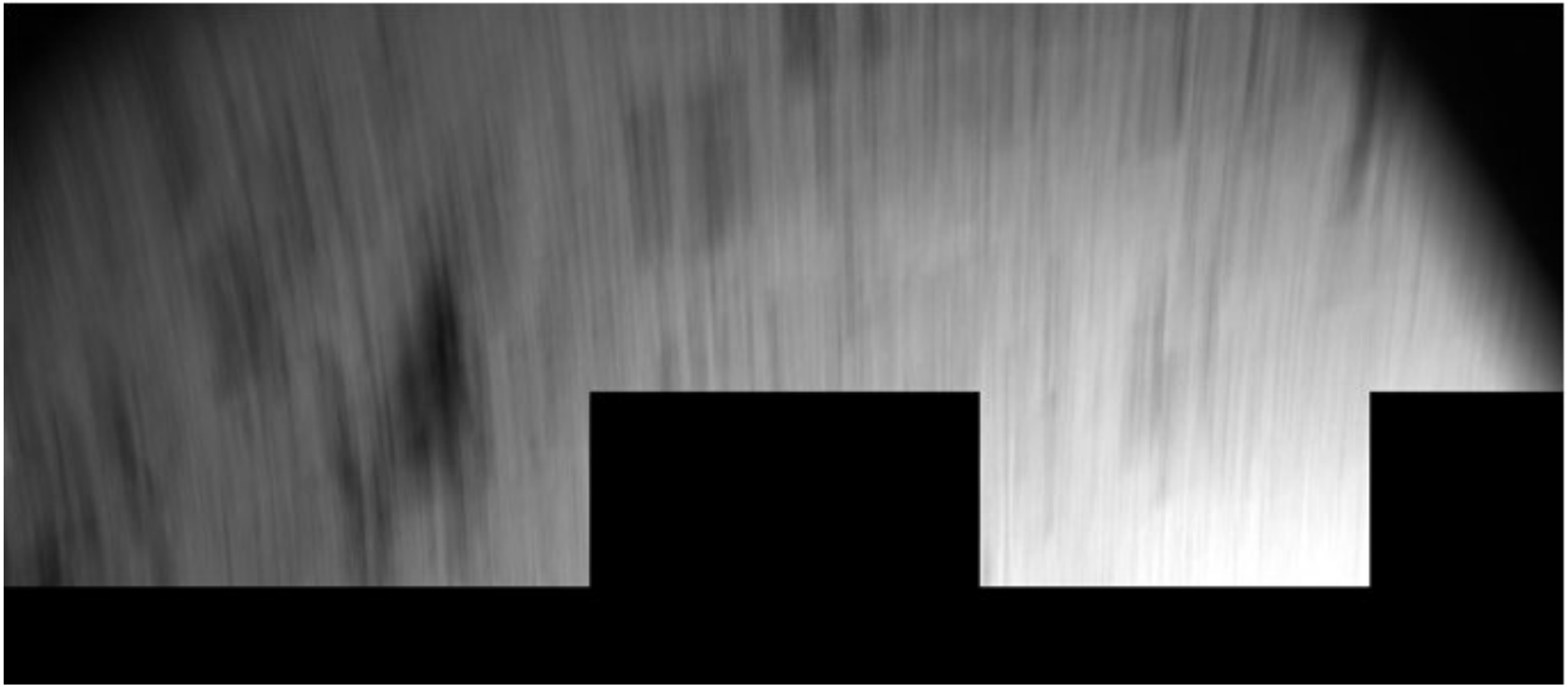
Champagne au DLR

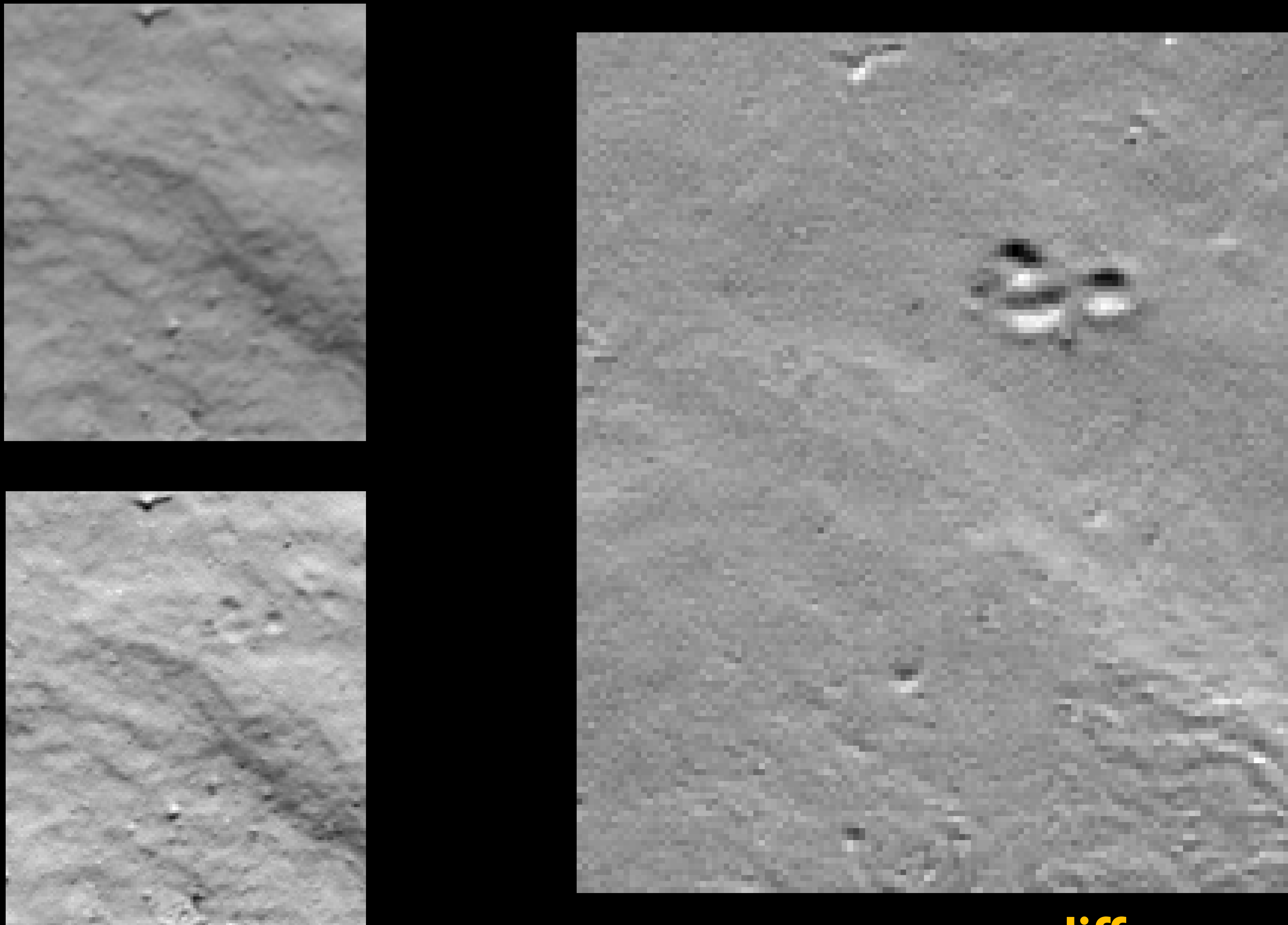
François Hollande à la Cité des Sciences



François Hollande à la Cité des Sciences

First CIVA image after landing




before
after
difference

The COSAC experiment onboard Rosetta/Philae

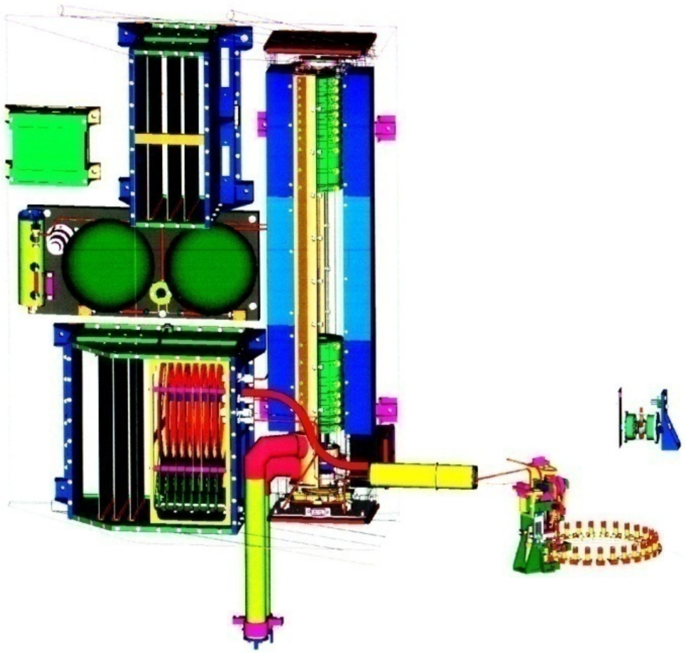


Fig. Schematic view of the GC-TCD-MS instrumentation for the COSAC experiment onboard RoLand.

Fig. The COSAC instrument includes two spherical 330-cm^3 tanks for the helium carrier gas in the center of the image, the cylindrical device that contains the calibration gas and is located to the left of them, a GC box that contains the multi-column gas chromatograph below, and the linear TOF-MS, which is mounted vertically on the right with the ion source on the bottom and the multi-sphere plate detector on the top. Image credit: Fred Goesmann and the COSAC-team, Max Planck Institute for Solar System Research, Göttingen, Germany.

Goesmann, Meierhenrich et al. *Space Science Reviews* **128** (2007), 257.

Meierhenrich comments in *Nature* **505** (2014), 269-270 on Rosetta's chirality experiment

COSAC opening of venting pipes

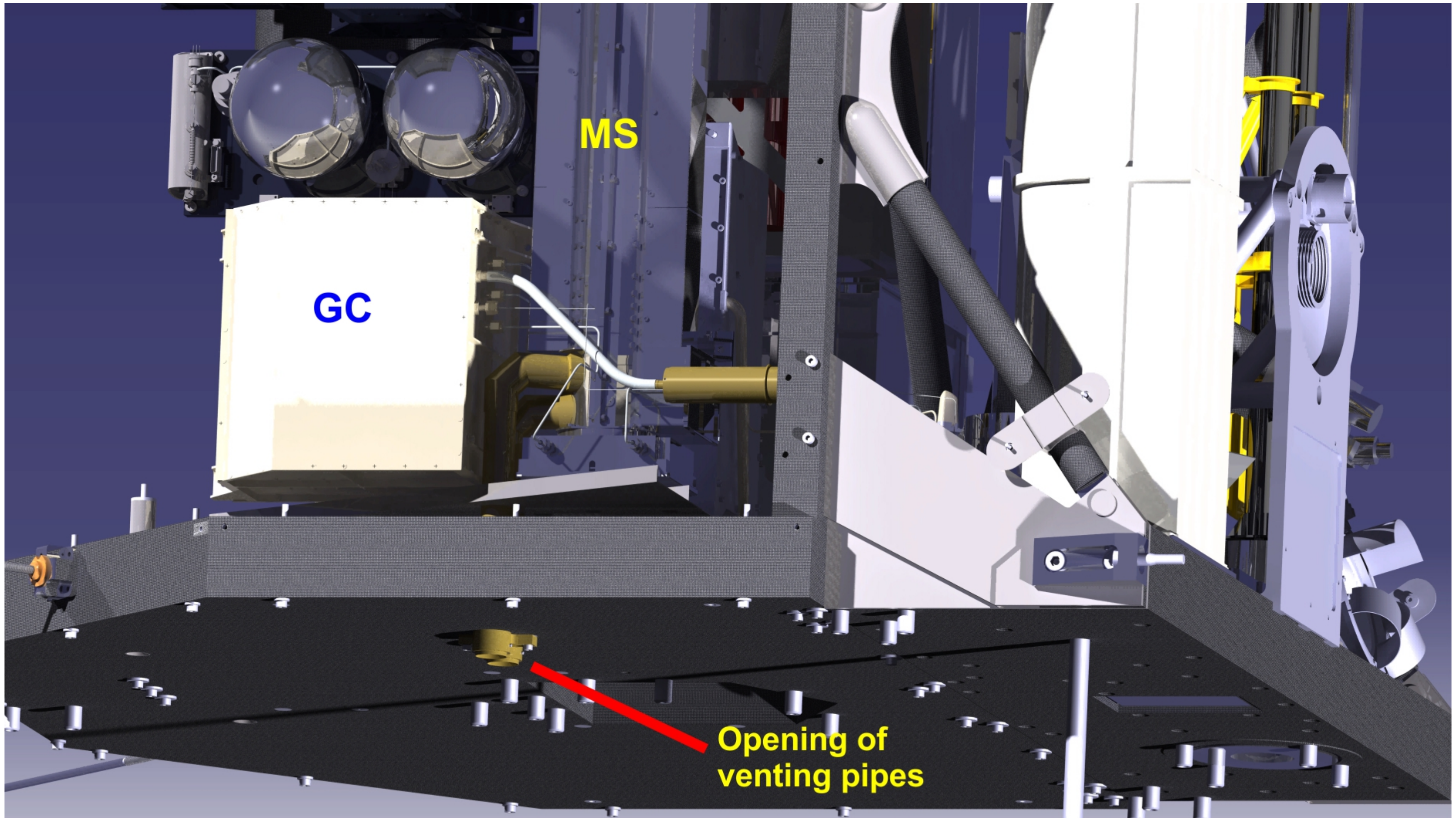
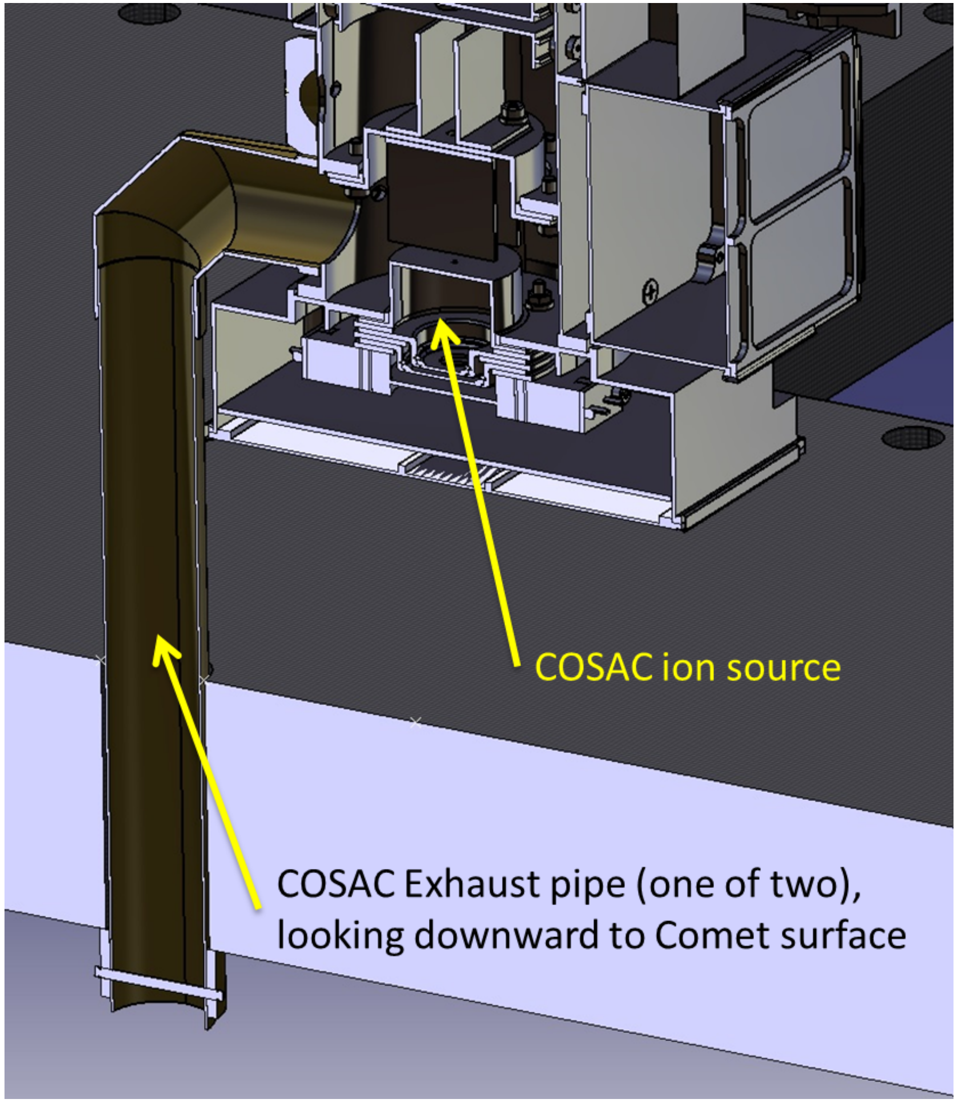


Fig. Lander body including COSAC elements and the venting pipes. The openings of the pipes are at the baseplate, pointing “downwards so that ejected material from the surface could easily enter. The grains would then stick somewhere on the inside surfaces of the pipes, where temperatures were around 12°-15°C.

Goesmann, Meierhenrich et al., *Science* **349** (2015), aab0689

Cross section of the COSAC exhaust

Fig. Cross section of the COSAC exhaust; the image shows one of the exhaust tubes in cross section (19 mm inner diameter) where cometary dust could have entered. It also shows the geometry of the ion source of the mass spectrometer.



Goesmann, Meierhenrich et al., *Science* **349** (2015), aab0689

Mass spectra taken by COSAC in MS-only mode

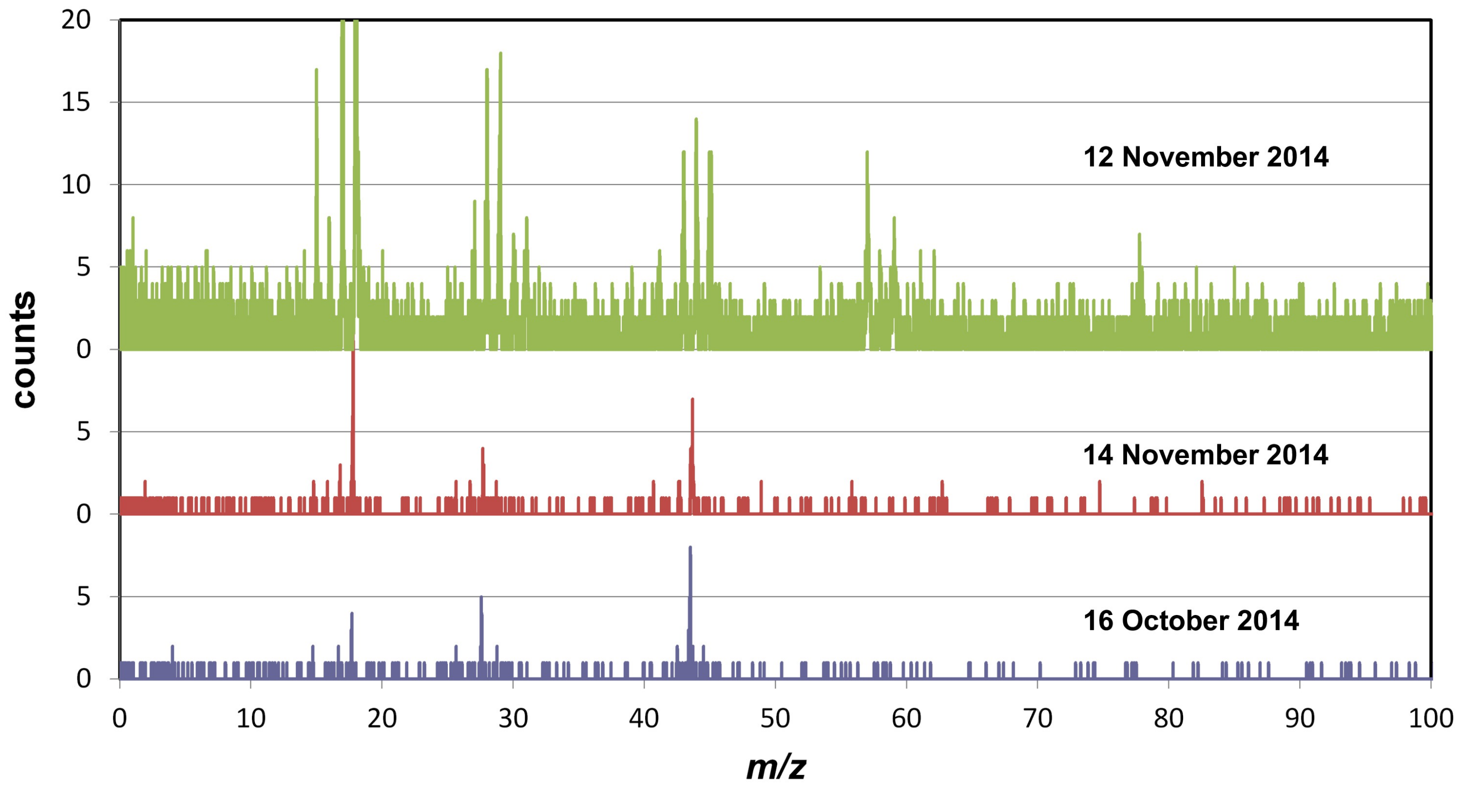


Fig. Top (green): spectrum taken 25 minutes after first touchdown; the *m*/*z* 18 peak reached a height of 330 counts, but the spectrum is truncated to show smaller peaks more clearly; middle (red): final spectrum, taken two days later at the current Philae position; bottom (blue) first spectrum, obtained in orbit 27 days prior to landing, from a distance of 10 km.

Goesmann, Meierhenrich et al., *Science* **349** (2015), aab0689

Mass spectrum taken by COSAC in MS-only mode

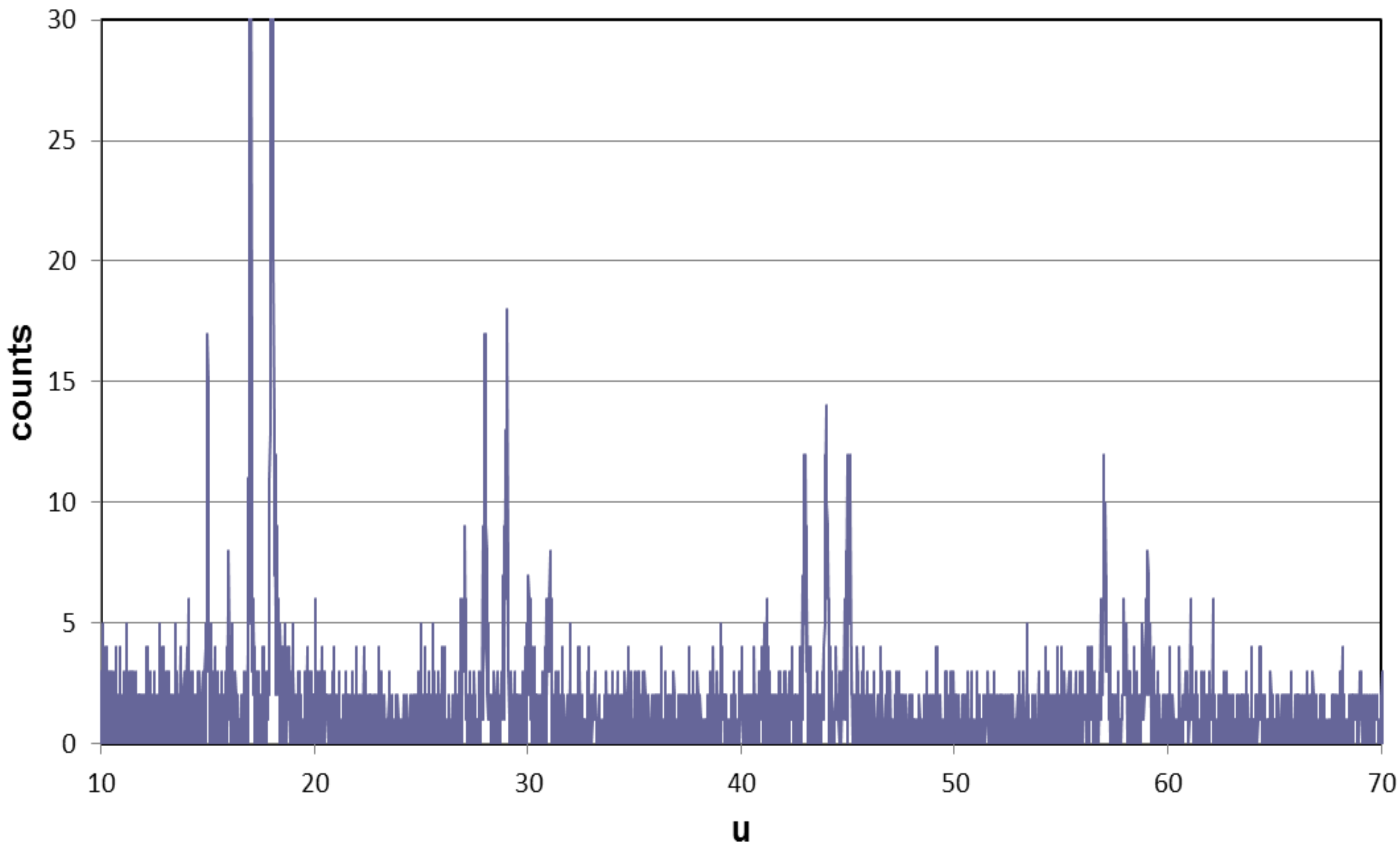


Fig. Mass spectrum taken 25 minutes after first touchdown; the *m*/*z* 18 peak reached a height of 330 counts, but the spectrum is truncated to show smaller peaks more clearly.

Goesmann, Meierhenrich et al., *Science* **349** (2015), aab0689

COSAC original mass spectrum und reconstructed fit

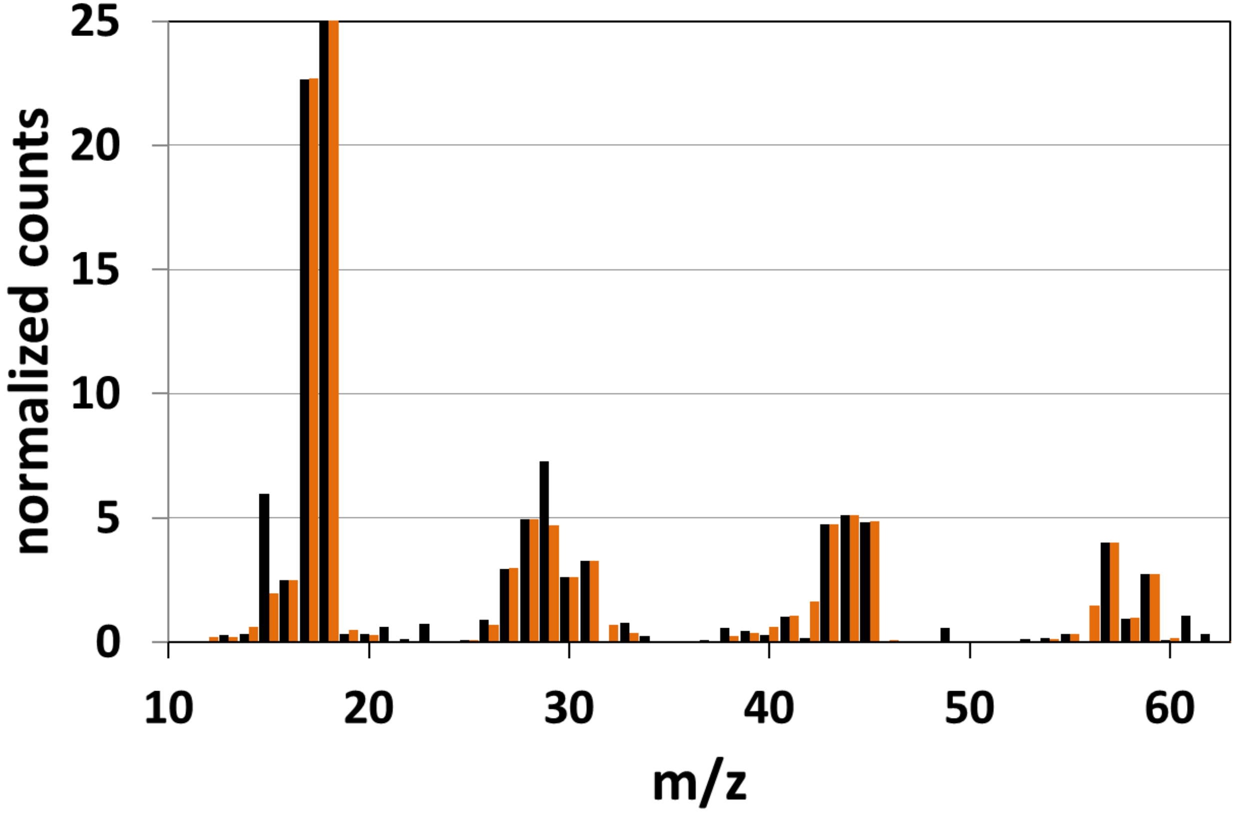


Fig. Comparison of the COSAC original mass spectrum (black bars for each integer mass) and the spectrum reconstructed from the best fit (orange bars to right of original signal). The peak heights are normalized to 100 for the *m*/*z* 18 peak (which has been truncated).

The sixteen molecules used to fit the COSAC mass spectrum

Name	Formula	Molar mass [u]	MS fraction	Relative to water
Water	H_2O	18	80.92	100
Methane	CH_4	16	0.70	0.5
Methanenitrile (Hydrogen cyanide)	HCN	27	1.06	0.9
Carbon monoxide	CO	28	1.09	1.2
Methylamine	CH_3NH_2	31	1.19	0.6
Ethanenitrile (Acetonitrile)	CH_3CN	41	0.55	0.3
Isocyanic acid	HNCO	43	0.47	0.3
Ethanal (Acetaldehyde)	CH_3CHO	44	1.01	0.5
Methanamide (Formamide)	$HCONH_2$	45	3.73	1.8
Ethylamine	$C_2H_5NH_2$	45	0.72	0.3
Isocyanomethane (Methyl isocyanate)	CH_3NCO	57	3.13	1.3
Propanone (Acetone)	CH_3COCH_3	58	1.02	0.3
Propanal (Propionaldehyde)	C_2H_5CHO	58	0.44	0.1
Ethanamide (Acetamide)	CH_3CONH_2	59	2.20	0.7
2-Hydroxyethanal (Glycolaldehyde)	CH_2OHCHO	60	0.98	0.4
1,2-Ethanediol (Ethylene glycol)	$CH_2(OH)CH_2(OH)$	62	0.79	0.2

Goesmann, Meierhenrich et al., *Science* **349** (2015), aab0689

Generalized formation scheme of 67P-compounds identified by COSAC

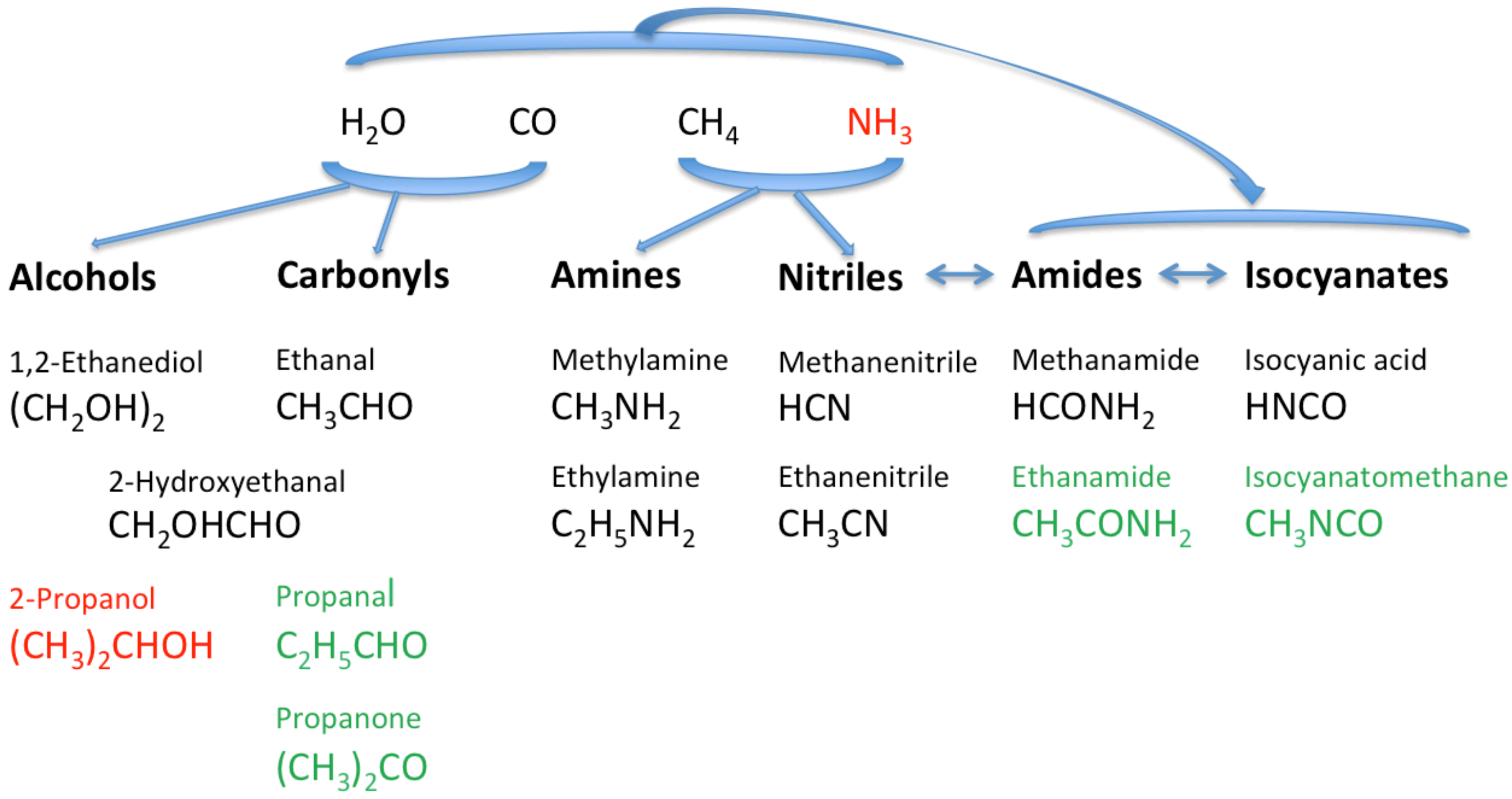
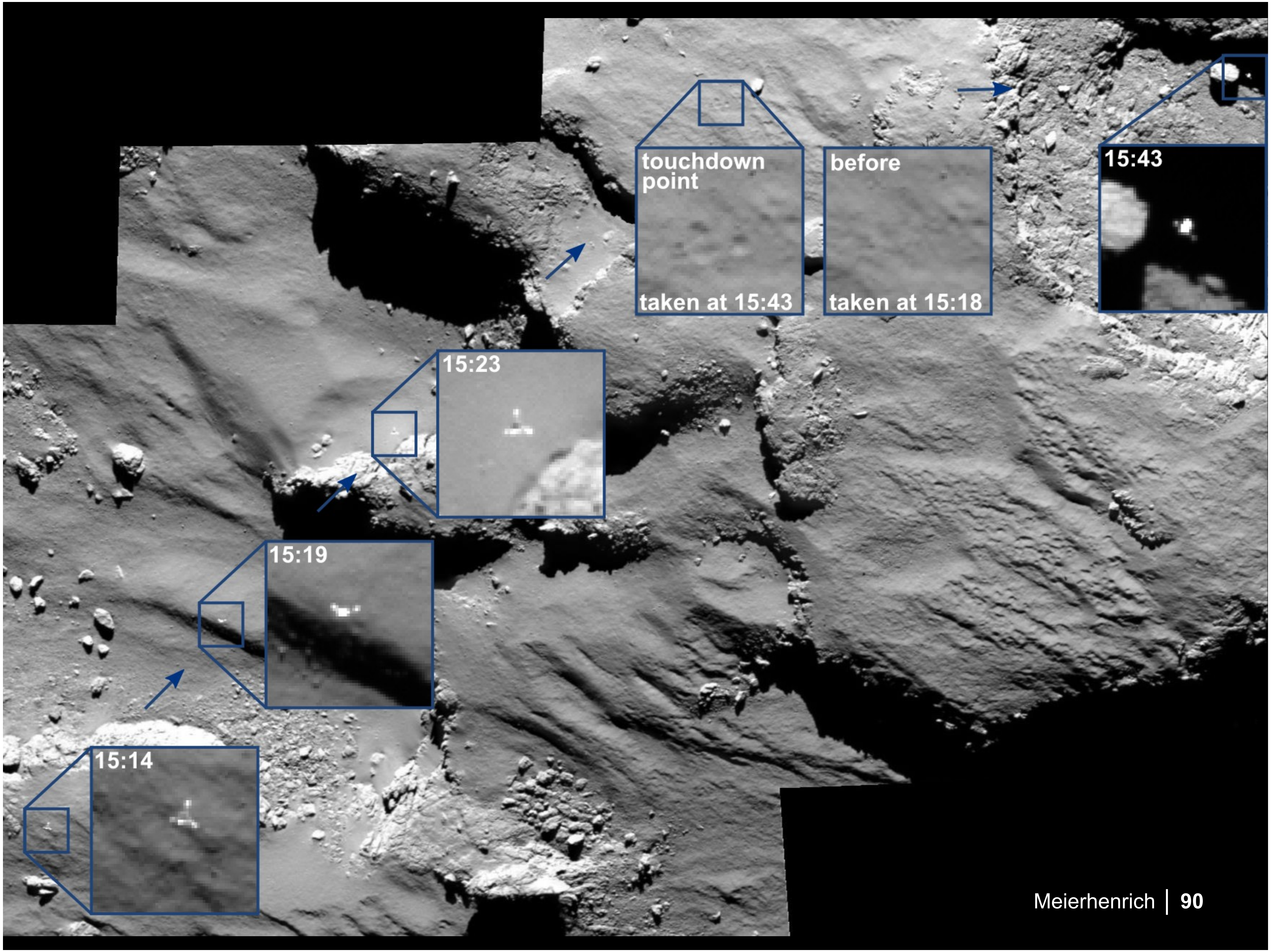
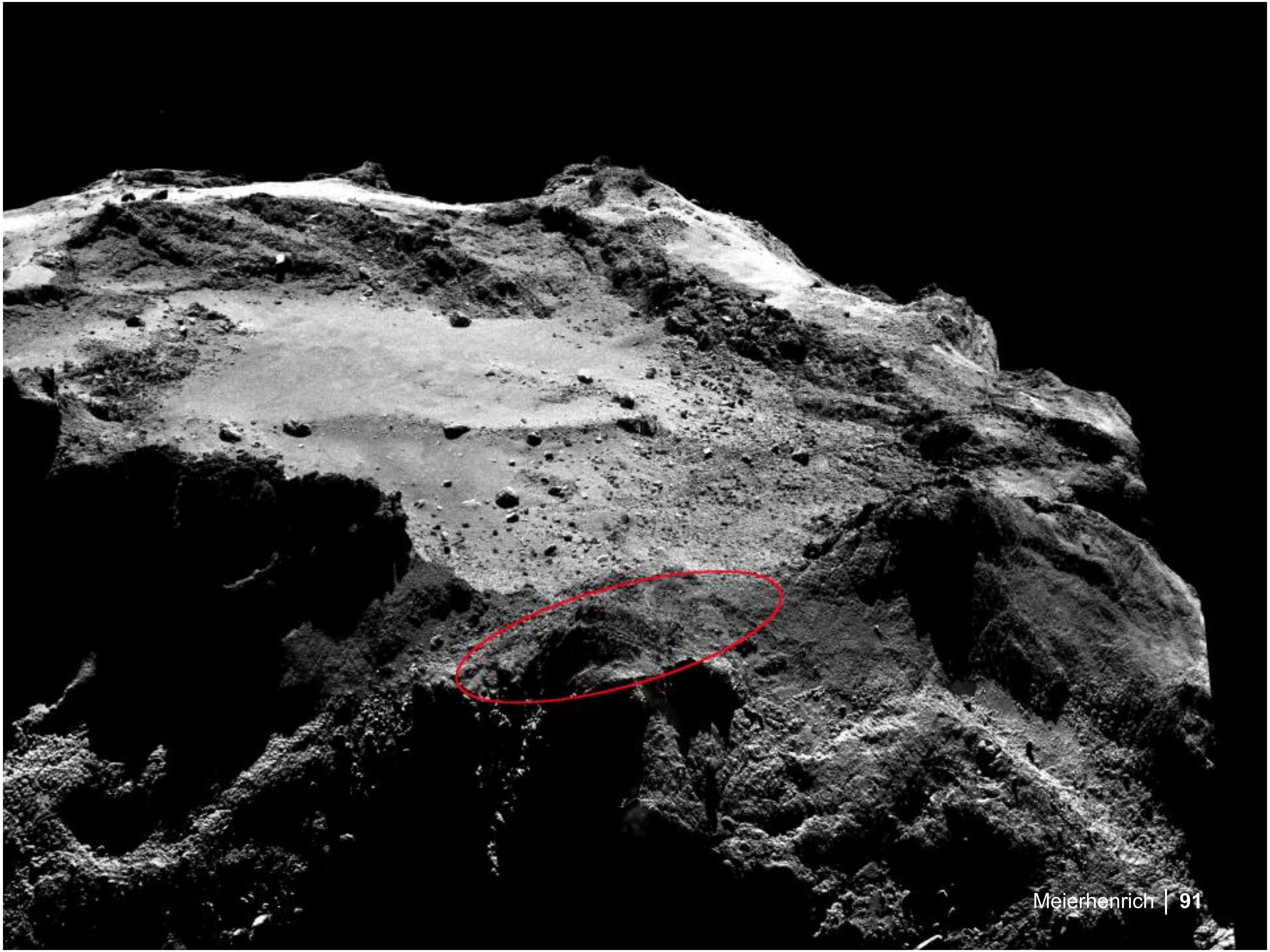
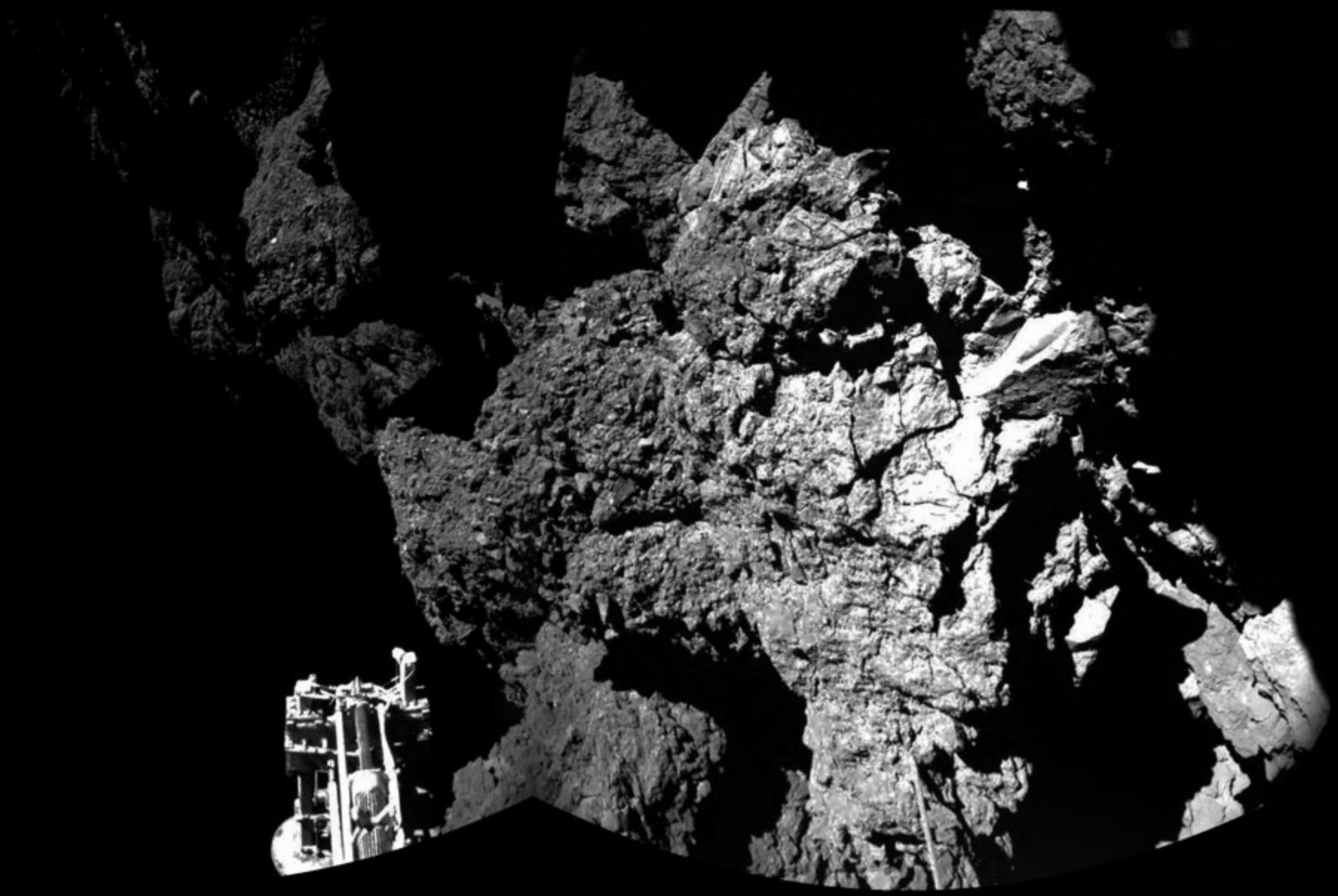


Fig. Possible formation pathways of COSAC compounds. Species in red not confidently identified, species in green reported for the first time in comets by COSAC.

Goesmann, Meierhenrich et al., *Science* **349** (2015), aab0689


touchdown point
taken at 15:43
before
taken at 15:18
15:43
15:23
15:19
15:14



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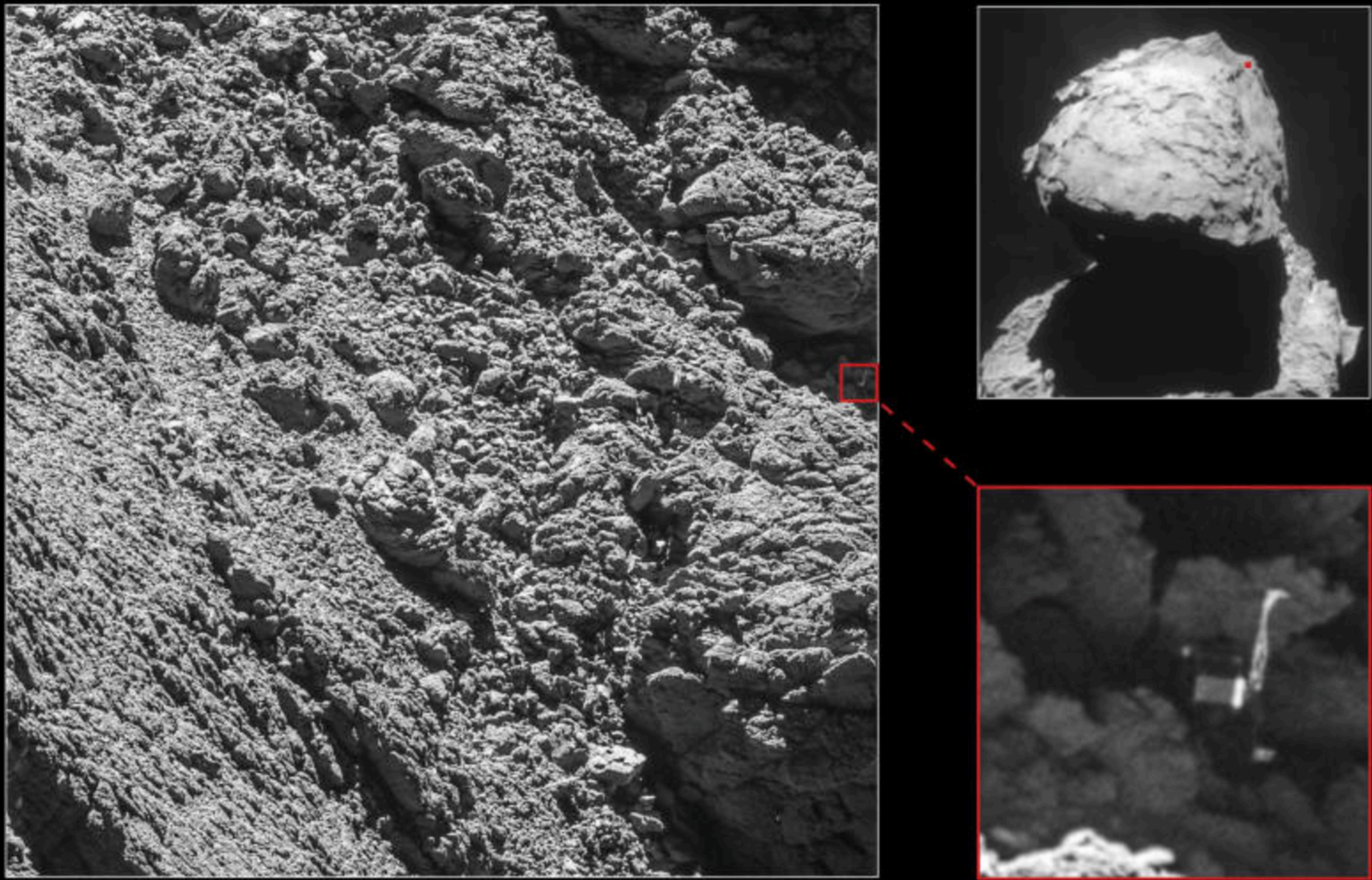
Philae's first look
Reporting back from the surface of comet 67P



COSAC onboard Rosetta's Philae Lander

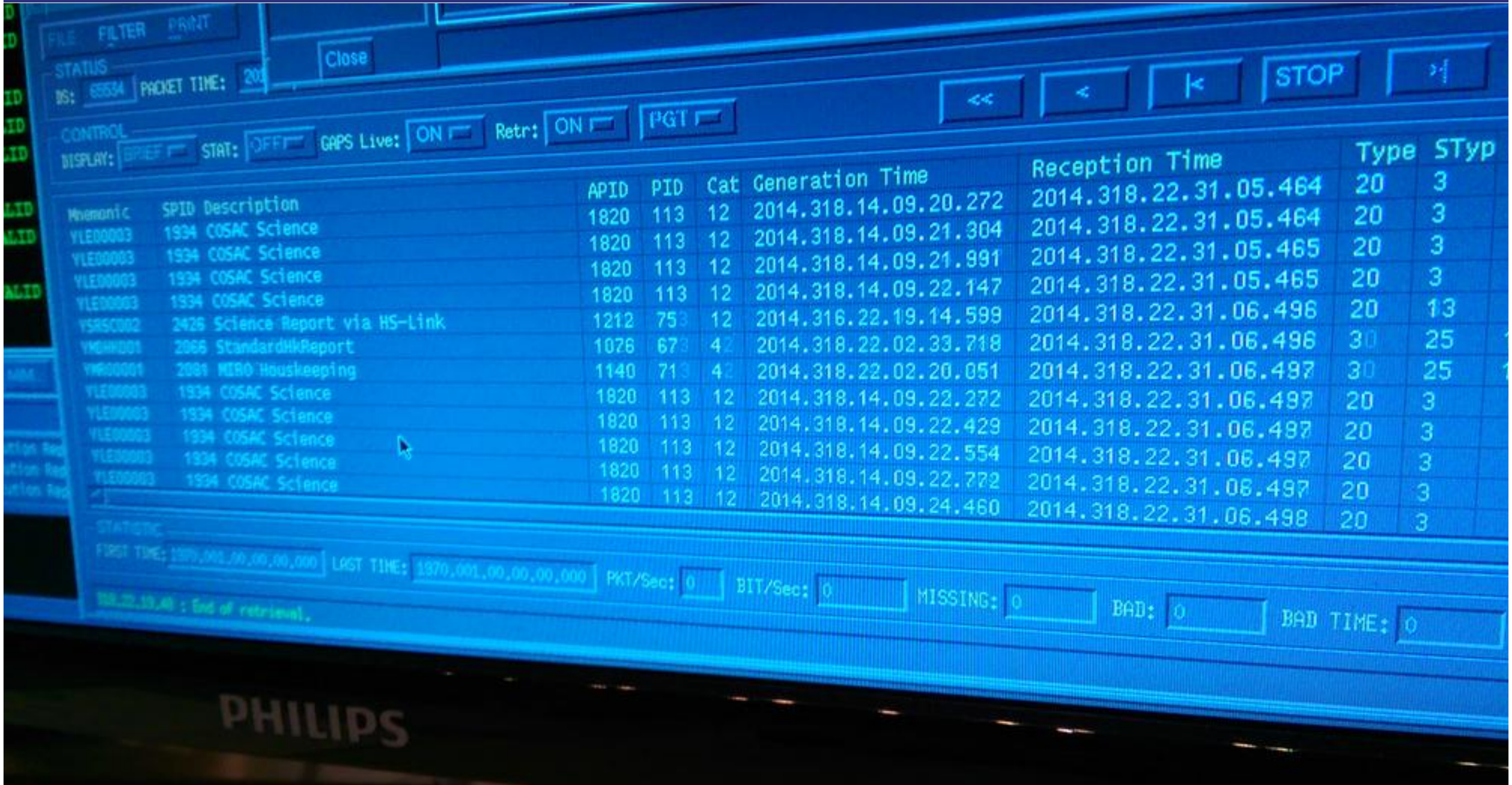
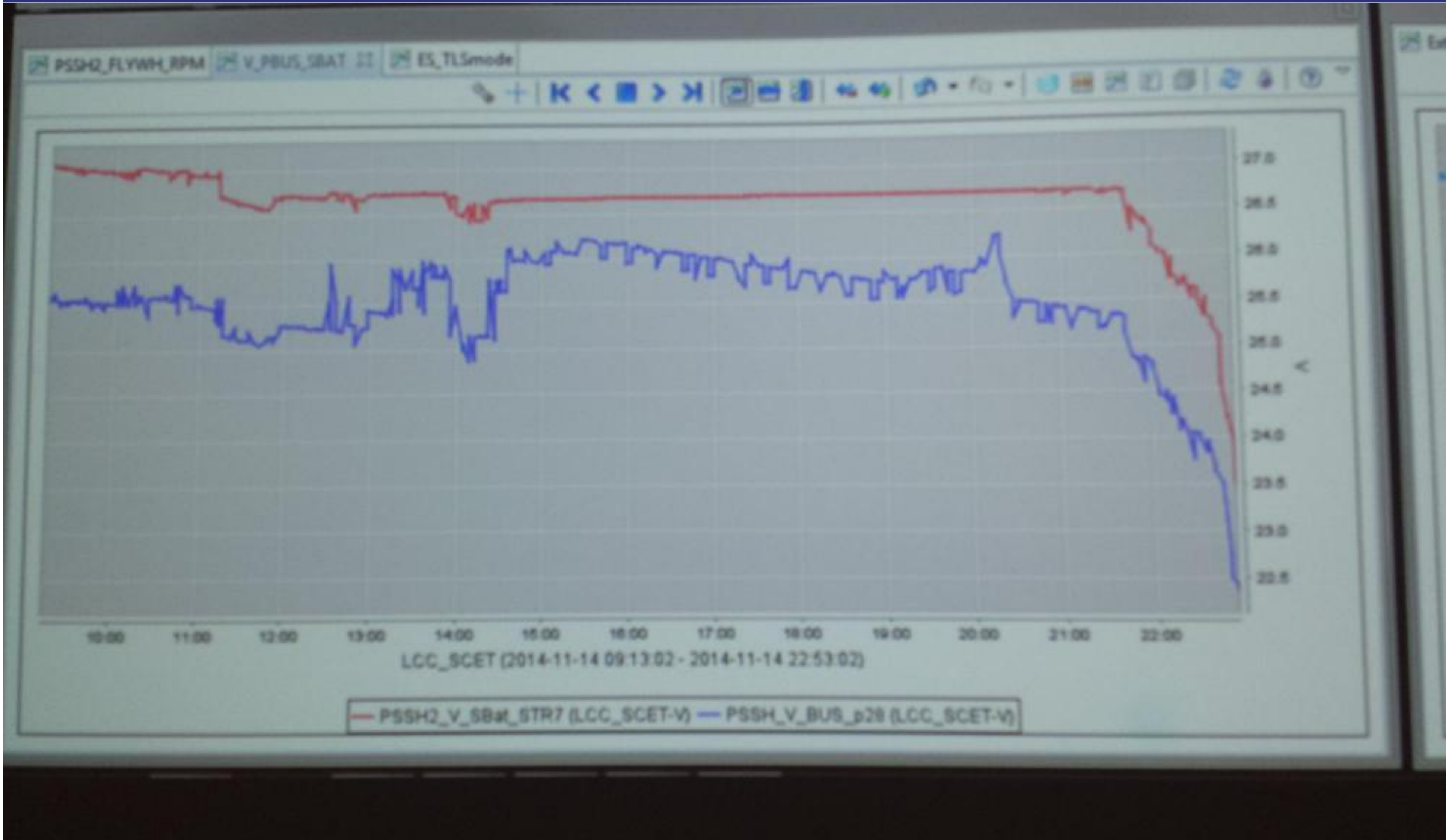


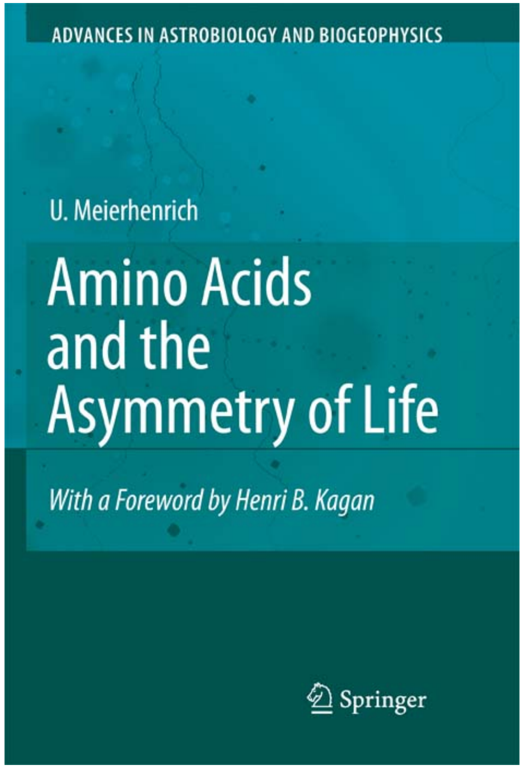
Fig. COSAC sequences come in at the ESA control center. A gas chromatogram was recorded and successfully transmitted along with 427 mass spectra.

COSAC onboard Rosetta's Philae Lander



Meierhenrich comments in *Nature* **552** (2015), 263-264 on Philae wake-up

Meierhenrich Monographies



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Foreword by Henri Kagan

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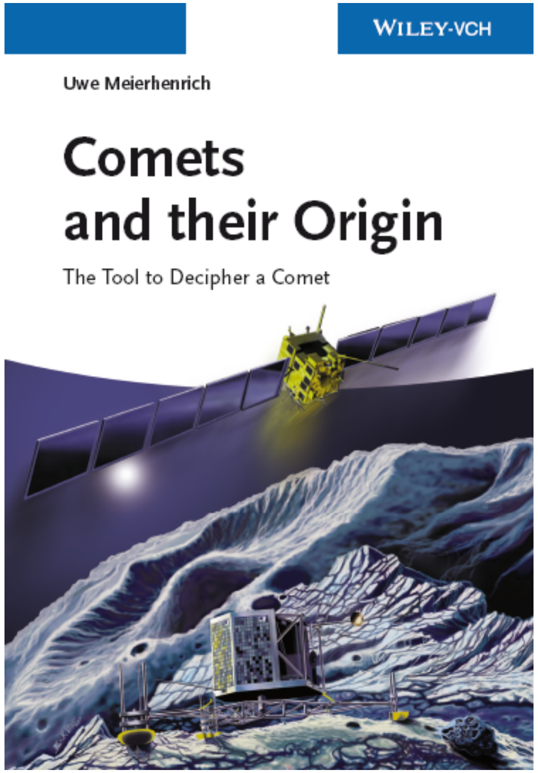

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Forewords by A'Hearn & Schwehm

Advertised in *Science*

Meierhenrich: *Amino Acids and the Asymmetry of Life*. Springer (2008)
Meierhenrich: *Comets and their Origin*, Wiley-VCH (2015)

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