Identification of Inorganic and Organic Inclusions in the Vostok Lake Ice with Raman Spectroscopy

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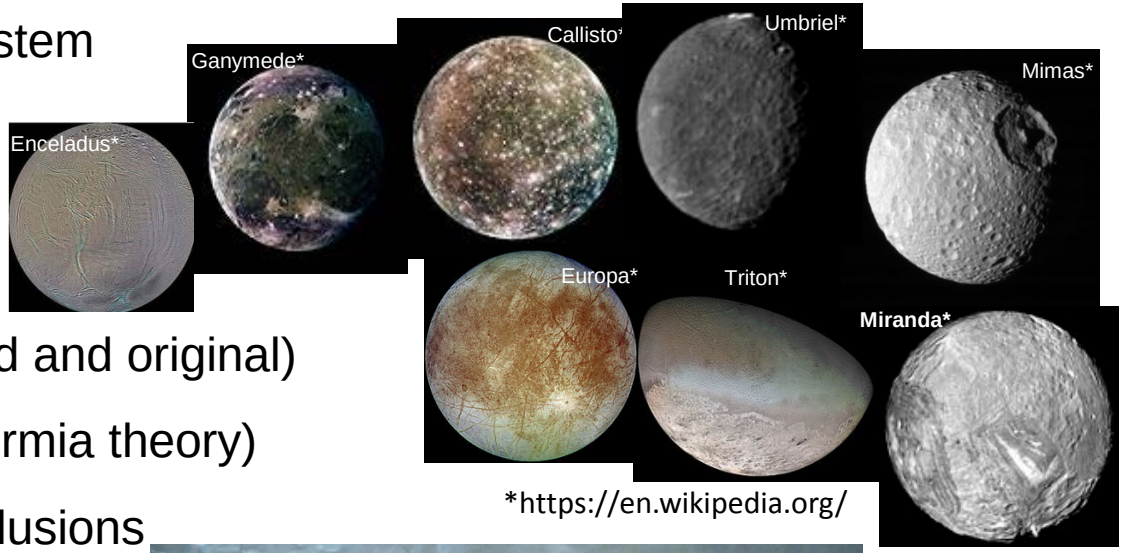
DLR

Motivation

- Search for life and habitable worlds in the Solar System (planetary research)
  - Icy moons in our solar system
  - Pole region of Mars
  - Pole region of Moon



*https://en.wikipedia.org/

- Study of inclusions (untouched and original)
  - Micrometeorites (panspermia theory)
  - Inorganic and organic inclusions
  - Sample return from Solar System bodies

- Learn to measure

  and to work in ice for future missions

! Investigation of inclusions with context preservation !

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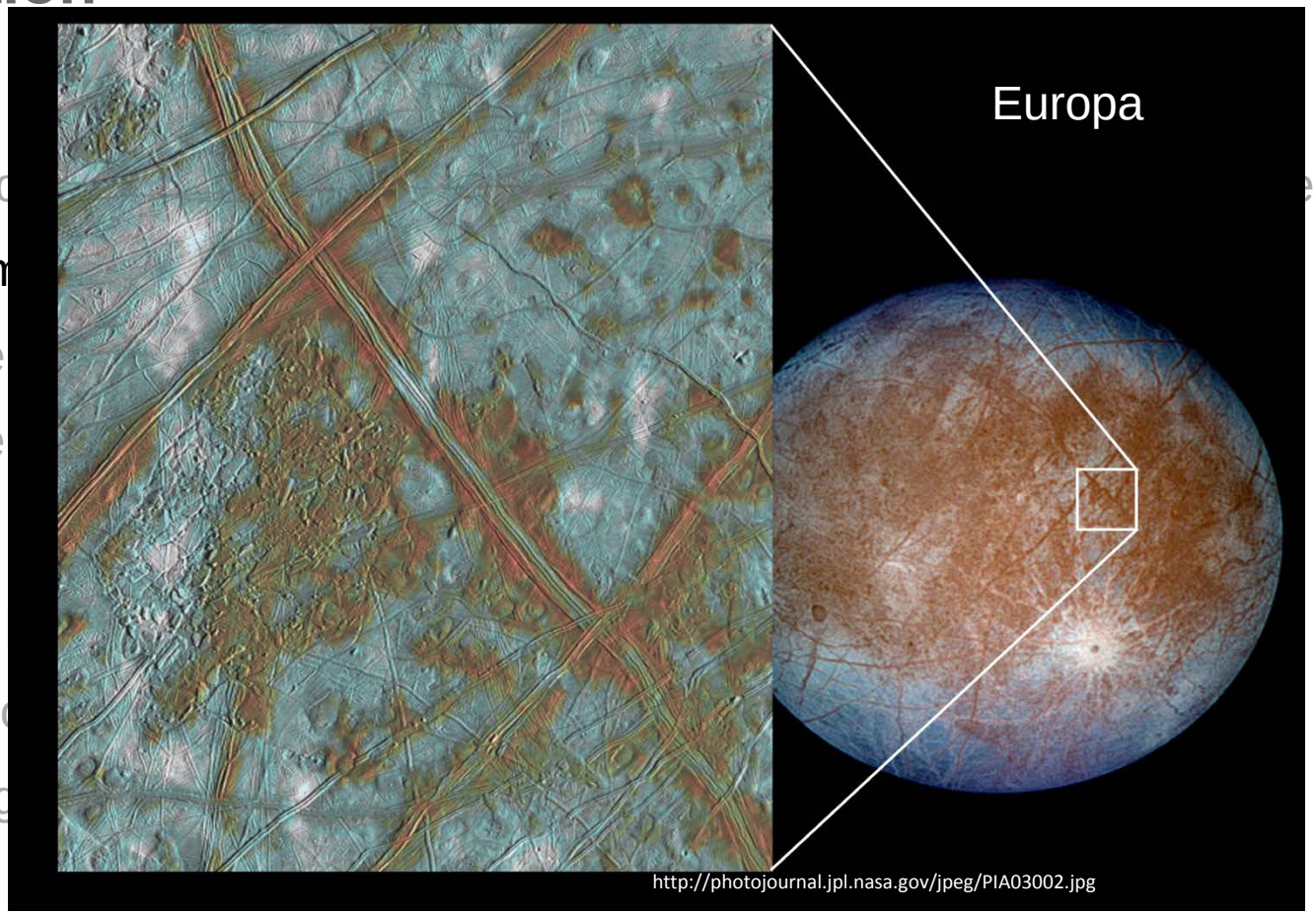

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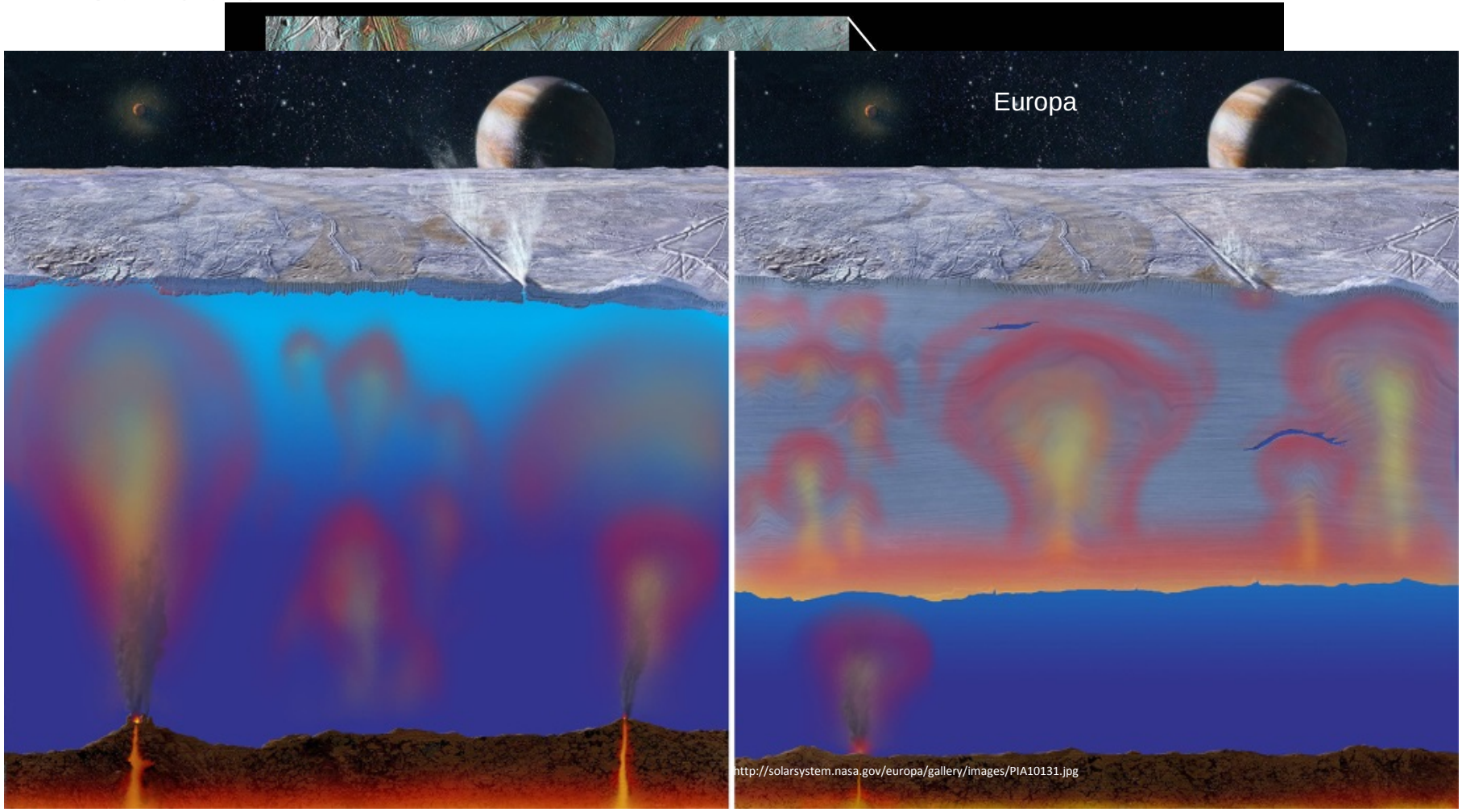
Europa
http://solarsystem.nasa.gov/europa/gallery/images/PIA10131.jpg

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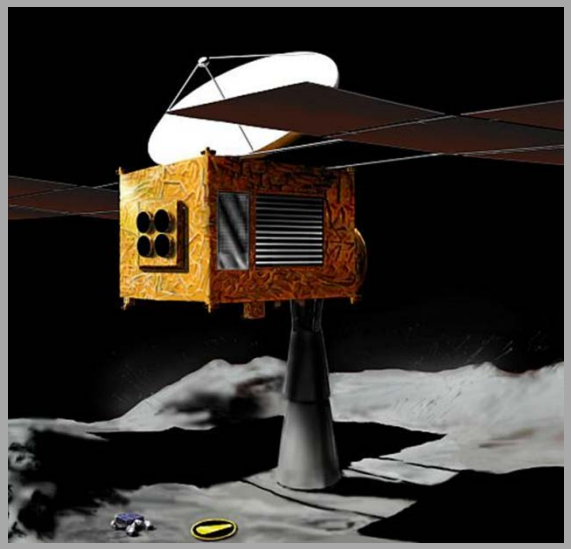
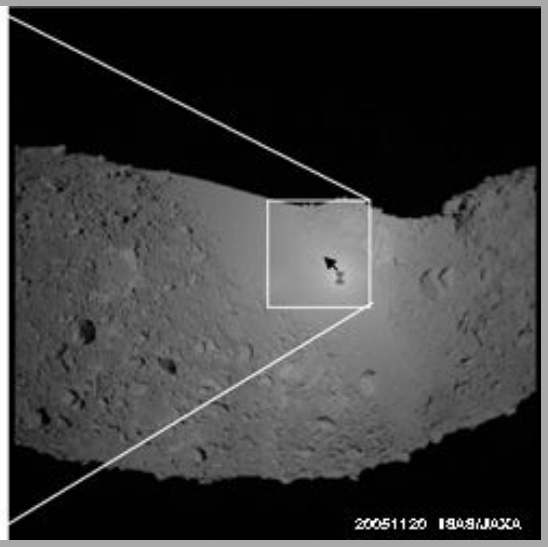
Hayabusa Mission



2003 Launch
2005 Visit
two “touchdowns” (100 m apart) at Muses-C region
Problems while sampling
2007 Start back to Earth
2010 Landing in Australia

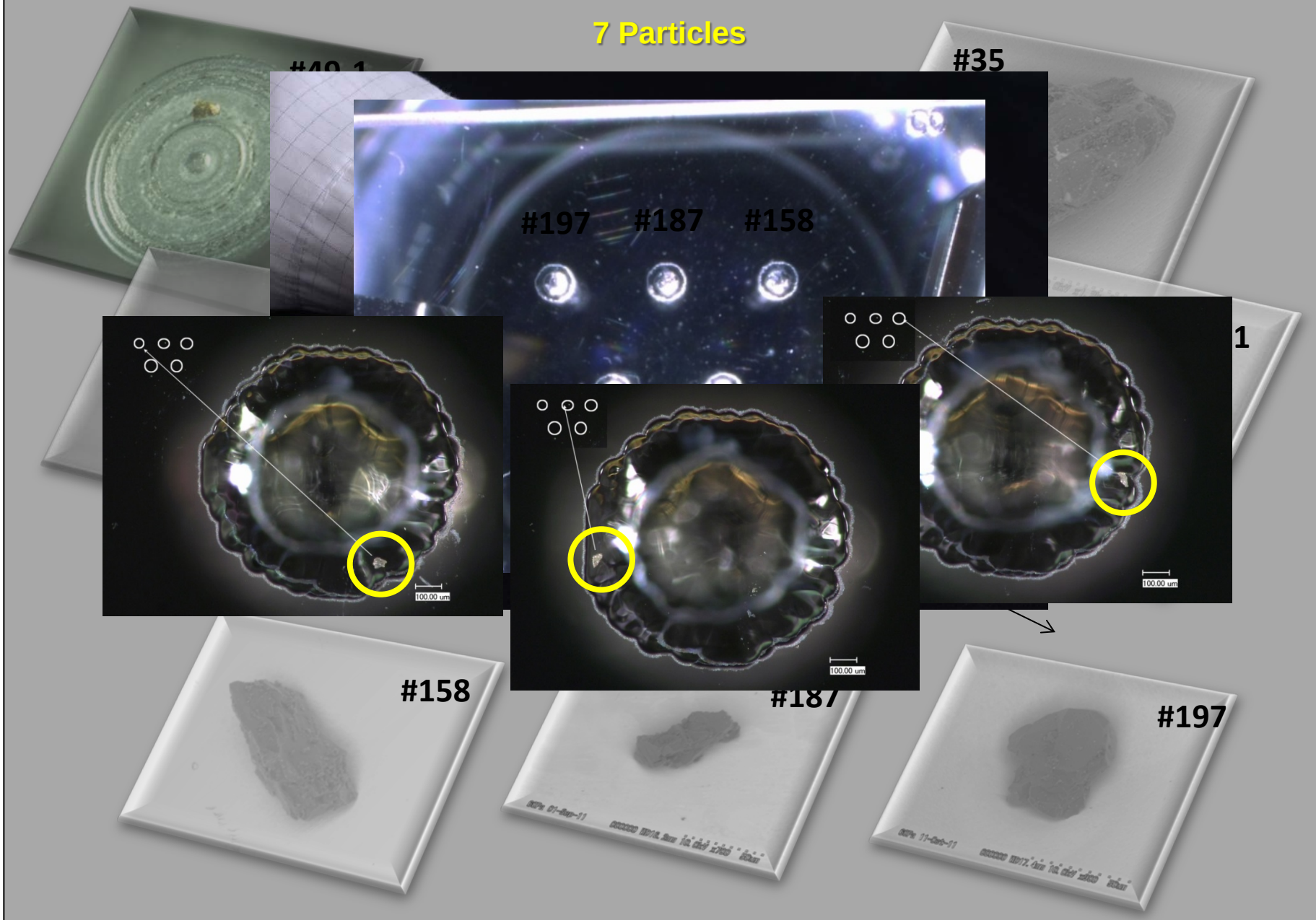


Itokawa

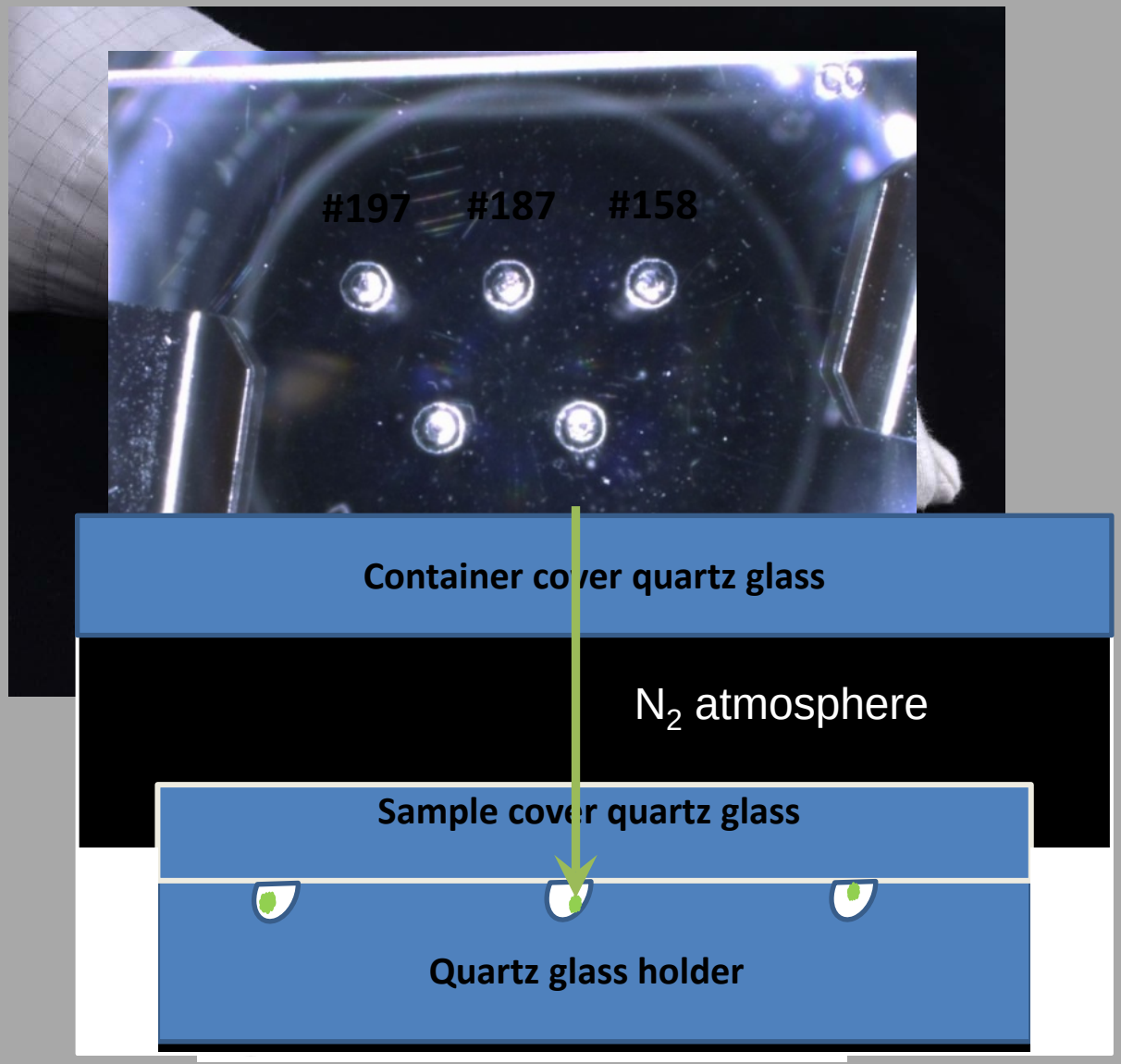
- **S-type near-Earth asteroid**
- ~535 m x 250 m
- perihelion 0.95 AU, semi-major axis 1.3 AU
- rubble pile

- head – body, different densities (2.9 & 1.8 g/cm3)
- contact binary?
- **regolith** between main fragments (“Muses-C”)

7 Particles



3 grains in N_2 atmosphere covered with two cover glass plates



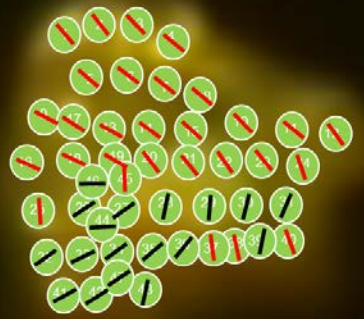
3 grains in N_2 atmosphere covered with two cover glass plates

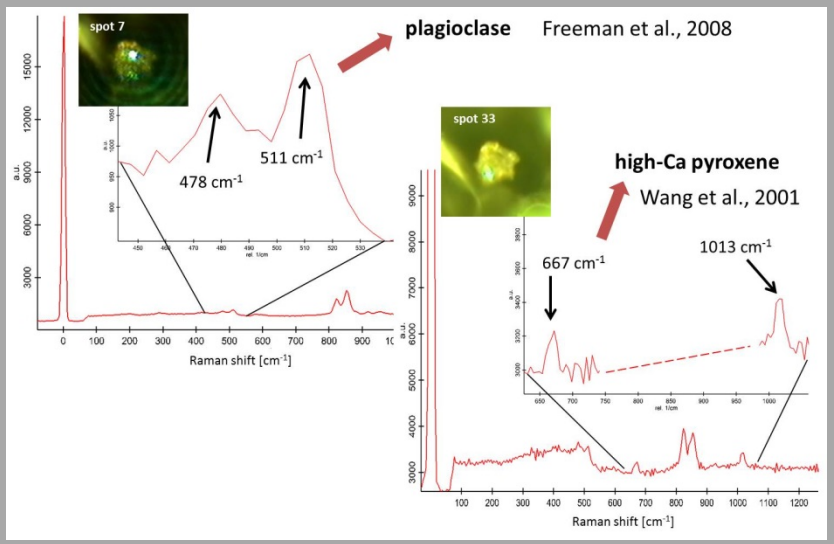
#197

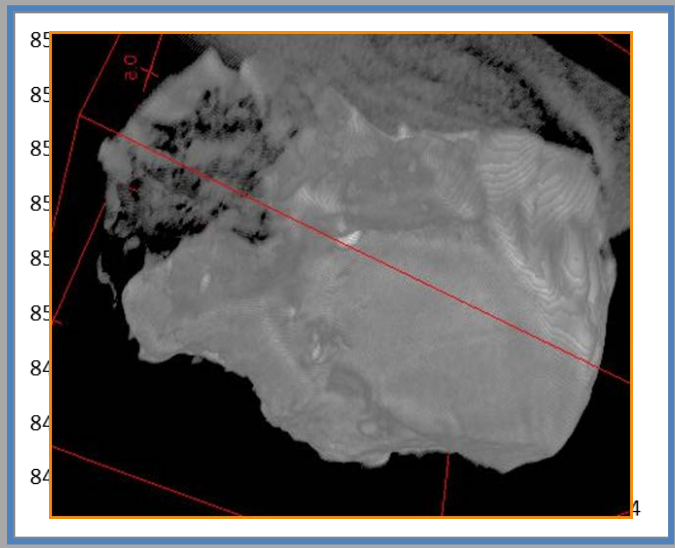
- Olivine
- Plagioclase
- Pyroxene

Mineralogy

Orientation







Raman Spectroscopy to characterize inclusions in ice first attempt

- Raman (inelastic scattering of light) spectroscopy
  - Nondestructive method
  - Fingerprint spectra for material identification
  - Can look into transparent and translucent material – depth scan

- Application to inclusions in Vostok lake ice held at negative temperatures

- Procedure:
  - Performance test with selfmade samples of
    - Blank ice (tap water)
    - Mineral powder/particles (olivine) frozen in tap water ice
  - Measurements of Vostok lake ice without and with inclusions – first results

Sample preparation of Vostok lake ice with inclusions

2014 – 5G-3 3607m accretion I ice sample

8 - sample remaind in the cryo-container.

9 - The container was never opened, so the sample is in original air from the Grenoble-Lab

10 – returned back to Grenoble without warming up

Sample preparation of Vostok lake ice with inclusions

2014 – 5G-3 3607m accretion I ice sample

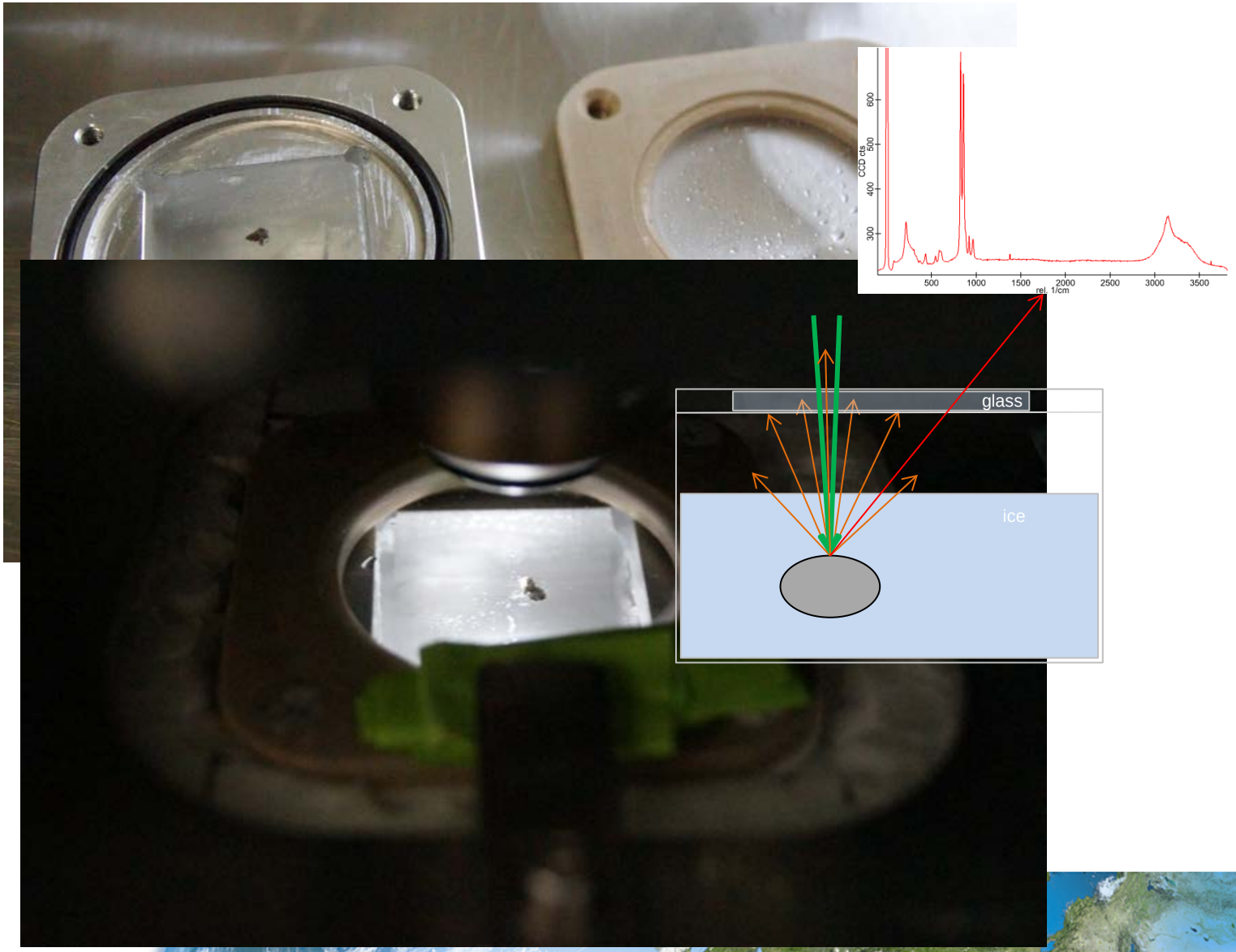
Procedures in the cold room No. 8 (-15oC) LGGE

1 – Metal container-ice holder from DLR (got frozen at -23°C)
(cleaned with ethanol – especially the glass window from the inside) at -15°C
2 – Ice segment was cut (roughly 2.5x2.5x2.5 cm) by circular saw (not a perfect cube!) and
washed with ethanol (to make it transparent)
3 – Ethanol was evaporated and ice cube was put inside the container with a drop of tape water put at the
bottom (to stick-freeze the ice cube)
4 – Container was covered with the lid and fixed with the screws
5 – Container was put into PE bag and sealed (kept at -23°C)
6 – Foam box with ice blocks (frozen at -43°C) surrounding the container with ice cube to send out
7 – arrived at DLR und was never warmer than -7°C
8 - sample remained in the cryo-container.
9 - The container was never opened, so the sample is in original air from the Grenoble-Lab
10 – returned back to Grenoble without warming up

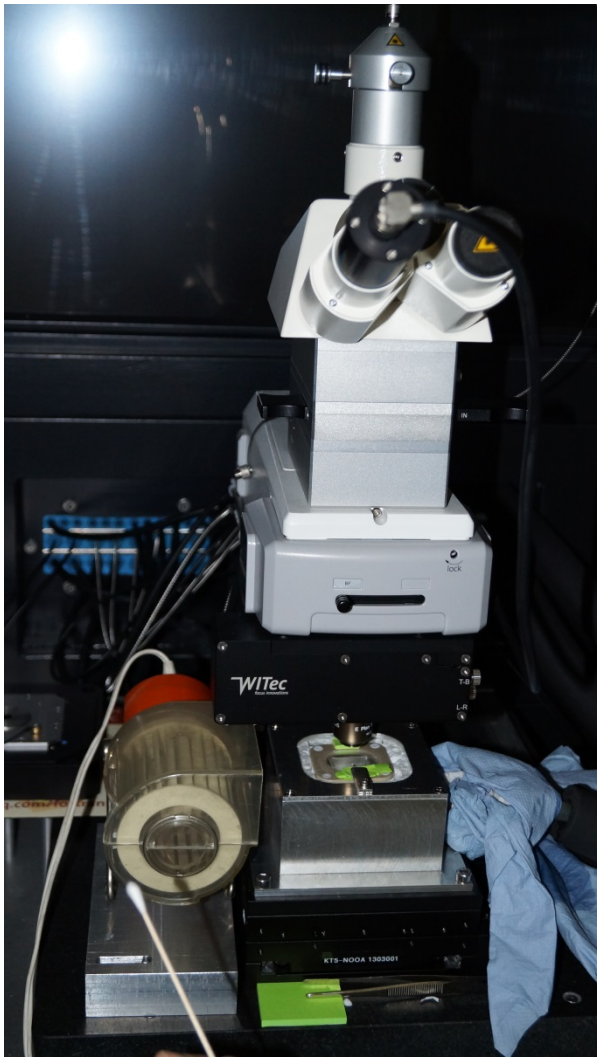
Raman measurements of inclusions in ice

Sample cryo-holder with Vostok lake ice with inclusion

Raman measurements of inclusions in ice



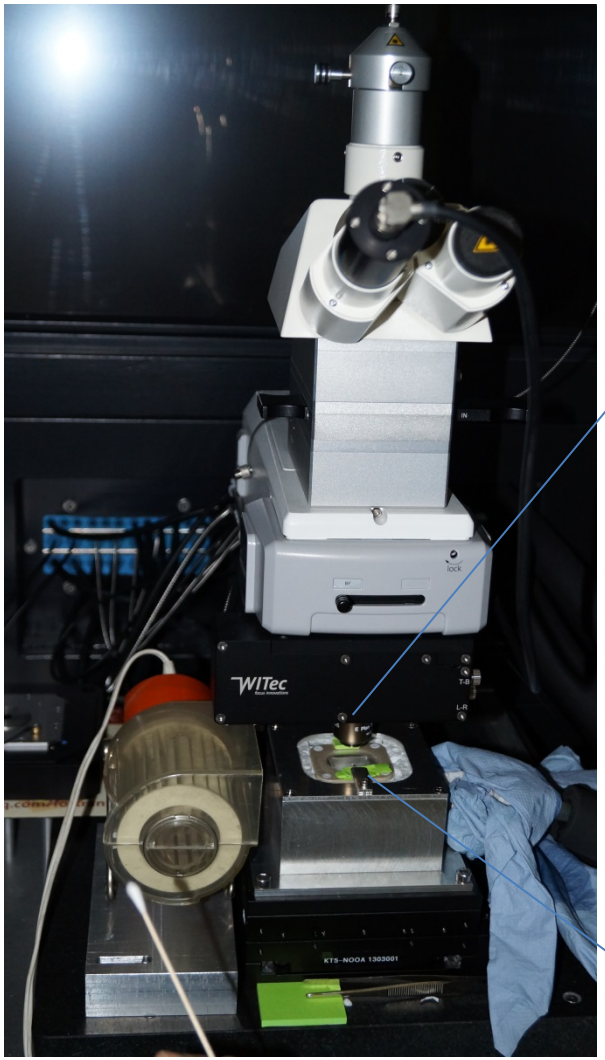
Raman measurements of inclusions in ice



Raman measurements:

- Witec Alpha 300 System
- Laser: 532 nm
- Laser Power: 0.5 mW
- Objective: Nikon10x LWD
- Measurement time: 10 s x 10 times :
- Spot in focus: ~ 1 µm
- Temperature of sample: < -20°C
- Window: quartz window, ~500 µm thickness

Raman measurements of inclusions in Vostok lake ice

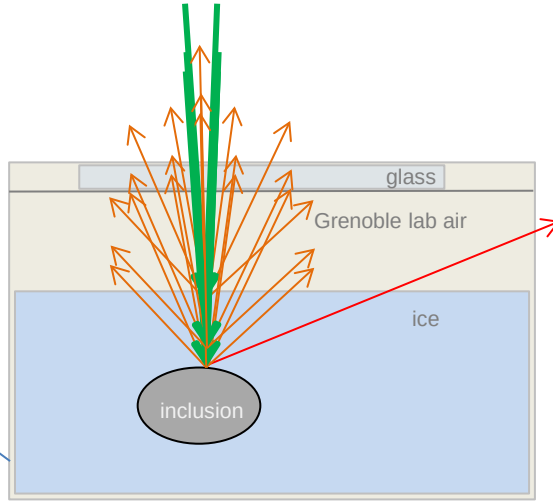


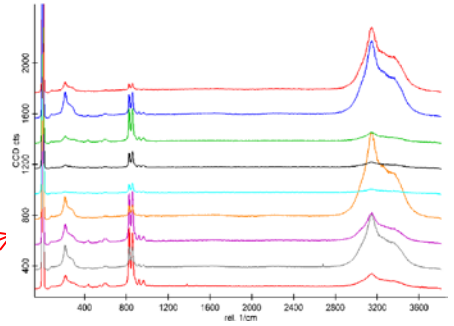
Measurement procedure:

- Manual depth scan from bottom side of cover quartz glass down to -7 mm
- Every measurement was repeated 2 times

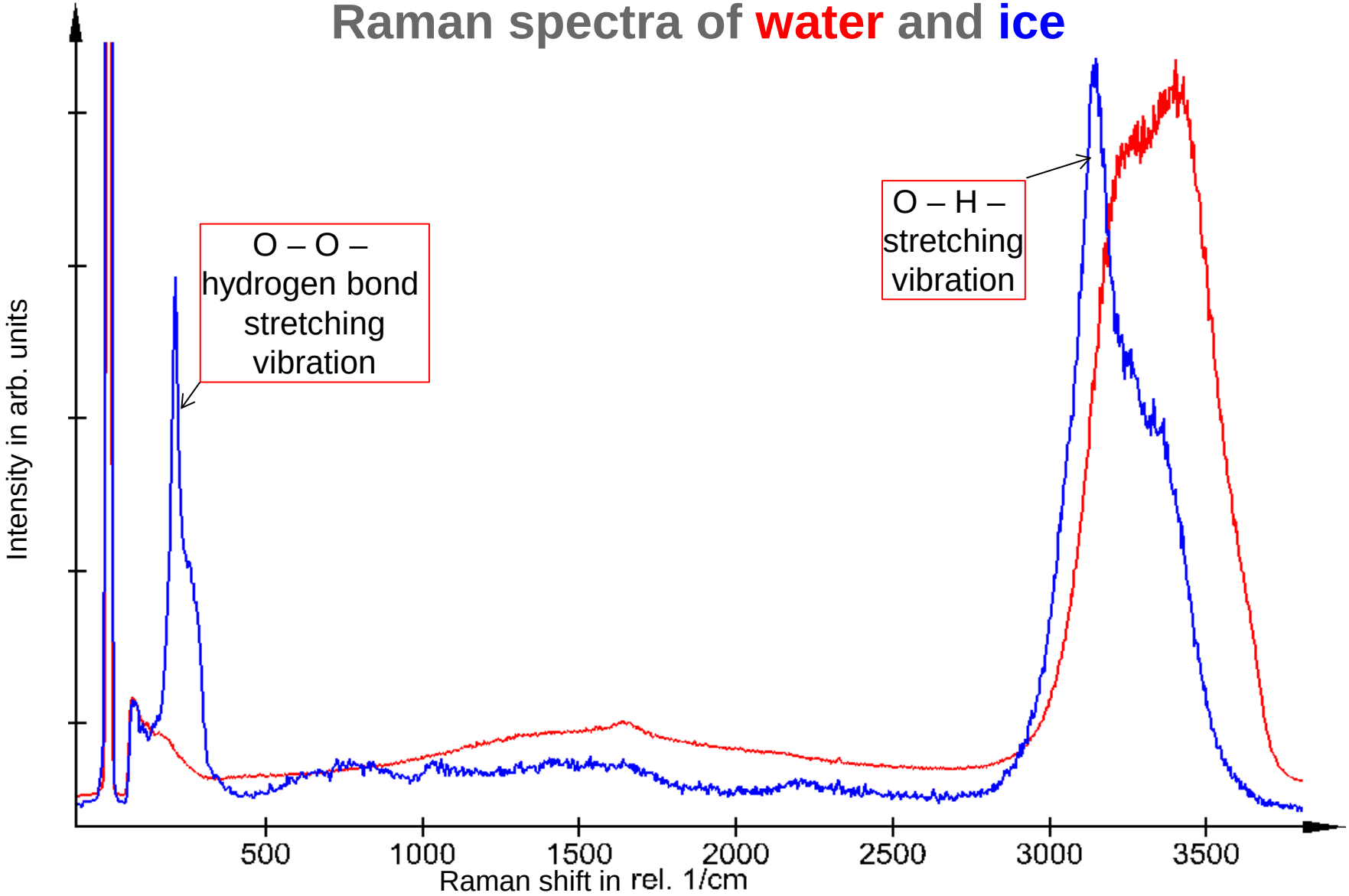
Problem:

The surface of ice is not visible by eye.

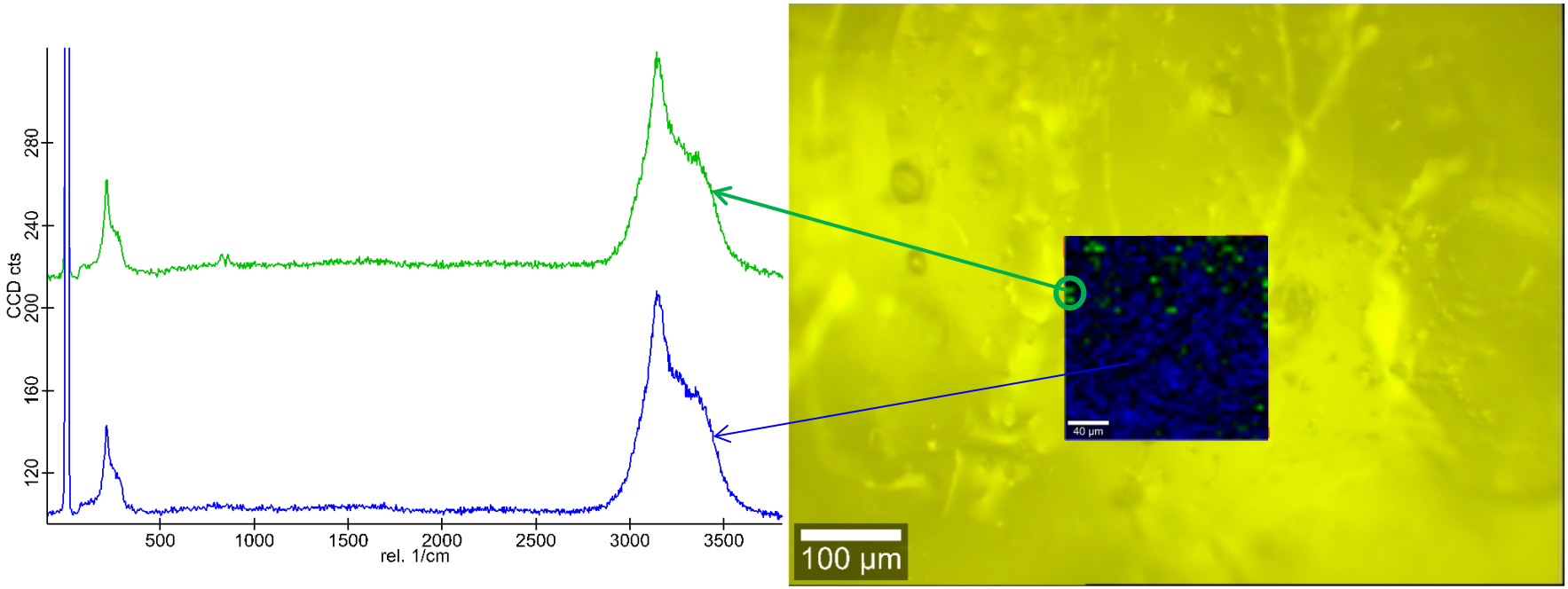




Raman spectra of water and ice



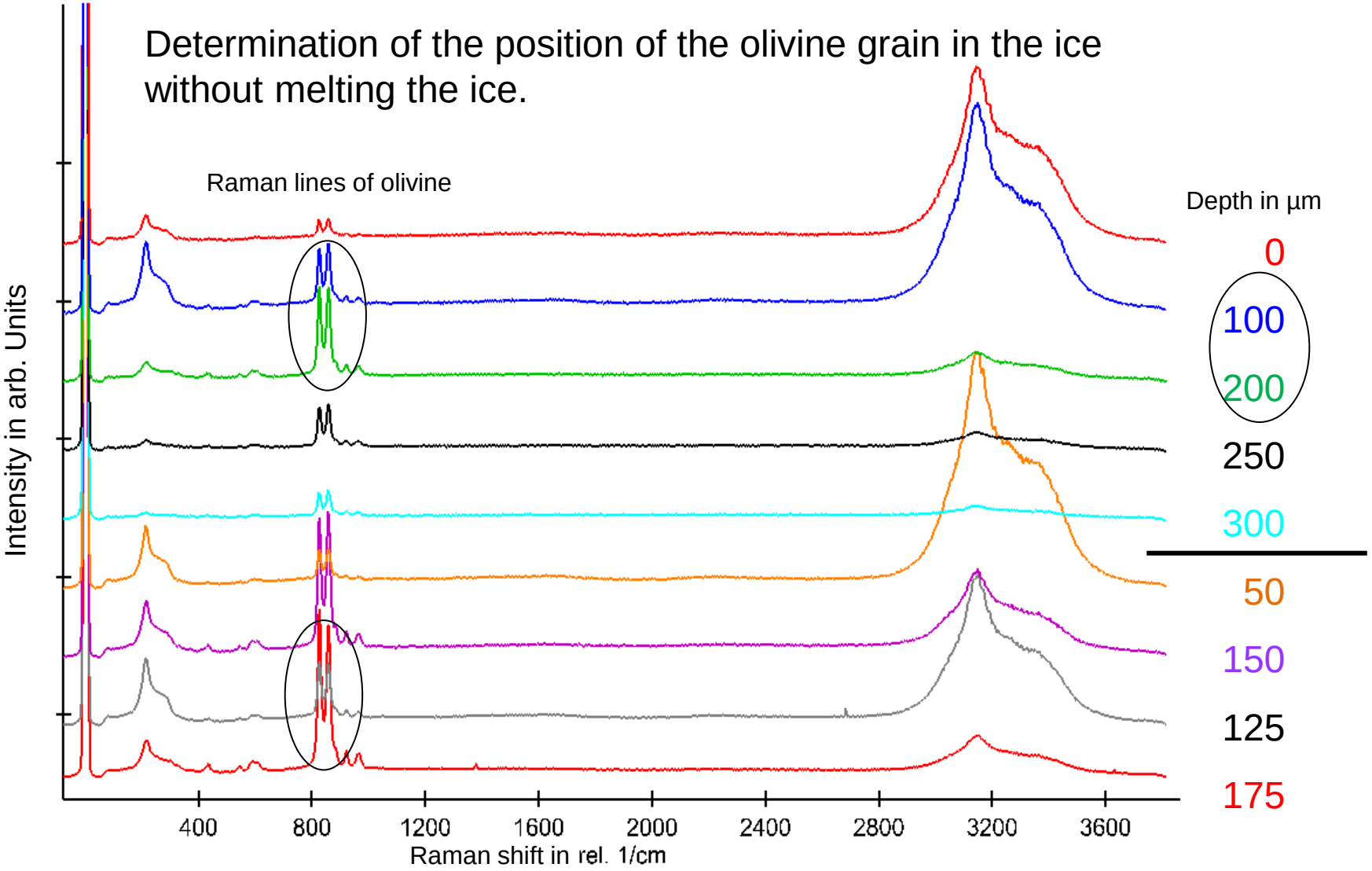
Performance test with selfmade samples of mineral (olivine powder <100 µm) frozen in tap water ice



Test, if inclusion can be seen in ice by Raman spectroscopy without melting the ice:

- Olivine grains were frozen in ordinary tap water in a simple cryo container
- Raman measurements were performed as described before

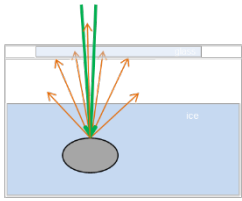
Determination of the position of the olivine grain in the ice without melting the ice.

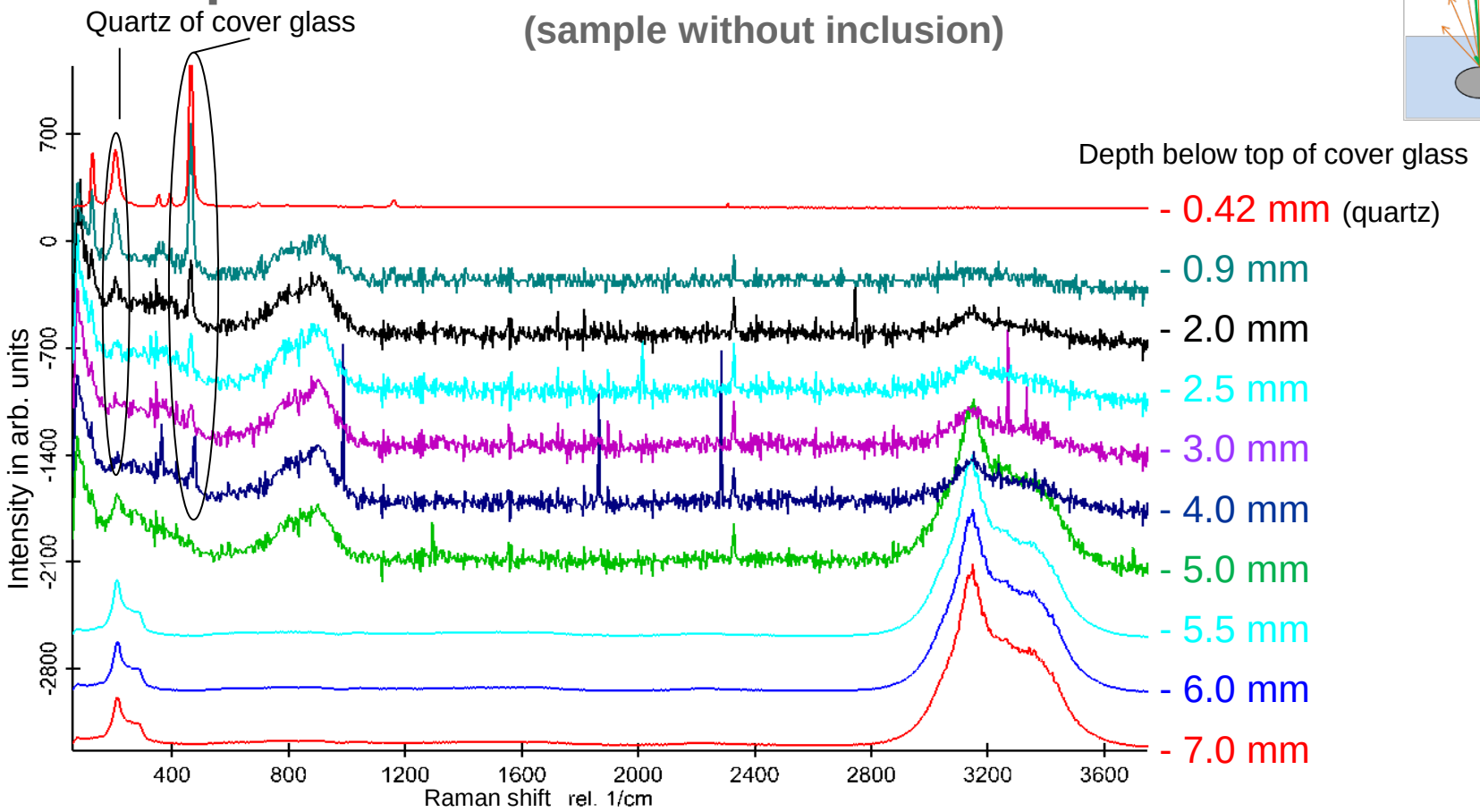


The olivine grain is located 175 µm below the ice surface.

Spectra taken at and in ice from Vostok lake

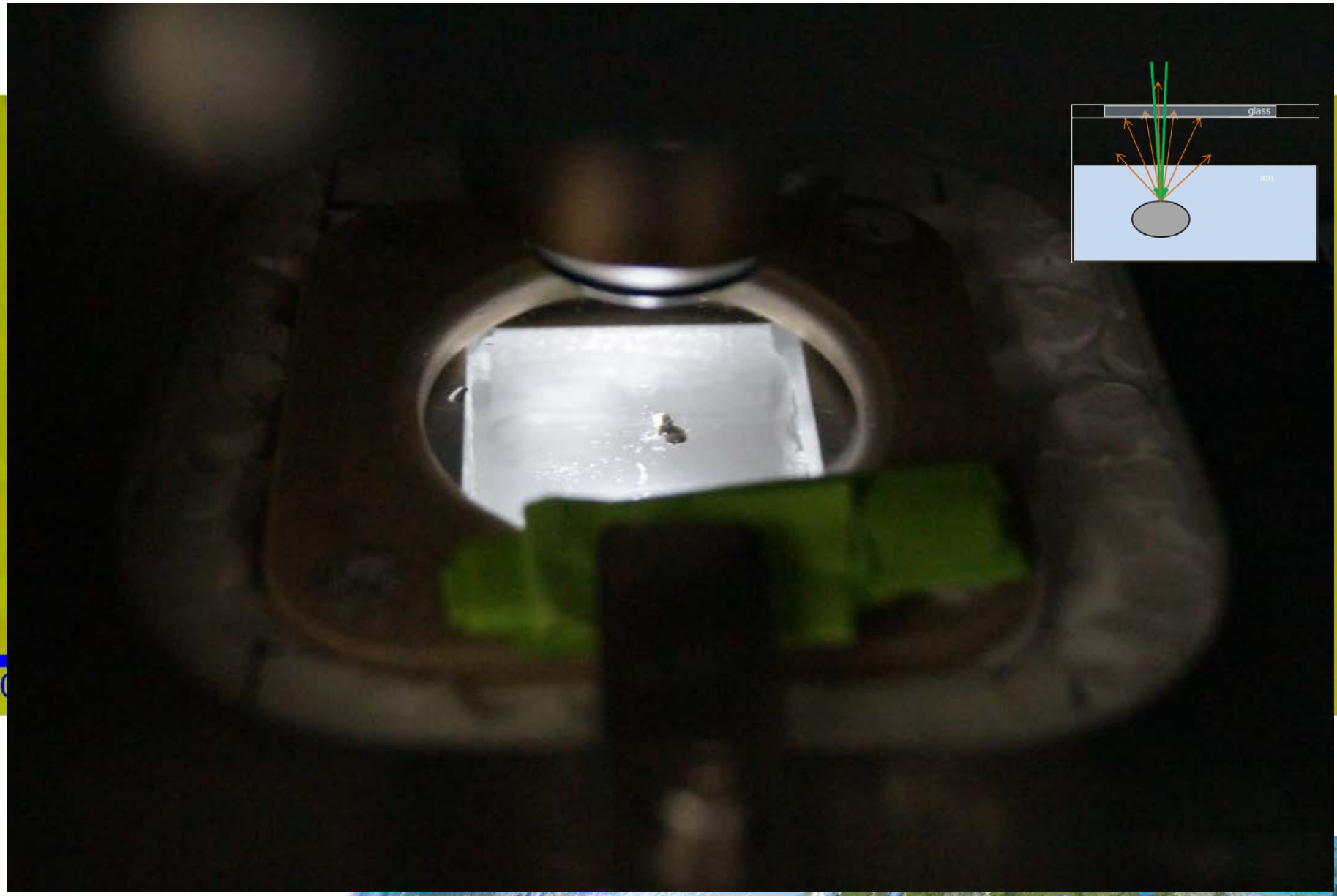
(sample without inclusion)



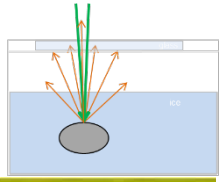


- Raman spectra taken through the quartz window changing the depth of the laser focus.
- The surface of ice is 5 mm below the bottom surface of cover window.

Spectra taken at and in Vostok ice with Inclusion

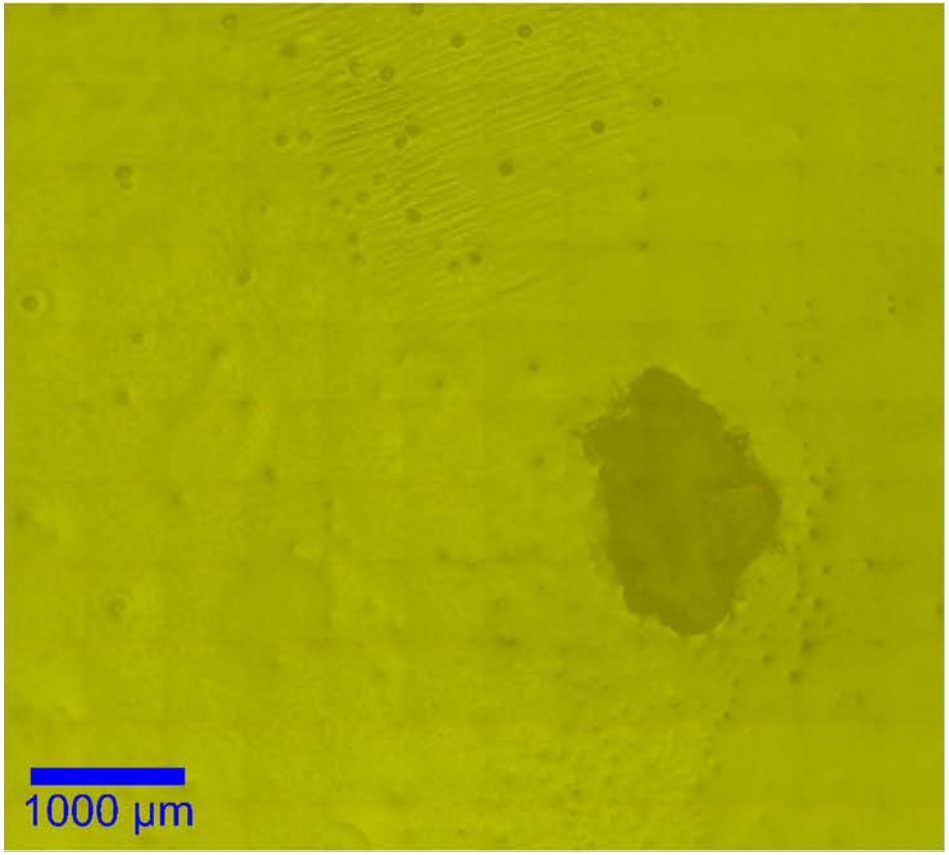


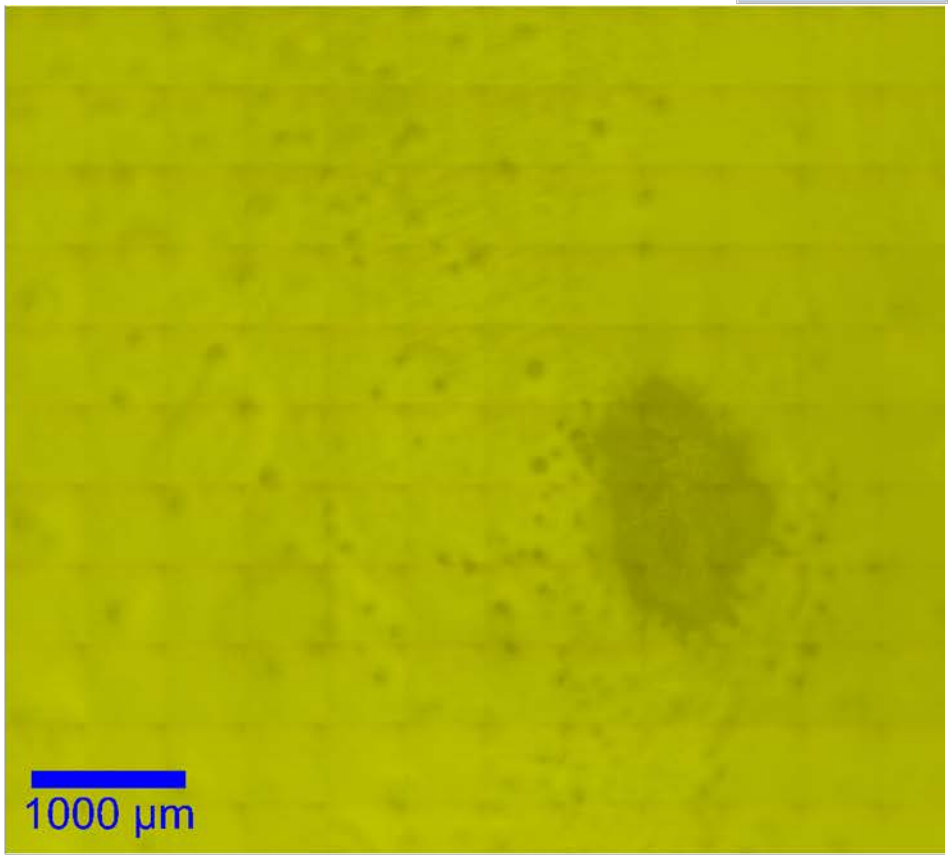
Spectra taken at and in Vostok ice with Inclusion



Microscopic images

Surface of ice is 2960 µm below cover quartz window

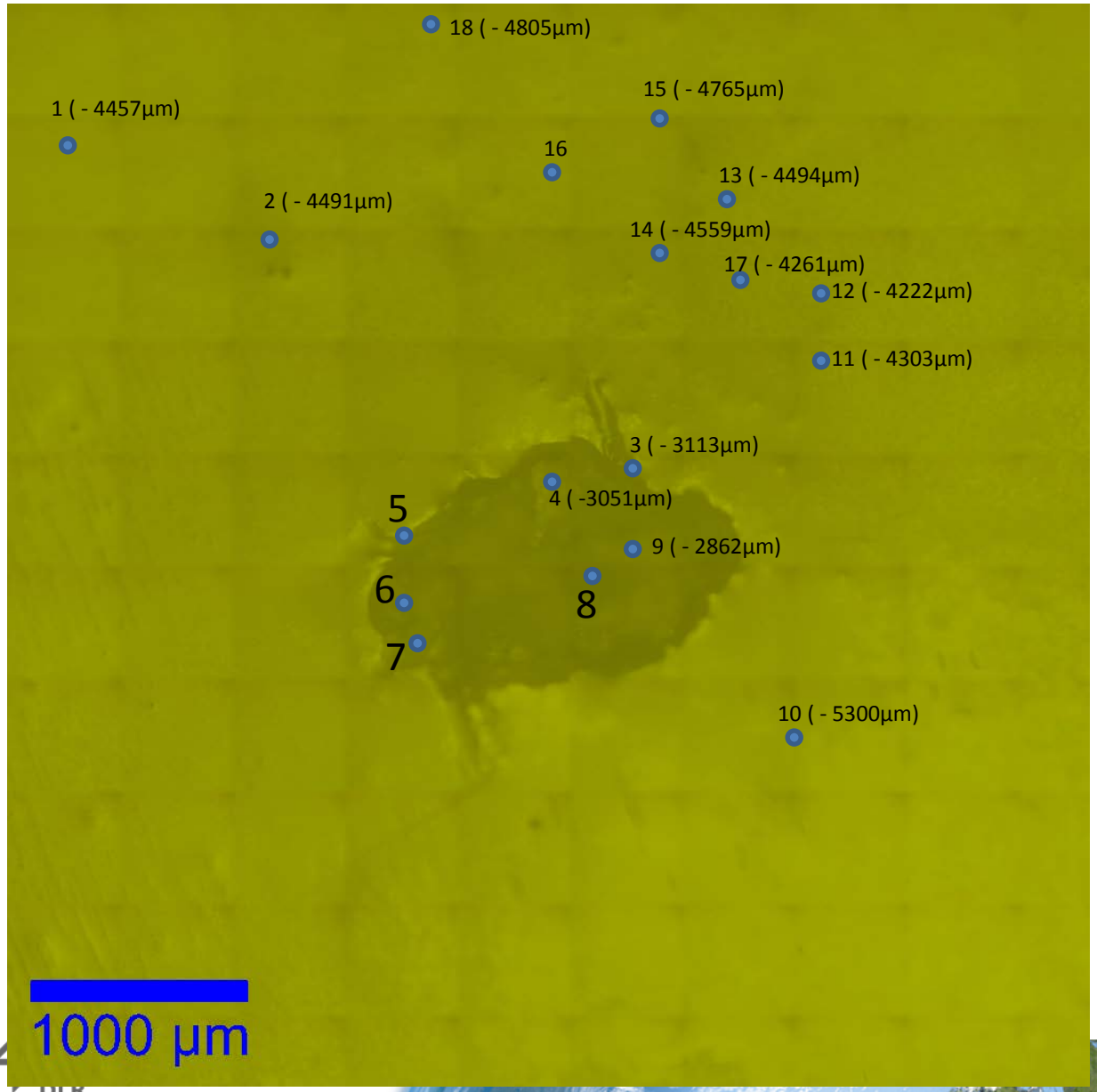




Surface of the surrounding ice
2960 µm under cover quartz window

Above the surrounding ice (+300µm)
2660 µm under cover quartz window

Vostok ice with inclusion

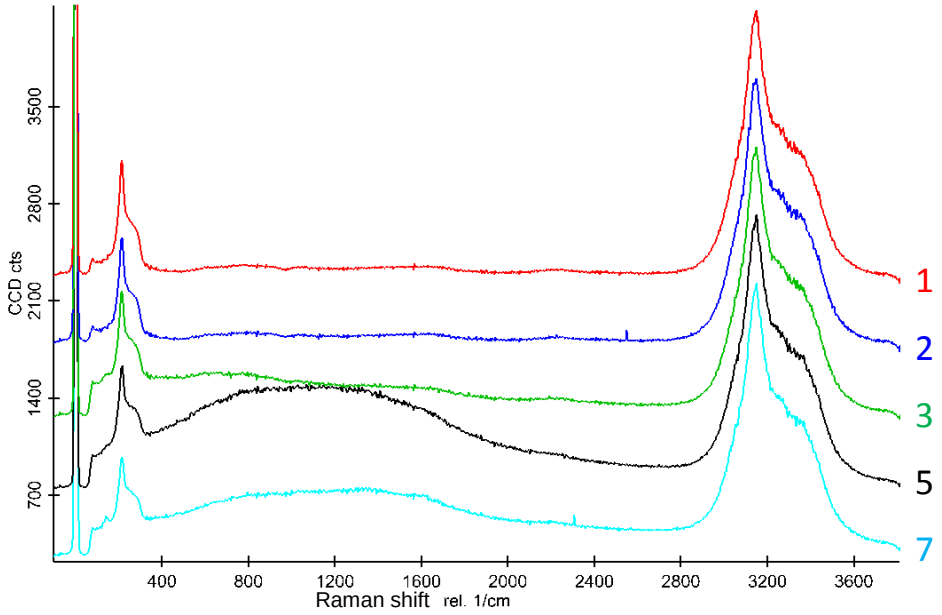


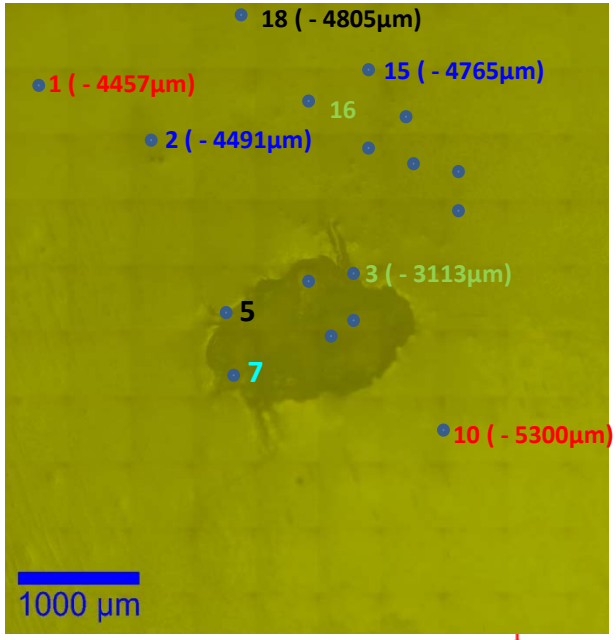
- Measurement points - in depth below cover glass

Surface of ice is at z = -3070 µm below cover glass

Laser power 500 µW
Objective 10x
Measurement time 100 s

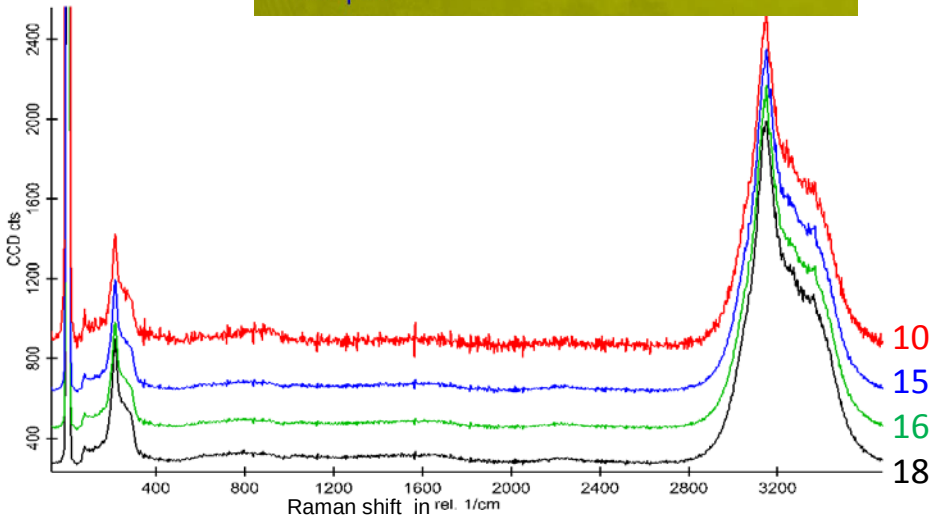
Spectra taken below ice surface, showing only ice



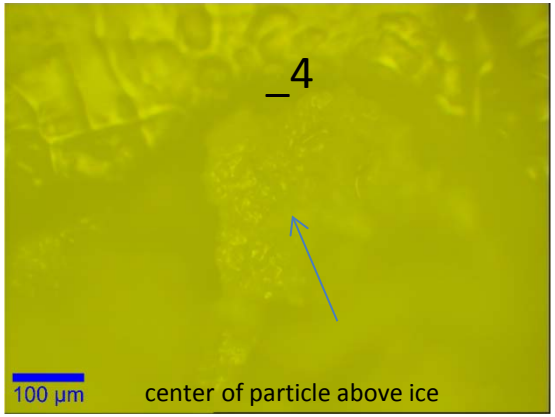


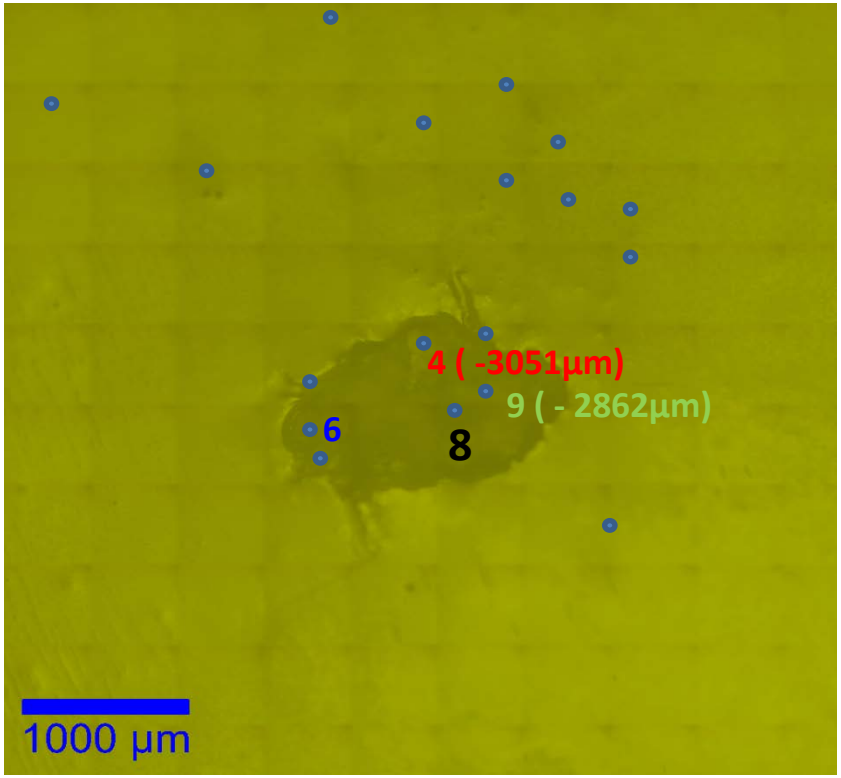
Only ice spectrum visible with some fluorescence on the particle (5, 7)

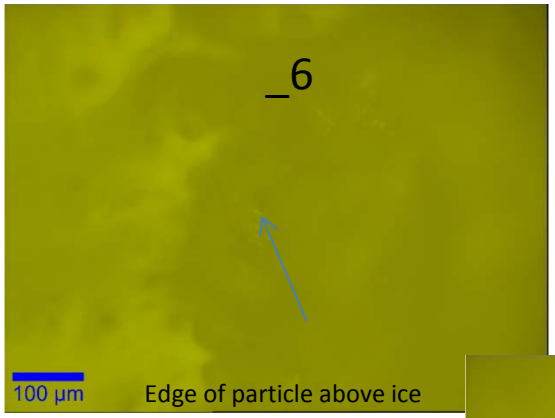
Surface of ice is at z = -3070 µm

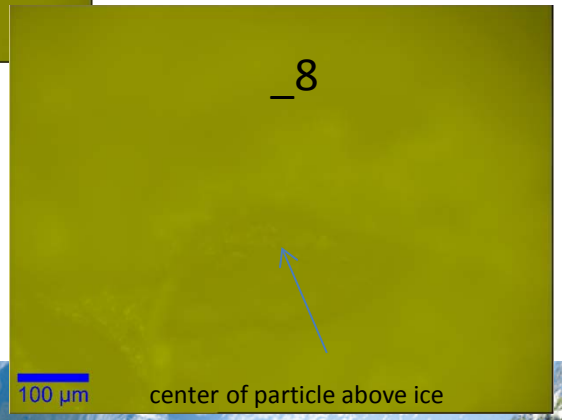


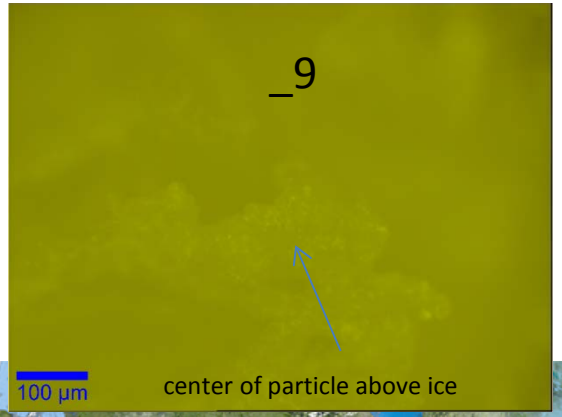
Spectrum on inclusion above ice surface



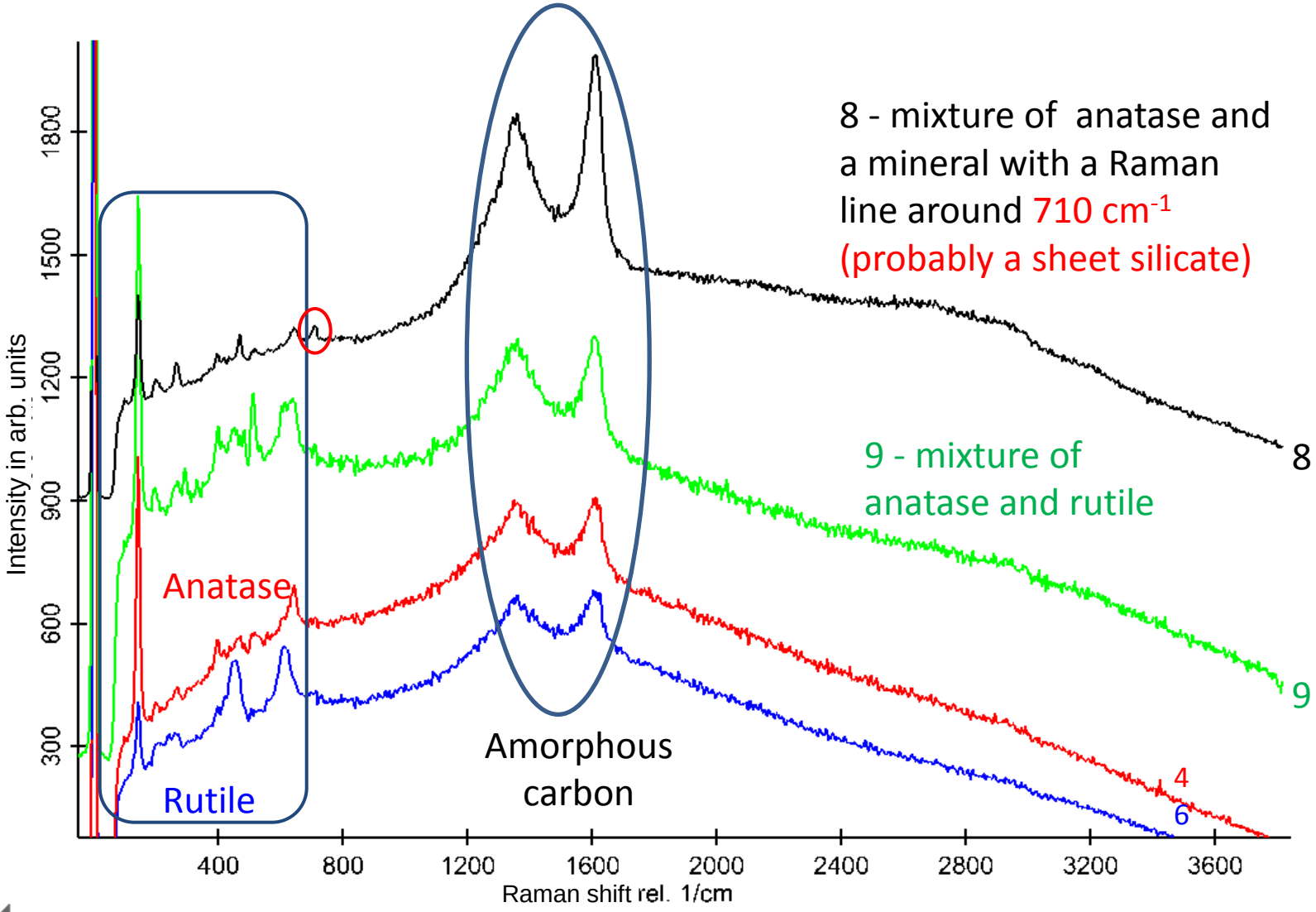




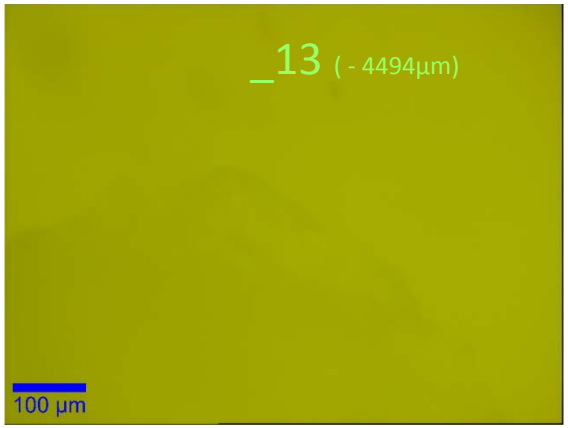


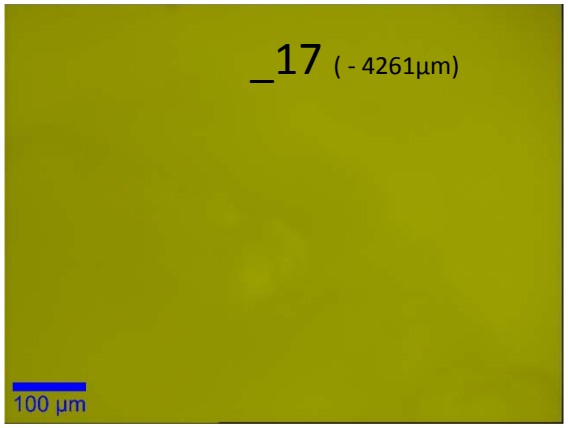


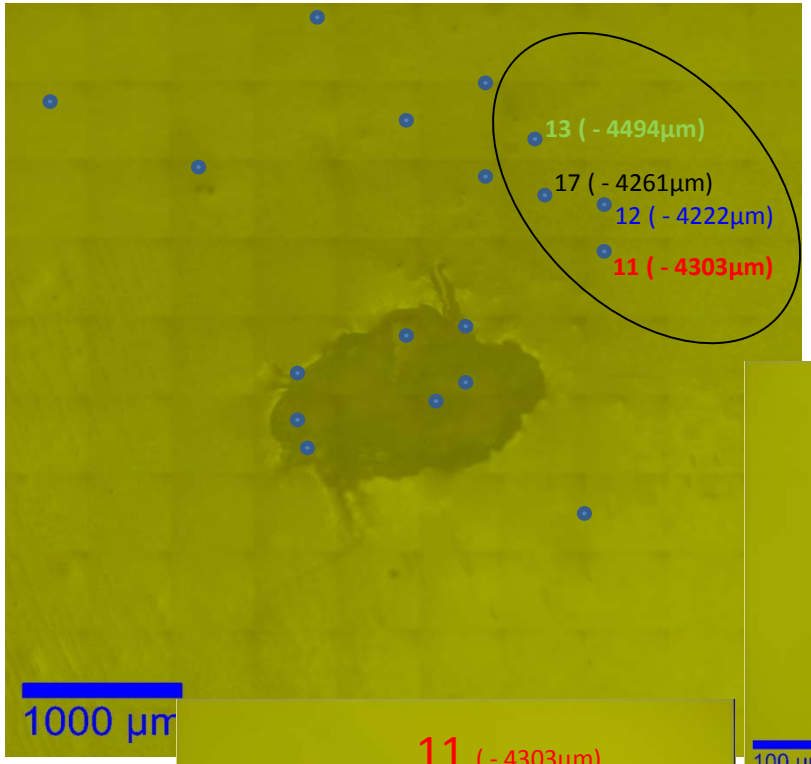
Spectrum on inclusion above ice surface

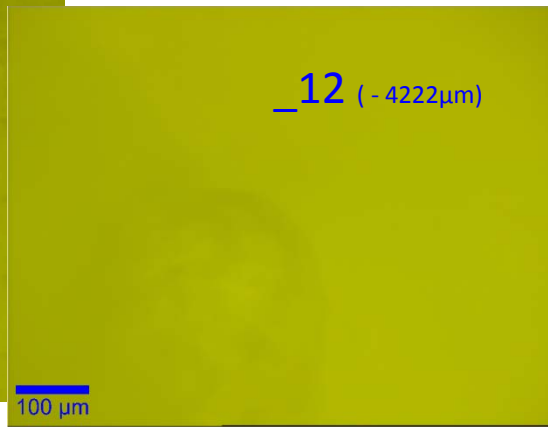


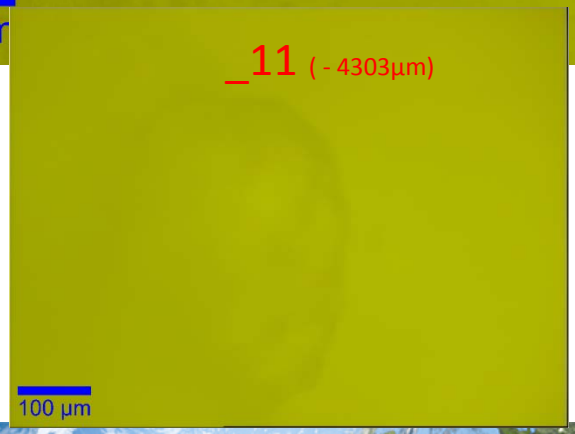
Vostok lake ice with Inclusion below ice surface



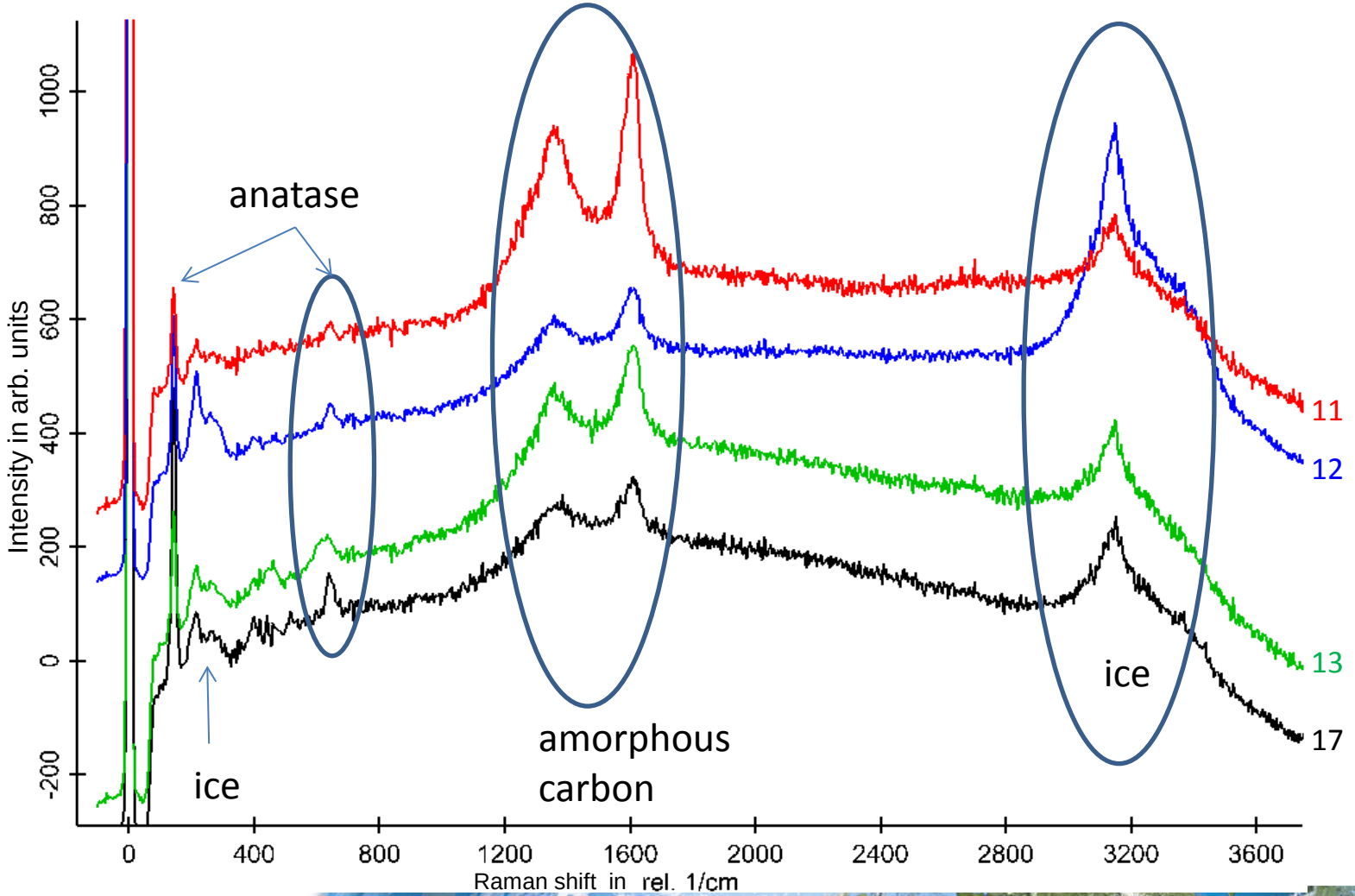








Spectra taken below ice surface on/in structures in ice showing more features than ice



Summary I

- Raman spectra on the surface of the big particle above ice, and below ice:
  either ice or anatase and rutile (TiO_2) and a sheet silicate combined with amorphous carbon (probably contamination).

- Raman spectra below ice surface pointing on structures below the ice surface, that were hardly seen in the microscopic image:
  - structures are stretched and oriented all into the same direction: only ice.
    (probaly gas inside these structures, but impossible to measure Raman of this gas).

  - other structure lookes different: spectra with amorphous carbon and anatase.
    (contamination can be excluded - structure is totally embedded in original ice and never (?) came in contact with the surface or atmosphere. As measurements near this structure in the ice don‘t show amorphous carbon or anatase - amorphous carbon and anatase are parts of the structure.

- So the origin of amorphous carbon is of high interest.

Summary II

- Raman spectroscopy is a usefull nondestructive method for material identification.
- It would be also a very usefull method for insitu measurements for the exploration of the Vostok lake
- Is planned to be used in future missions in space research (ExoMars, Mars 2020, Icy moons, …)
- Suggestion to co-operate with the space science community to test the space instrumentation under the extreme environment and conditions of the Vostok lake.

Thank you for your attention!
Спасибо за ваше внимание!