
Image: David Monniaux, Wikipedia

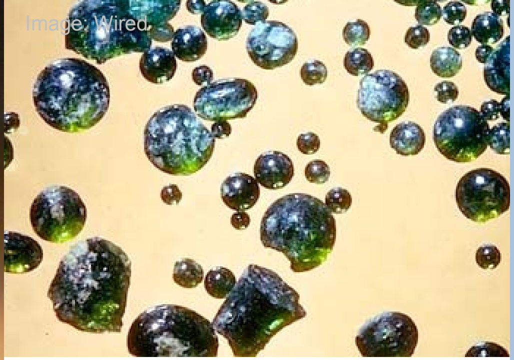


Image: Wired

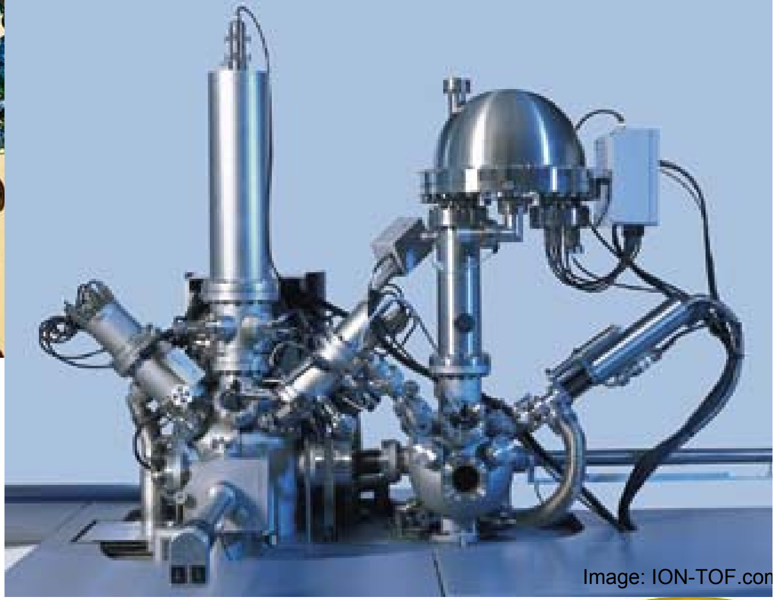


Image: ION-TOF.com

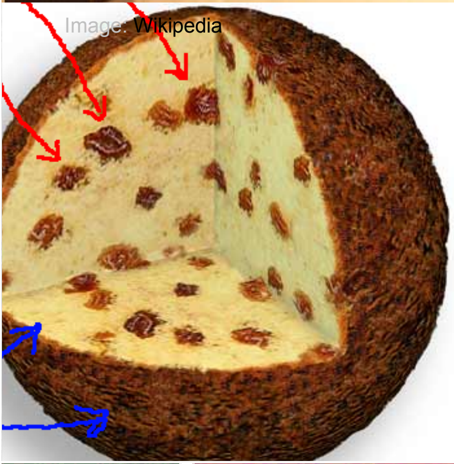


Image: Wikipedia

The Splendors (and no Miseries) of Mass Spectrometry

Theodore Alexandrov

Center for Industrial Mathematics,
University of Bremen

Winterseminar,
Alghero, Sardinia, Italy
23 Sep 2009

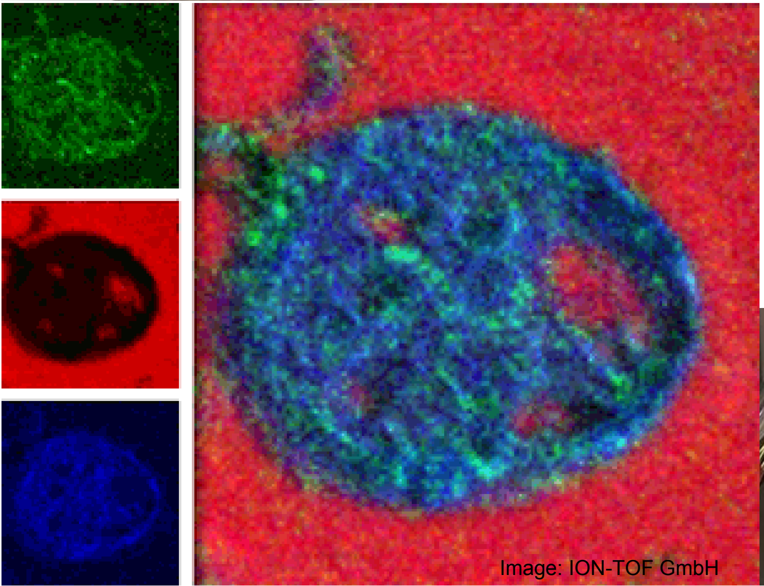
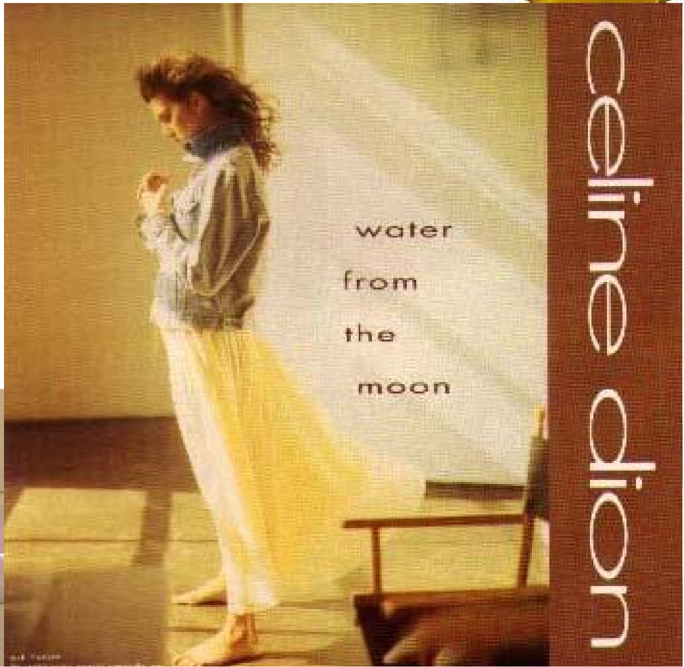


Image: ION-TOF GmbH


Image: www.electrotherapymuseum.com



Did you know that?

Mass spectrometry (MS) is a technique of analytical chemistry that identifies the elemental composition of sample based on mass-to-charge ratio of charged particles.

Did you know that MS is used to

- Detect and identify the use of drugs of abuse (dopings) in athletes
- Identification of explosives and analysis of explosives in postblast residues
- Analyse suspicious powders following the post 9/11 anthrax scare
- Monitor the breath of patients by anesthesiologists during surgery
- and …

T. Rex: just a big chicken?

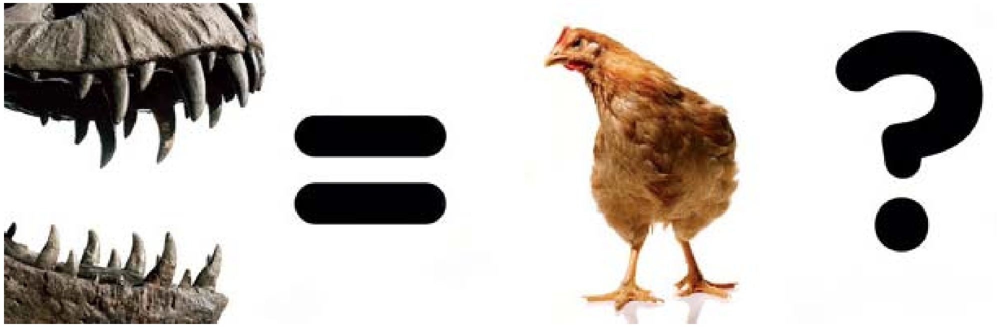
A sample of a bone of *Tyrannosaurus rex* was discovered in 2000 (sample MOR 1125)

68 million years old

Soft tissues were inside the bone

A sample was demineralized and studied in a mass-spectrometer

Several fragments were found which are very similar to collagen—the most common protein found in bones—from birds, specifically chickens!



Wired, 22.06.09 (http://www.wired.com/medtech/genetics/magazine/17-07/ff_originofspecies)

T. Rex: just a big chicken?

ore may be

optimizing
g of fossil
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according to
studies (*29*).
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Protein Sequences from Mastodon and *Tyrannosaurus Rex* Revealed by Mass Spectrometry

John M. Asara,[1,2]* Mary H. Schweitzer,[3] Lisa M. Freimark,[1] Matthew Phillips,[1] Lewis C. Cantley[1,4]

Fossilized bones from extinct taxa harbor the potential for obtaining protein or DNA sequences that could reveal evolutionary links to extant species. We used mass spectrometry to obtain protein sequences from bones of a 160,000- to 600,000-year-old extinct mastodon (*Mammut americanum*) and a 68-million-year-old dinosaur (*Tyrannosaurus rex*). The presence of *T. rex* sequences indicates that their peptide bonds were remarkably stable. Mass spectrometry can thus be used to determine unique sequences from ancient organisms from peptide fragmentation patterns, a valuable tool to study the evolution and adaptation of ancient taxa from which genomic sequences are unlikely to be obtained.

Obtaining genome sequences from a number of taxa has dramatically enhanced our abilities to study the evolution and adaptation of organisms. However, difficulties in the acquisition of DNA or RNA from ancient extinct taxa limit the ability to examine molecular evolution. Recent advances in mass spectrometry (MS) technologies have

Early history of MS

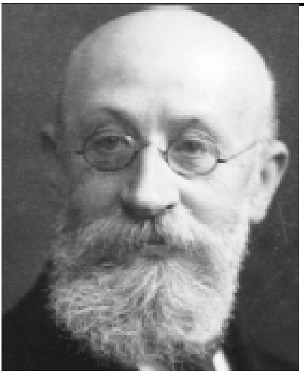
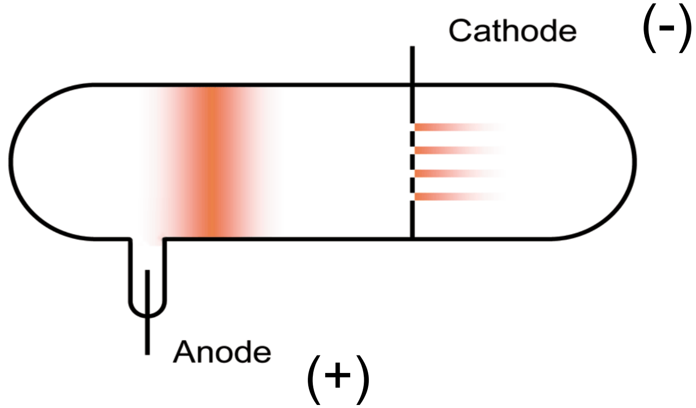


Image: Michael Hedenus, *Der Komet in der Entladungsröhre*

Eugen Goldstein (Potsdam)

1886: invented Kanalstrahlen (anode/channel/positive rays)



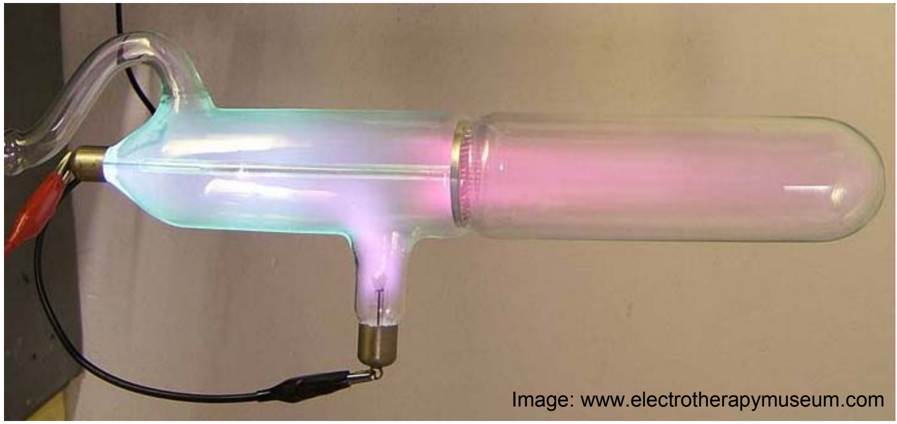


Image: www.electrotherapymuseum.com

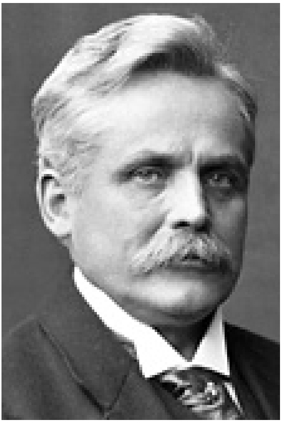


Image: Wikipedia

Wilhelm Wien (RWTH Aachen,Würzburg,Munich)

experimented with anode rays in a magnetic field
separated canal rays (ions) according to their mass-to-charge ratio

It might be expedient to “abandon the terms cathod rays, canal rays and positive light and to speak only of positive and negative particles".
Wien (1898) Ann. Physik 65, 440

1911: Nobel Prize in Physics for the work on heat radiation

Early history of MS, J.J.Thomson

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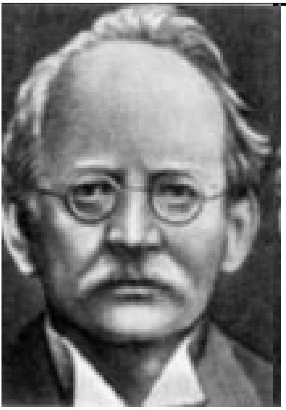
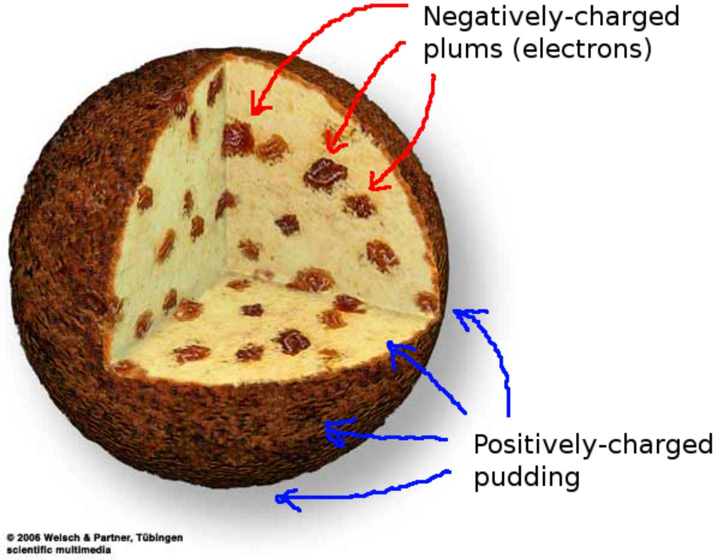


Image: http://masspec.scripps.edu

Sir Joseph John Thomson (UK,Cambridge)

Experiments with cathode rays, discovery of the electron (“corpuscles“)

“Plum pudding model of the a

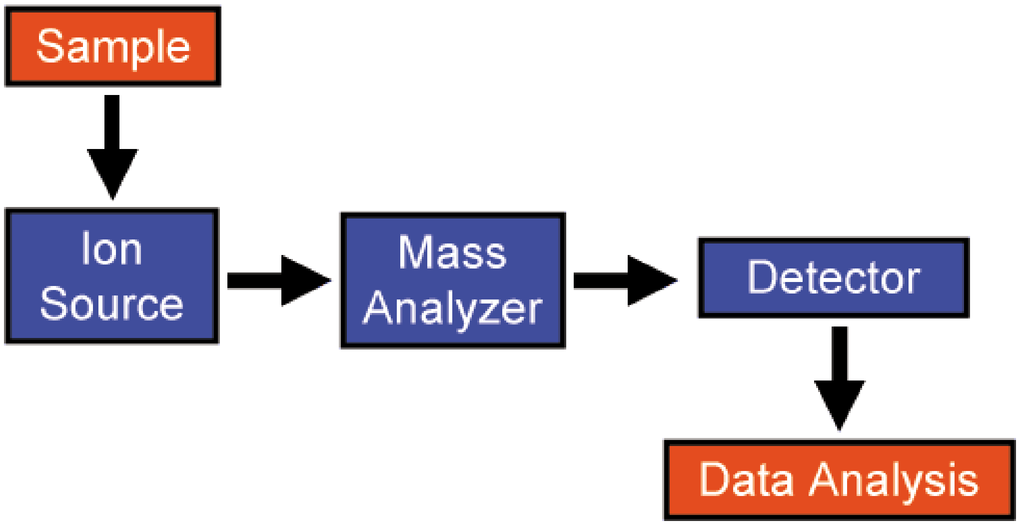


1898: Measured mass-to-charge ratio of the electrone

1906: Nobel Prize in Physics for the discovery of the electron and his work on conductivity in gases

1913: the first mass spectrometer

Principles of MS



- Ions (atoms without several electrons →positively charged) are created
- Their mass-to-charge ratios are measured

Image: Wikipedia

Ion sources

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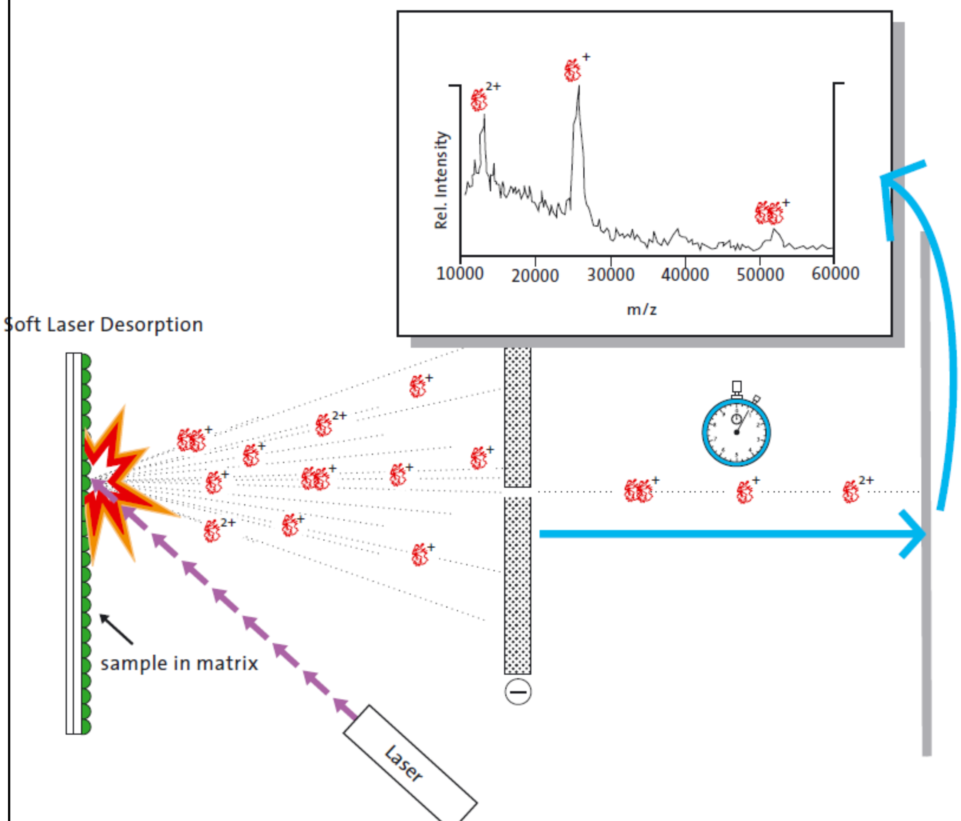
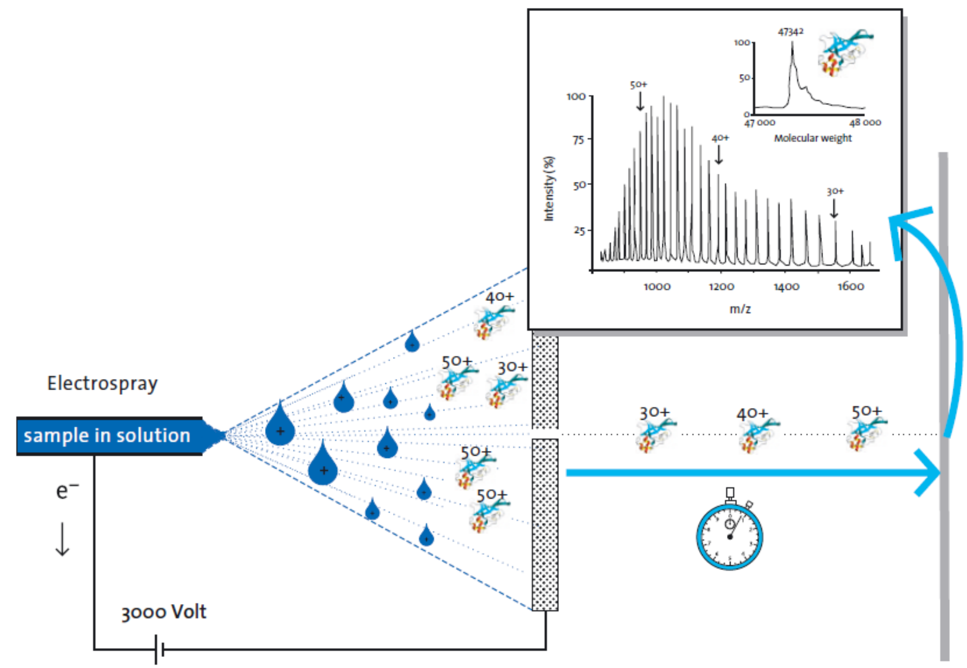
1988: Matrix-Assisted Laser Desorption Ionisation (MALDI)



1989: Electrospray Ionisation (ESI)



Images: Advanced information on the Nobel Prize in Chemistry 2002, 9 October 2002

Water from the Moon?

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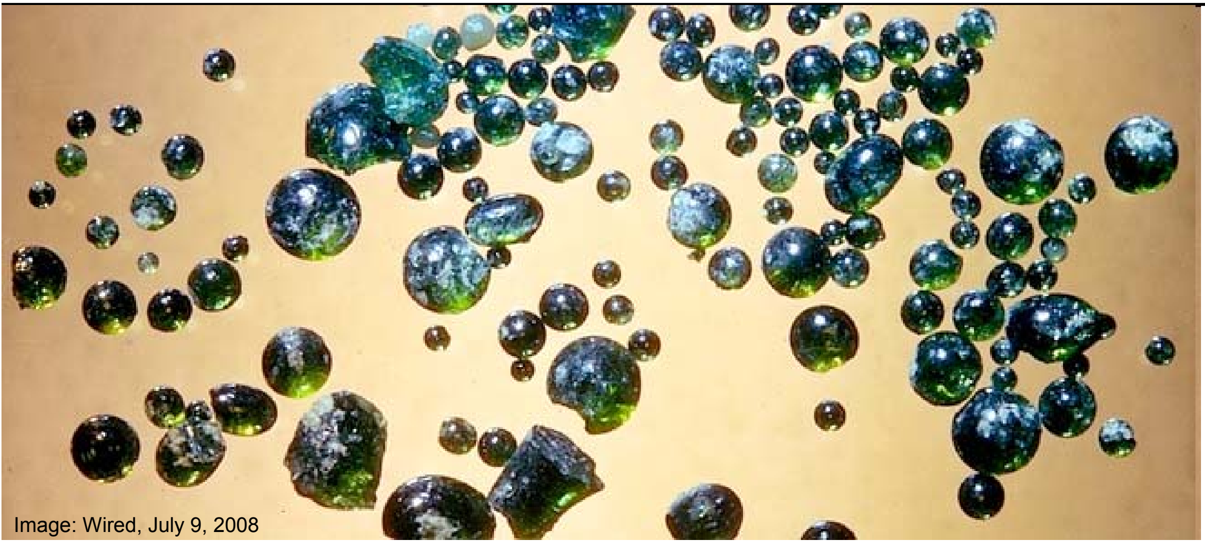

Image: Wired, July 9, 2008

US Apollo missions in the late 1960s and early 1970s brought lunar volcanic glasses, pebble-like beads

In 2008, Saal et al. used **Secondary Ion Mass Spectrometry** (SIMS) to detect a minute quantities of water

"We developed a way to detect as little as five parts per million of water. We were really surprised to find a whole lot more in these tiny glass beads, up to 46 parts per million."

Erik Hauri (Carnegie Institution, Washington DC)

1 parts per million (ppm) = 0.0001%

Celine Dion(1993) Water From The Moon. TechReport ☺

Water from the Moon?

Center for Industrial Mathematics

nature Vol 454 | 10 July 2008 | doi:10.1038/nature07047

LETTERS

Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior

Alberto E. Saal[1], Erik H. Hauri[2], Mauro Lo Cascio[1], James A. Van Orman[3], Malcolm C. Rutherford[1] & Reid F. Cooper[1]

The Moon is generally thought to have formed and evolved through a single or a series of catastrophic heating events[1], during which most of the highly volatile elements were lost. Hydrogen, being the lightest element, is believed to have been completely lost during this period[2]. Here we make use of considerable advances in secondary ion mass spectrometry[3] to obtain improved limits on the indigenous volatile (CO_2, H_2O, F, S and Cl) contents of the most primitive basalts in the Moon—the lunar volcanic glasses. Although the pre-eruptive water content of the lunar volcanic glasses cannot be precisely constrained, numerical modelling of diffusive degassing of the very-low-Ti glasses provides a best spectrometry (SIMS)) have had relatively high detection limits, particularly for H_2O and CO_2. Recent substantial advances in SIMS provide improved detection limits for H_2O, CO_2, F, S and Cl, up to two orders of magnitude lower than electron microprobe, FTIR and earlier SIMS instrumentations (see Supplementary Information). Here we report, by virtue of the new SIMS technique[3], improved limits on the indigenous volatile (CO_2, H_2O, F, S, Cl) contents of the lunar volcanic glasses and evaluate the processes controlling their variation within and between glass beads. Our results represent the first evidence for the presence of indigenous water in the lunar interior.

Secondary Ion Mass Spectrometry (SIMS)

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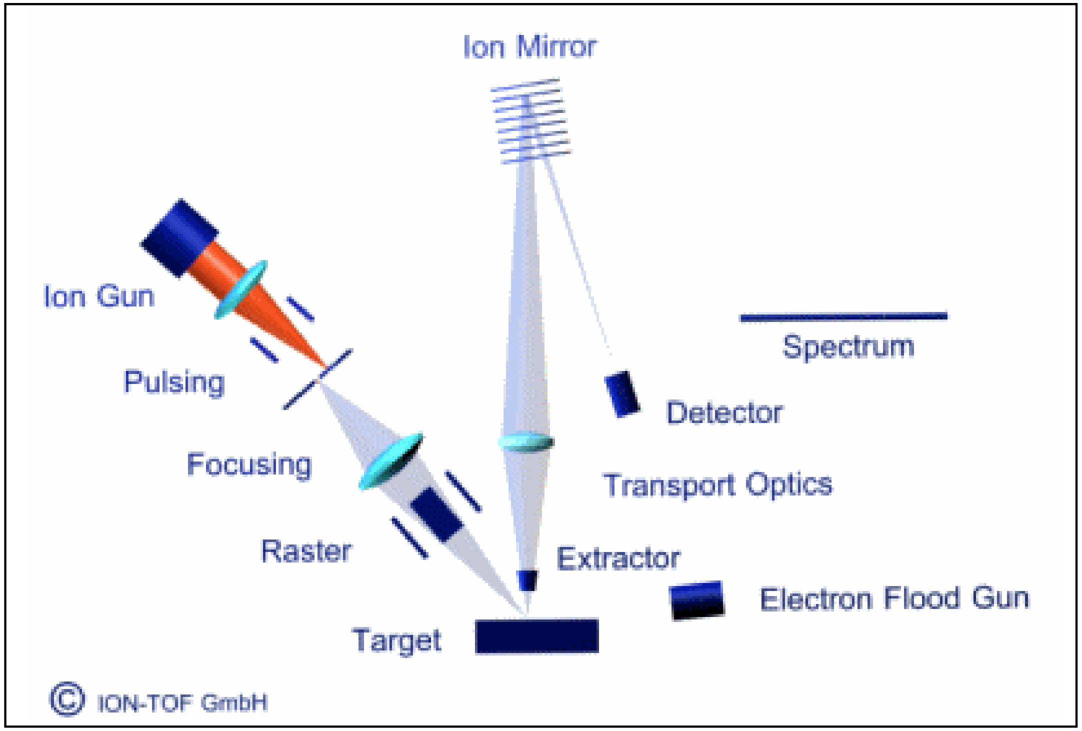


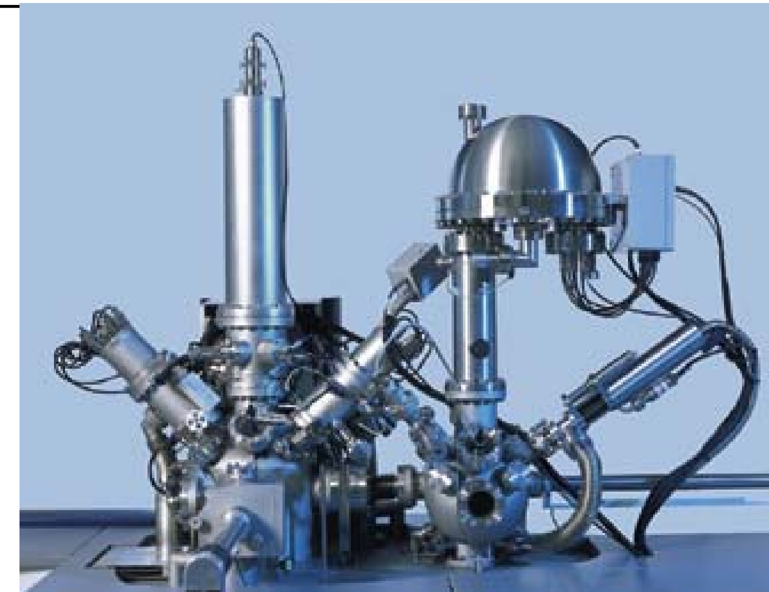


Image: www.iontof.com

SIMS is used in materials science and surface science

The most sensitive surface analysis technique (ppb range!)

1 ppb = 0.0000001%

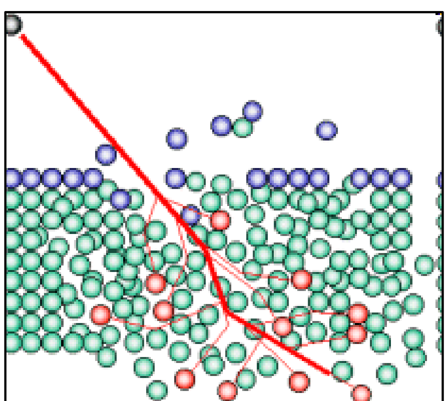


Image: www.cameca.com

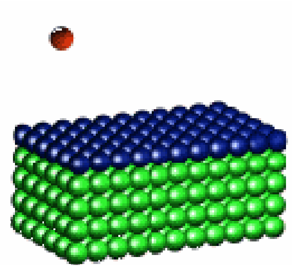
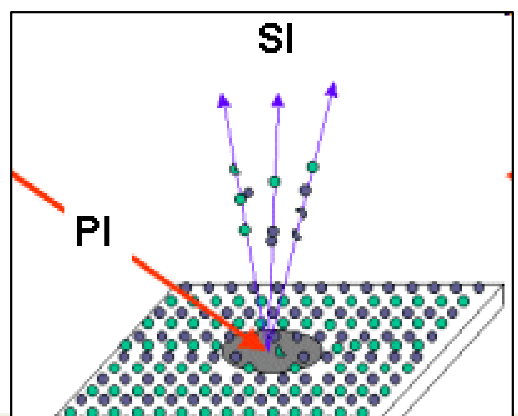


Image: www.iontof.com

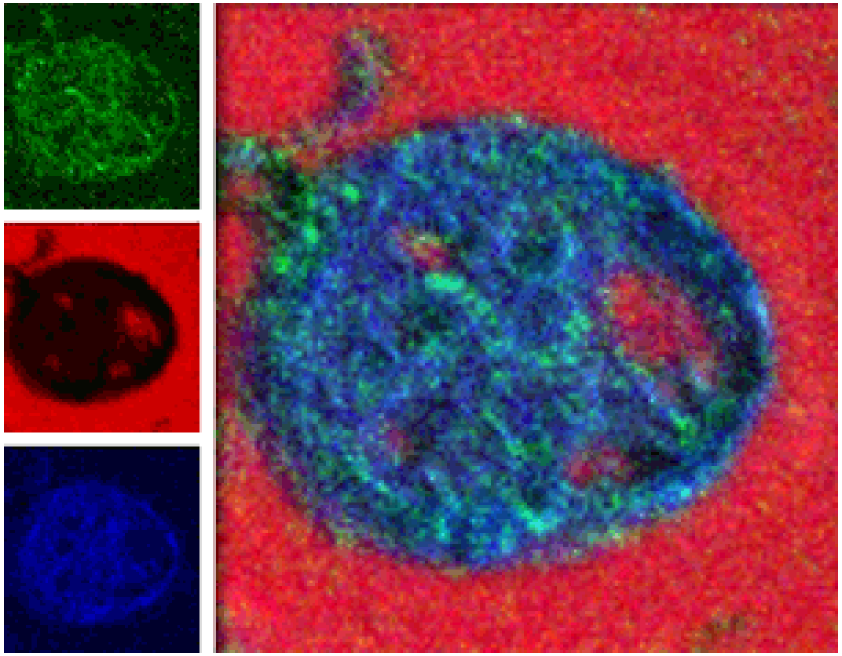


In gray is damaged area.
Image: www.cameca.com

SIMS imaging

Typical sizes	
11 nm	ribosome
100 nm	large virus
150-250 nm	small bacteria
2 µm	E.coli - a bacterium
9 µm	human red blood cell
10-30 µm	eukaryotic animal cells
10-100 µm	eukaryotic plant cells

- SIMS can be rasterized with lateral resolution of 40 nm, 1 nm=10^{-9} m
- SIMS imaging



The spatial distribution of sodium (red), lecithin (green) and serine (blue) within a placenta cell.

The spatial distribution of CN (red), CNO (green) and palmitate+stearate (blue) on the paper surface.

Images: www.ion-tof.com

SIMS depth profiling

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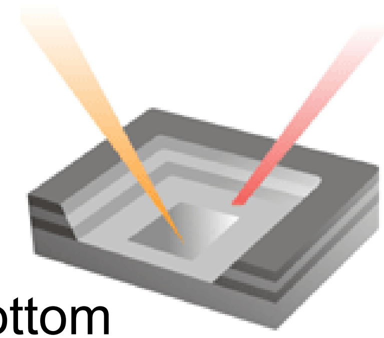
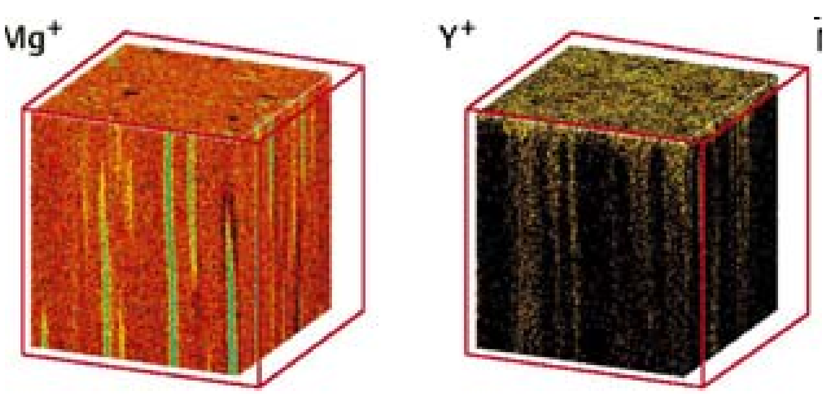
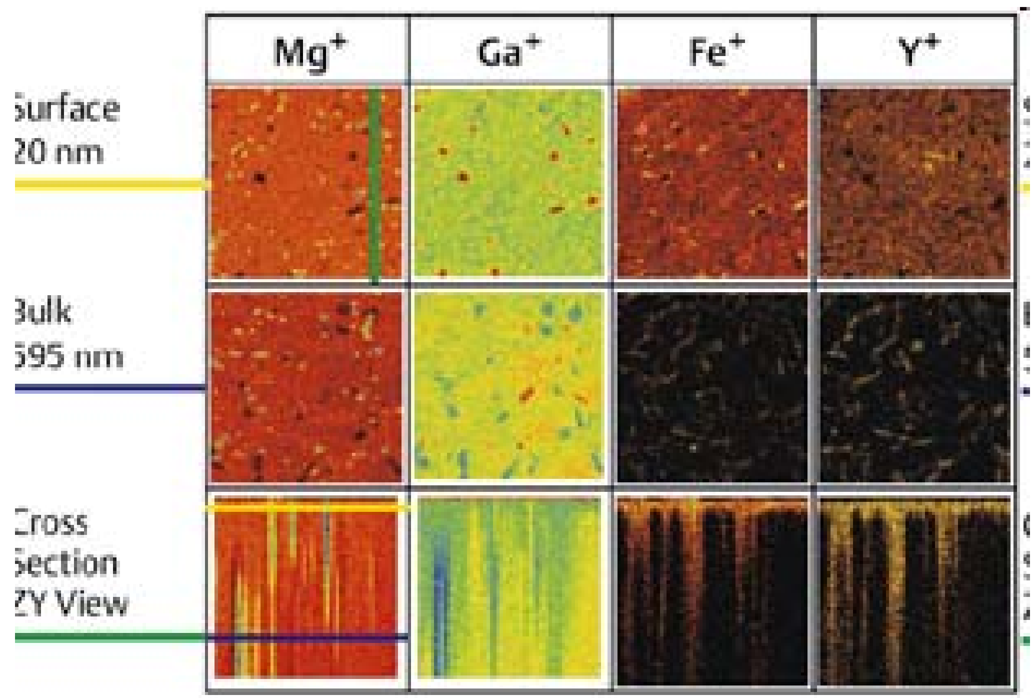
- SIMS depth profiling
  - Two ion beams
    - First beam is sputtering a crater
    - Second one is progressively analyzing the crater bottom



3D image





Images: www.ion-tof.com

Mass spectrometry art

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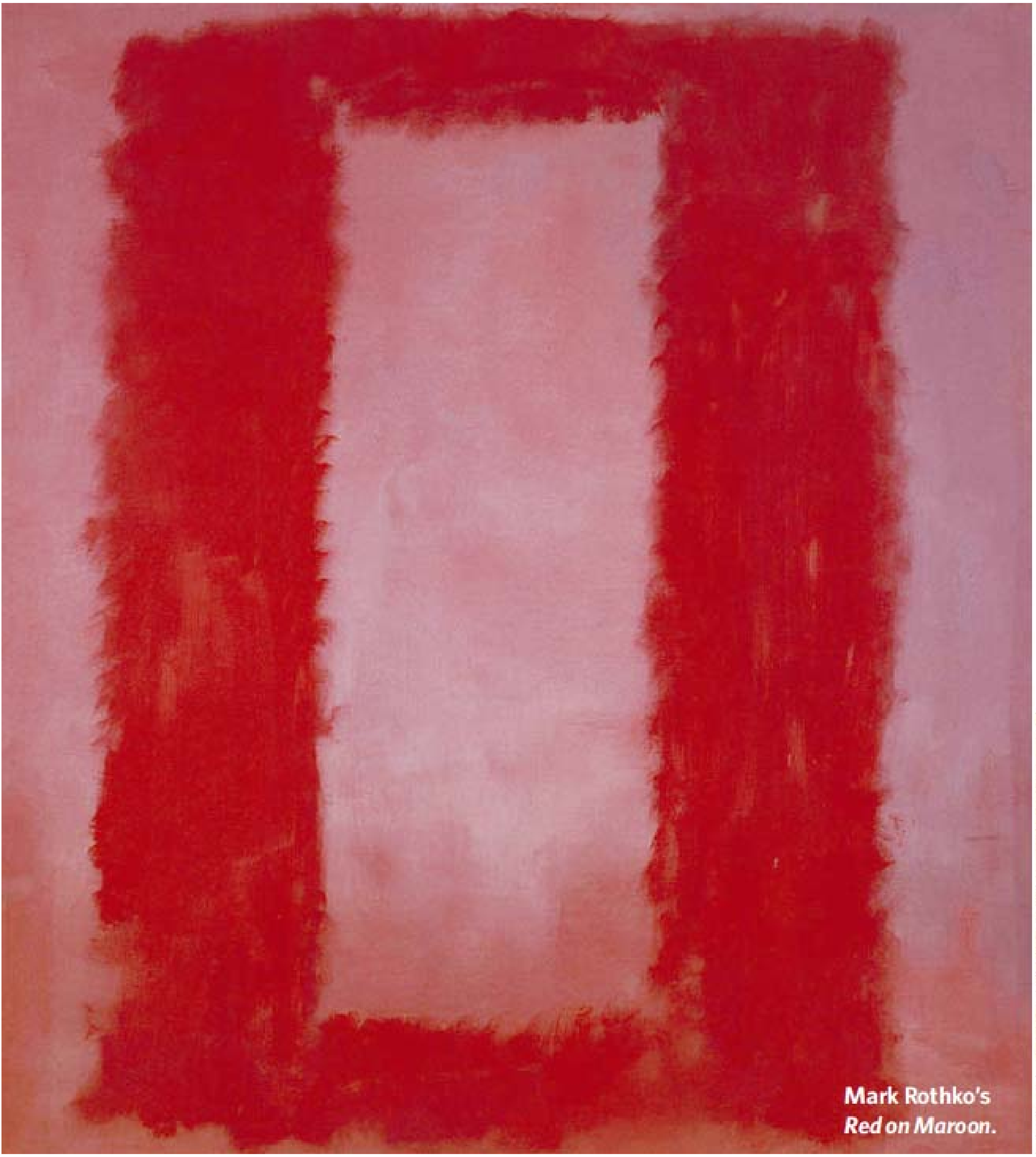
Mark Rothko's *Red on Maroon.*

Mark Rothko

Was famous for his translucent colors and for his secrecy about his methods

Conservators at the Tate Modern studied his murals with mass spectrometry and found out that

Rothko used materials far beyond the conventional range sold for artists including egg, glue, …