

# Marine nanoparticles



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# Outline

## **Background:**

Small stuff matters

Submarine tailings deposition

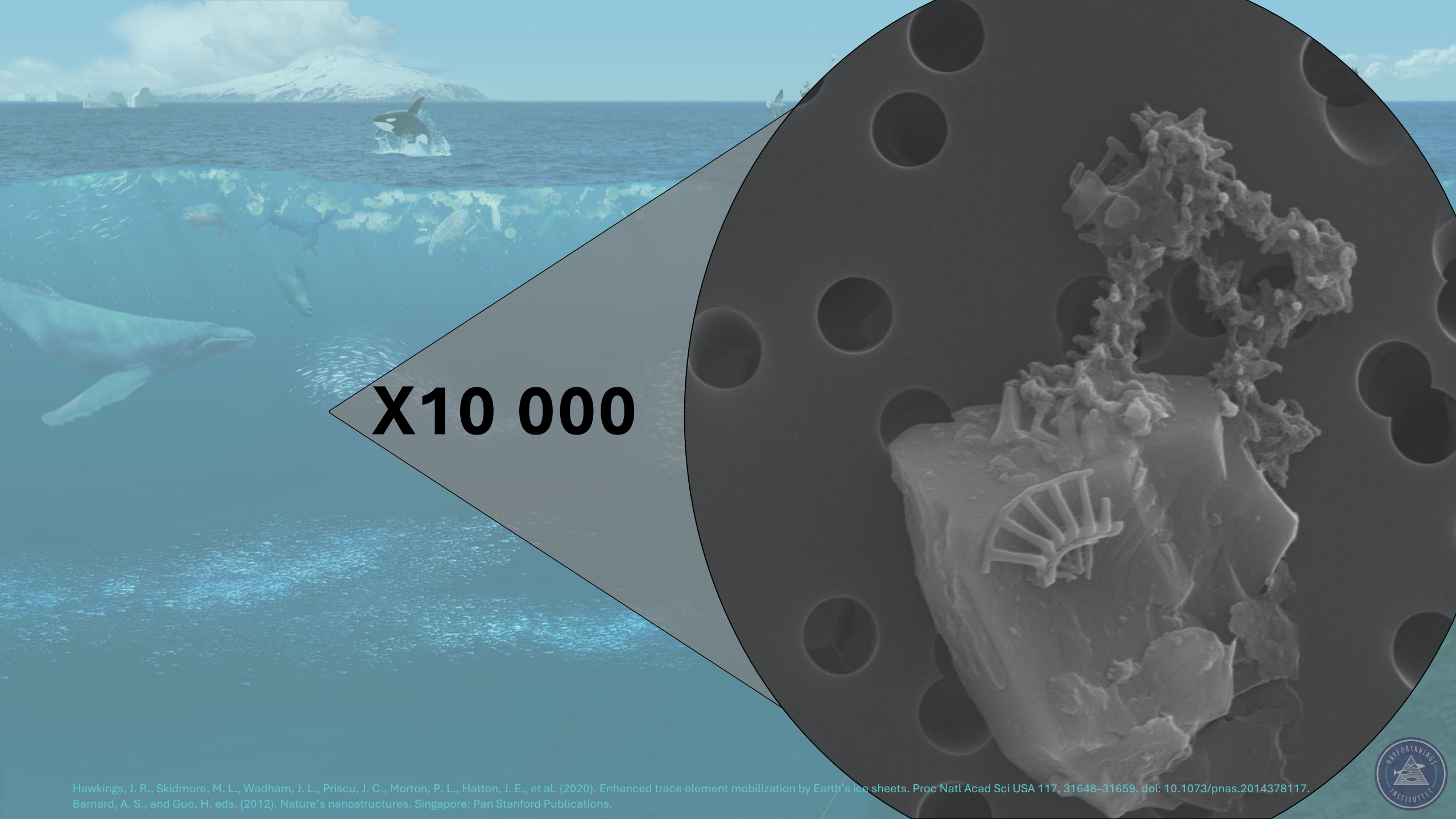
## **Distribution of inorganic NPs in a Norwegian fjord:**

Methods

New data

# Background





**X10 000**

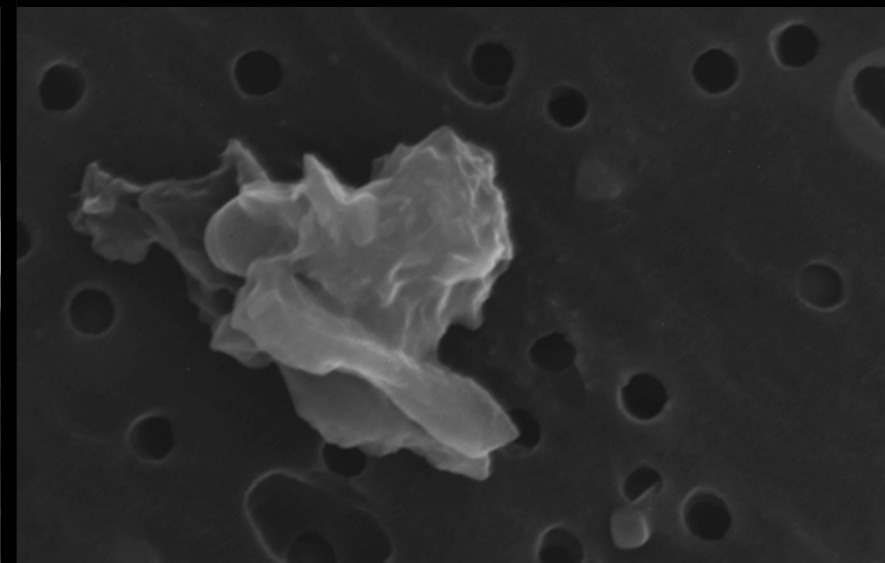
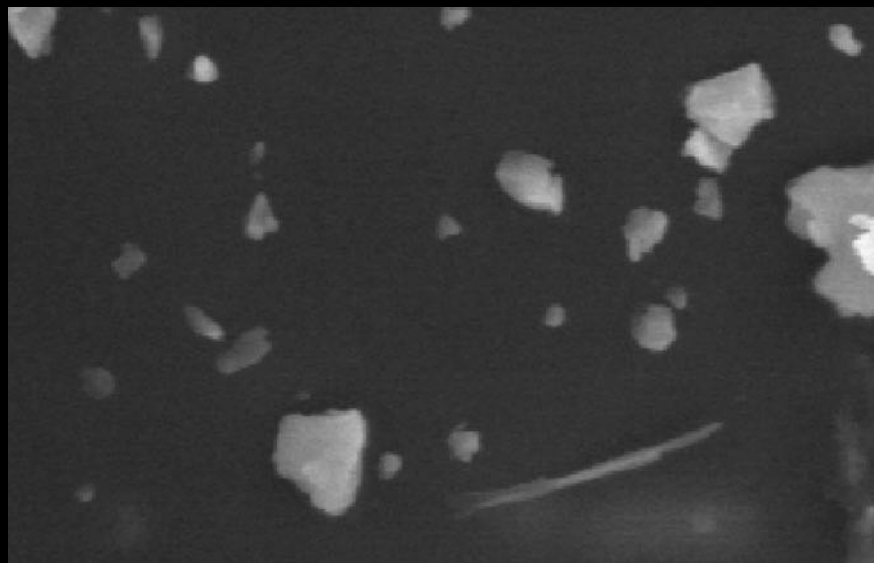
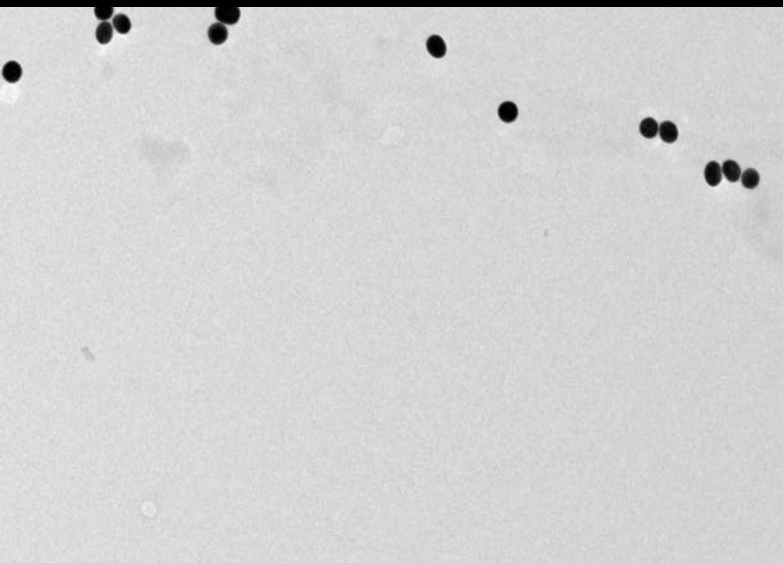




**ENGINEERED**

**INCIDENTAL**

**NATURAL**







Available online at [www.sciencedirect.com](http://www.sciencedirect.com)



International Journal of Pharmaceutics 355 (2008) 150–163

INTERNATIONAL JOURNAL OF  
**PHARMACEUTICS**

[www.elsevier.com/locate/ijpharm](http://www.elsevier.com/locate/ijpharm)

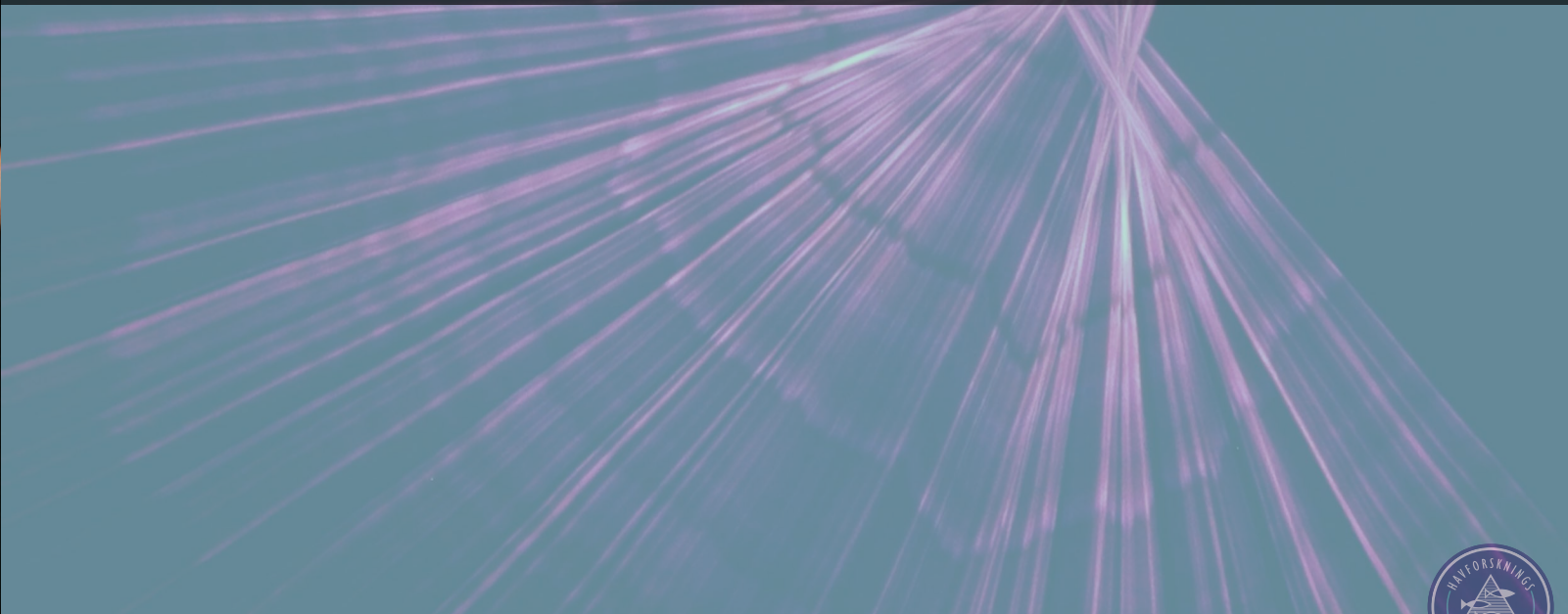
## Size analysis of submicron particles by laser diffractometry—90% of the published measurements are false

Cornelia M. Keck\*, Rainer H. Müller

*Department of Pharmaceutical Technology, Biopharmaceuticals & NutriCosmetics, Free University of Berlin,  
Kelchstrasse 31, 12161 Berlin, Germany*

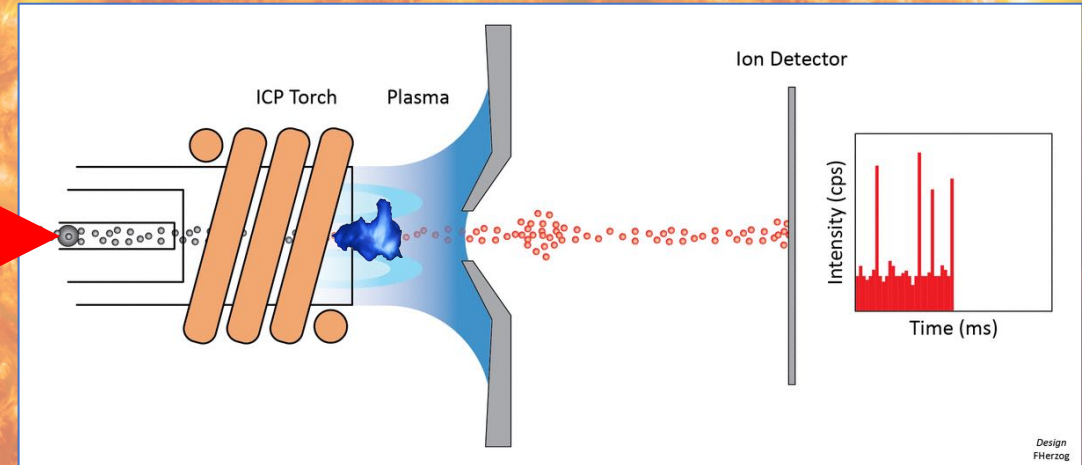
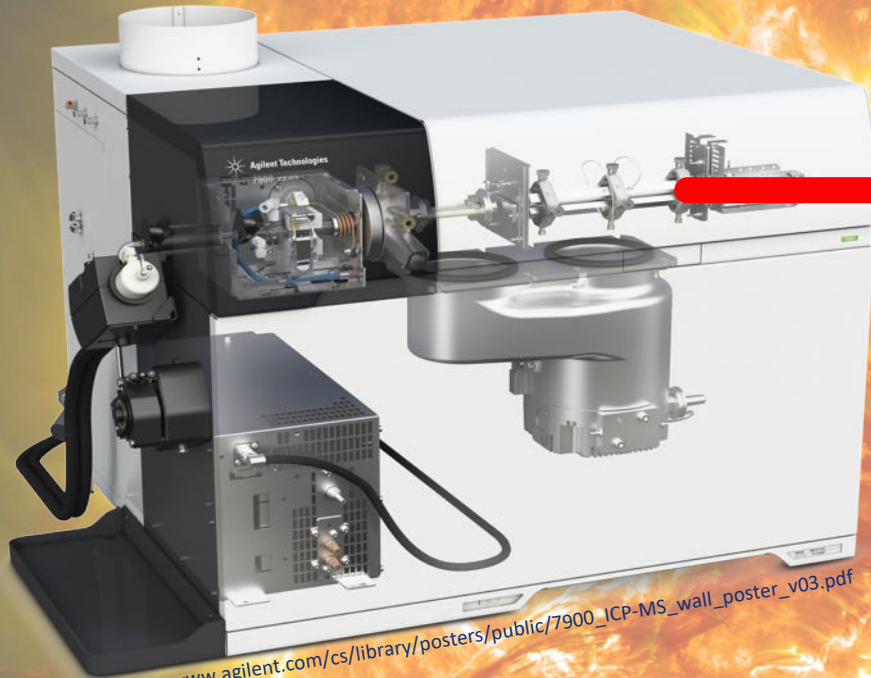
Received 10 September 2007; received in revised form 3 December 2007; accepted 4 December 2007  
Available online 15 December 2007

clays – colloids - submicrometer particles – nanoparticles (NPs)





# single particle-ICP-MS



From [www.webdepot.umontreal.ca/Usagers/wilkinsk/MonDepotPublic/single-particle-inductively-coupled-plasma-mass-spectrometry-\(sp-icpms\).html](http://www.webdepot.umontreal.ca/Usagers/wilkinsk/MonDepotPublic/single-particle-inductively-coupled-plasma-mass-spectrometry-(sp-icpms).html)

Adapted from [www.agilent.com/cs/library/posters/public/7900\\_ICP-MS\\_wall\\_poster\\_v03.pdf](http://www.agilent.com/cs/library/posters/public/7900_ICP-MS_wall_poster_v03.pdf)





# Submarine tailings disposal (STD)

## Dei skal lenke seg fast for å stoppe dumping i fjorden

Ungdom er klare til kamp for å stanse anleggsmaskinene som kjem til Førdefjorden.



Bård Siem  
@BardSiem  
Journalist

Bergens Tidende

Lokalt Lokalt v

Jan Grimeland  
Jan

Nå begynner forarbeidet til gruvedepoiet i Førdefjorden. Her har 15 ungdommer flyttet inn, og forbereder seg på sivil ulydighet.

Aksjonistene vil hindre at Nordic Mining får rive 23 bygninger ved Engebøfjellet.

er fra Vevring, Sunnfjord  
24. feb. kl. 06:38  
124. feb. kl. 07:25



– Engebøprosjektet er et enormt naturinngrep, og det er frustrerende at politikerne ikke tør å ta en

## Vil stanse gruvedrift – det kan koste staten milliarder

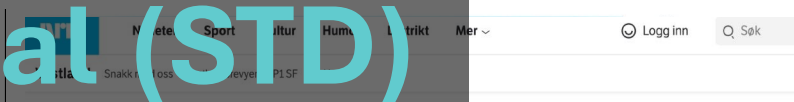
SV lover stans av gruvedriften i Repparfjorden etter valget. Hvis nestleder Torgeir Knag Fylkesnes får Stortinget med på det, kan det koste staten flere milliarder kroner i erstatning.



Christian Kråkenes  
Journalist  
Irmelin Kulbrandstad  
Journalist

## Opposisjonen vil forby all dumping i sjøen

SV, Rødt, MDG og Venstre fremjar felles forslag til Stortinget om å forby all dumping av gruveavfall i sjøen.



## Jakter etter mineraler til flere milliarder

Et selskap mener å ha funnet kvarts for flere titalls milliarder kroner ved Årnes i Kvinnherad.

## Ørjan har aksjonert mot gruvedrift i 15 år – til liten nytte

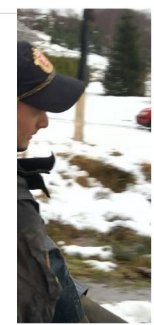
Søk Meny

Aftenposten A-magasinet Oslo Sport Meninger

Norge Miljø og klima

## Lenker seg fast mot omstridt gruvedrift i Finnmark

Gruveselskapet har ingen planer om å anmelde aksjonistene: – Vi vil løse dette gjennom dialog.

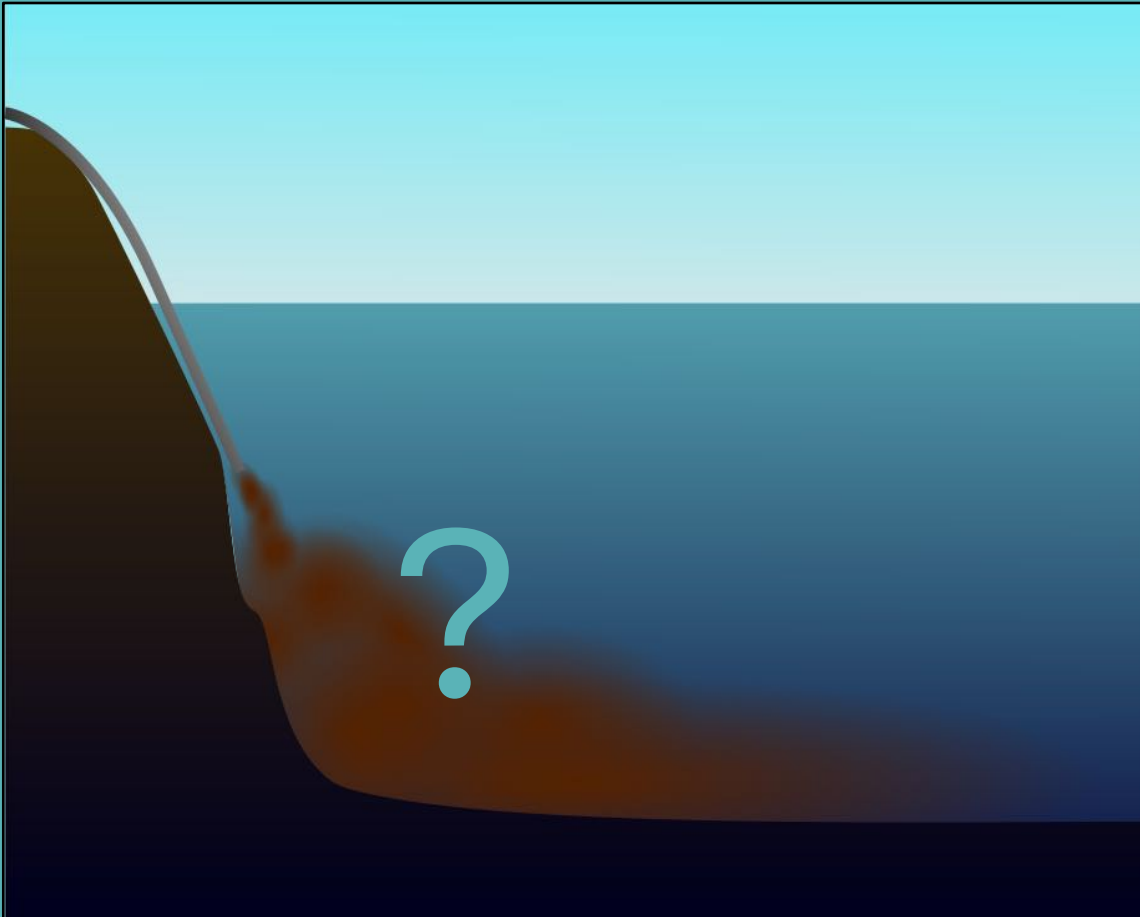


Håvard Nyhus  
Journalist  
Håvard Heggen  
Journalist  
Benedikte Grov  
Journalist  
Vi rapporterer fra Sunnfjord  
Publisert 17. feb. kl. 21:44

rt fjerna av politiet.



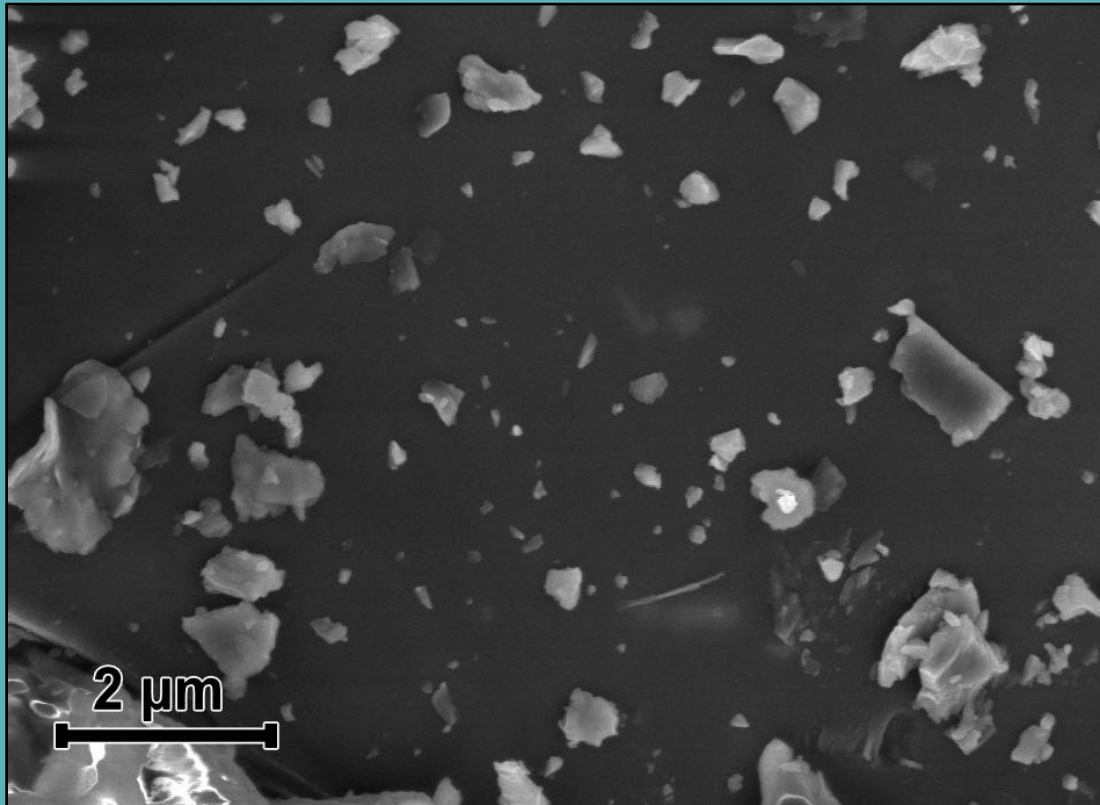
# Submarine tailings disposal (STD)



- Megatonnes (MT) waste per year
- 16 sites **worldwide**<sup>1</sup> - four **NO**
- Controversial and poorly understood
- Long term impact(?)



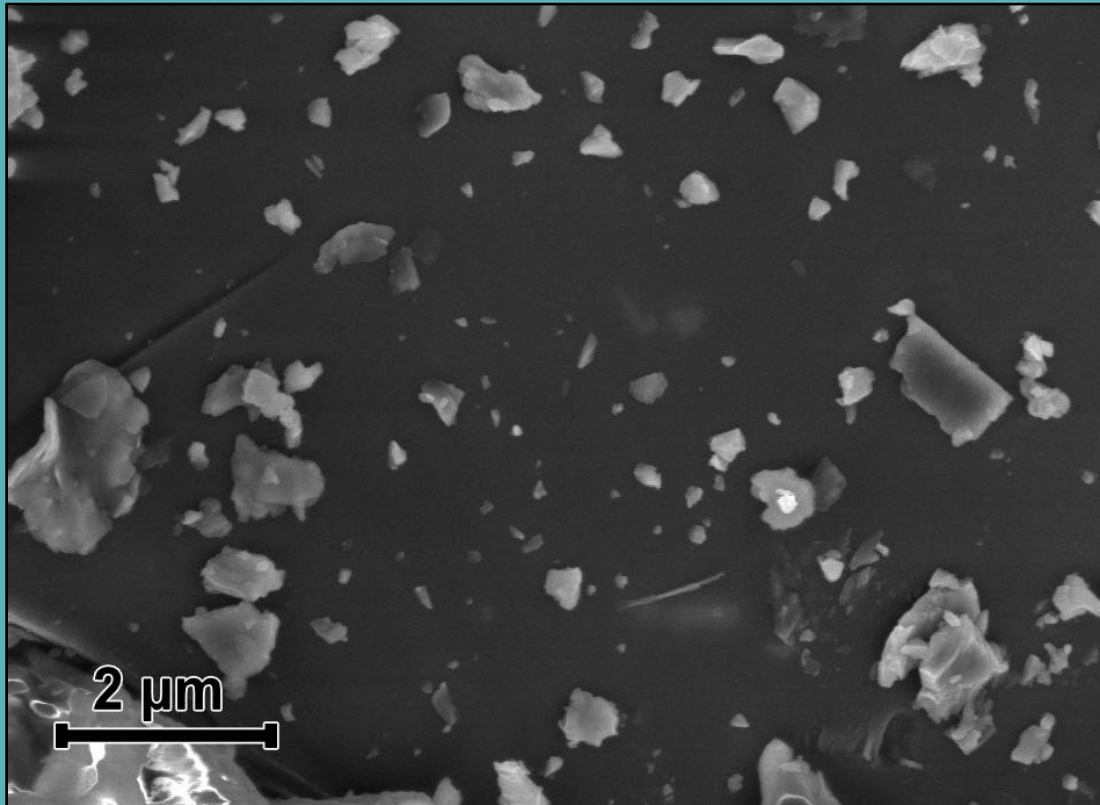
# Submarine tailings disposal (STD)



- Global **Natural** NP flux:  
~  $10^3$ s MT/year<sup>1,2</sup>  
(Atmospheric, riverine, glacial, hydrothermal)
- **Incidental** NPs from one STD?  
4 MT/yr x 30%  $\approx$  1.2 MT/yr



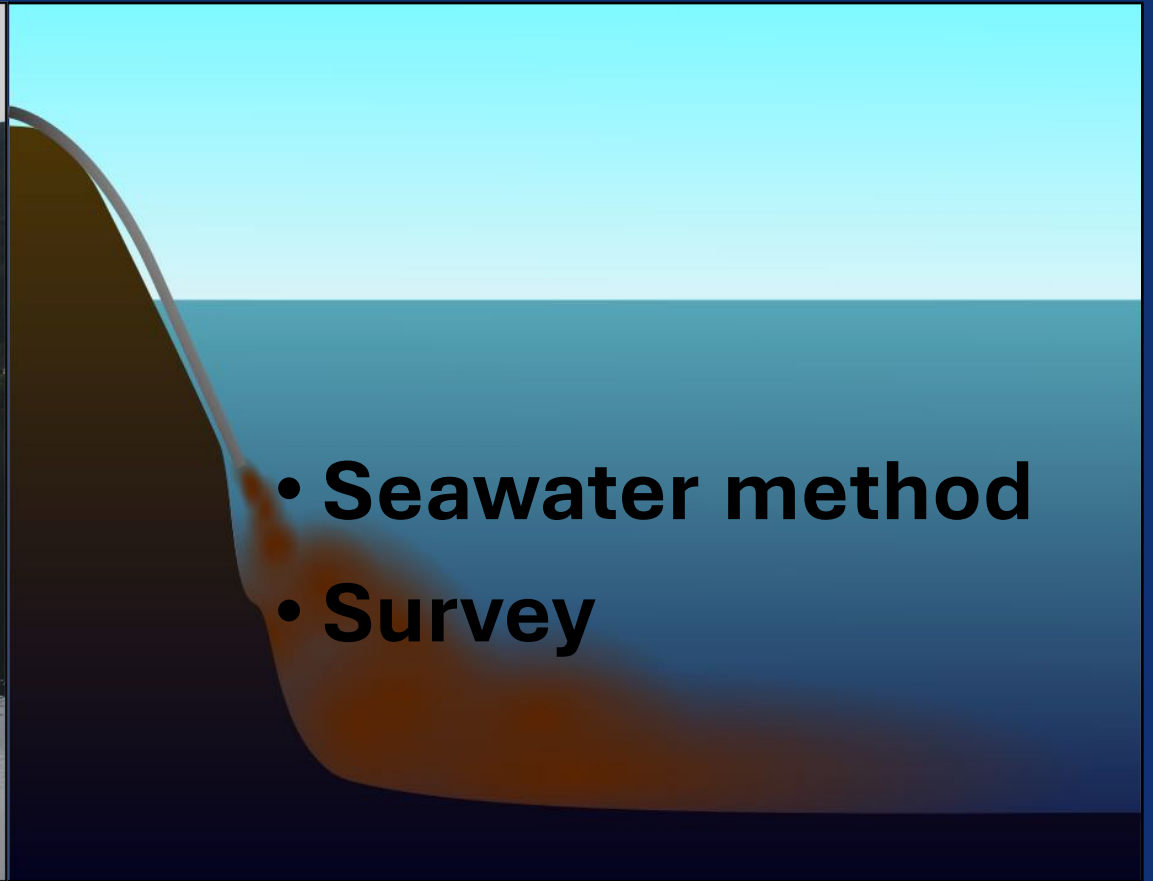
# Submarine tailings disposal (STD)



- Global **Natural** NP flux:  
~  $10^3$ s MT/year<sup>1,2</sup>  
(Atmospheric, riverine, glacial, hydrothermal)
- **Incidental** NPs from **one STD**:  
~ **1‰** of total **GLOBAL** input!  
Estimate based on estimates...



# “Distribution of inorganic nanoparticles in a Norwegian fjord”



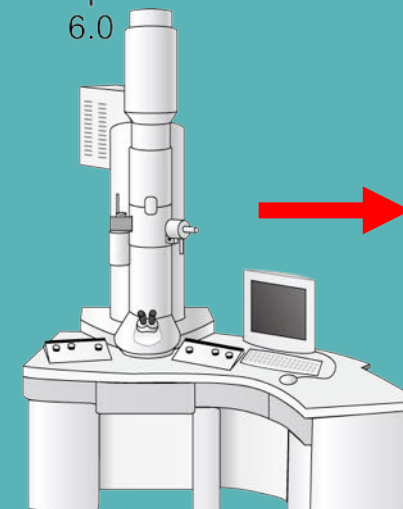
- Seawater method
- Survey

# Methods: data acquisition



## Quantitative data

- Single particle
- Total metals
- 16 selected elements



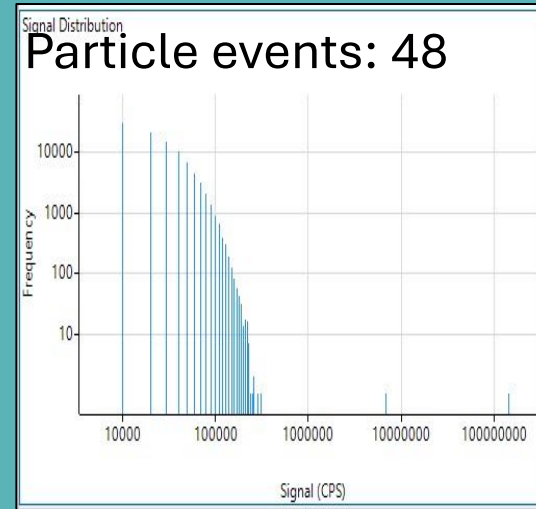
## Qualitative data

- autoSEM
- All elements



# Methods: processing **COMMERCIAL**

- **Commercial signal processing:**
  - Black box & proprietary
  - Bugs
  - Type I & II errors



Well-defined NPs, no noise  
(n papers 100++):



Seawater: background, matrix effects  
(n papers 2-3):

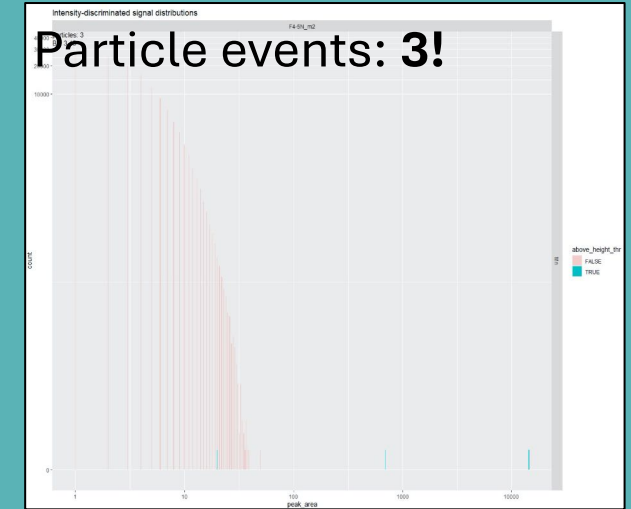


# Methods: processing



/arebruvold/fordefjorden\_distribution

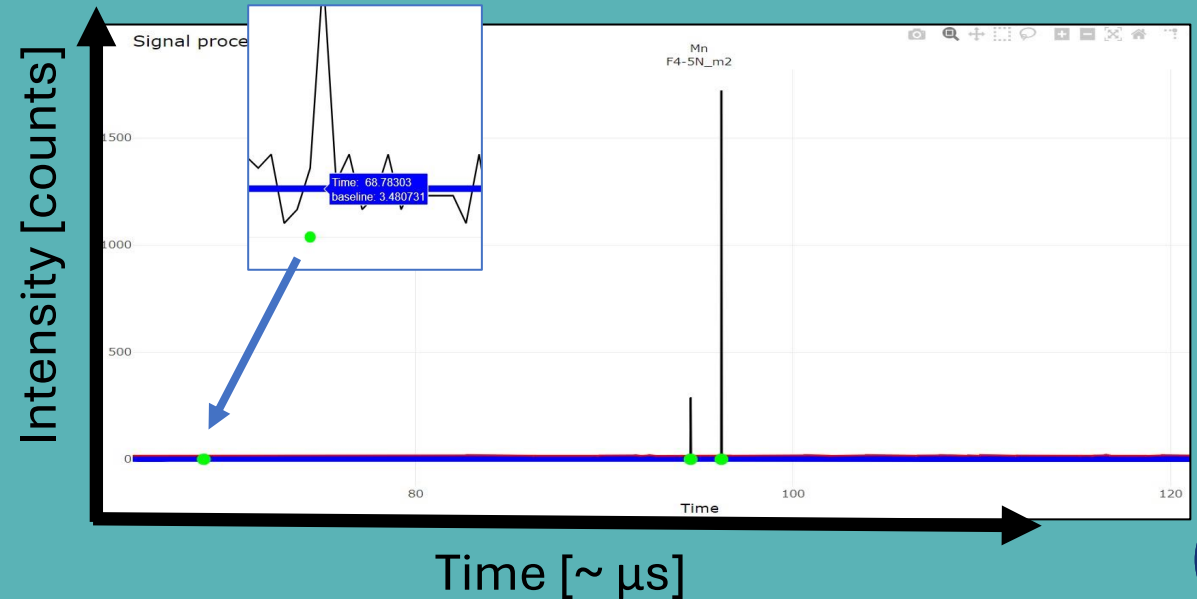
- **Novel signal processing:**
  - Open source/ transparent
  - Automated
  - **Minimizes** errors type I & II
  - Statistically defined critical level ( $\alpha$ )



Well-defined NPs, no noise  
(n papers 100++):



Seawater: background, matrix effects  
(n papers 2-3):





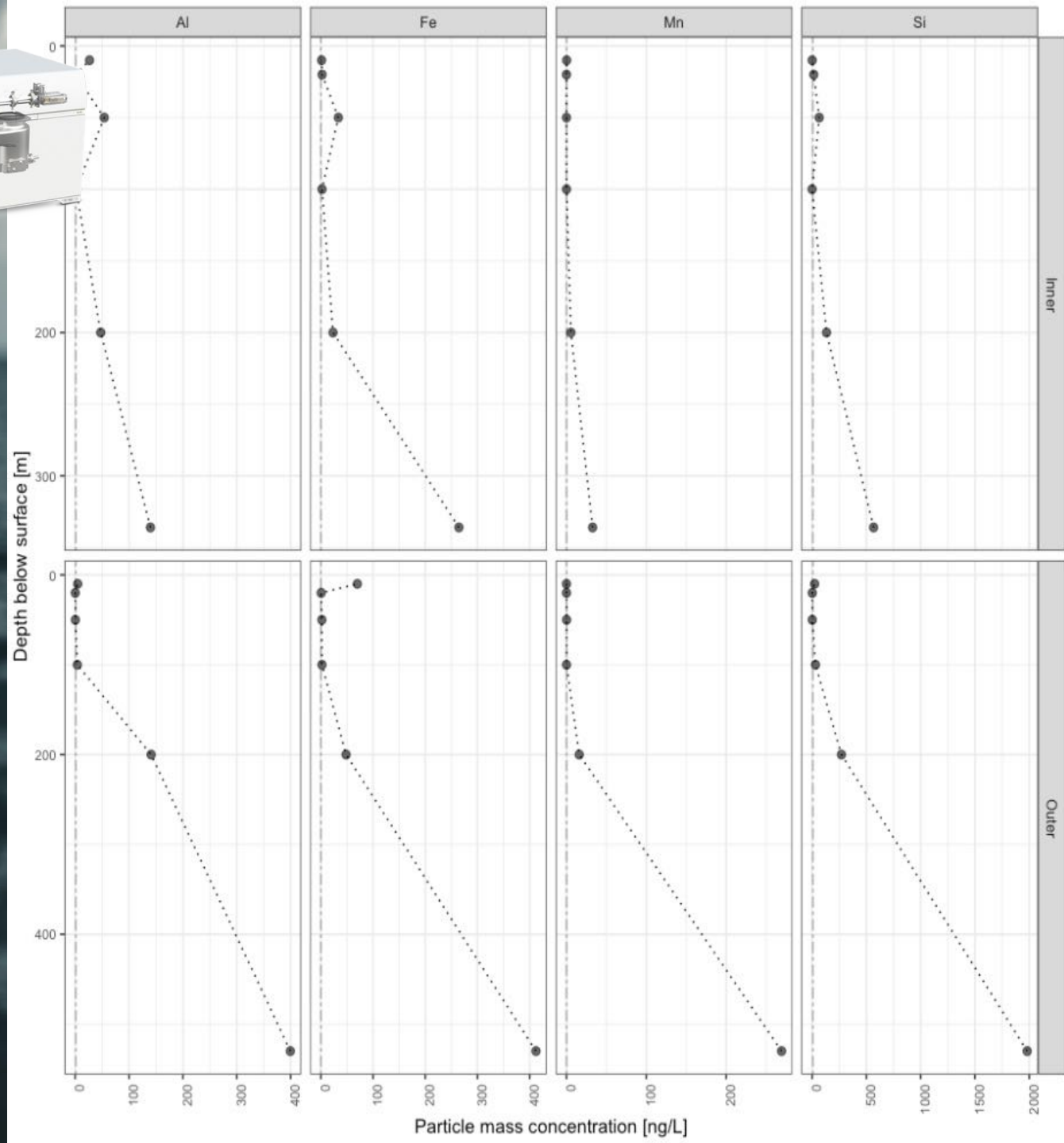
# Results & discussion

# Single particle



Fe Mn Si Al

$n < 10^8$  / liter





# Single particle vs total metals

## Total metals

- Higher conc., ~ as reported<sup>1,2,3,4</sup>
- More variability
- Fjords: large spatiotemporal variations<sup>3,5,6</sup>

## Inorganic particles

- Stronger depth dependence
- Minor inorganic fraction
- Not sufficient to generalize

1. Stolpe, B., and Hassellöv, M. (2010). Nanofibrils and other colloidal biopolymers binding trace elements in coastal seawater..., *Limnology and Oceanography* 55, 187–202. doi:10.4319/lo.2010.55.1.0187.

2. Simonsen et al. (2019). Modeling key processes affecting Al speciation and transport in estuaries. *Science of The Total Environment* 687, 1147–1163. doi:10.1016/j.scitotenv.2019.05.318.

3. Mason, R. P. (2013). *Trace Metals in Aquatic Systems: Mason/Trace Metals in Aquatic Systems*. Chichester, UK: John Wiley & Sons, Ltd doi:10.1002/9781118274576.

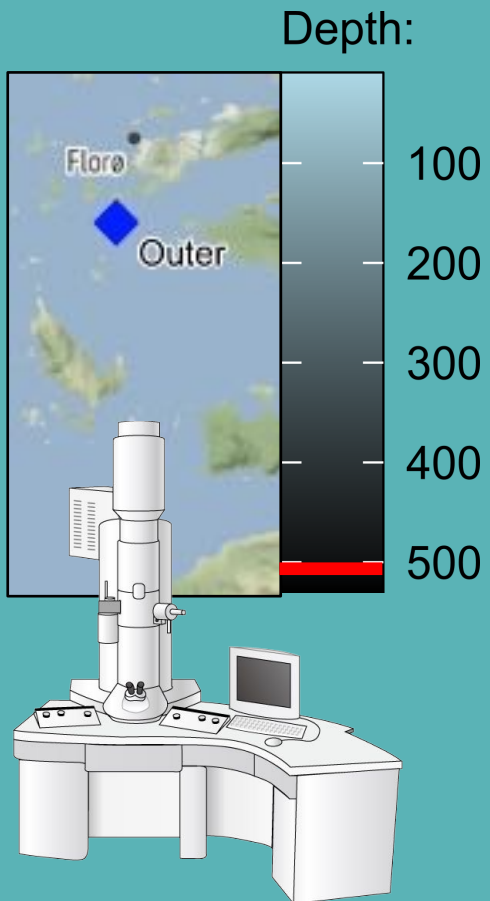
4. Botté, A., Zaidi, M., Guery, J., Fichet, D., and Leignel, V. (2022). Aluminium in aquatic environments: abundance and ecotoxicological impacts. *Aquat Ecol*. doi:10.1007/s10452021-09936-4.

5. Furness, R. W., and Rainbow, P. S. eds. (1990). *Heavy metals in the marine environment*. Boca Raton, Fla: CRC Press.

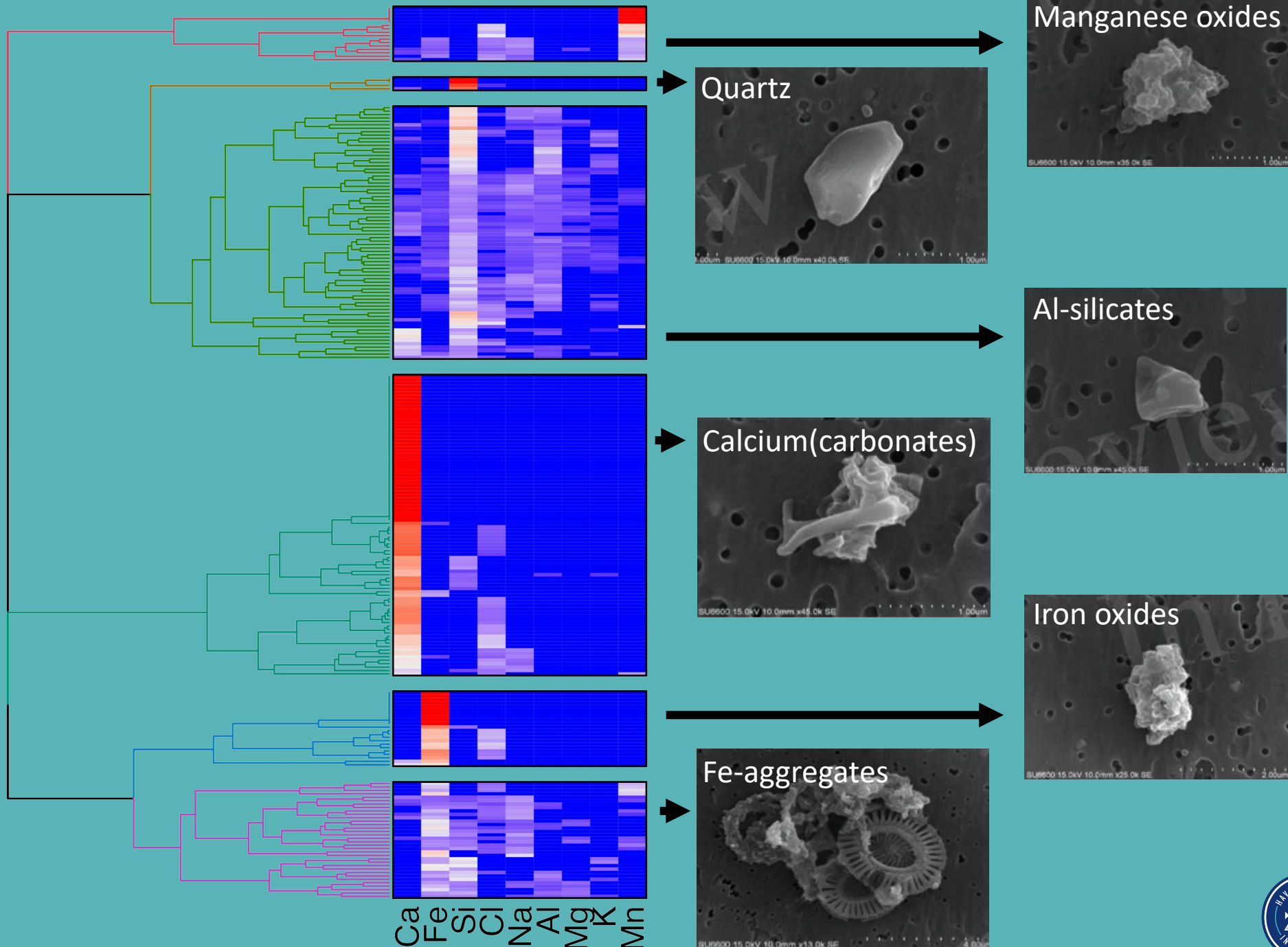
6. Elderfield, H. ed. (2006). *Treatise on geochemistry*. 6: The oceans and marine geochemistry / vol. ed. H. Elderfield. 1. ed. Amsterdam Heidelberg: Elsevier.



# SEM-EDX

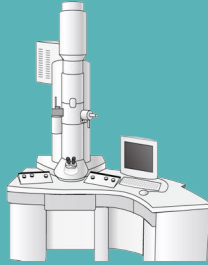


$N_{NP} = 238$





# SP-ICP-MS vs SEM-EDX



## In agreement:

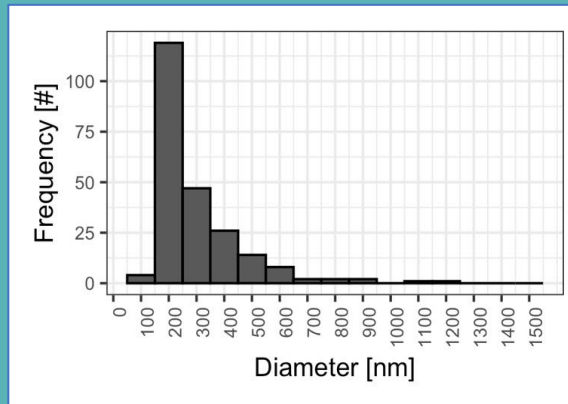
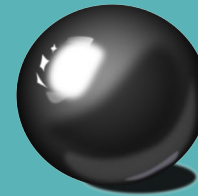
- Elements detected
- Relative elemental abundance

# SP-ICP-MS vs SEM-EDX

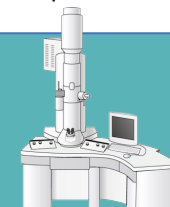
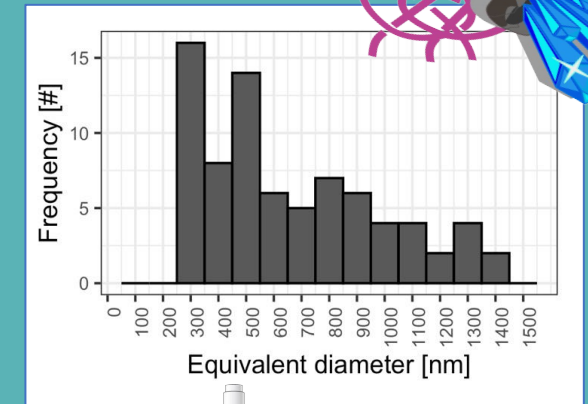
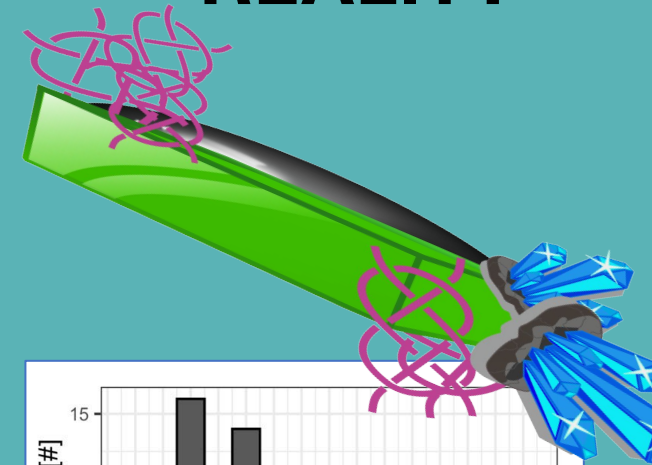
In agreement:

- Elements detected
- Relative elemental abundance
- **Size?**

## SP-ICP-MS



## REALITY





# Conclusion

- Low fraction of inorganic NPs (vs<sup>1,2,3</sup>)
- Particle diameters > 200 nm (conflicting<sup>4</sup>)
- Sensitive and precise platform for NP determination
- Explorative study, more data needed to generalize
- **New data on the distribution of inorganic NPs**

1 Wells, M. L., and Goldberg, E. D. (1993). Colloid aggregation in seawater. *Marine Chemistry* 41, 353–358. doi: 10.1016/0304-4203(93)90267-r.

2 Langen, P. J. V., Johnson, K., Coale, K., and Elrod, V. (1997). Oxidation kinetics of manganese (II) in seawater at nanomolar concentrations. *Geochimica et Cosmochimica Acta*, 10.

3 2 Barnard, A. S., and Guo, H. eds. (2012). *Nature's nanostructures*. Singapore: Pan Stanford Publications.

4 Wilkinson, K. J., and Lead, J. R. (2007). *Environmental Colloids and Particles: Behaviour, Separation and Characterisation*. John Wiley & Sons, Ltd.



# Thanks!

Slides to be posted @ [arebruvold.com/research.html](http://arebruvold.com/research.html)



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