



1^{ère} journée de microscopie dédiée aux applications géologiques

4 juin 2019

Maison internationale de la recherche
Université de Cergy-Pontoise



**Analyse des éléments mineurs et trace
à la microsonde électronique : état de
l'art et application à la pétrologie-
minéralogie**



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ISTeP

Petites quantités.....gros impact sur la santé

Les sources des éléments traces et des métaux toxiques

Évaluation du risque lié au Mercure dans l'alimentation

Dose Hebdomadaire Tolérable Admissible Provisoire (DHTP)
DHTP = DJTx7

Dose pouvant être consommée chaque semaine durant la vie entière, sans incidence sur la santé du consommateur

Évolution des DHTP (par OMS + FAO (JECFA)) entre 1978 → 2003

Norme : - 1978 : 3,3 µg/kg/poids corporel/semaine

→ Enfant (20kg): 66 µg/semaine

→ Homme (60kg): 200 µg/semaine

- 2003: 1,6 µg/kg/poids corporel/semaine

→ Enfant (20kg): 32 µg/semaine

→ Homme (60kg): 96 µg/semaine

200g de THON rouge (1mg/kg/poids frais) = 200 µg

Évaluation du risque lié au Cadmium dans l'alimentation

Dose Hebdomadaire Tolérable Admissible Provisoire (DHTP)

Norme : 7 µg/kg/poids corporel/semaine

→ Enfant (20kg): 140 µg/semaine

→ Homme (60kg): 420 µg/semaine

Évaluation du risque lié au Plomb dans l'alimentation

Dose Hebdomadaire Tolérable Admissible Provisoire (DHTP)

Norme : 25 µg/kg/poids corporel/semaine

→ Enfant (20kg): 500 µg/semaine

→ Homme (60kg): 1500 µg/semaine

Petites quantités.....merveilles minérales

Gem-corundum megacrysts from east Australian basalt fields: trace elements, oxygen isotopes and origins*

F. L. Sutherland, K. Zaw, S. Meffre, G. Giuliani, A. E. Fallick, I. T. Graham & G. B. Webb



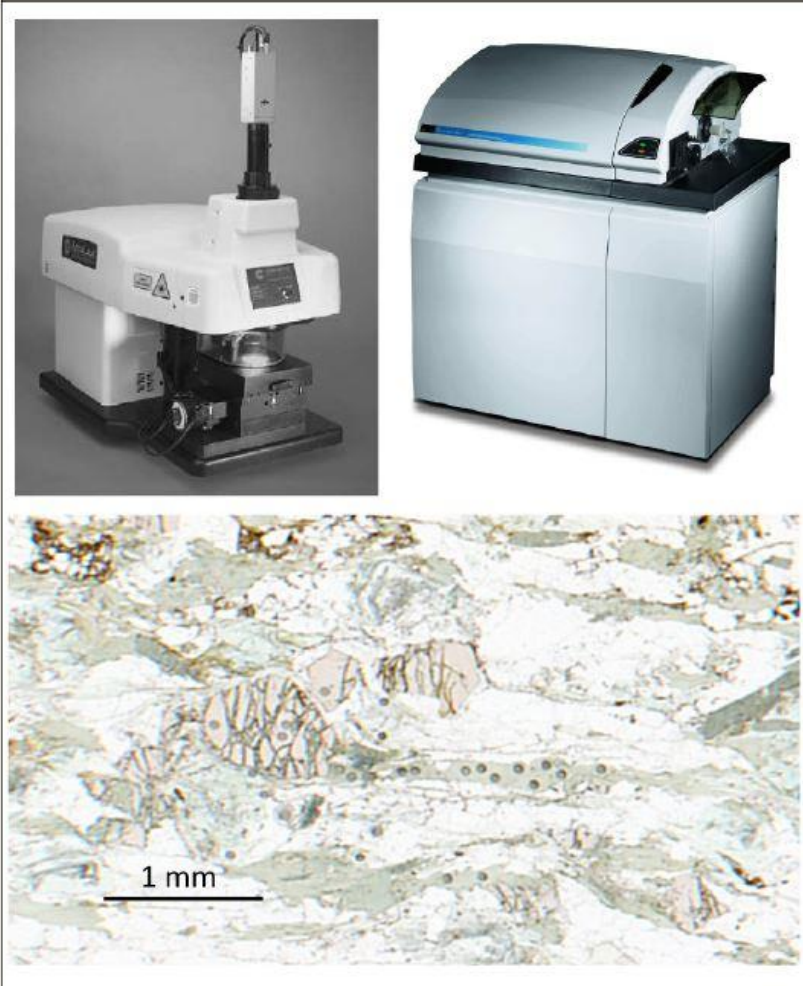
Table 5 Trace elements (ppm), LA-ICP-MS analyses, Yarrowitch corundum. (rubis, saphirs)

Sample	Fe	Cr	Ti	V	Ga	Mg			
High-Mg (Mg > 35 ppm), Low-Ga (Ga < 25 ppm) Group (YAR 1.1-1.2, 1.4-1.6)									
Range (n = 10)	1740-2139	381-2563	28-238	5-19	16-22	36-95			
Average core (n = 5)	1956	1278	100	14	19	47			
Average rim (n = 5)	1941	1253	96	13	19	52			
Average (n = 10)	1949	1266	98	13	19	49			
High-Ga (Ga > 110 ppm), High-Mg (Mg > 70 ppm) Group (YAR 2.6)									
YAR 2.2 core (light blue) rim	6998	<0.9	262	2	158	5			
	6939	<0.8	177	2	157	4			
High-Ga (Ga > 110 ppm), Intermediate-Mg (Mg > 35 ppm) Group (YAR 2.1, 2.3-2.4)									
Range (n = 6)	11083-15078	1-16	59-70	2-12	114-226	35-105	527-710	0.005-0.130	1.34-4.40
Average core (n = 3)	12518	11	1262	4	163	66	558	0.069	2.90
Average rim (n = 3)	11967	2	845	5	145	45	635	0.016	3.35
Average (n = 6)	12243	6	1054	5	154	55	597	0.042	3.12

Analytical precisions (ppm): Fe, 7-8%; Cr, High-Mg group 9-12%, High-Ga group bdl-21%; Ti, 8-9%; V, 8-9%; Ga, 4-5%; Mg 6-7%; Si, 12-23%. bdl, below detection limit.

COMMENT LES ÉLÉMENTS TRACES ?

APPROCHE 1: LA-ICP-MS : Laser Ablation with Inductively Coupled Plasma Mass Spectrometry



Avantages:

- Simple d'utilisation et contrôle qualité
- Rapide ($\sim 1-2$ minutes / analyse)
- Précision (dépendante de la taille du laser)

Inconvénients:

- Méthode destructive
- Taille du laser $> 50 \mu\text{m}$
- Non adapté à la cartographie dans ces échantillons

COMMENT LES ÉLÉMENTS TRACES ?

Micro-X-Ray Fluorescence au synchrotron

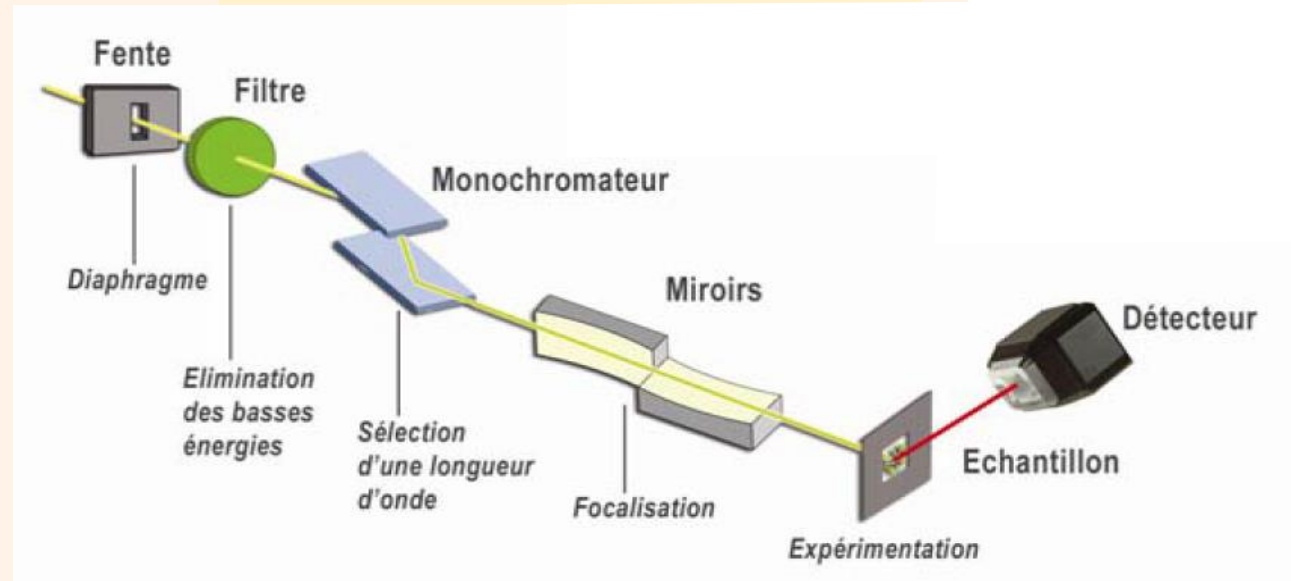
APPROCHE 2: μ - XRF SYNCHROTRON

Avantages:

- Méthode non destructive
- Taille du laser $< 1 \mu\text{m}^2$
- Extrêmement rapide (2 Mpixels / heure)
- Orienté cartographie élémentaire

Inconvénients:

- Accessibilité et traitement du signal
- Limites de détection ~ 100 ppm
- Pénétration du faisceau X $\rightarrow 10 \mu\text{m}$



COMMENT LES ÉLÉMENTS TRACES ?

APPROCHE 3: Microsonde électronique



Avantages:

- Méthode non destructive
- Ponctuel et cartographie élémentaire
- Faisceau d'e- < qqes μm^2
- Limites de détection ~ 30 ppm en ponctuel
- Accessibilité (remarque de B. Dubacq: « en face de mon bureau... »)

Inconvénients:

- Limites de détection ≥ 150 ppm en carto
- Présence d'un fond continu élevé

Surfaces analysées selon la technique utilisée

Eur. J. Mineral.
2003, **15**, 747–763

Trace elements in quartz – a combined electron microprobe, secondary ion mass spectrometry, laser-ablation ICP-MS, and cathodoluminescence study

AXEL MÜLLER¹, MICHAEL WIEDENBECK², ALFONS M. VAN DEN KERKHOFF³, ANDREAS KRONZ³
and KLAUS SIMON³

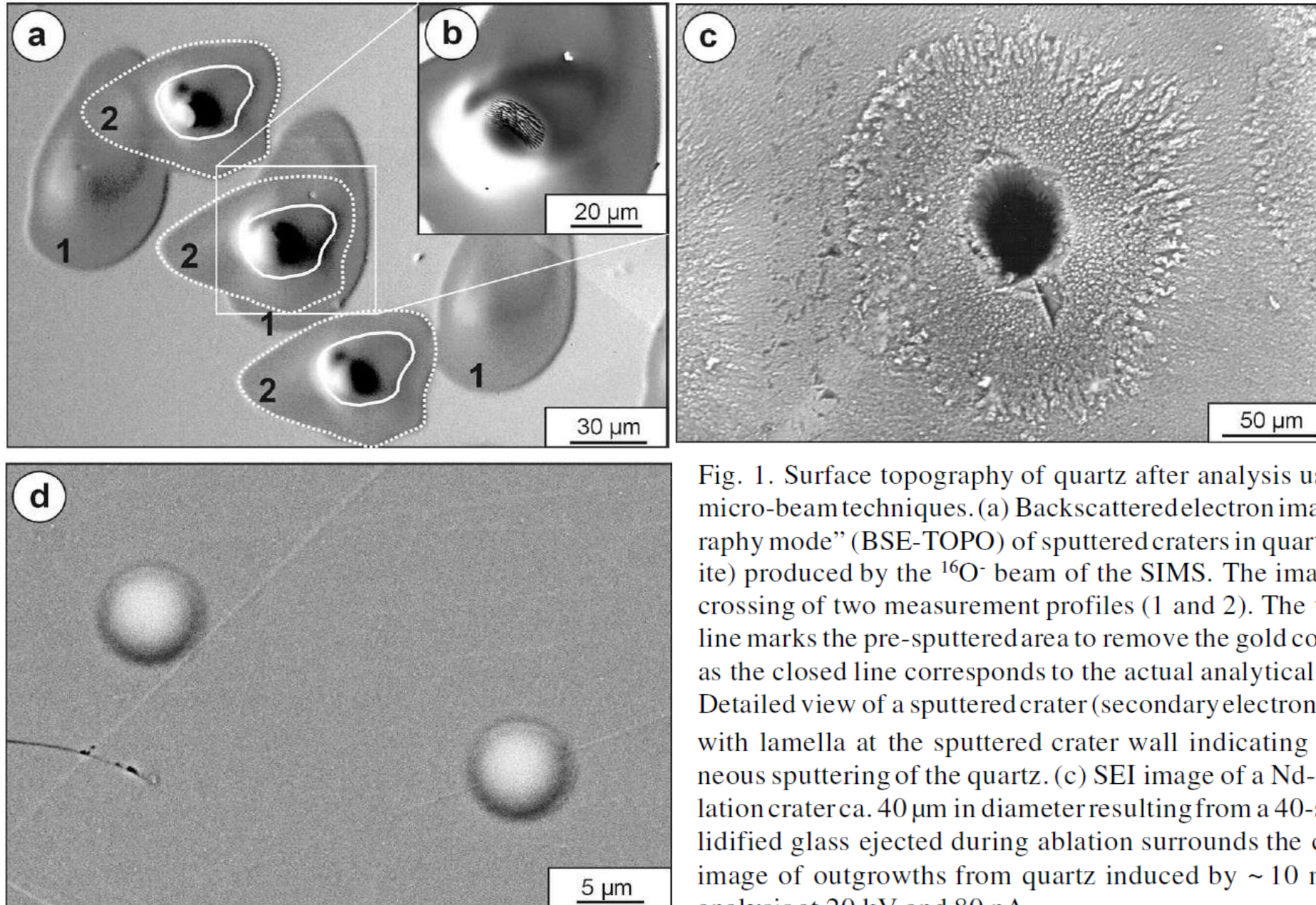


Fig. 1. Surface topography of quartz after analysis using different micro-beam techniques. (a) Backscattered electron image in “topography mode” (BSE-TOPO) of sputtered craters in quartz (Aue Granite) produced by the $^{16}\text{O}^-$ beam of the SIMS. The image shows the crossing of two measurement profiles (1 and 2). The white spotted line marks the pre-sputtered area to remove the gold coating, whereas the closed line corresponds to the actual analytical spot size. (b) Detailed view of a sputtered crater (secondary electron image – SEI) with lamella at the sputtered crater wall indicating an inhomogeneous sputtering of the quartz. (c) SEI image of a Nd-YAG laser ablation crater ca. $40\ \mu\text{m}$ in diameter resulting from a 40-s-ablation. Solidified glass ejected during ablation surrounds the crater. (d) SEI image of outgrowths from quartz induced by ~ 10 minute EPMA analysis at 20 kV and 80 nA.

profondeurs analysées selon la technique utilisée

Eur. J. Mineral.
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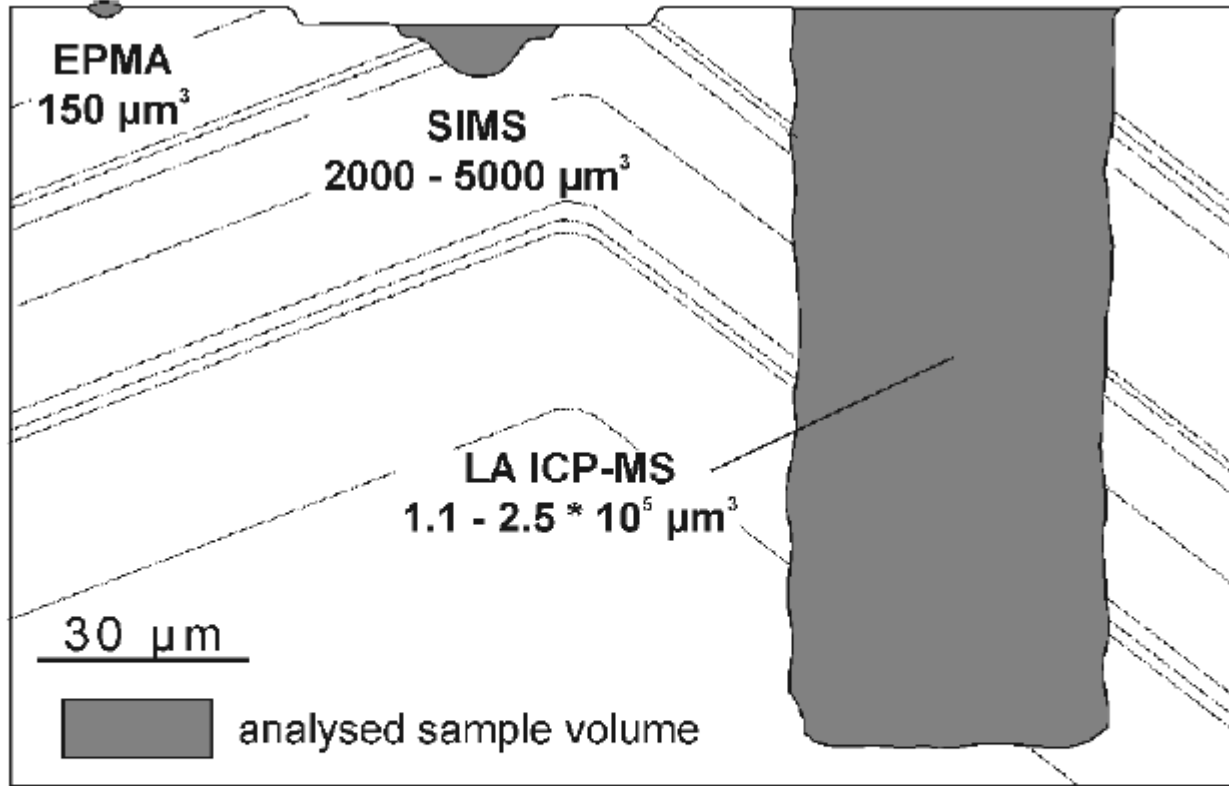
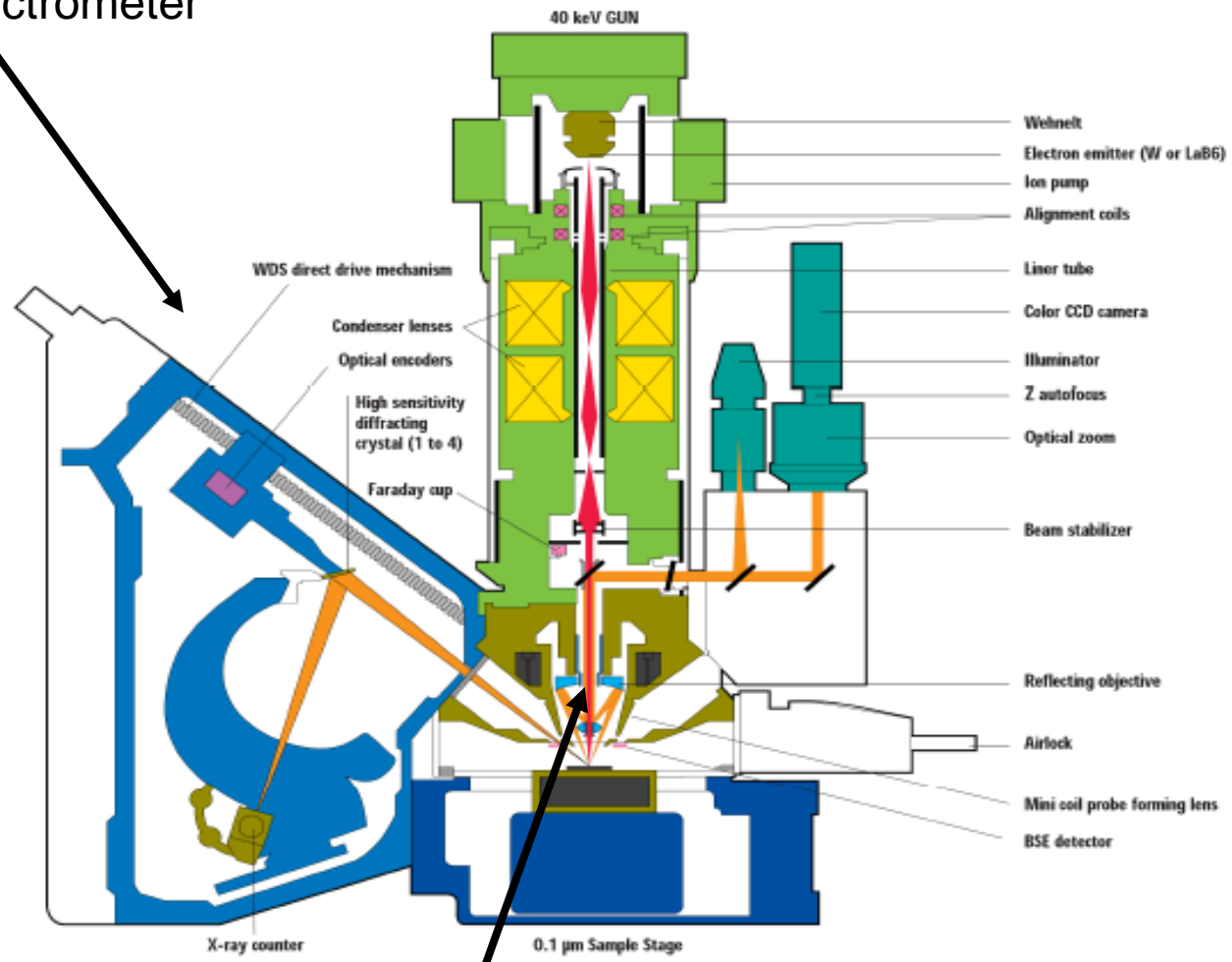
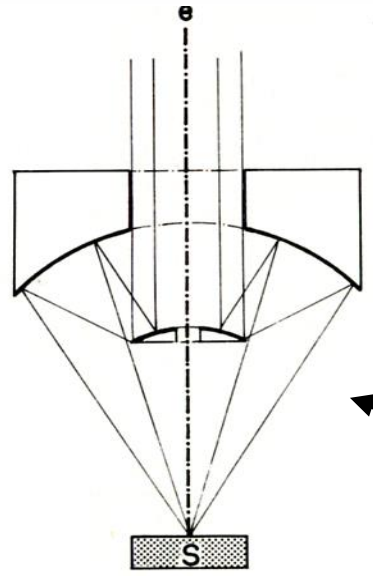
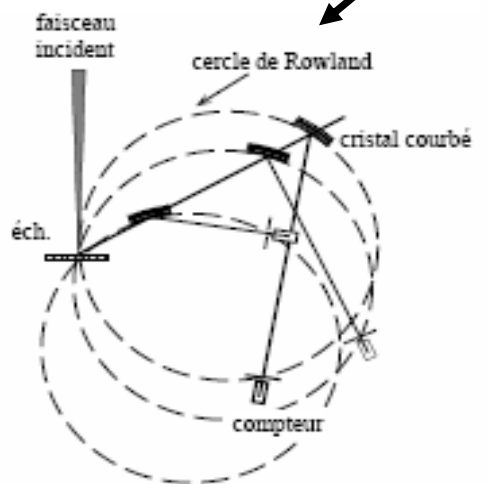


Fig. 3. Comparison of the sampling sizes of EPMA, SIMS, and LA-ICP-MS provided by our analytical conditions. Thin dashed lines represent typical growth zoning observed in magmatic quartz phenocrysts.

Electron Probe Microanalyzer (EPMA)

Wavelength Dispersive Spectrometer (WDS)



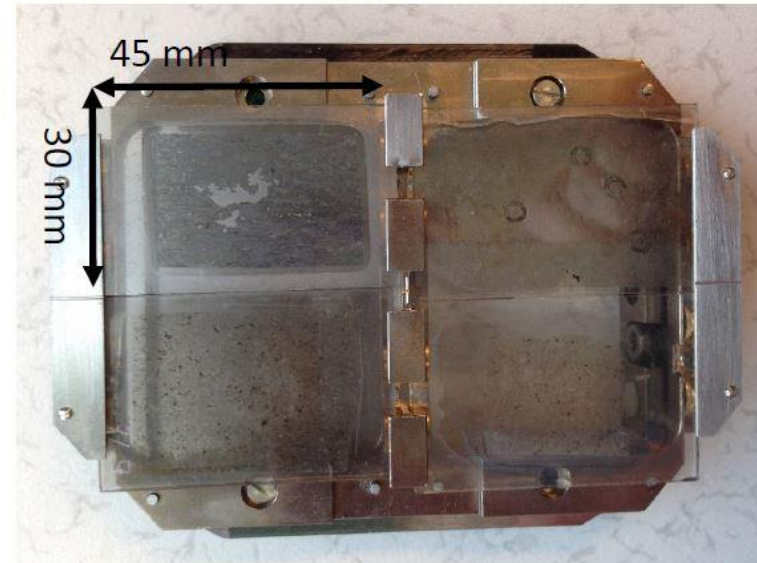
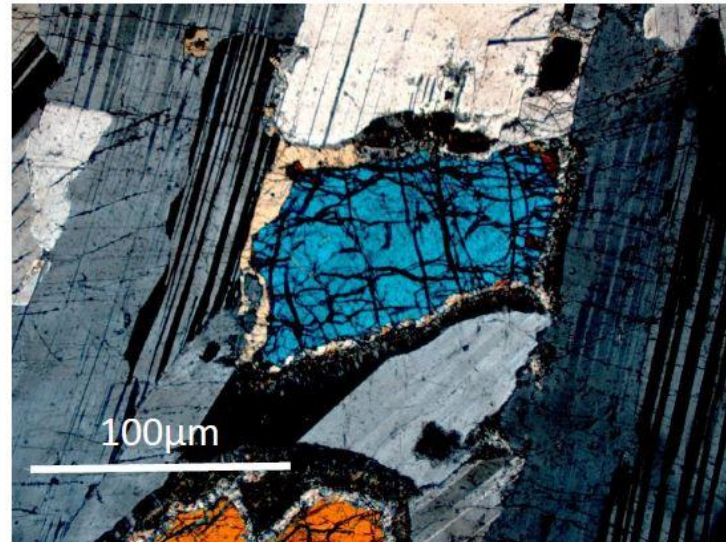
10 cm

Cassegrain optics (x400)

Electron Probe Microanalyzer (EPMA)



Détail d'une lame mince de gabbro (roche basaltique cristallisée en profondeur). (lumière polarisée et analysée)



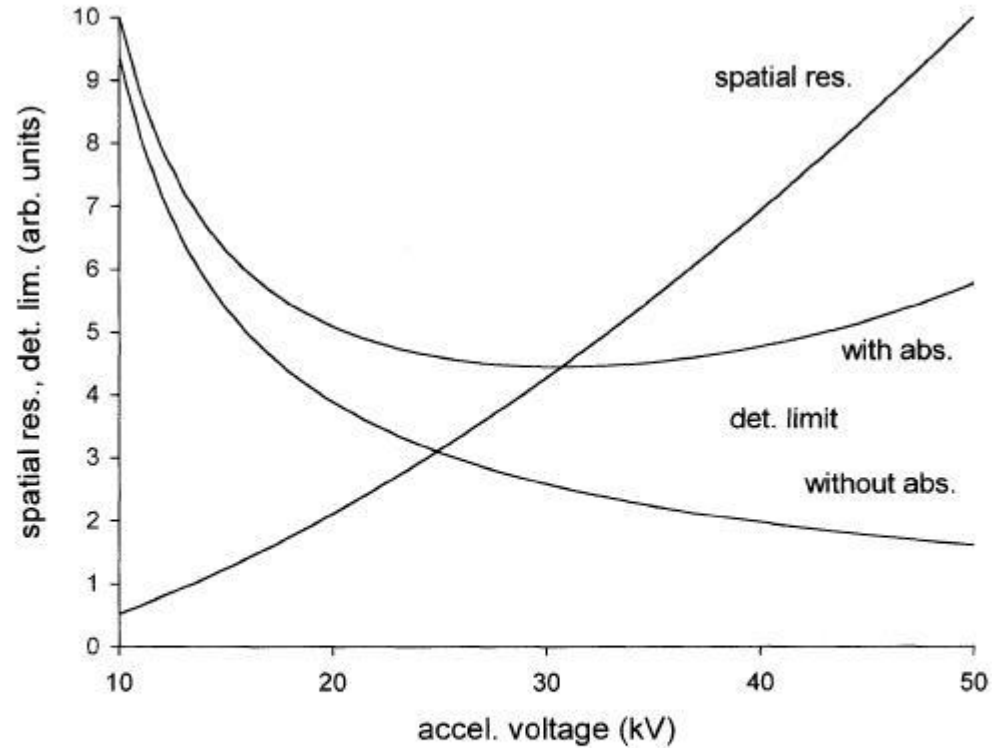


Fig. 1. Calculated relative spatial resolution and detection limit as function of accelerating voltage; detection limit shown with and without absorption in the sample (assuming arbitrary values of mass absorption coefficients for illustrative purposes)

Trace element analysis benefits equally from maximisation of peak intensity and peak-to-background ratio, both of which increase with increasing accelerating voltage (V_0), though in cases of high absorption the peak intensity passes through a maximum and then decreases owing to the increasing depth of X-ray production. However, electron penetration increases approximately as $V_0^{5/3}$, with a consequent worsening of spatial resolution.

LIMITE DE DETECTION

La plus faible concentration qui peut être détectée avec un certain niveau de confiance

Limite au-delà de laquelle on distingue une raie caractéristique du fond continu

METHODE DITE DES 3 SIGMAS :

raie caractéristique détectable :

Int. Raie $> 3 \times$ fluctuations stat. du FC
 $3 \times \sigma$ des valeurs de l'int. du FC

ESTIMATION DE LA LIMITE DE DETECTION

échantillon: $I = I_e - B_e$

- écart-type de la différence de deux intensités :

$$\sigma = \sqrt{I_e/t_e + B_e/\alpha_e t_e} = \sqrt{\frac{B_e}{t_e} \cdot \left(1 + \frac{1}{\alpha_e}\right)} = \sqrt{2} \cdot \sqrt{\frac{B_e}{t_e}}$$

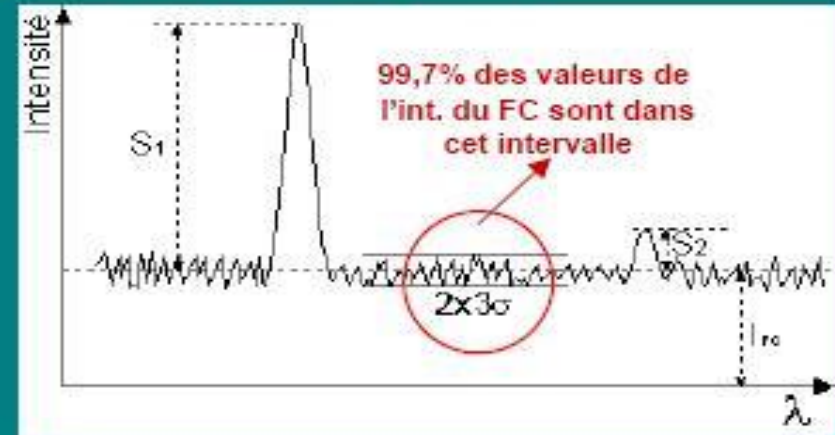
avec $I_e = B_e$, $\alpha_e = 1$

$$I_{\text{limite détectée}} = 3\sigma$$

- estimation de la concentration minimum détectable :

$$C_L = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot I_{\text{limite}} = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot 3\sigma = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot 3 \cdot \sqrt{2} \cdot \sqrt{B_e/t_e}$$

C_L dépend de la nature du matériau analysé



Modélisation du fond continu

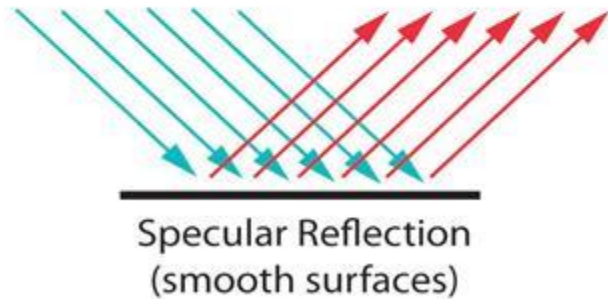
Bremsstrahlung = ralentissement des électrons incidents dans la cible
(loi de Kramer)

+

Réflexion spéculaire \neq

Réflexion de Bragg

Specular reflection is the mirror-like reflection of light from a surface, in which light from a single incoming direction (a ray) is reflected into a single outgoing direction.



+

Piémont de pic d'élément majeur

$$n\lambda = 2d \sin \theta.$$

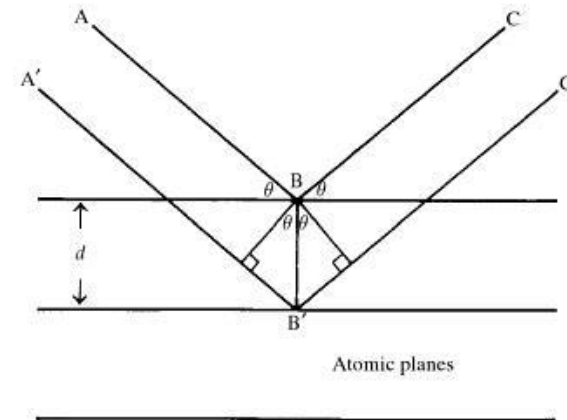
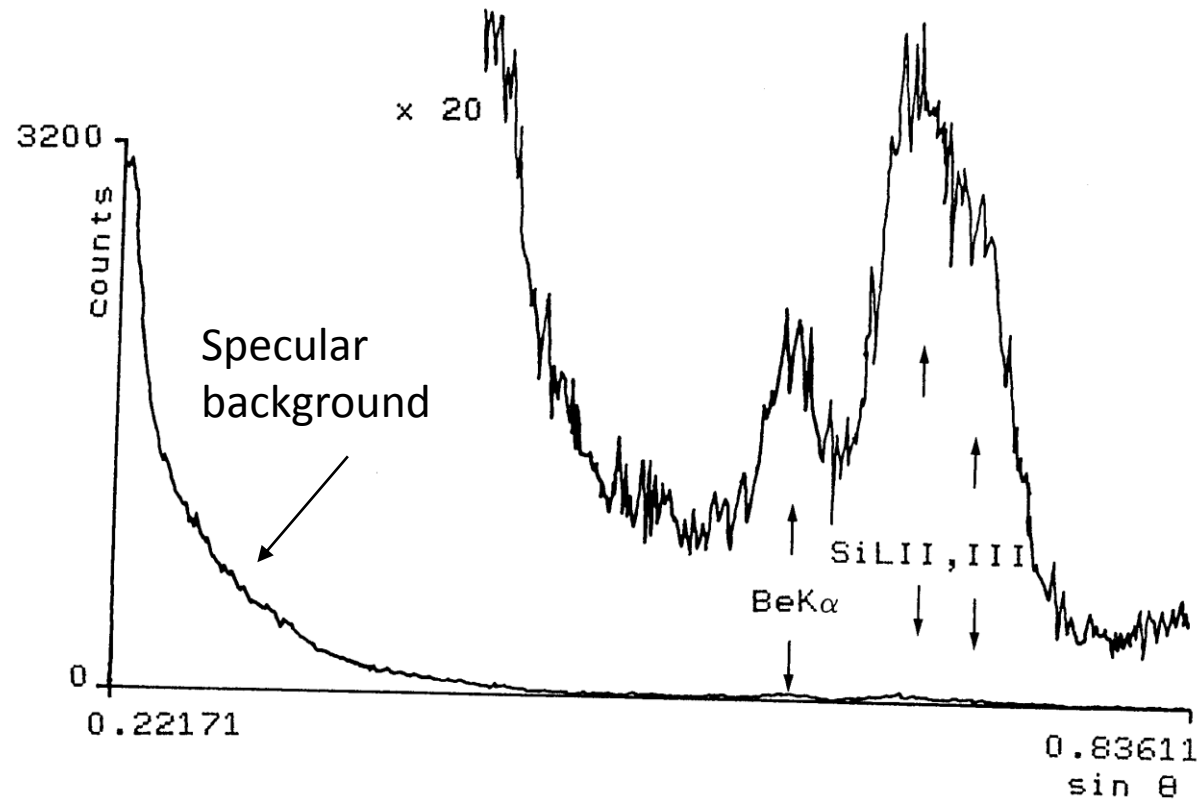


Fig. 5.11. **Bragg reflection**: diffracted rays are in phase when distance $A'B'C'$ differs from ABC by an integral number of wavelengths.

Modélisation du fond continu

Example 1: analysis of beryllium in silicates

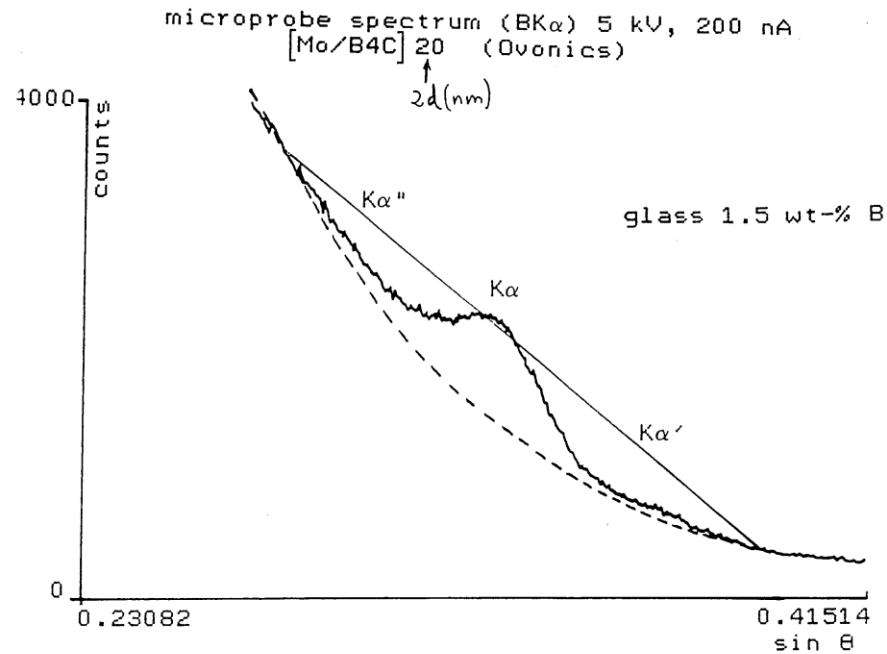
exp. spectrum (microprobe)
for beryl
10 kV, 100 nA,
[Mo/B₄C] 200 (Ovonics)



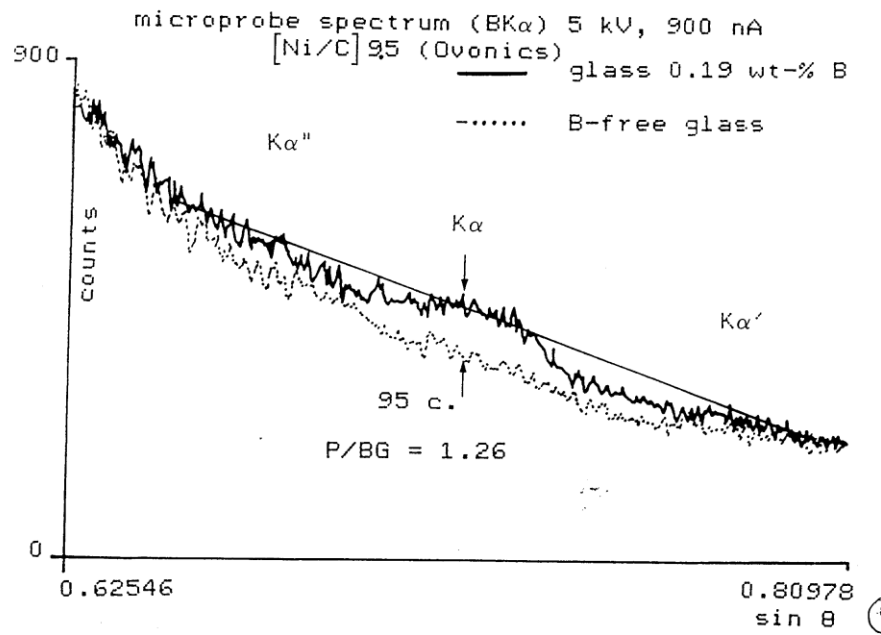
Specular reflection: X rays are totally reflected at the Surface of the LSM giving an intense signal for low Bragg angles. The higher the density of the LSM, the higher the specular reflection

Experimental spectrum recorded from beryl with Mo-B₄C LSM over the full mechanical range of a Cameca WDS. Note the high-level specular background compared with the height of the detected Bragg peaks.

Modélisation du fond continu



Using a Mo/B₄C LSM with 2d=20nm, the B K α peak (composed of a main peak and two satellite peaks K α' and K α'') is recorded over the low- θ range of the spectrometer. The specular background is large and strongly curved.



Using a Ni/C LSM with 2d=9.5nm, 1) lowers the density of the LSM and, 2) shifts the peak towards the high- θ range of the spectrometer where the specular background is reduced. The peak/background ratio for B K α emitted from a 0.19wt-% B glass is the same as that for the B K α peak emitted from the 1.5wt-% B glass with the Mo/B₄C LSM.

-> **detectability enhanced for the Ni/C LSM**

Modélisation du fond continu

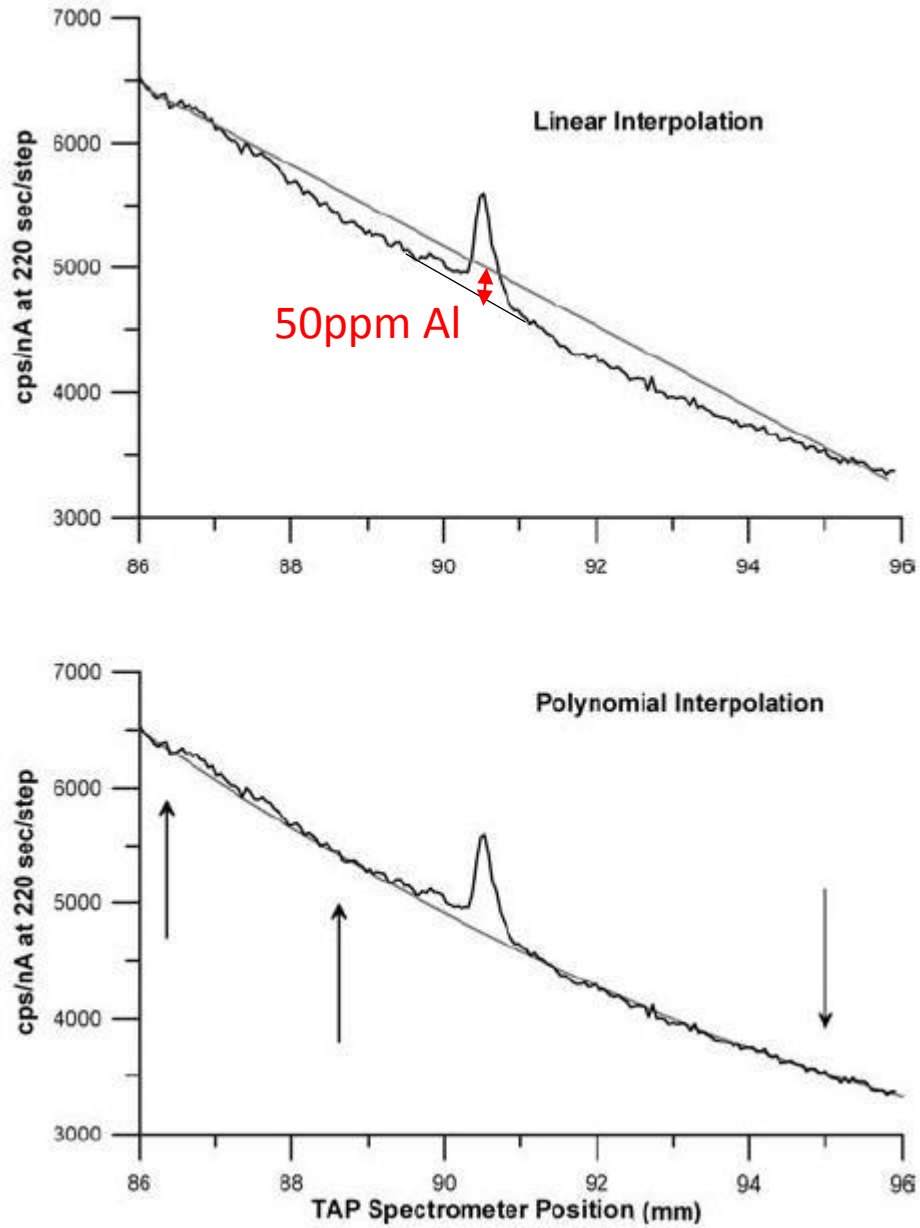
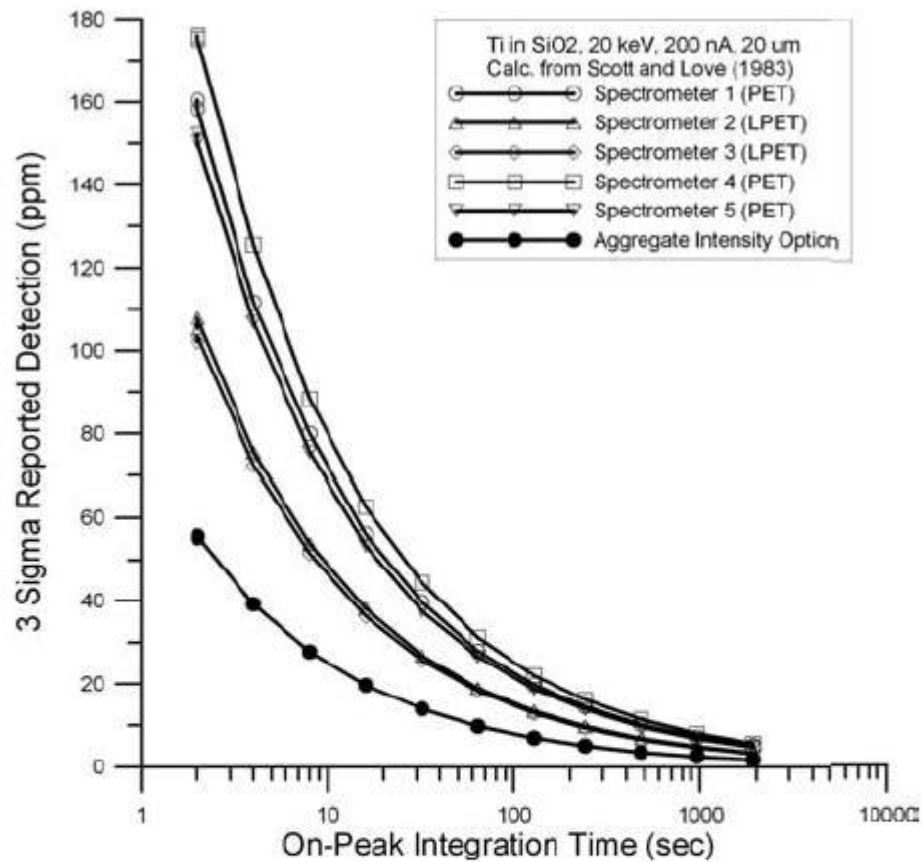
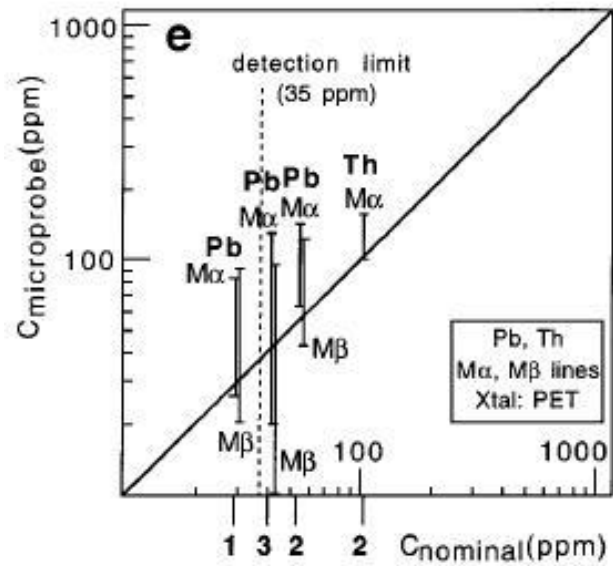
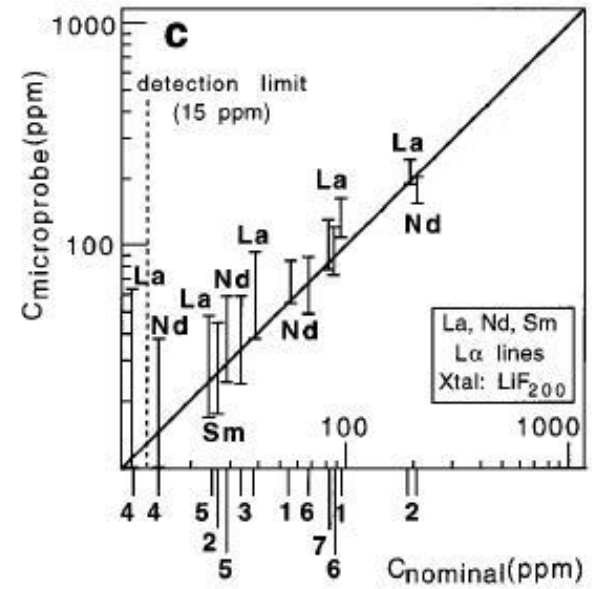
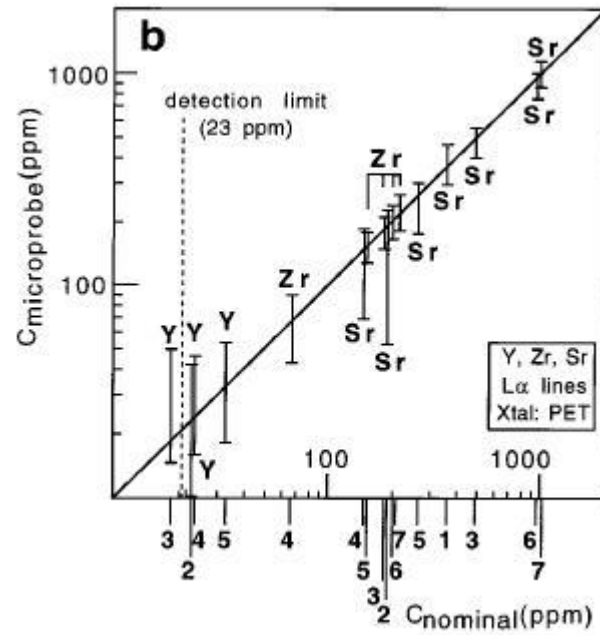
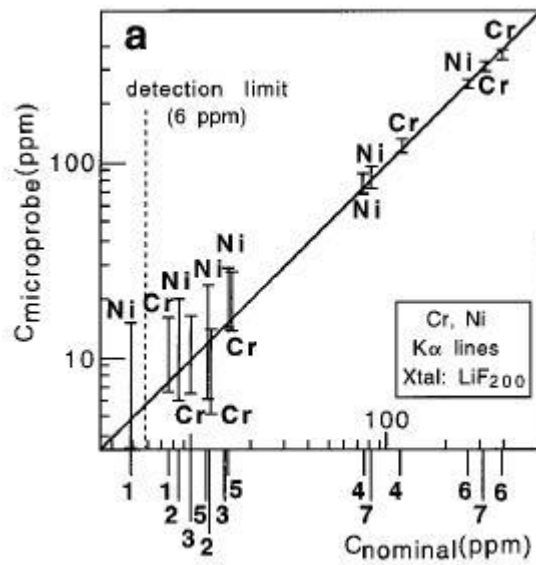


FIGURE 3. Wavelength intensity scan data on hydrothermal quartz in the range of the $AlK\alpha$ peak position (black lines). The gray lines represent different background models: linear (top) and polynomial (bottom). The arrows indicate the selected fit positions for the polynomial fit regression model. The choice of background model significantly affects the apparent Al abundance.



Mesure par couplage de plusieurs spectromètres

FIGURE 6. Comparison of individual spectrometer 3σ detection limits with the software-enabled “aggregate” intensity option as a function of counting time as measured on a pure SiO₂ “blank” (1.42 ppm Ti by ICP-MS). The aggregate intensity option reflects the combined intensities of all 5 individual spectrometers. Data was acquired on a Cameca SX-100 with 5 spectrometers using PET and LPET crystals. Note that the large area crystals produce the lowest detection limits for an individual spectrometer, but the aggregate intensity option curve consisting of the combined intensities from all 5 spectrometers greatly outperforms any individual spectrometer’s performance.



Verres étalons

35kV, 500nA, 10 μ m, t= 1000s (25sitesx40s/site)

Choix de l'intensité du faisceau électronique: dégâts d'irradiation

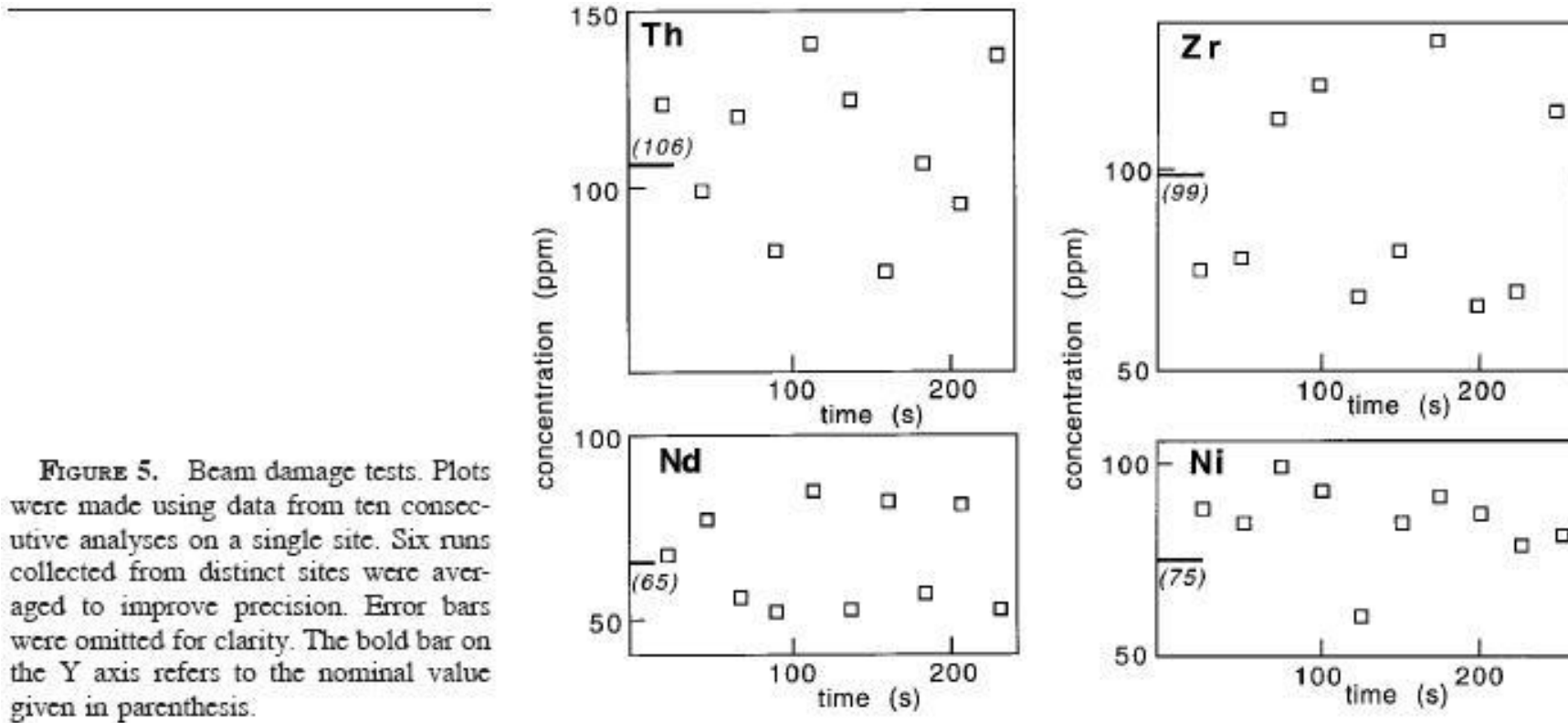


FIGURE 5. Beam damage tests. Plots were made using data from ten consecutive analyses on a single site. Six runs collected from distinct sites were averaged to improve precision. Error bars were omitted for clarity. The bold bar on the Y axis refers to the nominal value given in parenthesis.

Application: analyse à la microsonde électronique des éléments mineurs et traces pour comprendre l'histoire de la cristallisation des roches métamorphiques

Roches métamorphiques → issues de la transformation de roches sédimentaires sous l'effet de températures et/ou de pressions élevées.

→ apparition de nouvelles phases minérales

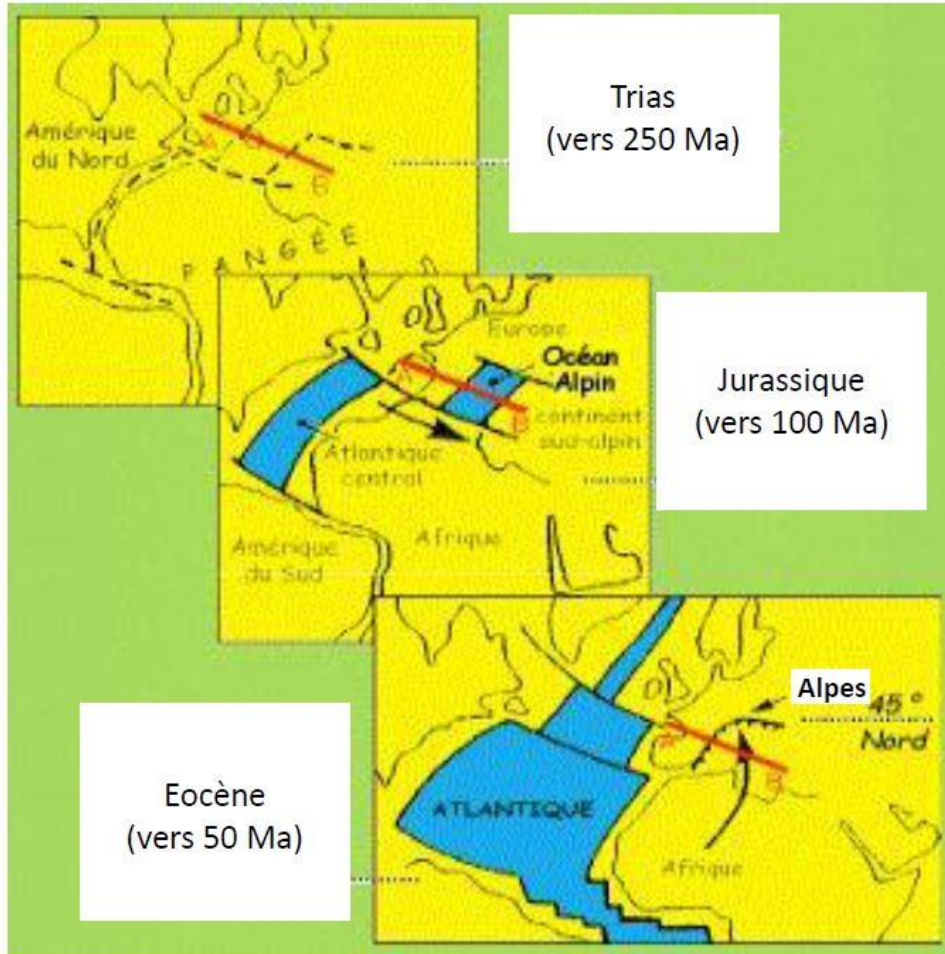
→ Élaboration de modèles thermodynamiques décrivant la chronologie de la cristallisation de la roche métamorphique

But de l'analyse des mineurs et traces : affiner les modèles thermodynamiques élaborés à partir de l'analyse des majeurs

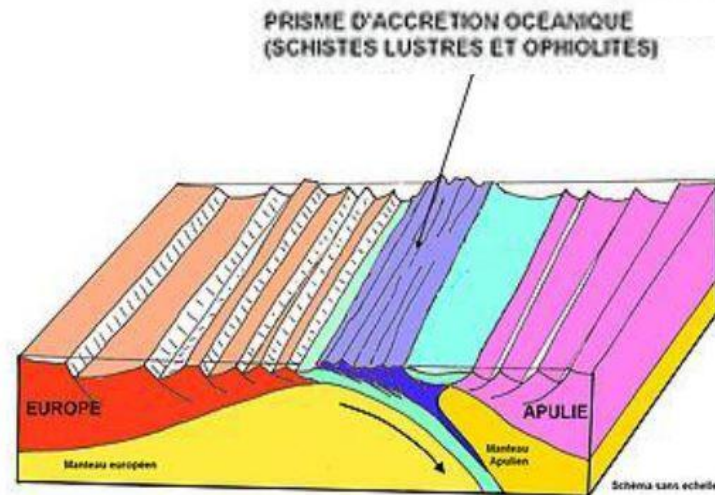
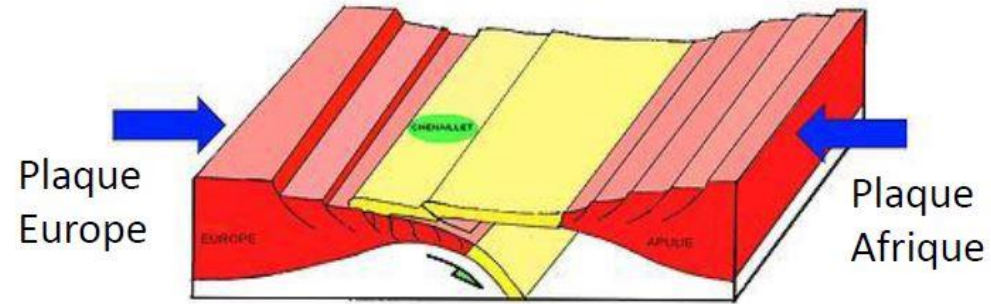
Éléments majeurs : Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K

Éléments mineurs (<1000ppm) et traces (<100ppm) : Sc, V, Cr, Co, Ni, Zn (métaux de transition de la 1^{ère} série)

Exemple : roches métamorphisées en zone de collision continentale dans les Alpes

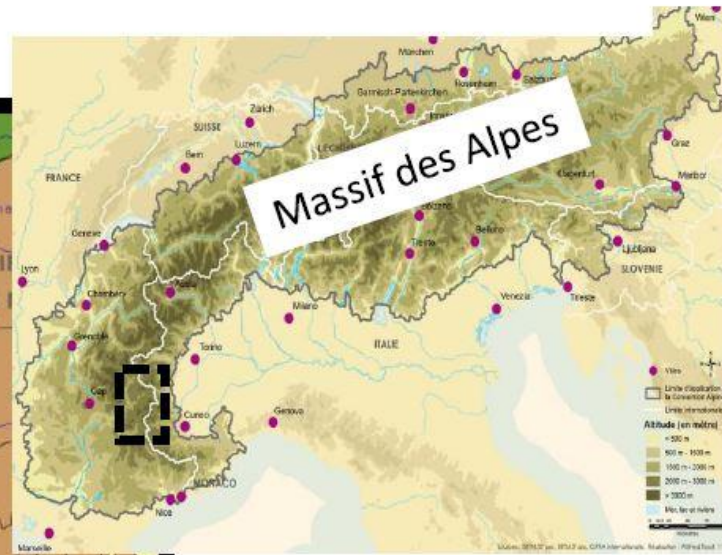
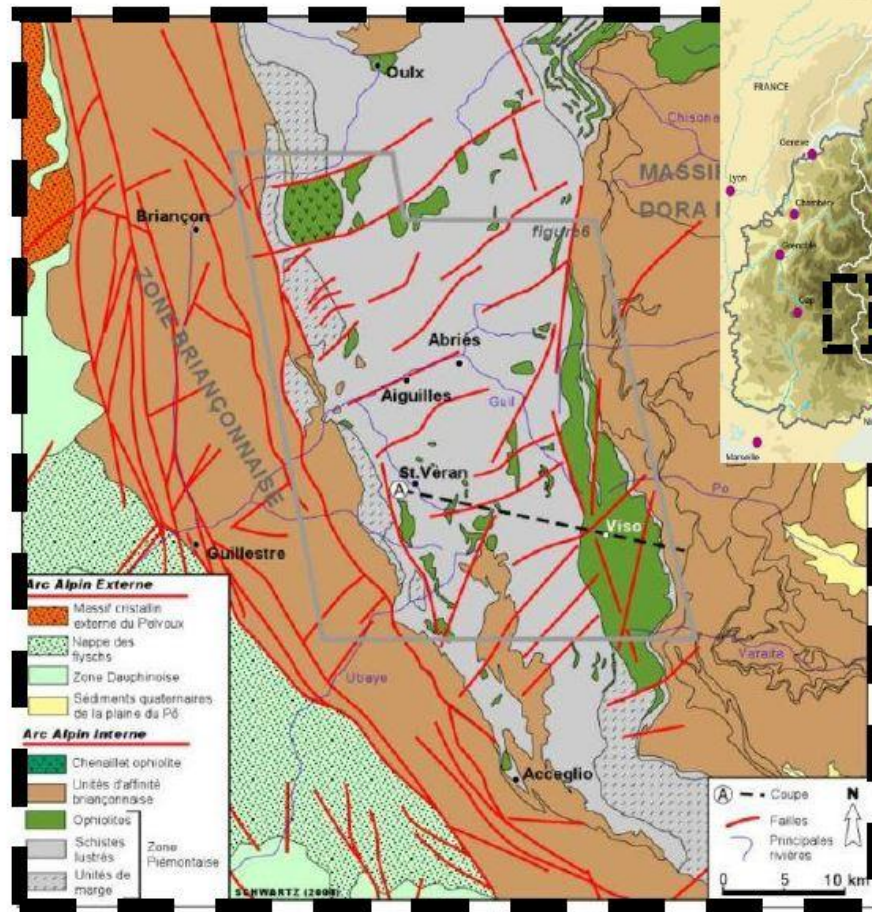


Tectonique des plaques



Schistes lustrés
=
Roche métamorphique
produite à HP-BT

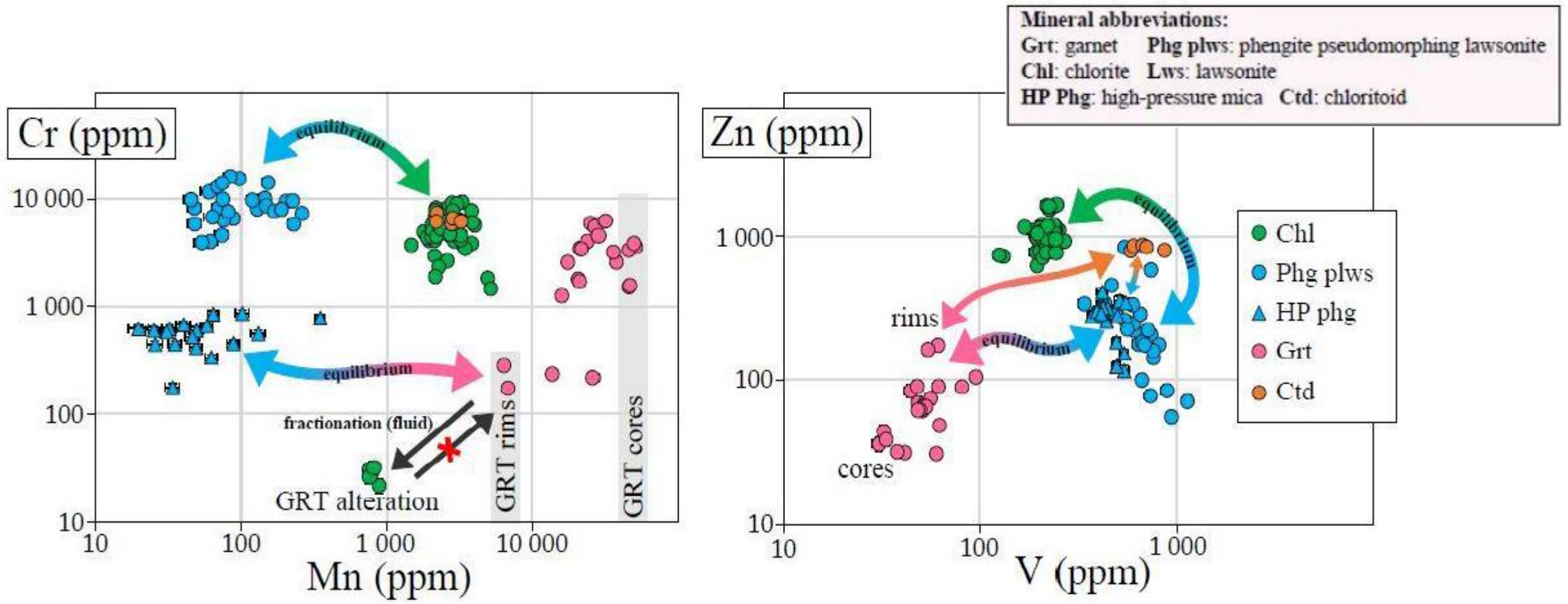
Arc alpin occidental



Aspect en 'nappe' des schistes lustrés



Trace and minor elements in a metapelite (Schistes Lustrés, French Alps)



TRACE ELEMENTS IN METAPELITES: Partitioning, Imaging and Use for Thermobarometry

BENOÎT DUBACQ^{1*}, VINCENT DE ANDRADE² & ALEXIS PLUNDER³



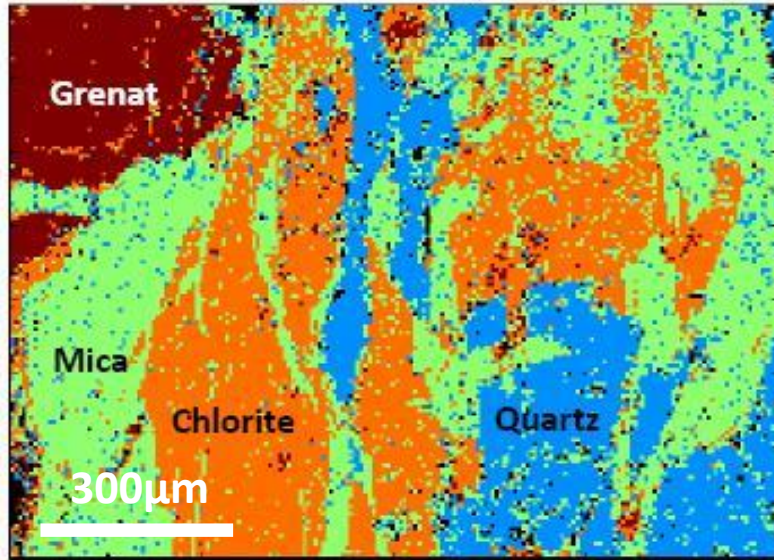
¹ CNRS-ISTeP, UMR 7193, Univ. Paris 6, case 129, 4 Place Jussieu, 75252 Paris France
² APS Argonne National Laboratory 9700 South Cass Ave. Bldg 438-B007 Lemont, IL. 60439
³ Dept. of Earth Sciences, Utrecht University, Heidelberglaan 2, 3584CS Utrecht, The Netherlands

*correspondence: benoit.dubacq@upmc.fr

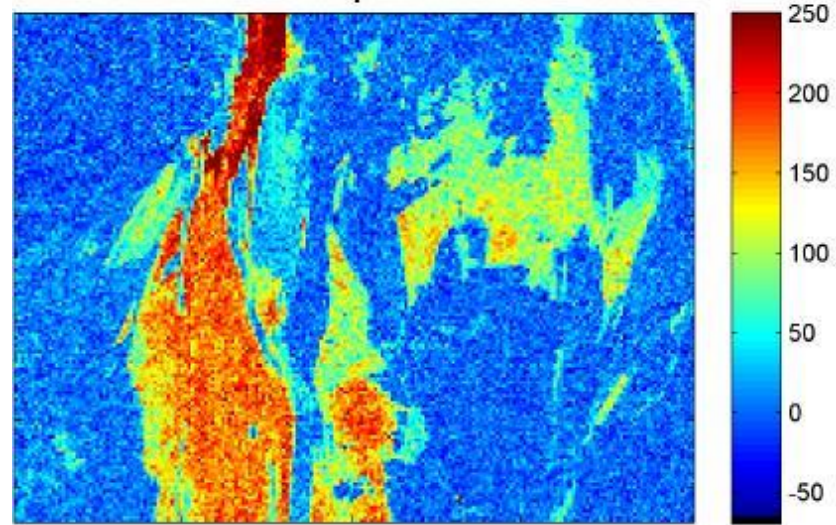


Ni $K\alpha$, 20kV, 250nA, 1LiF+2LLiF, 200x150 pixels, 150ms/pixel (2h50mn, P+BG)

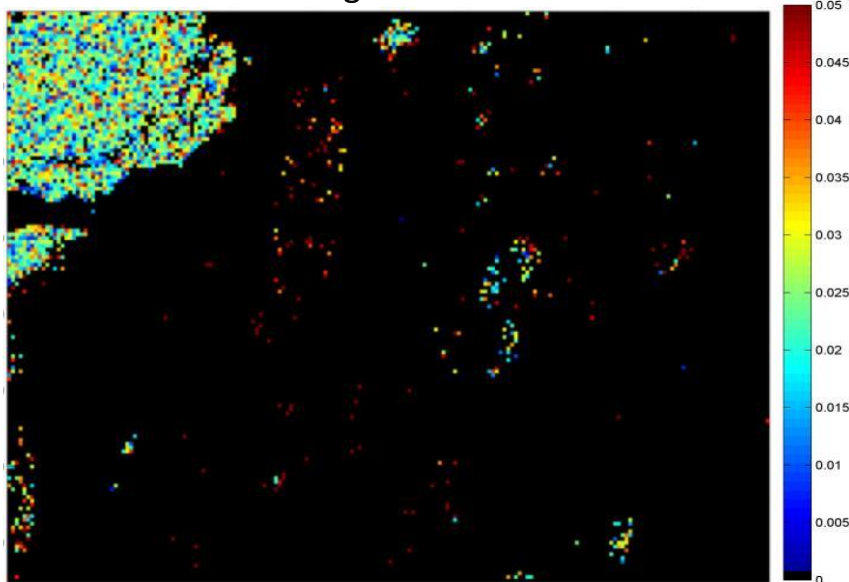
Carte des phases (d'après BSE)



Carte somme pics - somme fonds



Pixels grenat



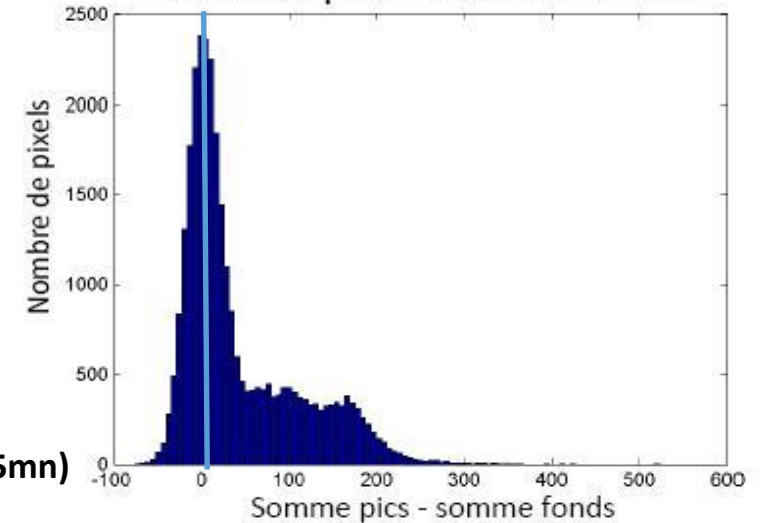
Grenat, 2888pixels (~15mn)

17+-6 ppm (2σ)

$C_{\min} = 4\text{ppm}$

Histogramme de fréquence

Somme pics - somme fonds



RÉSUMÉ

Conclusion 1 :

La mesure de certains éléments traces dans les phyllosilicates est possible, y compris en cartographie

Conclusion 2 :

La microsonde électronique offre un bon compromis entre résolution, précision et facilité d'analyse, complémentaire de μ XRF et LA-ICP-MS

Conclusion 3 :

Les éléments traces sont porteurs d'information pétrologique dans les roches de haute pression !

Conclusion 4 :

Les éléments traces vont être utiles pour vérifier puis affiner les modèles thermodynamiques