

# Investigating the Formation, Evolution, and Habitability of the Galilean Satellites with High Performance Mass Spectrometry

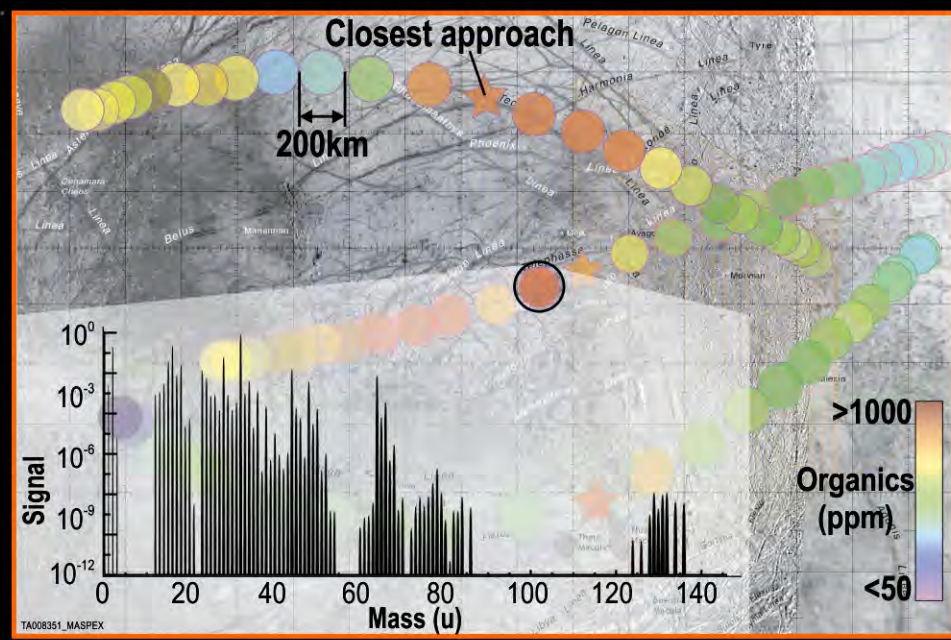


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## How High Resolution / High Sensitivity Mass Spectrometry Can Help Us Understand the Origin, Evolution and Habitability of Europa

### Objective 1: Measuring surface composition through direct sampling



Chemical and isotopic composition of the sputtered or outgassed material is analyzed using advanced mass spectrometry  
Cryosampling mode allows for detection at parts per trillion

#### Key Measurement Species

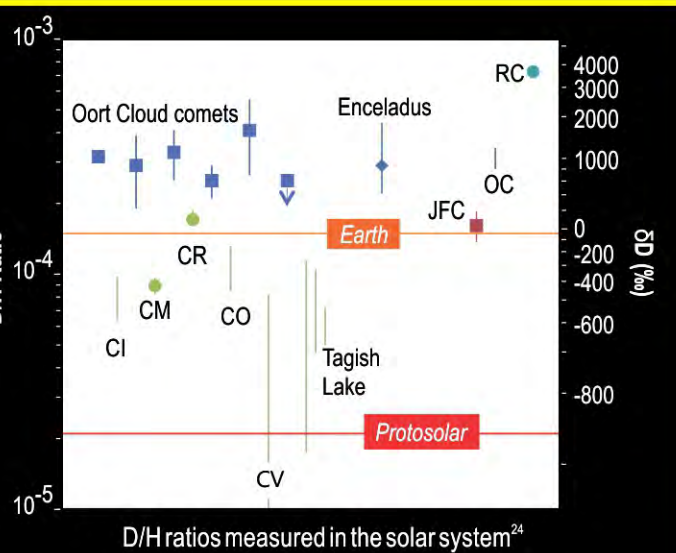
- H<sub>2</sub>O-ice abundances
- NH<sub>3</sub>, N<sub>2</sub>, CH<sub>4</sub>, HCN
- CO<sub>2</sub>
- SO<sub>2</sub>
  - In free ice, as trace component in water ice, as an adsorbate on other minerals, or as hydrated carbonate or bicarbonate
  - S allotropes, H<sub>2</sub>S (as a sputter product of surface H<sub>2</sub>SO<sub>4</sub>)
  - Noble gases
  - K, Na, <sup>40</sup>Ar
- Organics
  - Detection threshold set at 10 ppm based on Enceladus and Titan
  - Needed to distinguish between classes of organic compounds
  - Aliphatic and aromatic hydrocarbons
  - Nitriles
  - Oxygen-bearing hydrocarbons

Surface sampling simulation showing the spatial resolution of our instrument. Each circle represents a high resolution spectrum from which we derive abundances for organic content, H<sub>2</sub>, CH<sub>4</sub>, SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, etc. The spatial resolution shown is derived from simulations of a 100 km altitude flyby assuming compositions from Cassidy<sup>22</sup>.

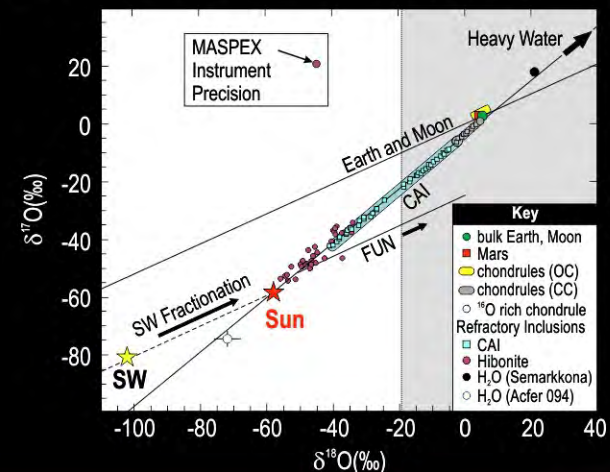
### Objective 2: Sources of Europa's Water

#### Critical measurements that bear on Europa's origin

- D/H ratio of water**
  - Primary tracer of solar system formation and dynamical evolution
  - Protosolar nebular formation vs. Jupiter subnebula formation
- Oxygen isotope measurements**
  - Oxygen in the Sun is dominated by <sup>16</sup>O relative to oxygen in the Earth-Moon system
  - Oxygen isotope measurements have not been made to date
  - Would provide evidence toward material origins for Europa
- Noble gases**
  - Important tracers of volatile evolution
  - Trapping/condensation at low temperatures in the nebula/subnebula
  - Non-reactive
  - Measures of Xe/O, Kr/O, and Ar/O will enable estimates of the extent of devolatilization

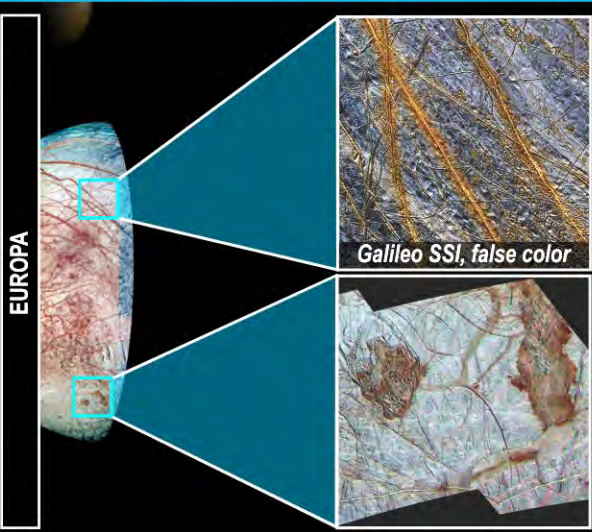


D/H ratios measured in the solar system<sup>24</sup>



Oxygen three isotope plot showing representative compositions of solar system matter, the solar wind (SW), and the value for the Sun<sup>25</sup>. All data fall predominantly on the slope-one line. The shaded area shows the best in situ oxygen isotope knowledge of icy bodies in the solar system from Giotto (δ<sup>18</sup>O range -51 to 128 per mil). No measurement of δ<sup>17</sup>O was obtained. In contrast, our instrument will provide measurements of both δ<sup>18</sup>O and δ<sup>17</sup>O with error bars the size of the dot indicated in the upper left inset.

### Objective 3: Linking surface geologic features with the interior



**KNOWN COMPOUNDS**  
H<sub>2</sub>O, SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, hydrate

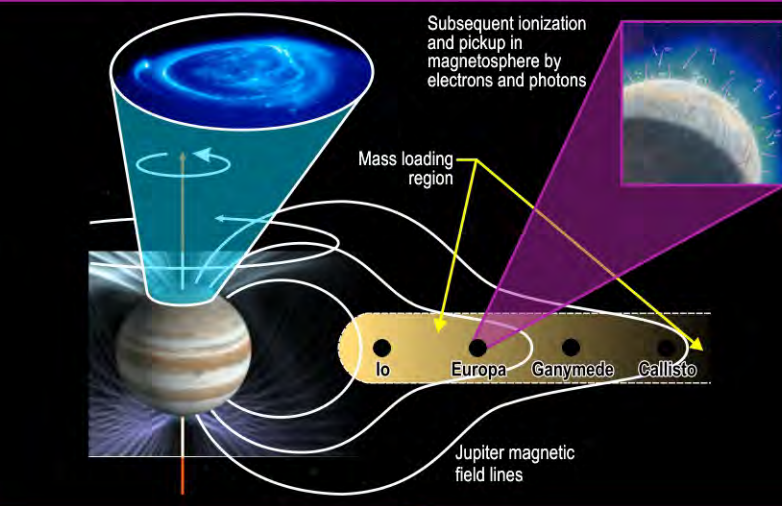
**EXPECTED OR SUSPECTED COMPOUNDS**  
Hydrates of MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, Na and K salts, S allotropes, organics

On earth, faults, fractures and folds are major controls on fluid and gas transport

Europa's large fault systems have likely served as pathways for volatile movement

- Measurements of H<sub>2</sub> and CH<sub>4</sub> that may be outgassed from interior
- Isotopic compositions may infer hydrothermal activity
- Noble gases, especially <sup>40</sup>Ar
- Provides constraints on geologic activity and rates of overturn

### Objective 4: Characterizing the exosphere and neutral clouds



- The neutral density plays a strong role in determining the nature and degree of plasma interaction with the satellite
- A relatively dense atmosphere/ionosphere will act to divert plasma around a satellite, reducing radiation dose
- Allows for characterization of exosphere/magnetosphere interactions, thus characterizing the radiation environment at Europa
- 3D neutral density distributions
- Spatial and temporal observations
- Determine sources and sinks of plasma in the magnetosphere

### References

R. W. Carlson et al., Europa's surface composition, In Europa, edited by Pappalardo et al., University of Arizona Press, pp. 283-327, 2009.

T. McCollom et al., The influence of carbon source on abiotic organic synthesis and carbon isotope fractionation under hydrothermal conditions, *Geochimica et Cosmochimica Acta*, 74, pp. 2717-2740, 2010.

M. J. Mumma and S. B. Charnley, The chemical composition of comets—Emerging taxonomies and natal heritage, *Annu. Rev. Astron. Astrophys.* 49, pp. 471-524, 2011.

J. Horita, Some perspective on isotope biosignatures for early life, pp. 171-186, 2005.

M. J. Whitticar, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chemical Geology*, 161, pp. 291-314, 1999.

A. S. Bradley and R. E. Summons, Multiple origins of methane at the Lost City hydrothermal field, *Earth and Planetary Sci. Lett.*, 297, pp. 34-41, 2010.

E. L. Shock, Geochemical constraints on the origin of organic compounds in hydrothermal systems, *Origins of Life and Evolution of the Biosphere*, 20(3-4), pp. 331-367, 1990.

E. L. Shock and W. B. McKinnon, Hydrothermal processing of cometary volatiles—applications to Triton, *Icarus*, 106, pp. 484-477, 1993.

E. L. Shock and M. D. Schulte, Organic synthesis during fluid mixing in hydrothermal systems, *J. Geophys. Res.* 103, 28,513-28,517, 1998.

T. M. McCollom and W. Bach, Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks, *Geochim. Cosmochim. Acta*, 73, pp. 856-875, 2009.

T. E. Mayhew et al., Hydrogen generation from low-temperature water rock interactions, *Nature Geosci.*, 6, pp. 476-484, 2013.

D. S. Kelley et al., A serpentine-hosted ecosystem: The Lost City hydrothermal field, *Science* 307, pp. 1428-1434, 2005.

J. Jouzel et al., Validity of the temperature reconstruction from water isotopes in ice cores, *J. Geophys. Res.*, 102(C12), pp. 26471-26487, 1997.

J. S. Kargel et al., Europa's crust and ocean: Origin, composition, and the prospects for life, *Icarus*, 148, pp. 226-265, 2000.

O. Mousis et al., A primordial origin for the atmospheric methane of Saturn's moon Titan, *Icarus*, 204, 749-751, 2009.

J. J. Kavelaars et al., On the formation location of Uranus and Neptune as constrained by dynamical and chemical models of comets, *Astrophys. J.* 724, pp. L20-L27, DOI 10.1088/2041-8205/724/2/L20, 2011.

T. Owen et al., Protosolar nitrogen, *Astrophys. J.* 553, pp. L177-L179, 2001.

O. Mousis, An estimate of the D/H ratio in Jupiter and Saturn's regular icy satellites—Implications for Titan Hygiene, *Astron. Astrophys.* 414, pp. 1165-1168, 2004.

J. H. Waite et al., Liquid water on Enceladus from observations of ammonia and 40Ar in the plume, *Nature*, 460, pp. 487-490, 2009.

K. D. McGrath et al., The oxygen isotopic composition of the Sun inferred from captured solar wind, *Science*, 332, pp. 1528-1532, 2011.

Zlotov, M. Y., Aquatic fluid composition in CI chondritic materials: Chemical equilibrium assessments in closed systems, *Icarus* 220(2): 715-729, 2012.

D. Hutcheon et al., New constraints on the delivery of cometary water and nitrogen to Earth from the 15N/14N isotopic ratio, *Icarus*, 204, pp. 346-348, 2009.

C. R. Glein et al., The oxidation state of hydrothermal systems on early Enceladus, *Icarus* 197, pp. 157-163, doi:10.1016/j.icarus.2008.03.021, 2008.

Brown, M. E. and K. P. Hand (2013), "Salts and radiation products on the surface of Europa," *Astronomical Journal* 145(4).

Alexander, C. M. O. D., et al., *Science* 337(6095): 721-723, 2012.

Zlotov, M. Y., *Aquatic fluid composition in CI chondritic materials: Chemical equilibrium assessments in closed systems*, *Icarus* 220(2): 715-729, 2012.

Dansgaard, W., 2004: *Frozen Annals*, Narayana Press, Odense, Denmark, 122 pp.

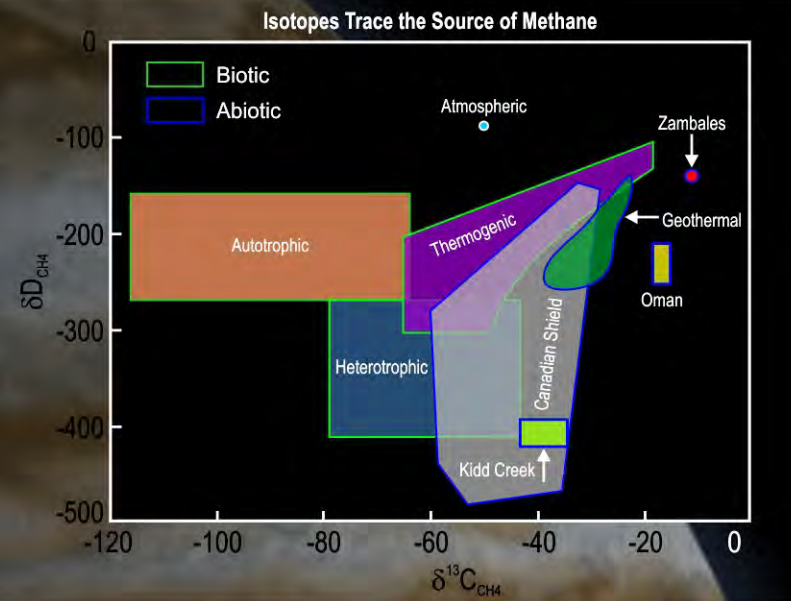
Cassidy, T. A., et al. (2009), "Trace constituents of Europa's atmosphere," *Icarus* 201(1): 182-190.

### Organic compounds as indicators of evolution and habitability on Europa

#### What are the origins of organics on Europa?

- External: from cometary and micrometeorite bombardment.
  - Internal: from hydrothermal processing or biogenic sources.
- #### What can the mass spectrometer detect?
- Heavy ion sputtering launches surface molecules to spacecraft altitude.
  - Radiolysis rapidly breaks surface organic molecules apart so large organic molecules are likely from newly exposed material.
  - Plumes provide a direct source of interior sampling unaffected by radiolysis.
- #### C and H isotopic ratios indicate habitability and evolution
- H<sub>2</sub>O and CO<sub>2</sub> isotopic ratios define the feedstock composition for organic synthesis.
  - Measurement of the C and H isotopic ratios of the organics provides insight into the creation processes e.g.
    - Fischer-Tropsch (abiotic)<sup>7</sup>
    - Cometary (primordial)<sup>8</sup>
    - Biological<sup>13</sup>
- #### Methane isotopic ratios are a key indicator for the source of organics<sup>6</sup>
- Studies of terrestrial hydrothermal vents enables the differentiation of abiotic and biotic sources.

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### Outgassing volatiles indicate the evolutionary state of an internal ocean

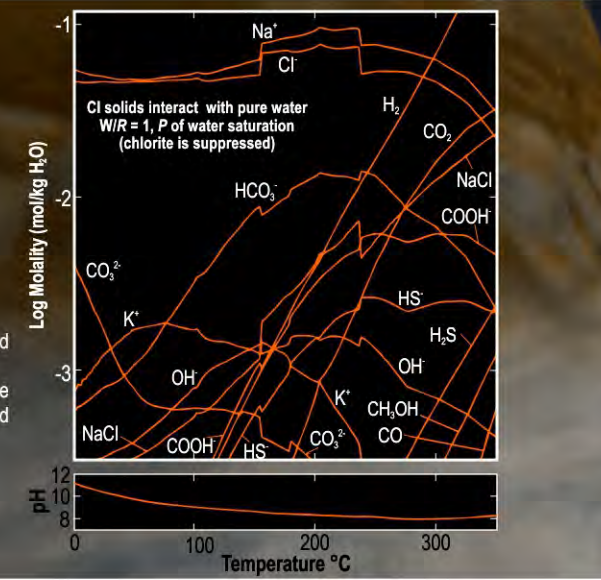
#### Evolved - volatile ratios in equilibrium indicate hydrothermal processing

- Equilibrium values indicate the oxidation state and fugacity of the mineral / solvent system<sup>7,8</sup>.
- Oxidation states more reducing than the fayalite-magnetite-quartz fugacity buffer (FMQ) can preserve and promote abiotic synthesis of complex organic compounds<sup>9</sup>.
- How does hydrothermal activity affect habitability?
  - Hydration of minerals produces hydrogen<sup>10,11</sup>, which can fuel microbial systems<sup>12</sup>.
  - Hydrothermal activity implies a primary source of energy and cycles biogenic elements in and out of the ocean.

#### Unevolved - volatile ratios in disequilibrium indicate a comet like body<sup>22</sup>

- Reactive primitive species e.g. CO and HCN indicate an unprocessed environment.

Models can predict the equilibrium ratios of dissolved volatiles in hydrothermal systems<sup>23</sup>. The figure shows the effect of temperature on the composition and pH of aqueous solutions equilibrated with Cl-type solids.



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### Isotopic ratios of NH<sub>3</sub> and N<sub>2</sub> show origin and evolution

#### Origin

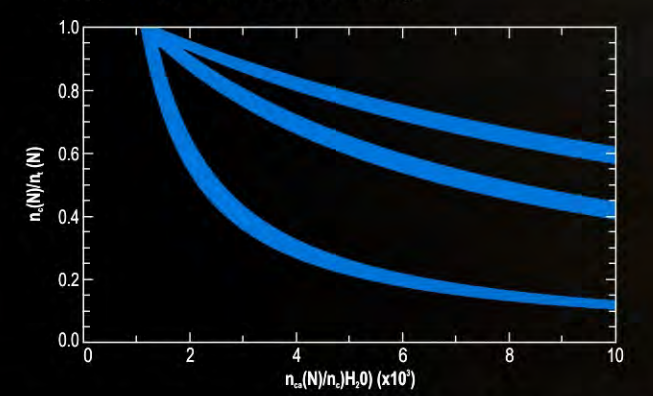
- The Galileo probe N<sub>2</sub> measurement<sup>20</sup> gives the origin N<sub>2</sub> isotopic ratio for the Jovian subnebula (primordial).

#### Evolution

- The Titan N<sub>2</sub> isotopic ratio is very different<sup>21</sup> due to its creation from NH<sub>3</sub> delivered in ices similar to comets<sup>22</sup>.

#### Europa's N<sub>2</sub> isotope ratio

- Comparison of Europa's N<sub>2</sub> isotope ratio with the Galileo value will indicate if the origin is purely primordial or contains a contribution from NH<sub>3</sub> hydrothermal processing (origin and evolution).
- N is more available for biogenic incorporation as NH<sub>3</sub> than as N<sub>2</sub> so the incorporation of cometary ices to Europa increases its habitability.



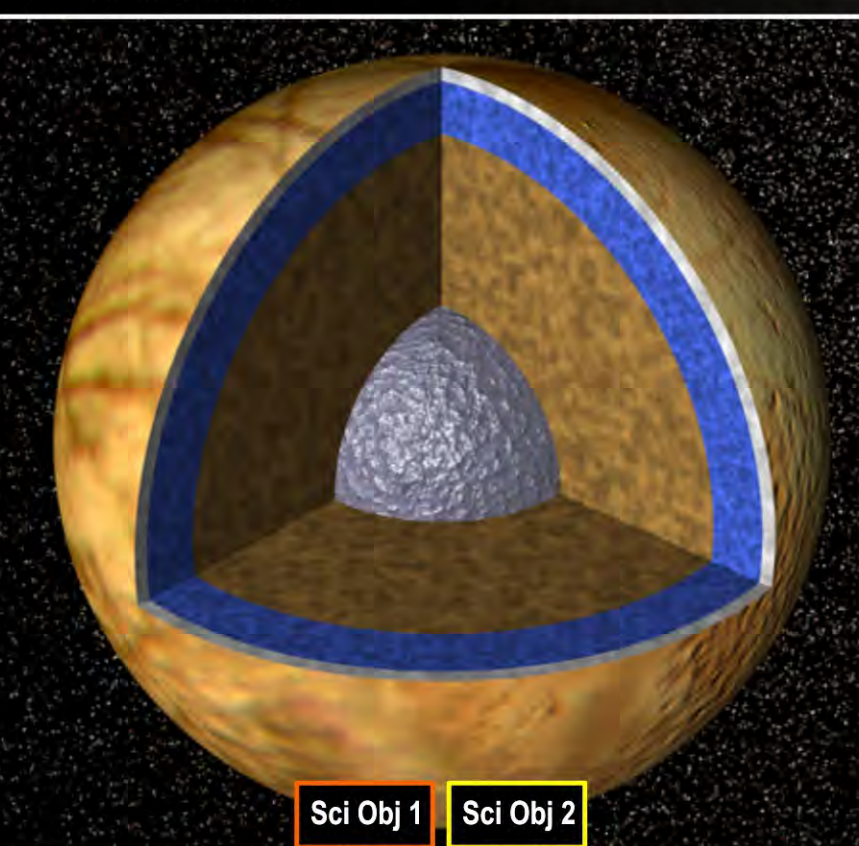
<sup>23</sup>The proportion of terrestrial nitrogen due to comets  $n_c(N)/n_t(N)$  as a function of the abundance of isotopically anomalous nitrogen in comets  $n_c(N)/n_c(H_2O)$ . Each curve corresponds to a different value of the primitive Earth nitrogen isotopic ratio: (<sup>15</sup>N/<sup>14</sup>N) = 2.3 × 10<sup>-3</sup>, 3.0 × 10<sup>-3</sup> and 3.55 × 10<sup>-3</sup> from top to bottom. The width of the curves accounts for the uncertainty on the measured cometary (<sup>15</sup>N/<sup>14</sup>N).

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### How active is Europa's interior?

#### <sup>40</sup>Ar release indicates overturn

- Decay of <sup>40</sup>K in rocks creates <sup>40</sup>Ar, which remains trapped until geologic activity releases it.
- Detection of <sup>40</sup>Ar is a measure of overturn and convection of the interior (evolution).

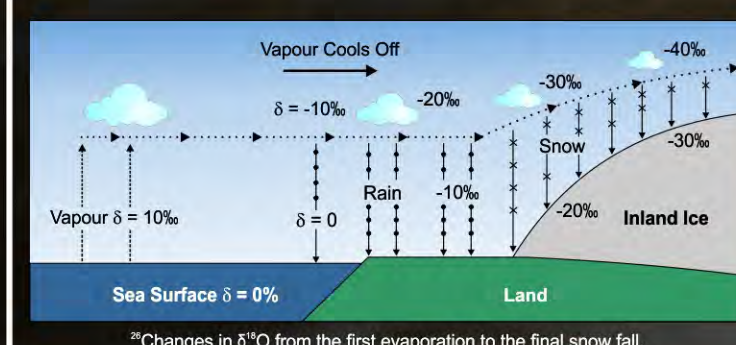


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### Isotopes of water trace origins

#### What are the origins of Europa's water<sup>2,16,17,18</sup>

- Devolatilization of carbonaceous chondrites<sup>14</sup> indicated by protosolar nebular ratios.
  - Icy planetesimals<sup>15</sup> indicated by cometary ices / Titan & Enceladus ratios.
- #### Can the spatial distribution of O isotopes identify oceanic upwelling?
- Vaporization and condensation of water fractionates the oxygen isotopes<sup>13,26</sup>.
  - Water vapor migration and condensation away from the source vent creates an O isotopic fractionation pattern on the surface that can be measured.



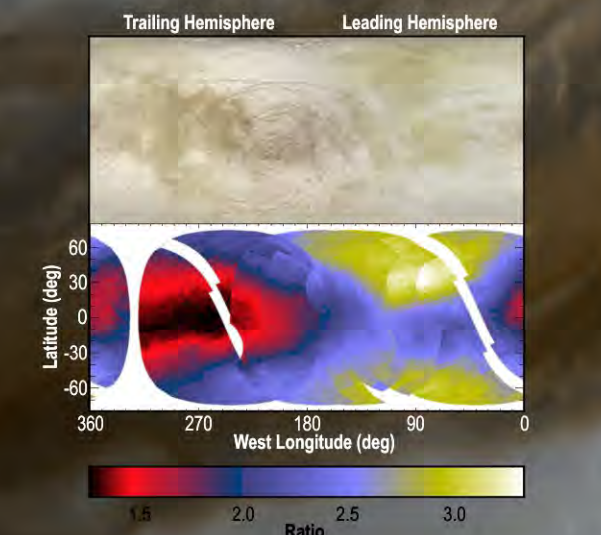
<sup>26</sup>Changes in δ<sup>18</sup>O from the first evaporation to the final snow fall.

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### Where does Europa's sulfur come from?

#### Is it native or transferred from Io?

- Compare isotopes from surface sputtering and SO<sub>2</sub> in the neutral cloud for similarities.
- Similar isotope ratios show that Europa's sulfur may be obtained from Io rather than from oceanic salts.



<sup>28</sup>The surface of Europa could contain the compositional imprint of an underlying interior ocean, but competing hypotheses differ over whether spectral observations from the Galileo spacecraft (top right) show the signature of ocean evaporates or simply surface radiation products unrelated to the interior. Recent Keck spectra (bottom right) show a previously undetected distinct signature of magnesium sulfate salts on Europa confined to the trailing hemisphere and spatially correlated with the presence of radiation products like sulfuric acid and SO<sub>2</sub>. This suggests that MgSO<sub>4</sub> is also a radiation product, rather than a constituent of a Europa ocean brine.

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### Analysis requirements for Europa's atmosphere observed during a 100km altitude flyby

The Europa Clipper Science Traceability Matrix requirement is outlined along with performance envelopes for the strawman instrument - NMS (Nozomi), Cassini INMS, Rosina RTOF and MASPEX (with and without cryotrapping)

