

REPORT ON PROJECT CH1568 :

Soluble and insoluble impurities mapping in the ice by X-ray Fluorescence.

CONTEXT OF THE STUDY

Interpretation of the climatic records trapped in polar ice requires the understanding of the interaction between the ice and the different impurities (soluble or insoluble). In this context, the knowledge of the localization of these impurities is of primary importance. In this project, we used the microfluorescence (μ X.R.F.) probe developed at the ID21 beam line to map the impurities distribution in the ice. In order to avoid sublimation and transformation of the ice sample we used a cryo cooled cell developed during the ME 481 experiment (1)(2). Soluble and insoluble impurities mapping in the ice by X-Ray Fluorescence have been realized and have begun to provide answers to a better understanding of impurities and ice interaction. The goal of this new experiment CH1568 was to improve the experimental procedure, validate previous results and study accreted ice from Antarctica. In this report we briefly describe the main results of this experiment; the results are detailed in two articles which are close to be submitted (3)(4).

SAMPLE PREPARATION

Samples have been prepared using the procedure developed for experiment ME481 (1) except that we have avoid the use of glue to fix the ultralene film which was suspected to be responsible for high chloride levels. Thus the ultralene film is simply pressed between the sample cell support and the lid with a o-ring.

Ice adjacent to the samples have been analysed by ion chromatography (table1) in order to get the mean concentration of the main ionic species of the melted

Two energies have been applied during the experiments:

- 2.5 keV to have the best sensitivity on S and to study the sulfur speciation.
- 4.1 keV to have the best sensitivity on Ca.

IMPROVEMENT AND BLANK TESTS

A) Blank of the experimental procedure and background estimation

To estimate the contamination introduced by the sample preparation, two kinds of tests have been performed :

- 1) Influence of the Ultralene film. As already mentioned in the previous experiments a large chloride signal was observed and we suspected that the glue used to fix the Ultralene film on the cell window or the Ultralene itself were at the origin of this signal. To test that and the influence of the film we have performed a spectrum of an empty sample cell. The results are presented in table two. Although a significant Chloride peak is present, the signal is about 10 times lower than in the ME481 experiment. This confirm that the main contamination arised from the glue.
- 2) Synthetic ice sample (S1) has been prepared from extra-pure water. They have been analysed by ion chromatography (see table 1) and XRF techniques (see table 2) under the same experimental conditions as for real polar ice samples.

These two tests give very similar results in particular for the Chloride peak. Since Ion chromatography for the S1 synthetic sample has not detected Cl, the Ultralene® film, very close to the sample surface is most likely the origin of the Cl peak.

When comparing the Ultralene to the synthetic ice, the Ultralene peak of all the other elements are slightly higher than the synthetic sample. This can be due to the influence of the aluminium cell which is empty and the cell signal is not absorbed by the sample. Thus we will consider the intensity of the « clean » synthetic sample as the background signal of the experiment. To consider an element as significantly present in polar ice, the μ X.R.F. signal should be at least two times higher than the synthetic sample signal.

B) Sample conservation during the experiment

The major risk of transformation of samples is sublimation. Sublimation can be due to a leak of the sample cell which is in a vacuum chamber. Figure 1 represents the μ X.R.F. spectrum from the sample cell filled with only air.

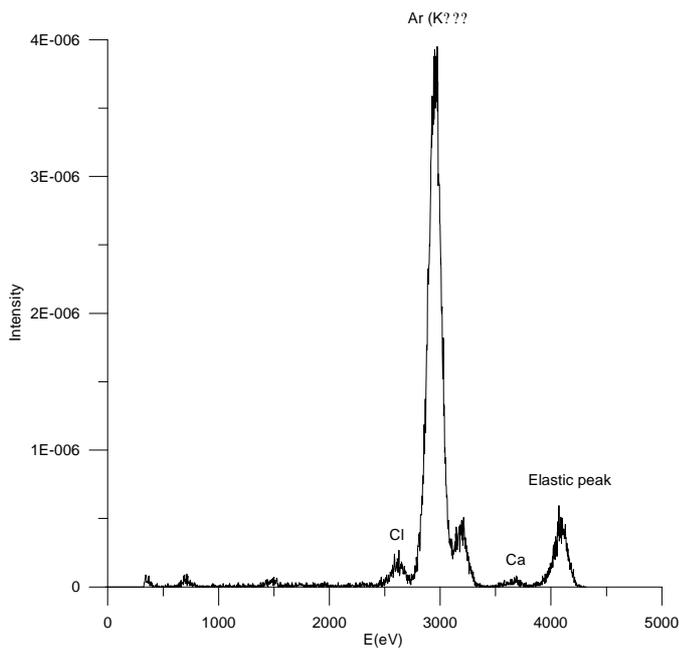


Figure 1 : μ X.R.F. spectrum from the sample cell containing air only.

The spectrum is dominated by a high peak from Ar. This result is due to the presence of air in the sample cell and hence its air tightness.

To check the stability of the sample and the reproducibility of the method, a particle has been examined three times with an interval of 2h 30mn. The Si intensity and shape are shown on figure 2a and 2b. The shape of the inclusion does not change and the intensity slightly decrease. This could suggest a slight evolution of the sample, but we can note that this decrease remains in the reproducibility range of the method.

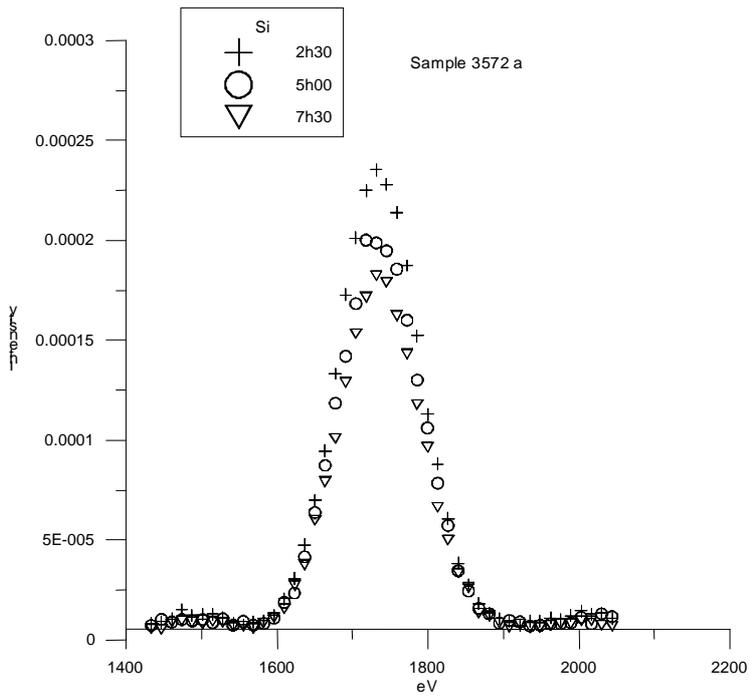


Figure 2a : evolution of Si intensity during an experiment

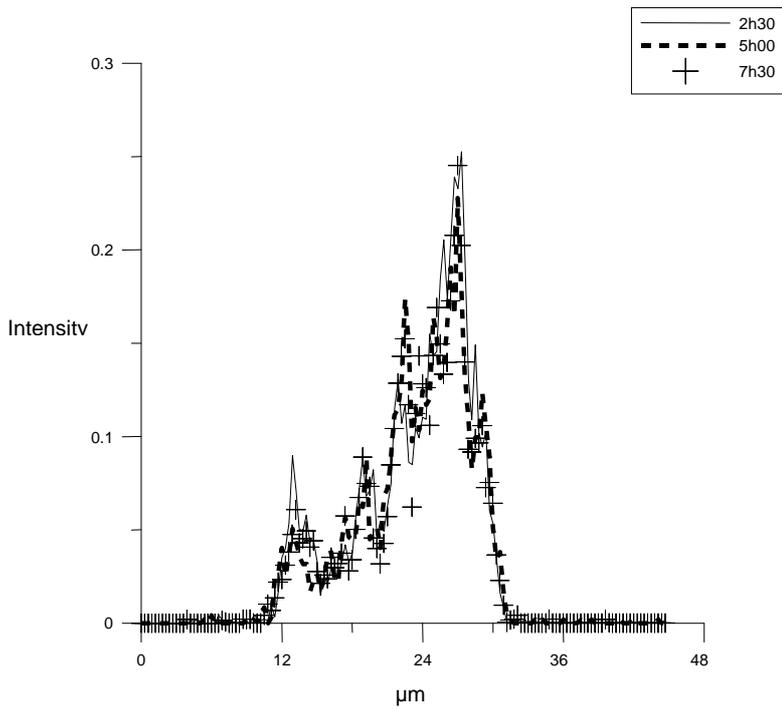


Figure 2b : Shape evolution of the Si

RESULTS

Natural samples of ice accreted from the lake Vostok which lies under the Antarctic ice sheet at about 3750 m below the surface have been analyzed. This ice is characterized by very large crystals and can include big aggregates (figure 3a)(5).

We present here results from two samples V1 and V2 taken at 3551m and 3572m depth respectively. V1 is in particular characterized by a large visible aggregate (aggregate 1).

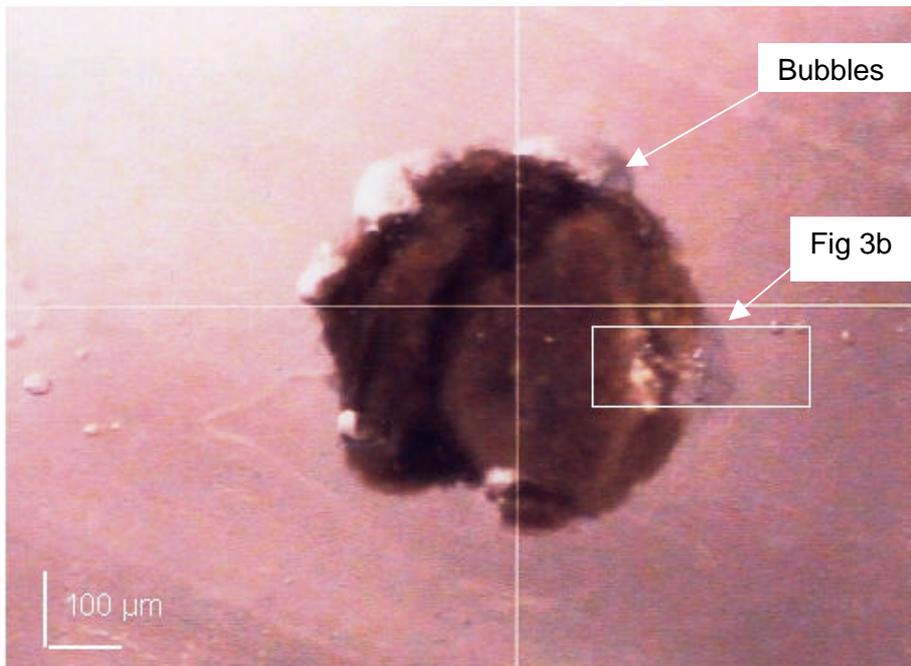


Figure 3a: aggregate 1 of the sample taken at 3551 m depth (V1)

This kind of inclusion, not seen in normal glacier ice is formed from the concentration of very fine particles locally accumulated during the accretion of the ice. The gas around the aggregate was initially at about 300 bar, thus the inclusion is highly unstable and μ X.R.F. measurement appears to be a unique way to get the in situ repartition of the elements. At the end of the experiment (after about 20 hours, this aggregate disappeared).

A) Chemical mapping

The figure 3b present chemical maps of the different elements measured

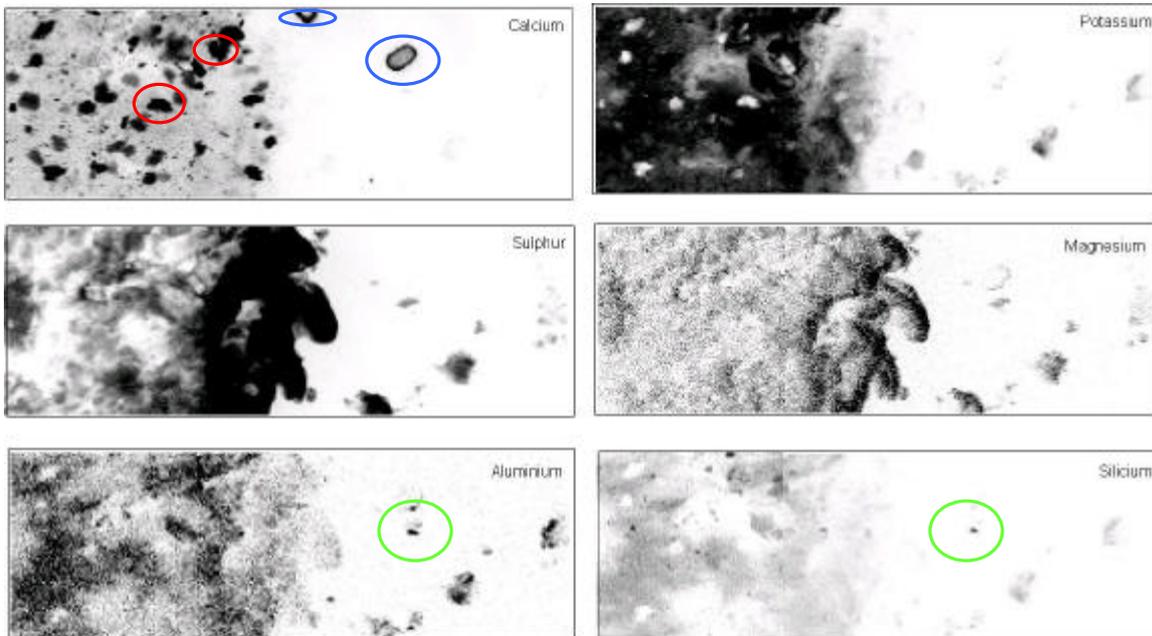


Figure 3b : map of Ca, K, S, Mg, Al, Si

Map size : 300 x 100 μ m, resolution 1 μ m, integration time 300 ms.

In the figure 3b the Calcium appears as large particles (red blue circles (about 15 μ m) but their shapes and their spectra are different whether they are inside or outside the visible inclusion The figure 3c shows the spectrum inside (red) and outside (blue) the large aggregate. The spectrum realized outside the aggregate is largely dominated by the Ca and is probably a CaCO₃ inclusion while inside the aggregate the Calcium is associated with other elements but seems to be anti correlated to the Potassium.

Sulfur is concentrated at the border of the aggregate and is associated with Magnesium and Aluminium in particular in the most external part of the aggregate.

Silicium is found as very small particles <1 μ m (green circle) and seems to be associated with Al (green circle) although the sensitivity to Al is very low.

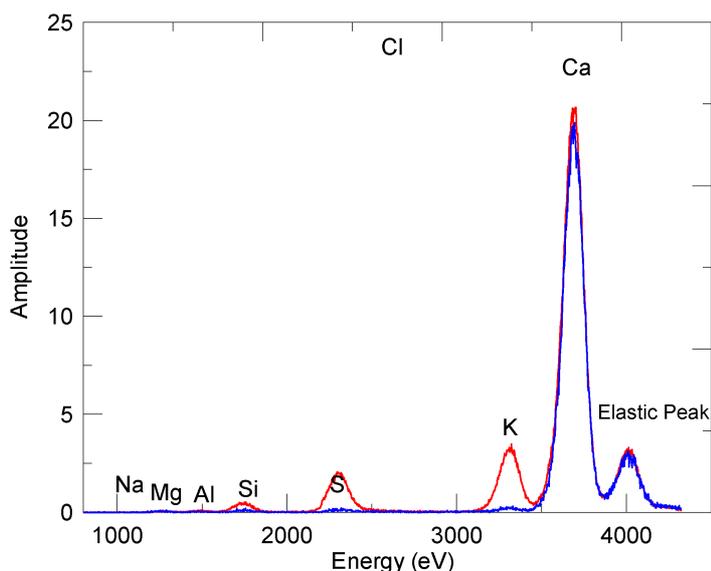


Figure 3c : μ X.R.F. spectrum of the particle of Ca inside and outside the visible inclusion.

B) Comparison with the ion chromatography : toward a quantitative interpretation

On Table 1 we report the ionic chemical composition of samples adjacent to those analyzed by μ X.R.F. Although taken at the same depth than the large aggregate, V1 did not contained visible inclusion. The two samples contained large amount of Chloride and Sodium. The main difference between the two samples being that V1 contained also large amount of Sulfate and Calcium.

Ionic species	Ca ²⁺	K ⁺	Cl ⁻	S		Si ²⁺	Al ³⁺	Mg ²⁺	Na ⁺	F ⁻	NO ₃ ⁻	NH ₄ ⁺
				MSA	SO ₄							
S1	0.87	0.28	<L.D	<L.D	0.30		<L.D	0.13	0.35	0.29	<L.D	0.21
V1	94.9	5.0	938	<L.D	215	-	<L.D	0.21	798	3.13	1.73	1.71
V2	14.6	9.0	721	<L.D	44.1	-	<L.D	4.51	623	2.33	1.97	0.45

Table 1 : Concentration (ng.g⁻¹) by ion chromatography :

Apart from the large aggregate described above, other parts of the sample have been mapped, in the ice matrix and some non visible inclusions have been discovered and mapped. Results are

presented in table 2 .The intensity of signal for each element as well as its ratio to the intensity measured on the synthetic ice are reported.

Elements	Ca	K	Cl	S	Si	Al	Mg	Na	F
Energy	3.69	3.31	2.62	2.31	1.74	1.48	1.25	1.04	0.67
Synthetic ice	3.52	0.35	11.1	1.77	1.02	0.86	0.22	0.31	1.93
Ultralene	3.19	1.598	10.6	-	2.4	3.2	1.59	-	3.19
	0.91	4.6	0.95	-	2.4	3.7	7.2	-	1.7
V1	4.74	0.37	25.4	2.74	1.05	0.85	0.49	0.24	1.72
ice matrix	1.4	1.1	2.3	1.6	1.0	1.0	2.2	0.77	0.89
V1	906	1965	27.2	772	562	46.7	27.2	2.3	3.8
Aggregate 1	257	5614	2.5	436	551	54	124	7.4	2.0
V1	1.63	2.45	299	12.9	2.46	0.82	0.82	3.28	3.28
Aggregate 2	0.46	7	26.94	7.29	2.41	0.95	3.73	10.58	1.7
V2	4.72	0.26	11.56	0.79	1.57	1.05	-	0.26	1.57
ice matrix	1.3	0.75	1.0	0.45	1.5	1.2	-	0.85	0.81

Table 2 : μ X.R.F. results. The energy correspond to the $K\alpha$ (keV) emission ray

normal characters: Analysis by μ X.R.F. Relative signal intensity ($\times 10^8$), I/I_0 where I is the signal emitted by the element and I_0 the original signal.

italic bold characters: ratio of the sample relative intensity to the relative intensity of the synthetic sample, taken as the experimental background.

The results from the ice matrix of the two samples are very similar and they are not significantly different than the synthetic results. As the ion chromatography of the synthetic ice has shown very low level of the species of interest, this suggest that these matrix are very clean and that all the impurities are strongly localized. It is interesting to note that the two aggregates have very different

composition. The sulfur is mainly contained in aggregate 1, while the Chloride is mainly in the aggregate 2. Furthermore, the results suggest that the aggregate 1 is formed of small mineral particles while NaCl is the main component of the aggregate 2.

C) Speciation

V2 has been used to show the potential brought by the new technique regarding speciation of the element. This is done by finely selecting the energy of the incident beam according to the oxidation number of the target element. Experiment has been done on a spot showing a particle including Si, Al, P and S (-II)and S(VI). The size of the image (fig 4) is 50x40 (μm), with resolution of 0.3 μm and integration time of 500ms. Size of the particle is 20x13.5 (μm). Figures 4a and 4b respectively show S (+VI) using 2.482keV and S (-II) with 2.473keV and their different localizations.

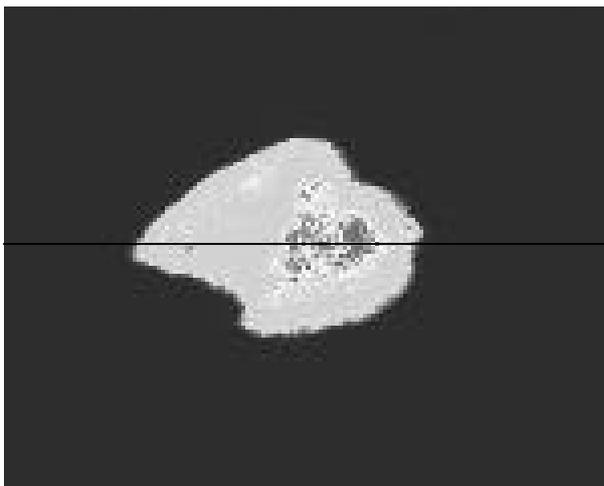


Figure 4a S(+VI)

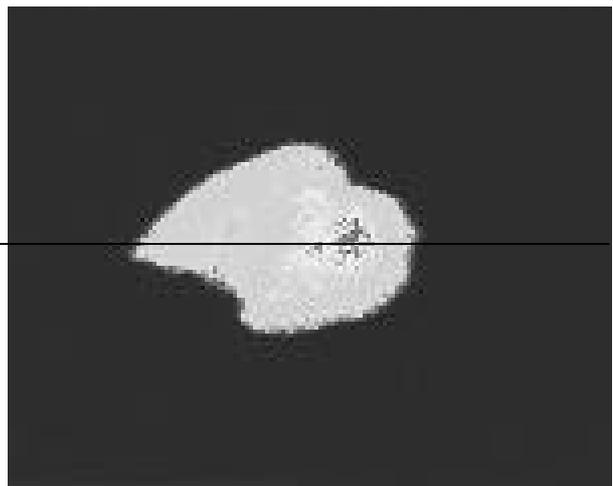


Figure 4b S(-II)

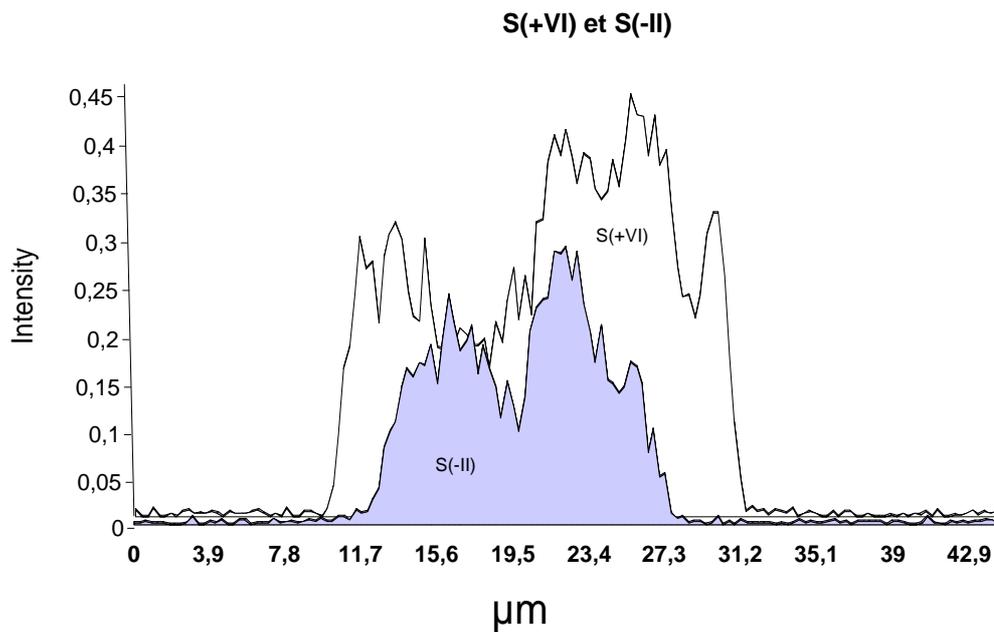


Figure 4c : S(+VI) and S(-II) (16,8µm) along the cross section of the particle

By supplying cartographies of elements for their different oxidation numbers the new technique adds useful information on the likely origins of impurities.

CONCLUSION

During this experiment, we have improved and normalised the experimental procedure developed in the ME481 project. In particular, we have removed the major source of Cl contamination and determined the background of the experiment by systematic analysis of synthetic samples. Being non invasive, this μ XRF technique allows to scrutinize unstable impurities and replicate experiments in order to confirm and refine results. Beyond the detection of elements within impurities the technique enables their speciation which may help finding the origins of impurities. As compared to SEM technique integration times are much shorter which enables large chemical mapping. Combined with ion chromatography , μ XRF analysis of synthetic samples comes out with an enhanced reliability of results and more quantitative interpretations. Results obtained from Vostok accreted ice show benefits gained from the new technique. For the first time, it has been possible to see the high chemical heterogeneity of this ice and to make visible the association of the different elements.

REFERENCES

- 1 Report Me481
2. Fourcade M.C, Barnola J.M., Susini J., Baker R. XRF elemental mapping of polar ice, Poster , International Congress on X-Ray Optics and Microanalysis, Chamonix France , 2003
- 3 Fourcade M.C., Barnola J.M., Susini J; Duval P., de Angelis M, New insights for study of impurities in polar ice by micro X-ray Fluorescence, *J. Glaciol.* to be submitted.
- 4 Fourcade M.C., de Angelis M, Barnola J.M., Susini J, Chemical Mapping in of polar ice from Antarctica by Micro X Ray Fluorescence at The European Synchrotron Radiation Facility, *Geophys Res. Lett.*, to be submitted.
- 5 Montagnat M., P. Duval, P. Bastie, B. Hamelin, O. Brissaud, M. de Angelis, J.R Petit and V.Y. Lipenkov, (2001), High crystalline quality of large single crystals of subglacial ice above lake Vostok (Antarctica) revealed by hard X-ray diffraction, *C.R. Acad.Sci.Paris, Earth. Planet. Sci.* 333, 419-425.