

REPORT ON PROJECT ME 481: SOLUBLE AND INSOLUBLE IMPURITIES MAPPING IN THE ICE BY X-RAY FLUORESCENCE.

The goals of this project:

Polar ice is a polycrystalline material including various impurities of different origins and forms:

- Soluble like sulfuric acid, derived from volcanic eruptions or from marine productivity,
- Insoluble like continental dust including calcium,
- Gaseous like CO₂ or CH₄, representative of the atmospheric composition trapped in air bubbles.

Location of these impurities, dispersed in the ice matrix or concentrated in the grain boundaries remains an open question with important implications in the interpretation of the environmental parameter records.

Previous studies have shown that sulfate ions are preferentially located at the grain boundaries (Mulvaney et al, 1988) and preliminary results of local tomography performed on the ID19 beamline (ME 297) results suggest that at least the biggest particles (> 3 µm) are not uniformly located in the ice.

Very recently, observation have been made with a low vacuum scanning electron microscope after a long ice sublimation in order to concentrate the impurities (Cullen and Baker, 2001). Although these results are very promising, the analytical conditions and sample treatment could lead to artifacts. In particular the sublimation can induce impurity migration. These results may not reflect the true chemical structure of the ice and it is important to develop a more direct analytical technique.

The X ray fluorecence technique developed at the ID 21 beamline is very sensitive and appears to be a unique mean to directly investigate the species of interest.

In this first experiment (ME 481), the goals were to:

- Design an adapted sample cell with a cryo- system in order to:
 - Preserve the sample without any transformation and sublimation, by maintaining the sample at low temperature as long as possible
 - Work in high vacuum in order to have the enough sensitivity
- Test the sample cell and set up the experimental procedure.
- Achieve a first direct mapping of sulphur and calcium compounds in the ice samples.

Experimental procedure

New sample cell and cryo-system :

Modifications of the ID 21 environmental chamber were necessary in order to add a specially designed dewar to cool the sample cell.

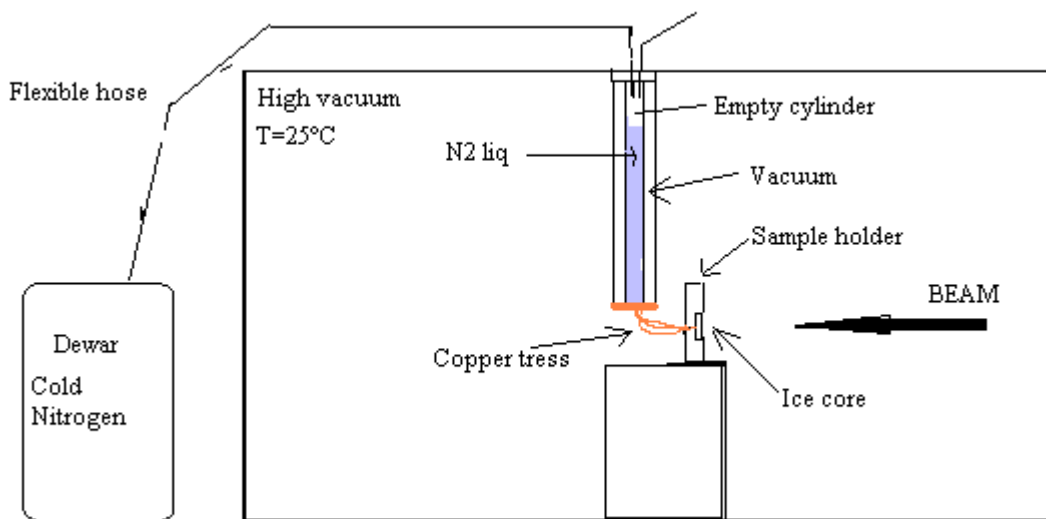


Figure 1 : schematic draw of the cryo-system, environmental chamber and sample cell.

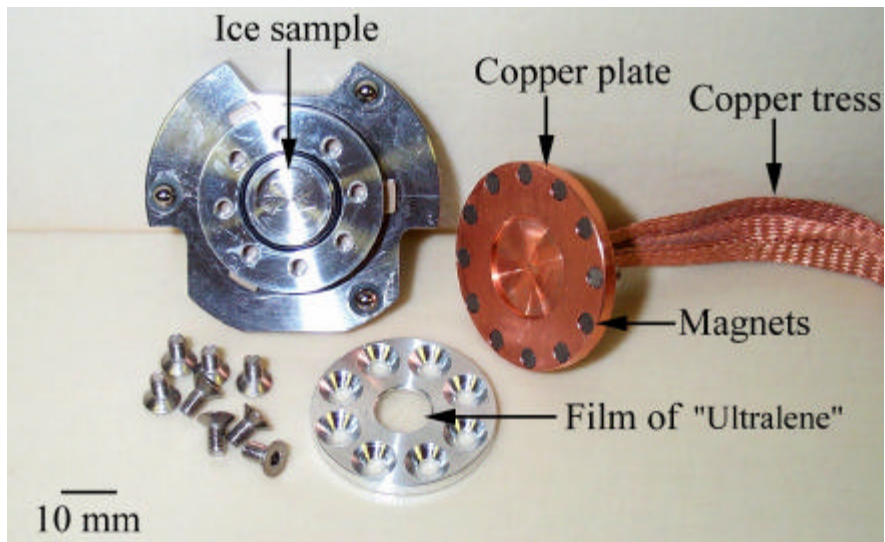


Figure 2 : details of the sample cell

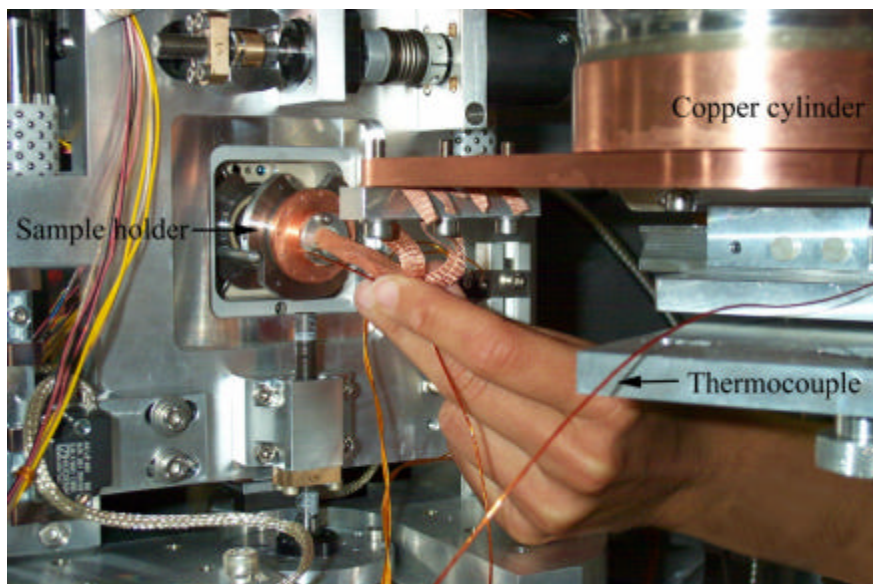


Figure 3 : the sample cell and its cooling system

Cooling system (Figures 1, 3)

The cooling system consists in a special 3 L dewar fixed to the roof of the vacuum chamber by a DN100 flange, automatically filled with liquid nitrogen. The base of the dewar is made of a thick copper cylinder coupled to a magnetised plate by a flexible copper tress, the sample cell being fixed to this plate by magnets. This system transfers the cold temperature from the bottom of Dewar to the ice sample. A Thermocouple is fixed on the copper plate to control the temperature during the experiment.

Sample cell (Figure 2):

The sample cell is made of aluminium in order to be light enough to be maintain in its position with magnets. The front window consists in a transparent film of Ultralene® and the cell is sealed with a viton O-ring to avoid sublimation of the sample during the experiment.

Sample preparation :

Samples have been prepared in the *Laboratoire de Glaciologie et Geophysique de l'Environnement* (LGGE) at constant temperature of -15°C to prevent condensation of water vapor on the sample surface. The ice sample was placed on a lathe and a cylinder of the diameter of the cell (1.1 cm) was machined. This cylinder was then put in the cell and its surface was adjusted with a microtome in order to exactly fill the cell. Once

the cell sealed, it was put into a Poly Carbonate box to avoid contamination of the Ultralene® film during the storage. All the samples were kept and brought to ESRF at a temperature of -38°C .

Sample set up

The critical point of the experiment is to prevent the presence of water vapor in the chamber which could be transformed into hoar on the cell window although it contains a very efficient water trap : the cold dewar. Thus two steps were necessary to set up the ice samples into the chamber.

The first step consists of cooling the dewar, the chamber being under vacuum (about 10^{-5} mbar, after half an hour) to avoid water condensation on the wall and on the tress. The dewar is filled with liquid nitrogen. At the end of this step the temperature of copper cylinder is about -160°C .

The second step consists in the introduction of the sample into the chamber.

After cooling the sample cell in its box into liquid nitrogen, the chamber is bring back to the atmospheric pressure by filling it with pure dry nitrogen. A flux of dry N_2 gas falls down in front of the door to keep away humidity from the chamber when the door is opened. The sample box is removed from the liquid N_2 , set into the chamber and opened. The cell is fixed with magnets to the copper plate and placed under the X ray beam. The door of the chamber is rapidly closed and the vacuum is made again.

Analyse

First, the surface of the sample is observed with an optical microscope in order to :

- Check the absence of hoar on the window.
- Look at the aspect of the ice and localise the grain boundaries.

Once a grain boundary is chosen a scan is done. Two energies have been applied during the experiments :

- 4.1 keV to have the best sensitivity on Ca (5 samples).
- 2.5 keV to have the best sensitivity on S (1 sample).

Experimental procedure is summarized table 1.

Mirror MO :	Ni	Angle:	8mrad
Monochromator:	Si 111	Energy:	4.1 keV
Zone plate:	KCl w2 $\varnothing=50$ drn=100	Central stop:	50 μm
Pinhole:		OSA:	25 μm
Detector:	Fluo HP Ge- trans diode		
IO detection:	Al foil		

Table 1 : experiment ME-481 information

Several maps with resolutions ranging from 2.6 to 0.5 μm have been performed. Trade off between size of map, resolution, and integration time has to be done in order to obtain the best image in a reasonable time.

Results

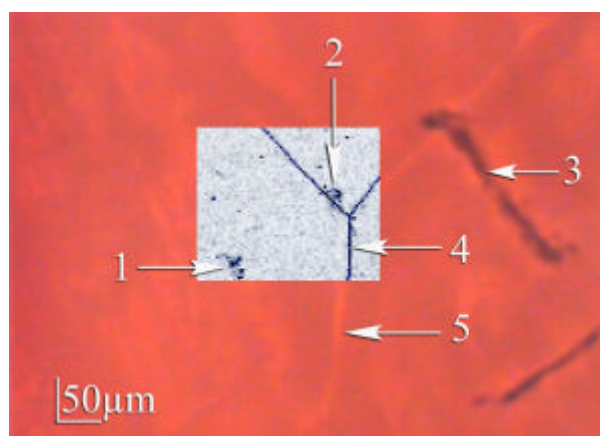
We have tested the sample holder and set up the experimental procedure, map different elements like potassium, sulphur and calcium compounds on 6 ice samples from Dome C (Antarctica) and had an outline of the possibility of this technique.

Choice of sample:

10 samples from 5 levels taken between 103 to 567 m depth on a Dome C (DC) (Antarctica) core have been prepared. Crystal areas and elemental concentrations have been taken in account to choose the samples. Since the crystals area of these samples was of the order of few square millimetres (Arnaud, 2000) the size of the window (10 mm) allowed to observe several grains. Moreover ice adjacent to the samples had been analysed by ionic chromatography to get the mean concentration of the major anions and cations. The soluble impurities concentration are well below 1ppm, that is below the detection limit of the X ray microfluorescence, but they correspond to a mean measured on melted samples. For a successful observation, impurities have to be focussed in a region of the sample. If we suppose that they are concentrated into the veins, a 10^6 factor to the concentration should be applied and impurities can be detected.

Mapping results

We propose to describe in this report the result of sample 1031 taken at 567 m depth. On the microscopic image (Fig.4), apart from the grain boundary, the surface appeared homogeneous.



- (1) Particle with K,Ca, S
- (2) Particle with Si, Al, K, Ca, S
- (3) Default from optic microscopy
- (4) K along the grain boundary
- (5) Grain boundary

Figure 4 : image of the sample 1031a by optic microscopy, and associated Potassium map. The map resolution is 2.6 μm and the integration time of each pixel is 3.3 s.

The area mapped corresponds to an area of 200 x 200 μm . The resolution is 2.6 μm and the energy is fixed to Ca and the results are discussed below :

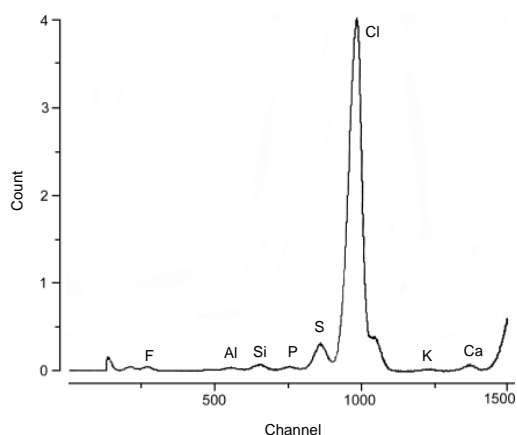


Figure 5 : XRF Spectrum of the area with the energy fixed to Ca and a resolution of 2.6 μm

The elemental spectrum (Fig 5) is dominated by a large peak of Cl followed by much smaller peaks of S, Ca, Si, P and K. Even if it's difficult to quantify the microfluorescence response to chemical concentration, comparison between the peak height to the ionic chromatography results (table 3) shows that, at least the relative amplitude of each element is in the same order. However the chloride peak seems too large and this could be due either to a very high sensitivity of the technique to this element either to a contamination. To test the last hypothesis, we have rinsed ultralene film and glue with ultra clean water and analysed this water. We found that after the contact with the ultralene film the water was clean while after the contact with the glue the water contained high amount of chloride. Thus the glue used to fix the ultralene film on the cell window contaminates the ice sample.

	F	S				Cl	NO ₃	Na	NH ₄	K	Mg	Ca
		MSA	S *	SO ₄	S	SO ₄	S *					
Concentration (ppb)												
Ionic chromatography	1,73	20,80	7,01	200,90	54,34	220,04	73,35	114,72	-	8,55	29,45	72,74
XRF analysis	n.d.	0.29				4.10	-	n.d.	-	0.03	n.d.	0.05

n.d; : not detected.

Table 2 : Comparison Ionic Chromatography results (de Angelis, Pers. Com.) and XRF results.

For each pixel the response of each element (signal intensity in count) is recorded. With these data it's possible to trace the repartition along lines of the elements on the maps (figures 6 and 7) to show the relative repartition of the elements in the different part of the sample (crystal, grain boundary, particles).

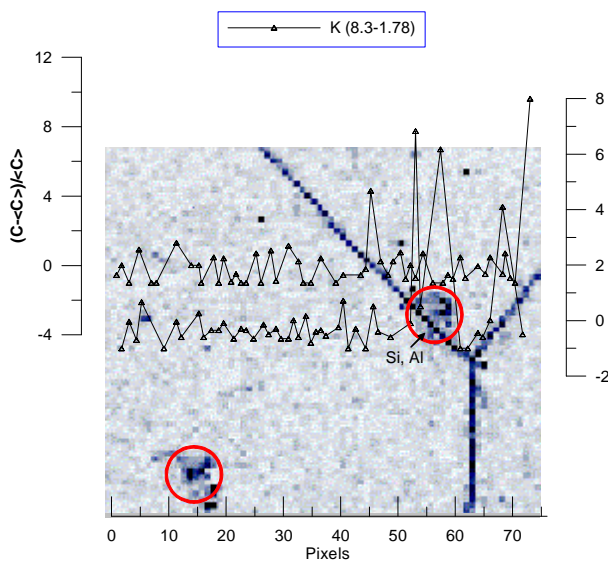


Figure 6 : K map and its repartition

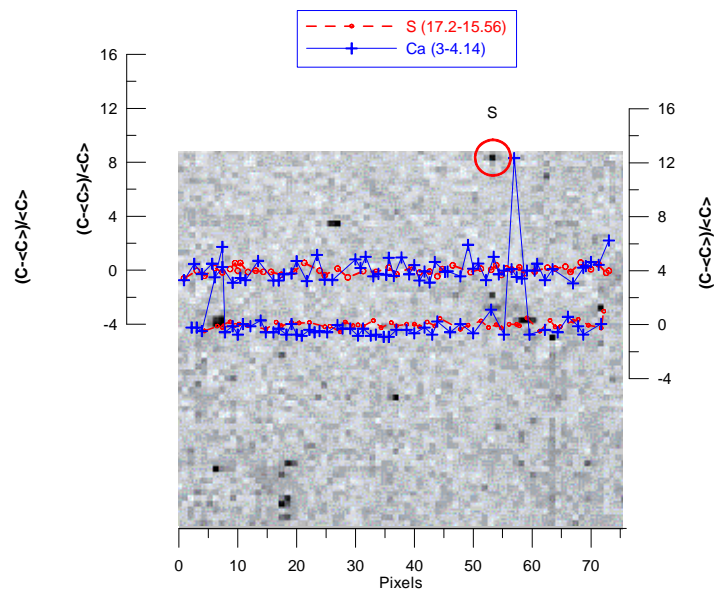


Figure 7 : Ca map and repartition of S and Ca.

The most striking result is the strong concentration of K along the grain boundary. This was expected since K is in most cases not in a soluble form and should be preferentially along the grain boundary or associated with insoluble particles (figure 6).

Results on Ca (figure 7) are less pronounced than K. If slightly more Calcium is along the grain boundary the deviation from the mean is very small, and its concentration can be considered has homogeneous in the ice matrix or associated with Si, Al near the triple junction.

The repartition of S (figure 7) shows that S is homogeneous into the ice matrix and the grain boundary. In this case, S comes probably as H₂SO₄. Only one very intense spot (2000 count) is found in the ice matrix (circle figure 6) associated with Ca corresponding most probably to an insoluble particle (CaSO₄). In this experiment, it's not possible to distinguish the response of the different state of sulphur. However, with an energy fixed on the pre energy of the S K-edge, it's possible to map the sulphur oxidation state, allowing identify the different chemical combinations of sulphur. This technique is illustrated on Figure 8 where the peak (1) is a sulphide (2) correspond to the sulphate.

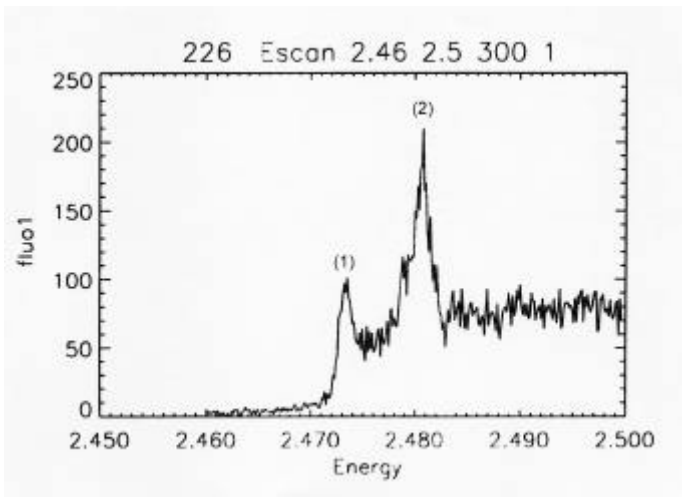


Figure 8 : example of a pre energy diagram in order to know which element is associated to S.

(1): 2,473 keV to determine (2) 2,480 keV SO_4^{2-}

Remarks on the experimental conditions :

Time of experiment may be very short and this is one of the big advantage in comparison with S.E.M technique. A first and rapid map can be done to locate interesting points and then high resolution (up to 0.5 μm in our case) mapping of these area can be performed. In this case, long integration times have to be used to be sensitive enough and the experiment can last up to 12 hours. It is thus important to know if our set up can maintain the integrity of the ice sample.

The design of the cryo system and sample cell allows to maintain the sample at a temperature of about -130°C during up to 29 hours without visual change of the ice. Microscopic observation of the Ultralene® film after 20 hours of experiment (sample 1011a) and comparison with new film pointed out only a slight ageing of the surface. Sealing of cell has been inadvertently tested when a sample (1031a) melted. Melted ice stayed into the cell in the evacuated chamber at least 5 hours proving the tightness of the cell and the quality of the Ultralene® film. It's thus reasonable to think that ice samples can be kept along the experiment without major change. However, tests have to be done to check that the long integration time doesn't modify the composition and the structure of the sample.

Conclusion:

Results of this first experiment are very promising. We tested the sample holder and set up the experimental procedure. A direct mapping of several elements in the ice has been obtained. Concentration of them was estimated around 50 ppb. Even if elements are localised and then more concentrate, observation of them have shown the good sensitivity of this technique. More, we had obtained the first chemical mapping of S in polar ice.

We also began to provide answers to a better understanding of impurities and ice interaction. These results confirm that technique developed at the ID 21 beamline is very sensitive, softer for the sample and faster than SEM, and appears really to be unique to analyse and map impurities in polar ice core sample.

News experiments would be done in order to confirm some results.

References

- Mulvaney R. E.W. Wolff and K.Oates, Sulfuric acid at grain boundaries in Antarctic ice, *Nature*, 331, 247-249, 1988.
- Cullen D. and I. Baker, Observation of Impurities in Ice, *Microscopy Research and Technique*, 55, 198-207, 2001.
- Arnaud L., Weiss J., Gay M., Duval P., Shallow-ice microstructure at Dome Concordia, Antarctica, *Annals of glaciology*, 30, 8-12, 2000.