

# Location and composition of micro-inclusions in deep ice from the EDML ice core (Antarctica) using optical microscope and cryo-Raman spectroscopy

Jan Eichler<sup>1,2</sup>, Ina Kleitz<sup>1</sup>, Maddalena Bayer-Giraldi<sup>1</sup>, Daniela Jansen<sup>1</sup>, Sepp Kipfstuhl<sup>1</sup>, Wataru Shigeyama<sup>3,4</sup>, Christian Weikusat<sup>1</sup>, Frank Wilhelms<sup>1,5</sup> and Ilka Weikusat<sup>1,2,6</sup>

<sup>1</sup> Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Germany; <sup>2</sup> Department of Geosciences, Eberhard Karls University Tübingen, Germany; <sup>3</sup> Department of Polar Science, SOKENDAI (The Graduate University for Advanced Studies), Japan; <sup>4</sup> National Institute of Polar Research, Japan; <sup>5</sup> Georg-August-Universität Göttingen, Germany; <sup>6</sup> Utrecht University, Netherlands.

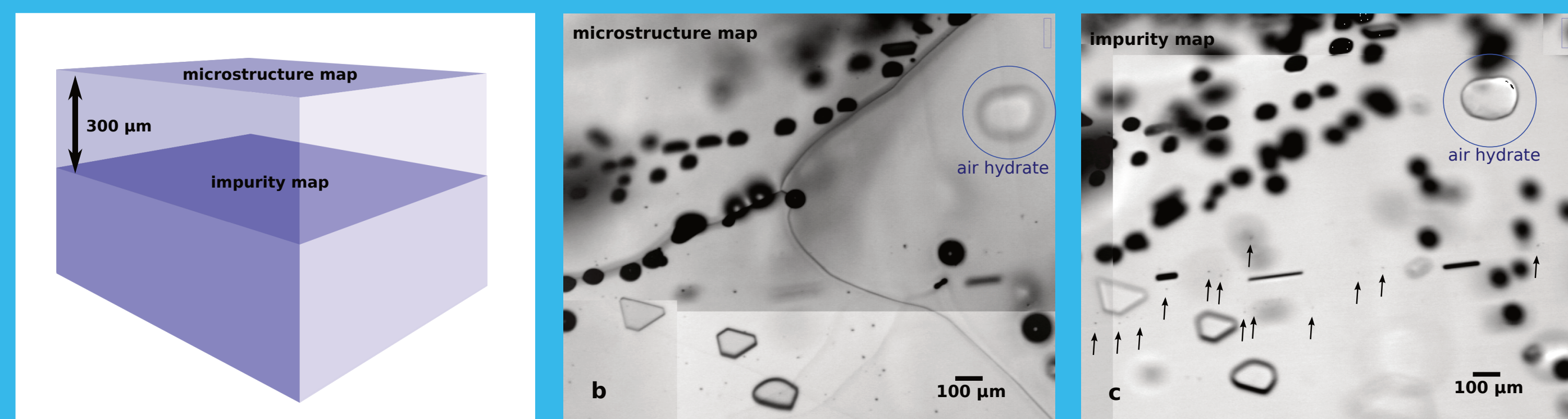
## Motivation

The impurity content in meteoric ice from polar regions is relatively low compared to other natural materials. However, it controls a variety of physical properties of ice - from dielectric response to its mechanical behavior. Links between impurity concentration, changes in ice microstructure and deformation rate have been reported on several scales. In order to approach the responsible mechanisms, a better understanding is needed regarding the in-situ form, location, and distribution of the different species within the polycrystal.



mechanism (theory)	phenomenon (expected)
electrolytic conduction along GB (Wolff, Mulvaney,...)	high concentration of specific impurities along GB and triple junctions
protonic defect density (Jaccard)	Impurities incorporated into the ice-lattice substituting H2O molecules or interstitials (F, Cl, Na, NH4)
grain-size sensitive flow, changes in GB mobility (e.g., Zener pinning)	
dislocation mobility via protonic defects (Glen, Jones)	impurity concentration correlates with high dislocation densities
dislocation density (e.g., via Frank-Read sources)	

## Impurity maps



### Method

Surfaces are polished with a microtome knife and exposed to air for a few hours. Sublimation smoothens the surface and creates grooves at sites of high energy, where grain and subgrain boundaries intersect the surface. In this way 2D maps of grain boundary networks and subgrain structures can be created (microstructure maps). When focusing into the ice volume and choosing transmission light mode  $\mu$ -inclusions appear as dark dots of the size of few microns.

### Samples

Three samples from the EDML ice core (Antarctica) were analyzed:

Depth (m)	Age (ka)	Period
2371.4	129	interglacial
2371.9	129	interglacial
2392.2	138	glacial

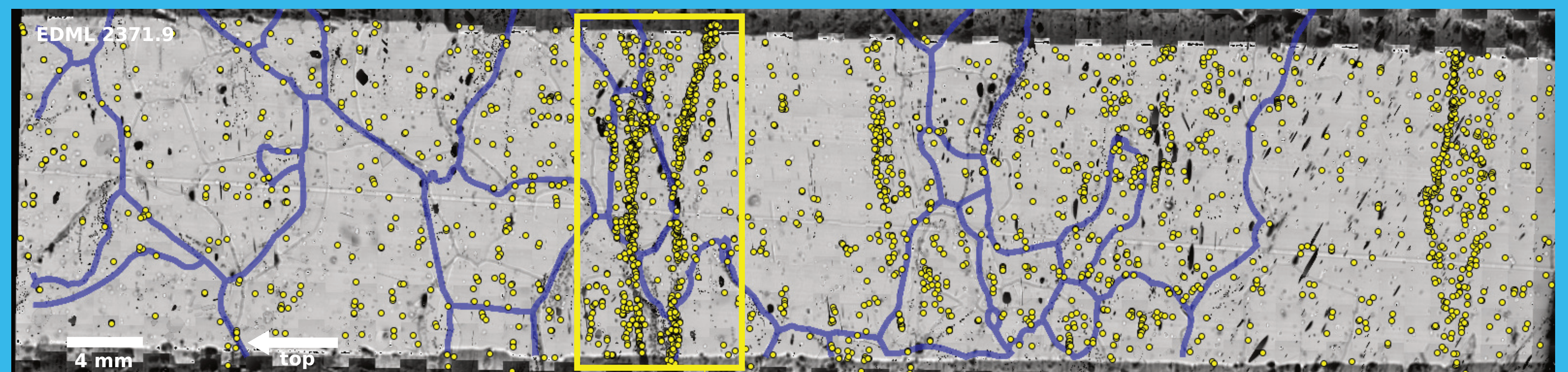
**Distribution of micro-inclusions** is inhomogeneous (Eichler et al., 2017). In the warm-period samples horizontal layers can be distinguished with concentration reaching 40,000 particles/cm<sup>3</sup>. On the  $\mu$ -mm scale, small clusters and chains are frequent. In general no correlation between micro-inclusions and grain boundaries could be detected. Only around 10% of  $\mu$ -inclusions are located within the distance of 300  $\mu$ m to a grain boundary. More than 90% of  $\mu$ -inclusions are found in the grain interiors. The concentration of  $\mu$ -inclusions and clusters seems not to depend on shape, size or crystal orientation of individual grains. Instead, high accumulations of secondary gas inclusions along grain boundaries are observed. These micro-bubbles do not occur insitu, but are secondary artifacts due to relaxation of the material.

### Zener pinning

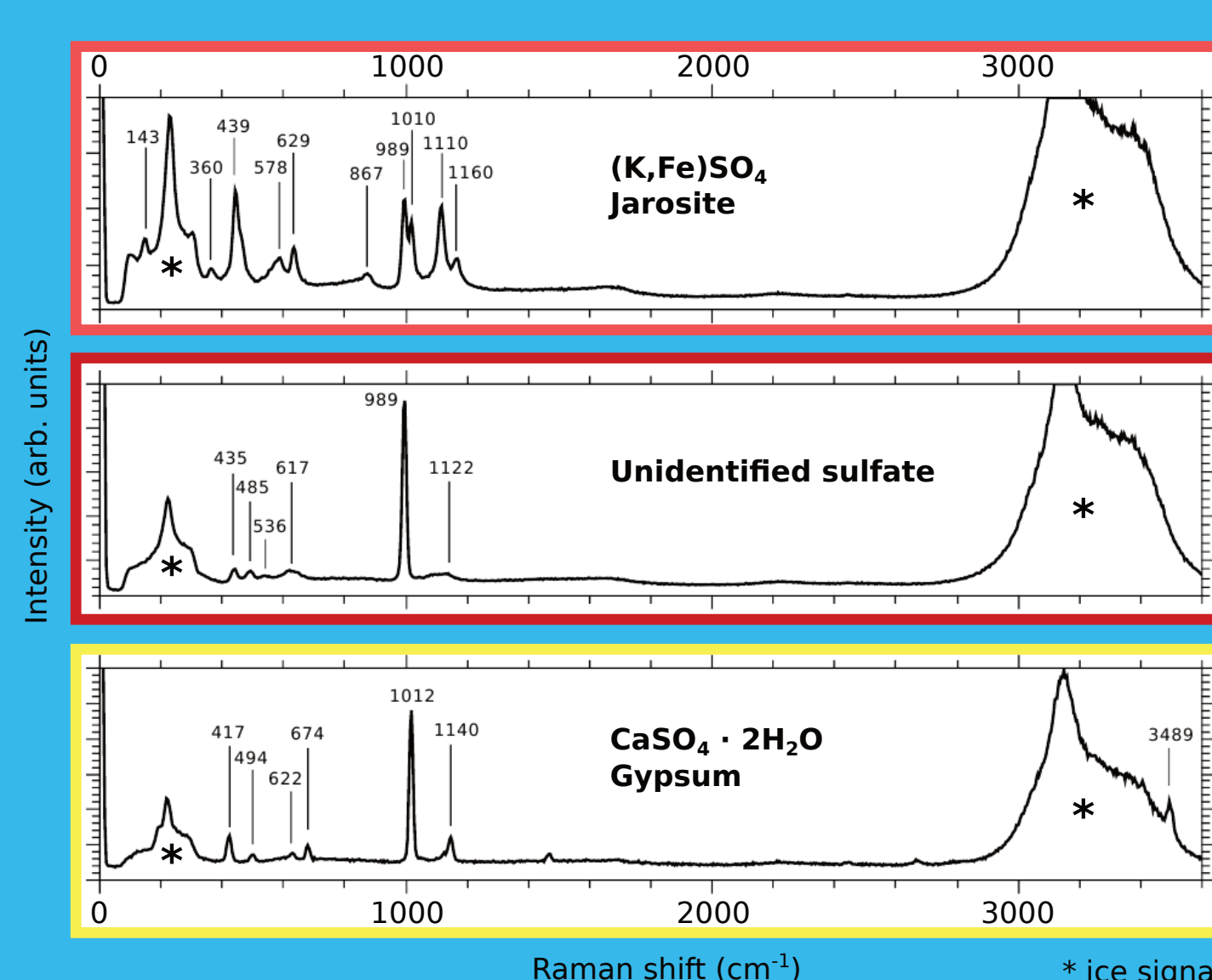
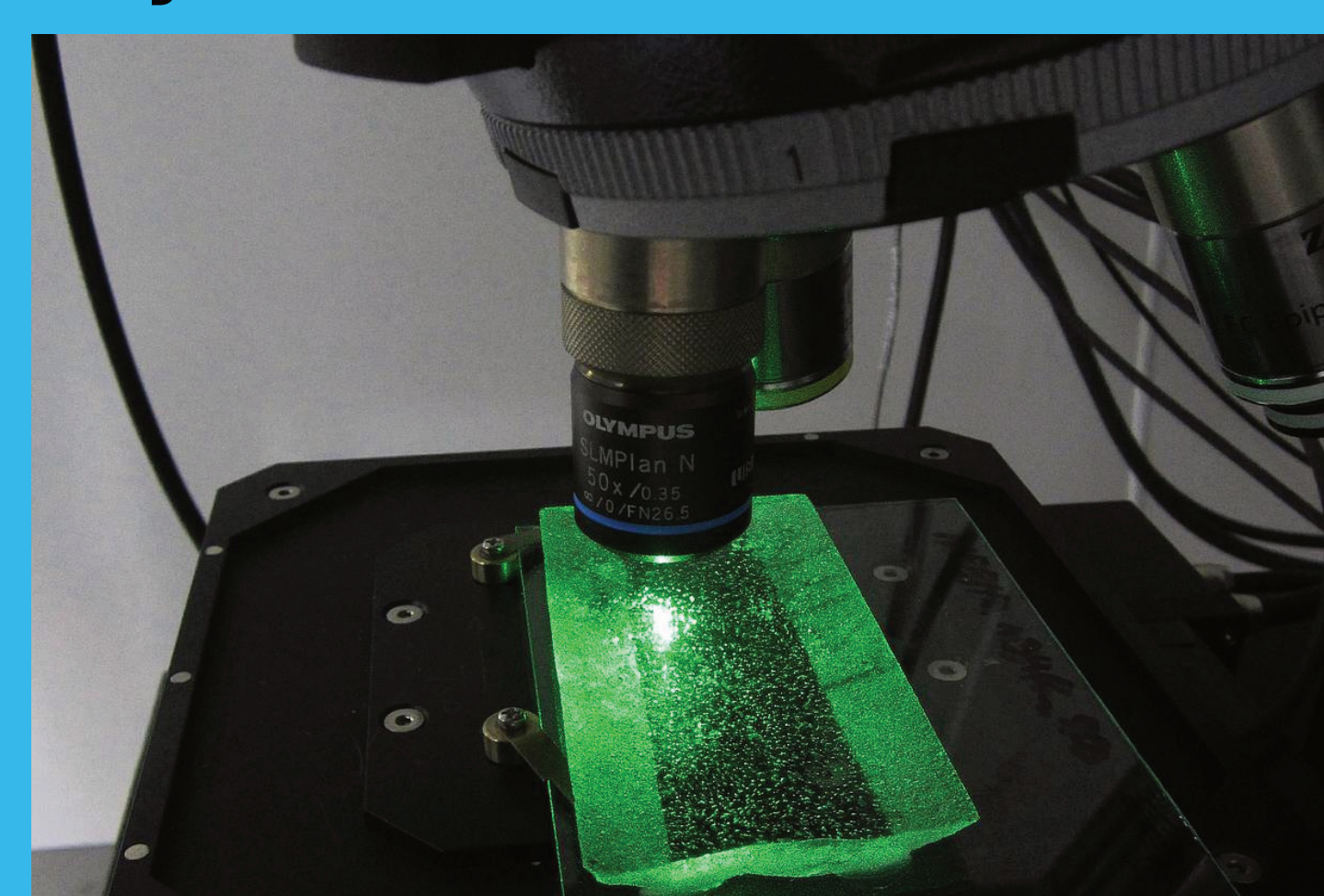
The observations indicate that the Zener interaction is not strong enough to cause harvesting and dragging of  $\mu$ -inclusions by grain boundaries - "slow mode pinning" (Alley et al., 1986). In contrast, fast mode pinning - i.e., temporal particle-boundary interaction can still reduce the driving force for grain boundary migration.

### Conclusion points and questions

- No slow mode pinning.
- No redistribution of  $\mu$ -inclusions by Zener drag.
- Other links between  $\mu$ -inclusions and grain size?
- Other links between  $\mu$ -inclusions and deformation rate?
- What is the role of dissolved impurities?



## Cryo-Raman



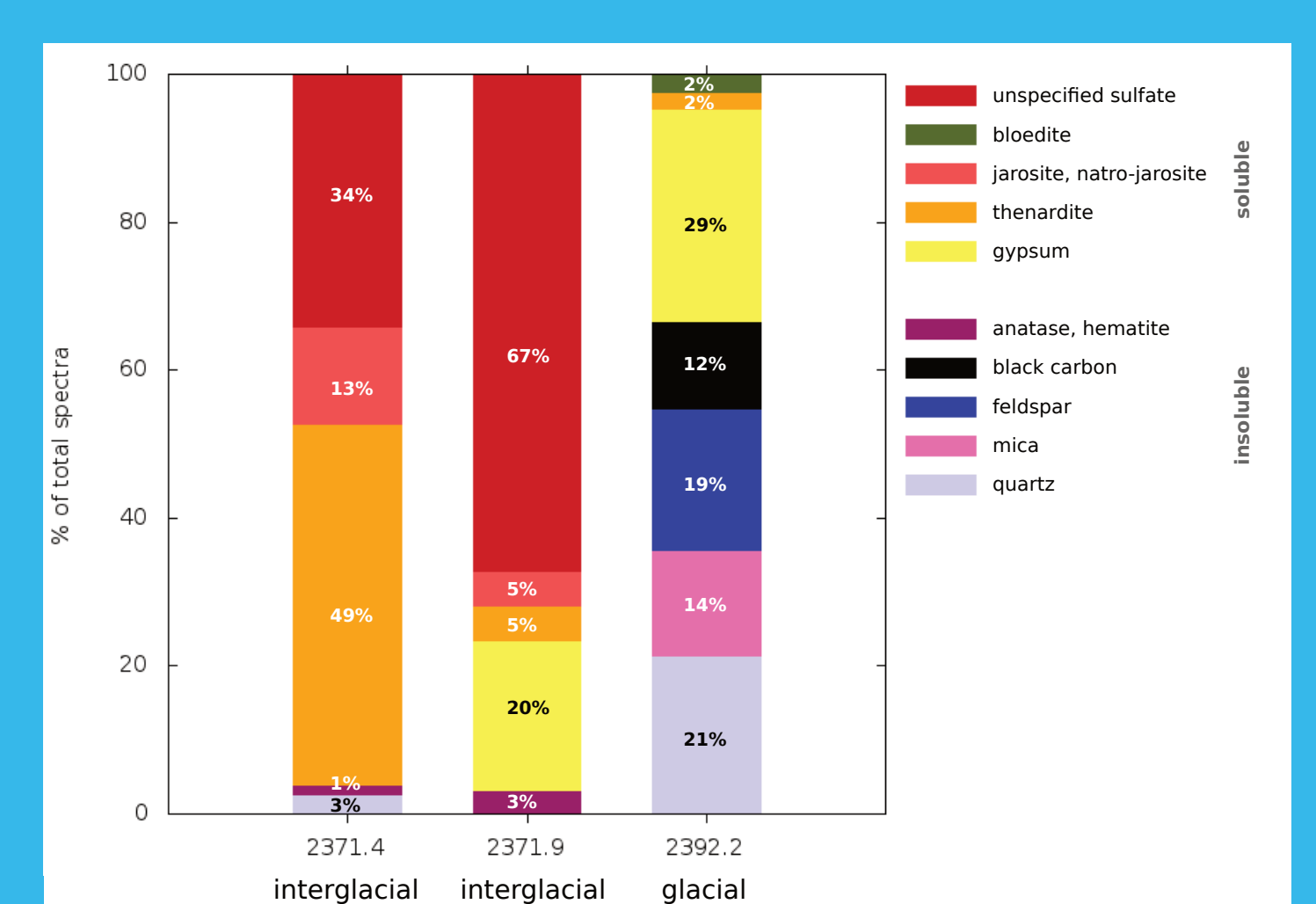
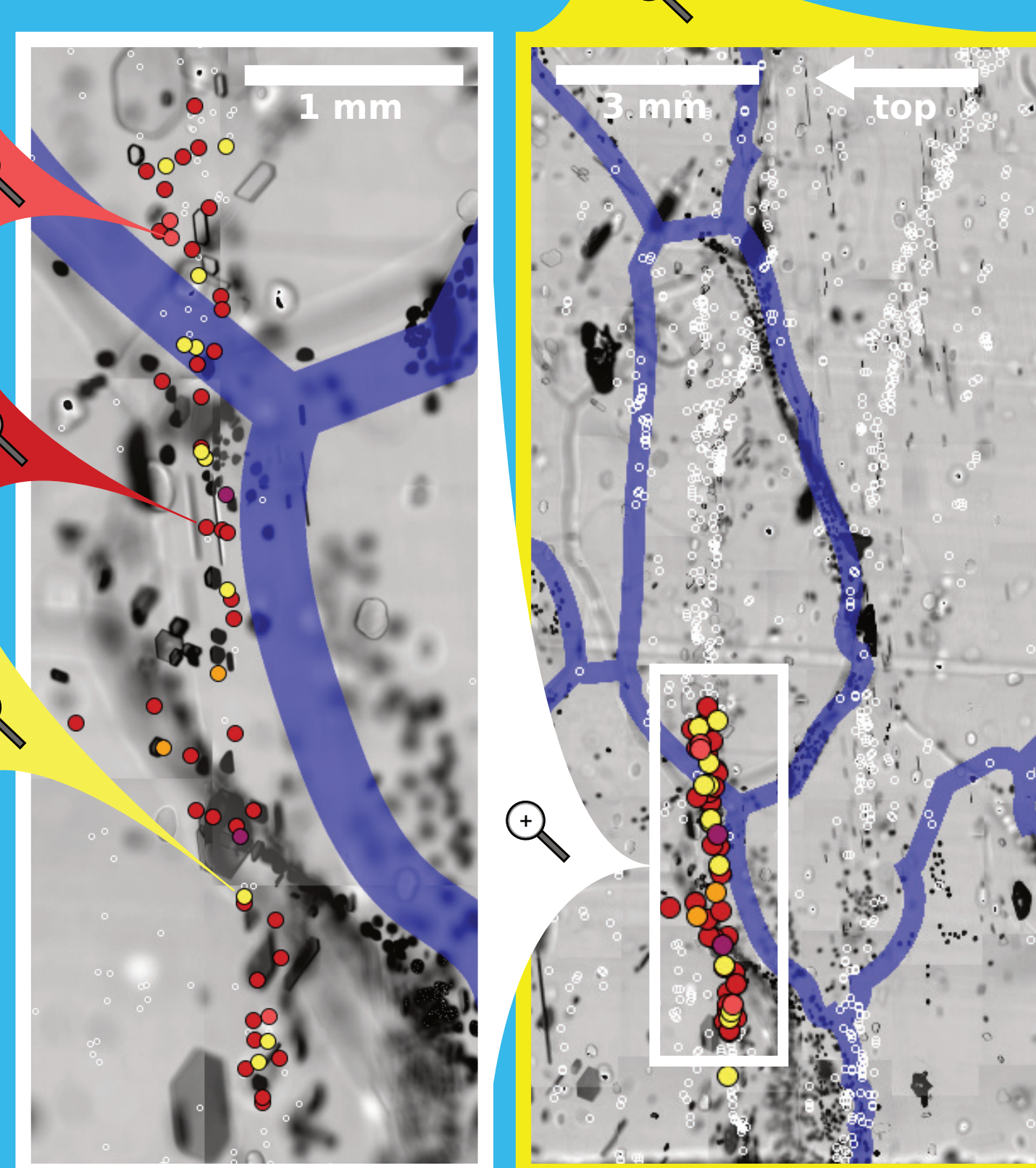
### The Cryo-Raman system

WITec alpha 300 M+ with UHTS 300 spectrometer and Nd:YAG laser (532 nm) set up in the AWI cryolab at  $-15^{\circ}\text{C}$ .

**Raman spectra** are decomposed into discrete vibrational modes and compared to reference spectra. A good quality spectrum includes several modes which enable confident identification of the species.

### Measured spectra

soluble	insoluble	Chemical Formula
unspecified sulfate	anatase, hematite	$\text{TiO}_2, \text{Fe}_2\text{O}_3$
bleoedite	black carbon	C
jarosite, natro-jarosite	feldspar	
thenardite	mica	
gypsum	quartz	$\text{SiO}_2$
		$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
		$(\text{F,K})\text{SO}_4$
		$\text{Na}_2\text{SO}_4$
		$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$



### Impurity composition

The glacial ice (2392.2) contains mostly insoluble particles such as silicates and black carbon.

Interglacial samples (2371.4, 2371.9) contain almost exclusively sulfate salts such as  $\text{Na}_2\text{SO}_4$  (thenardite),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) and others.

The different species are well mixed. No evidence of segregation or special partition has been found.

## References

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