



# Dégâts d'irradiation: conséquences sur la microanalyse des fluor-apatites

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Réunion thématique: MEB - Matériaux naturels et Environnement  
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# Utilisation

- **Sciences des matériaux**: déchets nucléaires; piégeage des métaux lourds; fertilisants
- **Sciences du vivant**: dents; tissu osseux (naturel et synthétique)
- **Sciences de la terre**: volatiles et fluides pendant une cristallisation magmatique; datation radiométrique Rb–Sr (Fluorstrophite);





# “APATITE”

- **Werner (1786) – le nom derive de  $\alpha\pi\alpha\tau\alpha\omicron$  = tromper**

- **Formule generale:  ${}^{\text{IX}}\text{M}1_4 {}^{\text{VII}}\text{M}2_6 ({}^{\text{IV}}\text{TO}_4)_6 \text{X}_2$**   
Où

M =  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Bi}^{3+}$

T =  $\text{P}^{5+}$ ,  $\text{As}^{5+}$ ,  $\text{V}^{5+}$ ,  $\text{Si}^{4+}$ ,  $\text{S}^{6+}$ ,  $\text{B}^{3+}$

X =  $\text{F}^-$ ,  $(\text{OH})^-$ ,  $\text{Cl}^-$

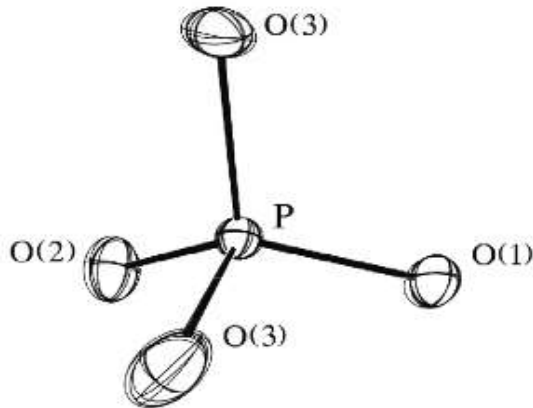
- **3 termes plus importants: hydroxy- fluoro- et chloro-apatites**

	M1/M2	(TO4) <sub>6</sub>	X <sub>2</sub>	Formule et nom usuel (et domaines d'application)
Substitutions stoechiométriques	Ca <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup>	OH <sup>-</sup>	Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> (biomatériaux) Hydroxyapatite <sup>[38]</sup>
			F <sup>-</sup>	Fluoroapatite <sup>[34]</sup>
			Cl <sup>-</sup>	Chloroapatite
	Ca <sup>2+</sup> / Cd <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup>	OH <sup>-</sup>	Ca <sub>10-x</sub> Cd <sub>x</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> hydroxyapatites calcocadmées <sup>[39]</sup>
Pb <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup> ou VO <sub>4</sub> <sup>3-</sup>	Cl <sup>-</sup>	Pb <sub>10</sub> (PO <sub>4</sub> ,VO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub> Pyromorphite, Vanadite <sup>[40, 41]</sup>	
			(Piégeage de métaux lourds)	
Ca <sup>2+</sup> / Ln <sup>3+</sup> ou Ca <sup>2+</sup> / Rn <sup>3+</sup>	PO <sub>4</sub> <sup>3-</sup> / SiO <sub>4</sub> <sup>4-</sup>	F <sup>-</sup>	Ca <sub>10-x</sub> (Ln,Rn) <sub>x</sub> (PO <sub>4</sub> ) <sub>6-x</sub> (SiO <sub>4</sub> ) <sub>x</sub> F <sub>2</sub> Britholites (piégeage de métaux lourds, conditionnement de déchets nucléaire) <sup>[42, 43]</sup>	
Ln <sup>3+</sup> / Ca <sup>2+</sup>	SiO <sub>4</sub> <sup>4-</sup> ou GeO <sub>4</sub> <sup>4-</sup>	O <sup>2-</sup>	(Ca,Sr,Ba) <sub>2</sub> Ln <sub>3</sub> (SiO <sub>4</sub> ,GeO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> Oxyapatites (SOFC)	
Substitutions non stoechiométriques	Ca <sup>2+</sup> / lacune	PO <sub>4</sub> <sup>3-</sup> /CO <sub>3</sub> <sup>2-</sup>	OH <sup>-</sup> / lacune	Ca <sub>10-x</sub> □ <sub>x</sub> (PO <sub>4</sub> ) <sub>6-x</sub> (CO <sub>3</sub> ) <sub>x</sub> (OH) <sub>2-x</sub> □ <sub>x</sub> Hydroxyapatites carbonatées de type B (biomatériaux) <sup>[37]</sup>
	Ca <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup> /SiO <sub>4</sub> <sup>4-</sup>	OH <sup>-</sup> / lacune	Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6-x</sub> (SiO <sub>4</sub> ) <sub>x</sub> (OH) <sub>2-x</sub> □ <sub>x</sub> Hydroxyapatites silicatées (biomatériaux) <sup>[44]</sup>
	Ln <sup>3+</sup> / lacune	SiO <sub>4</sub> <sup>4-</sup> ou GeO <sub>4</sub> <sup>4-</sup>	O <sup>2-</sup>	Ln <sub>9,33</sub> (SiO <sub>4</sub> , GeO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> Oxyapatites (SOFC)

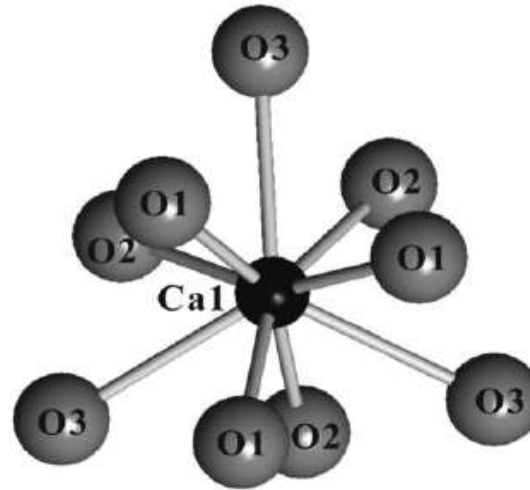
\* Ln<sup>3+</sup> : Terre rare, Rn<sup>3+</sup> : radionucléides

# Cristallographie d'une apatite

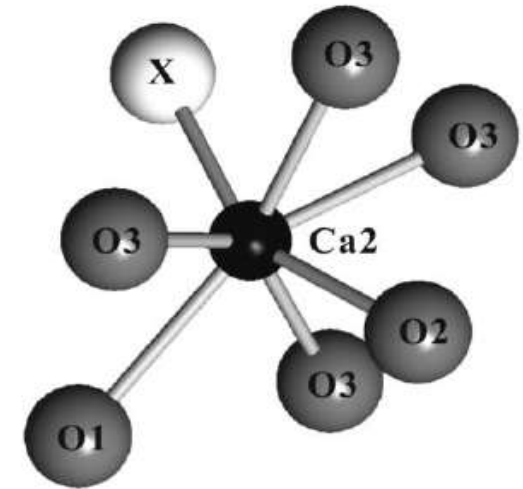
## Tétraèdre PO<sub>4</sub>



## Polyèdre Ca<sub>1</sub>O<sub>9</sub>



## Polyèdre Ca<sub>2</sub>O<sub>6</sub>X



Système hexagonal Groupe spatial P6<sub>3</sub>/m

$$a = b = 9.398 \text{ \AA}$$

$$c = 6.878 \text{ \AA}$$

Hughes, J.M. and Rakovan, J. (2002) The Crystal Structure of Apatite: Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH,Cl). In: Phosphates: Geochemical, Geobiological and Materials Importance, Kohn, M., Rakovan, J., Hughes, J.M. (eds). Reviews in Mineralogy and Geochemistry. Mineralogical Society of America. Washington, DC. V. 48, 1-12

Yun Luo, John M. Hughes, John Rakovan, and YuanMing Pan - Site preference of U and Th in Cl, F, and Sr apatites - American Mineralogist, Volume 94, pages 345–351, 2009

## Plateforme analytique commune ISTO-BRGM



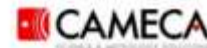
**Microsonde CAMECA SX FIVE**



**MEB-RAMAN (TESCAN-RENISHAW)**

## Quel Crystal analyseur choisir pour le dosage du Fluore?

SX 100 Crystals and their wavelength coverage



\* Most commonly used crystals

█ K Lines  
█ L Lines  
█ M Lines

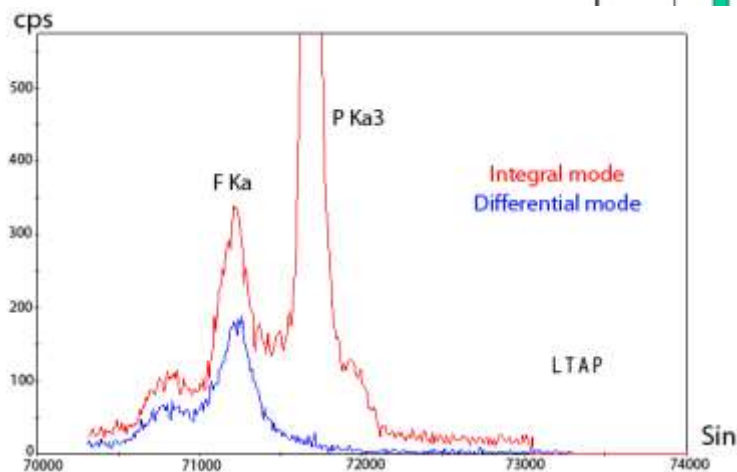
Z	LiF* LiF*	PET* LPET*	TAP* LTAP*	PC0 LPC0	PC1 LPC1	PC2* LPC2*	PC3 LPC3
	4207nm	3742nm	2.576nm	4.5nm	6nm	10nm	20nm
10		14 S	9 F 15 P 25 Mh	7 S 11 Mh	6 C 9 F	5 B 8 O	4 S 3 B
20	21 R						

Valeurs  $\sin \theta$  de  $FK\alpha$ :

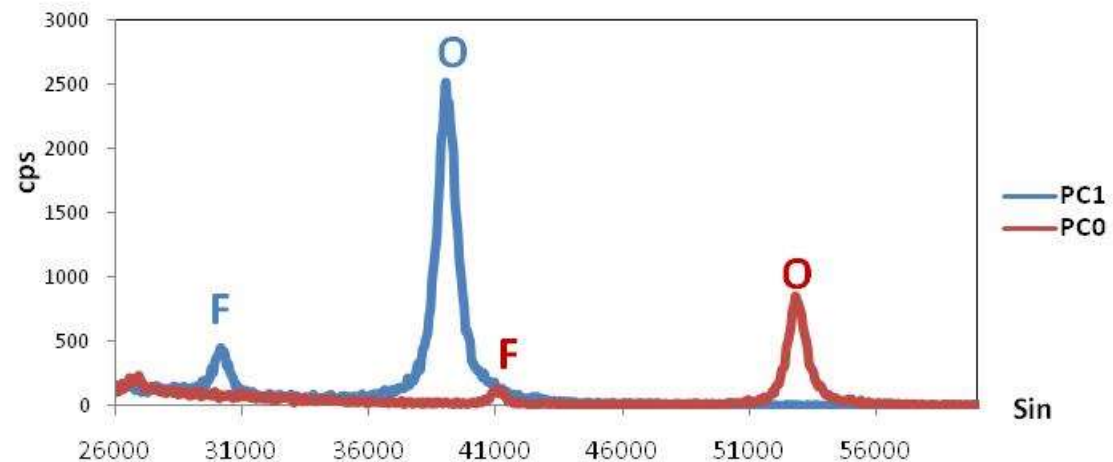
TAP: 71157

PC0: 40710

PC1: 30182

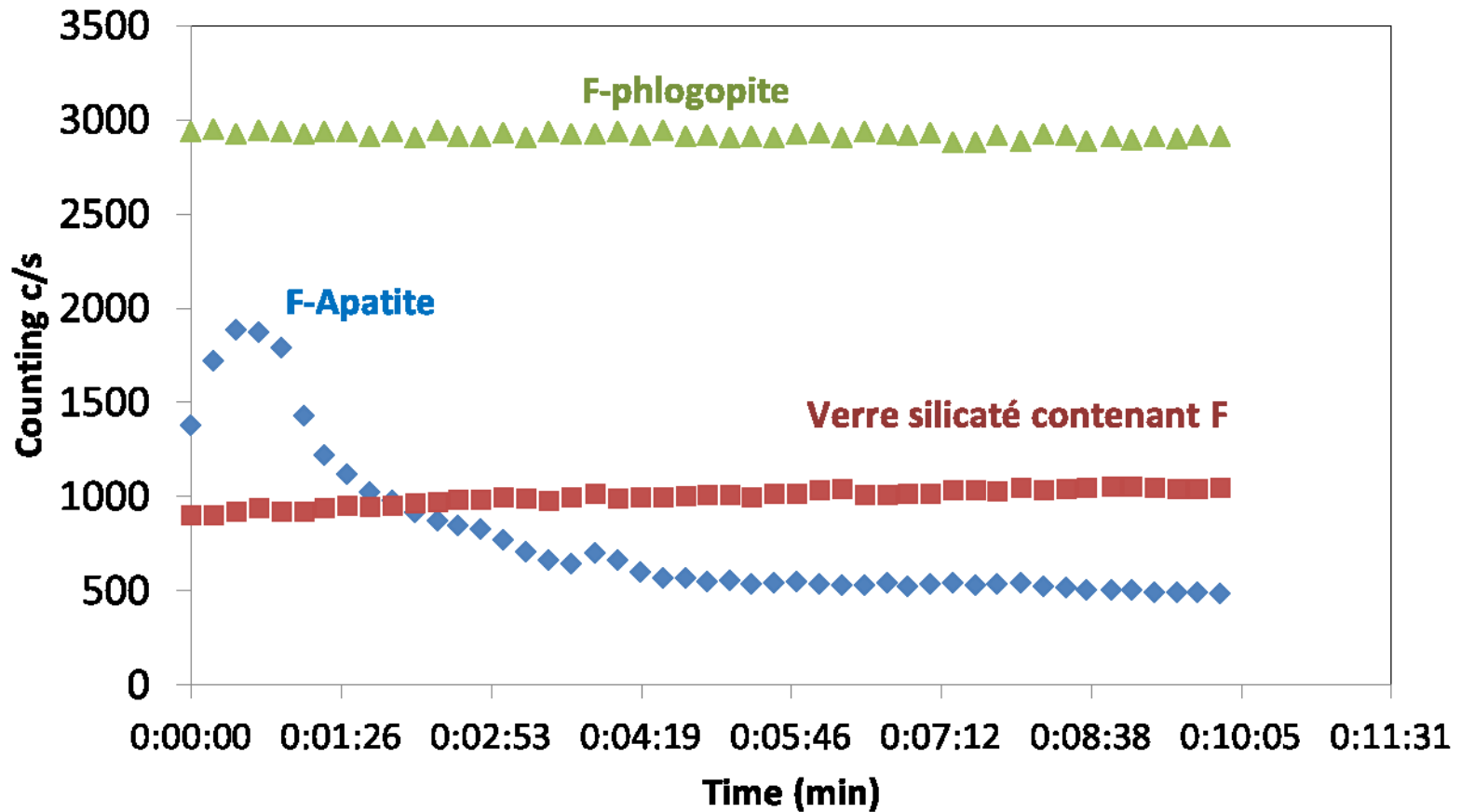


15 kV – 100 nA – faisceau defocalisé 50  $\mu$ m



15 kV – 20 nA – faisceau focalisé

## F K $\alpha$ de différents matériaux réalisé avec un cristal multicouche PC1 (2d = 60.732)

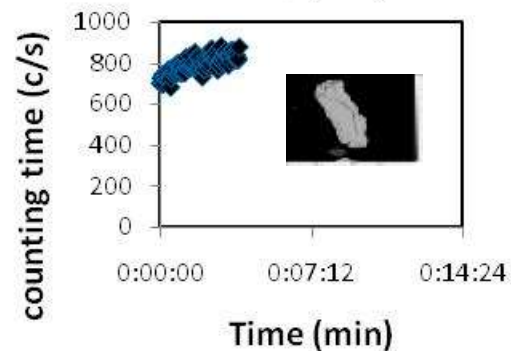
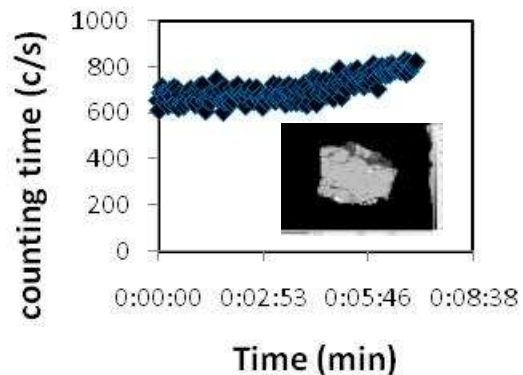
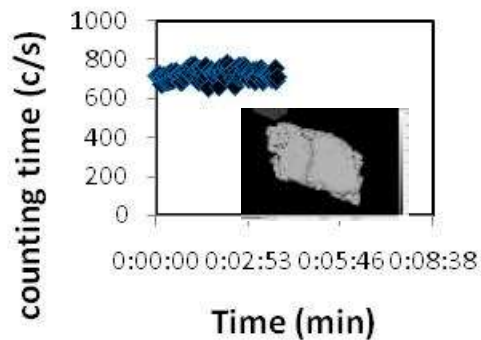
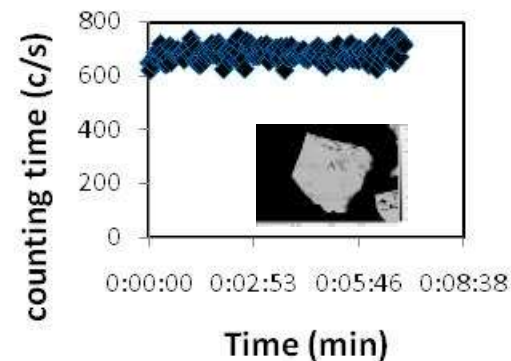
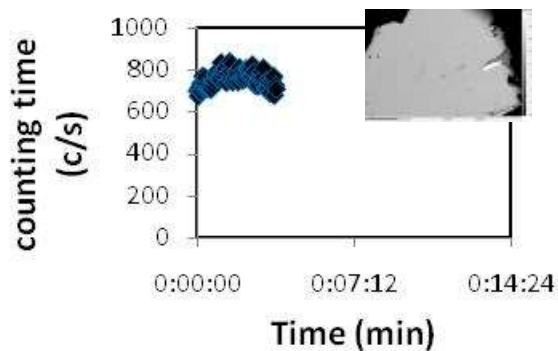
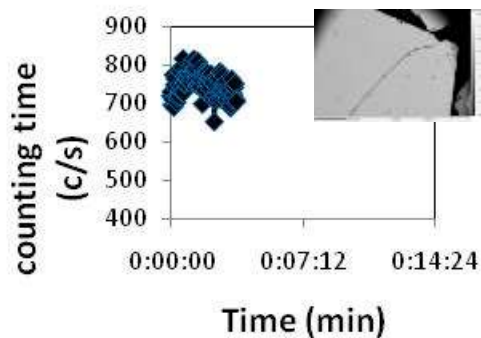
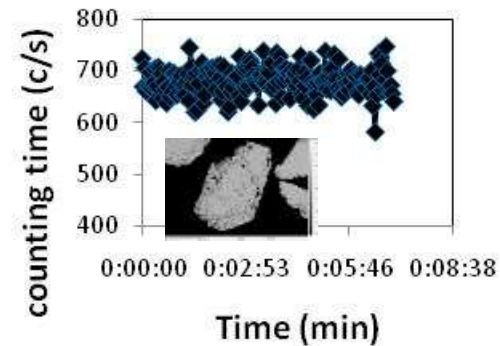
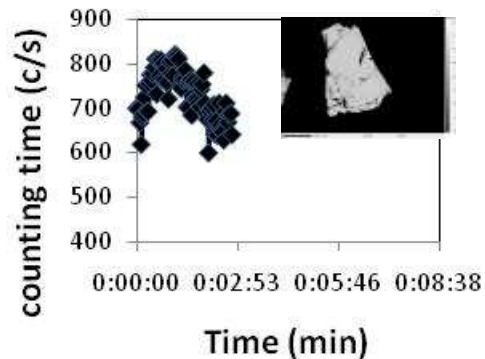
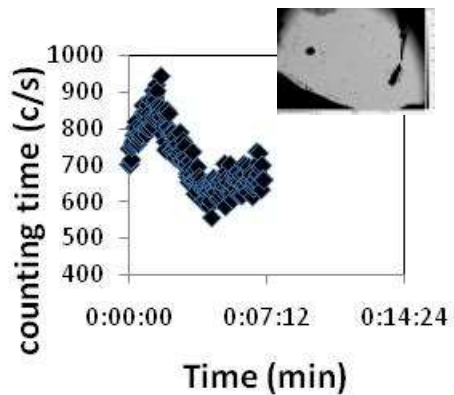




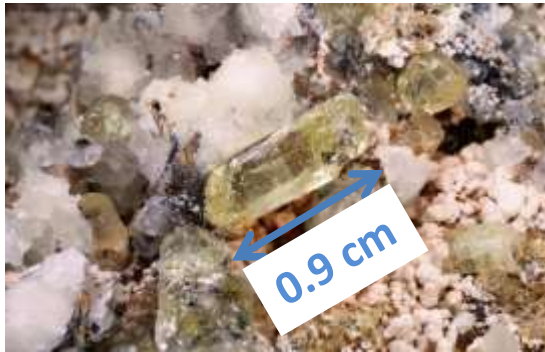
Institut des Sciences de la Terre d'Orléans



7 kV - 20 nA - faisceau focalisé

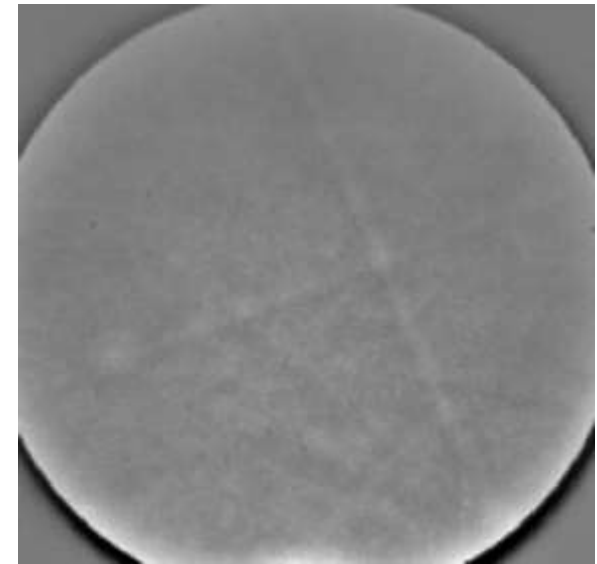


# Apatite Jumilla (faisceau électronique $\perp$ axe c)

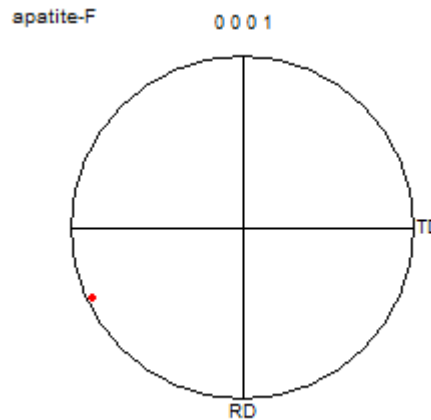
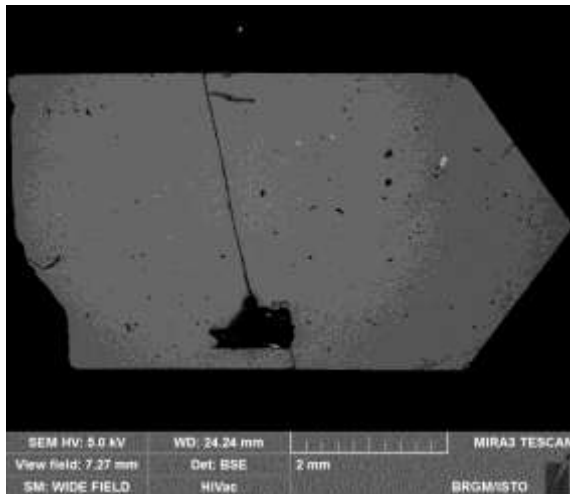


Jumilla, Murcia, Espagne  
Mina Nuestra Señora del Carmen

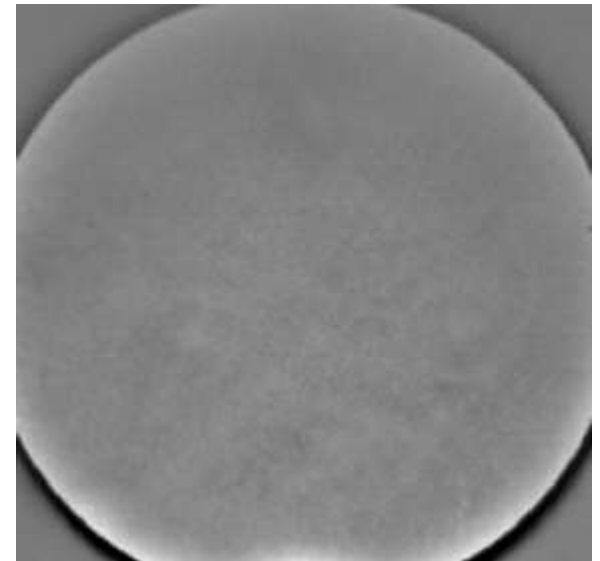
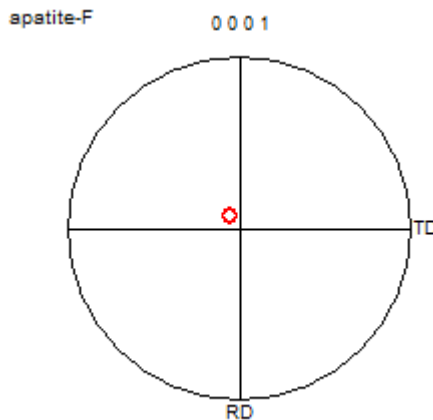
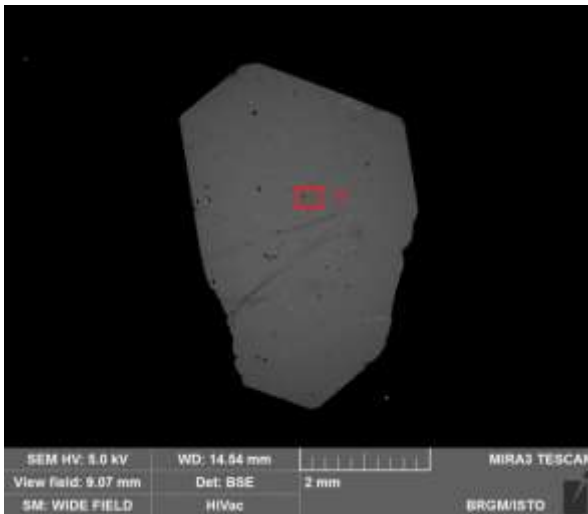
HV=25 kV BI=15 Low Vac WD=20mm



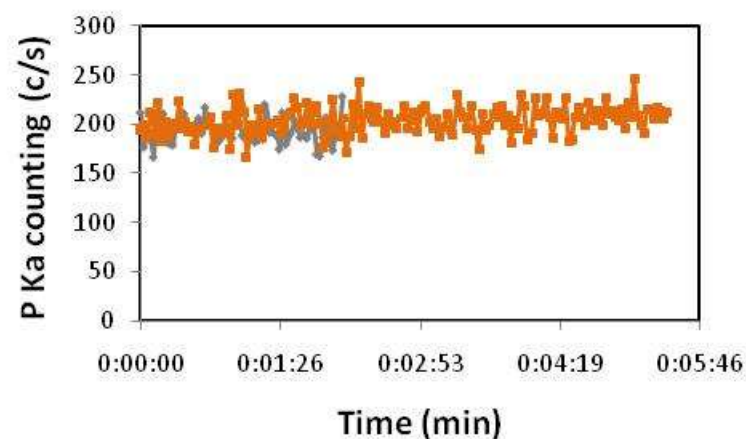
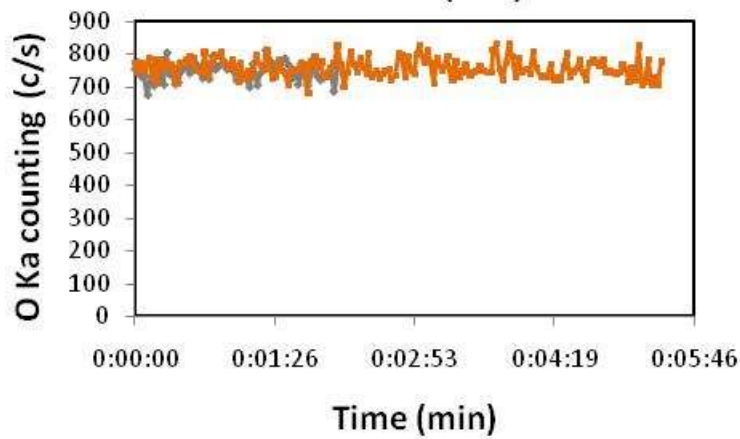
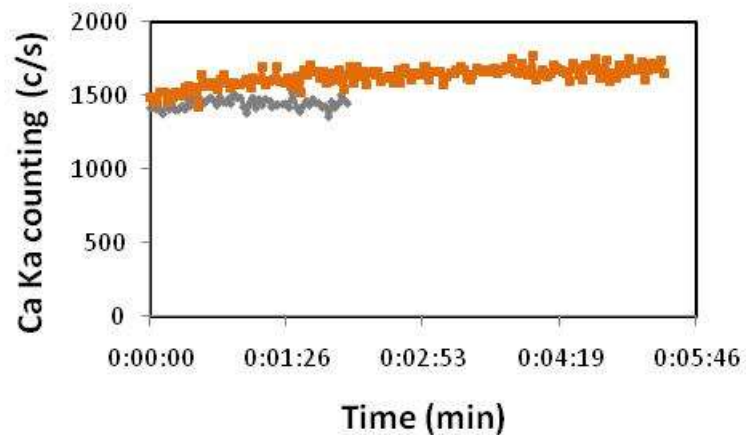
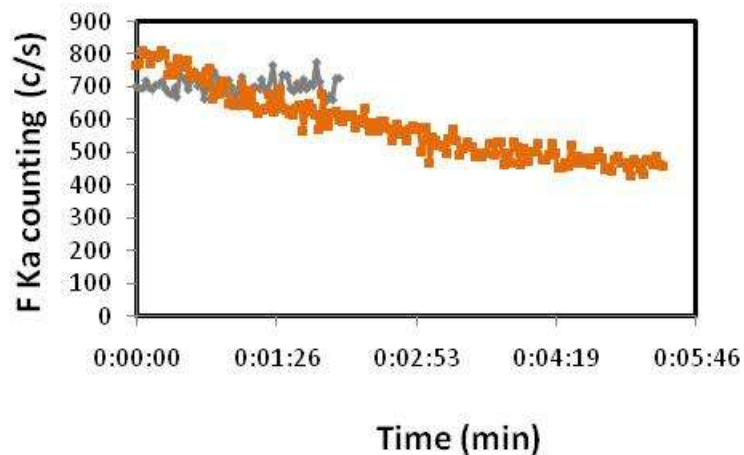
10 Pa



# Apatite Jumilla (faisceau électronique $\parallel$ axe c)



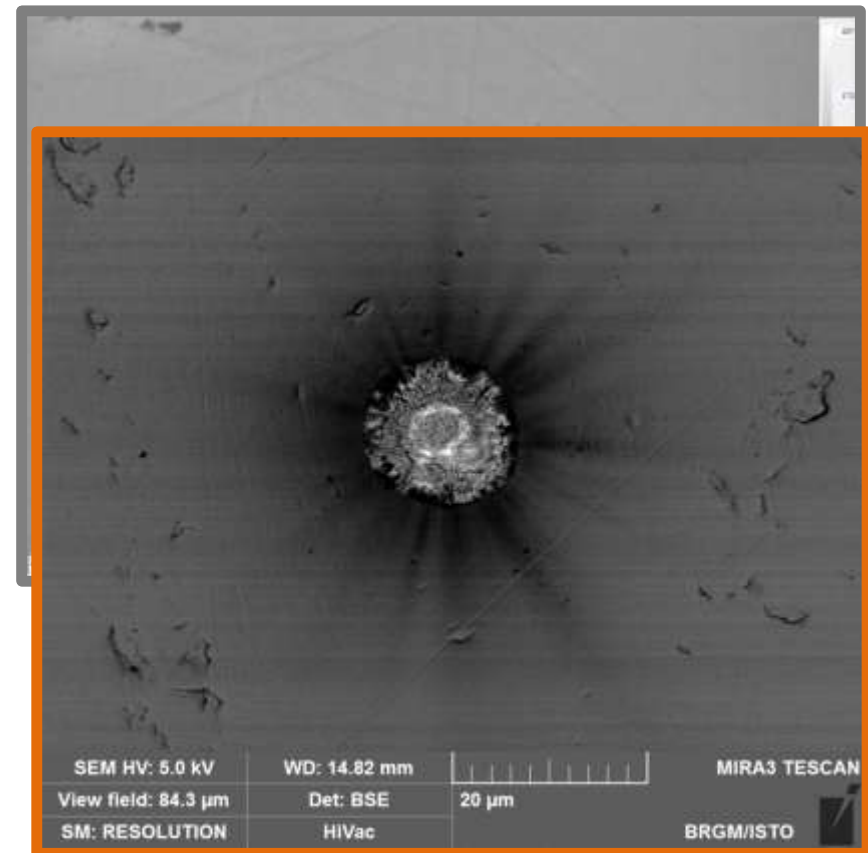
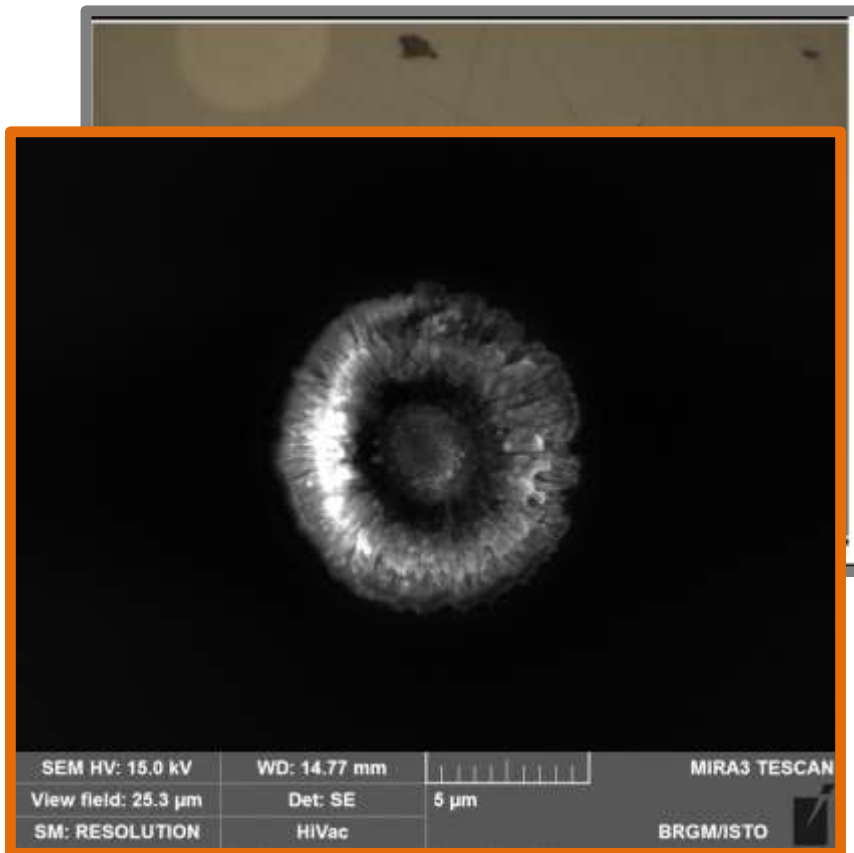
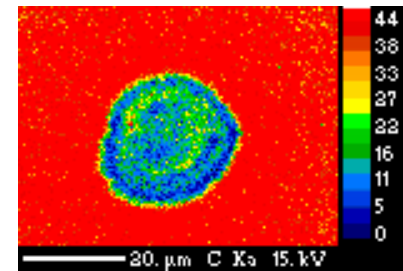
## 7 kV - 20 nA - faisceau focalisé



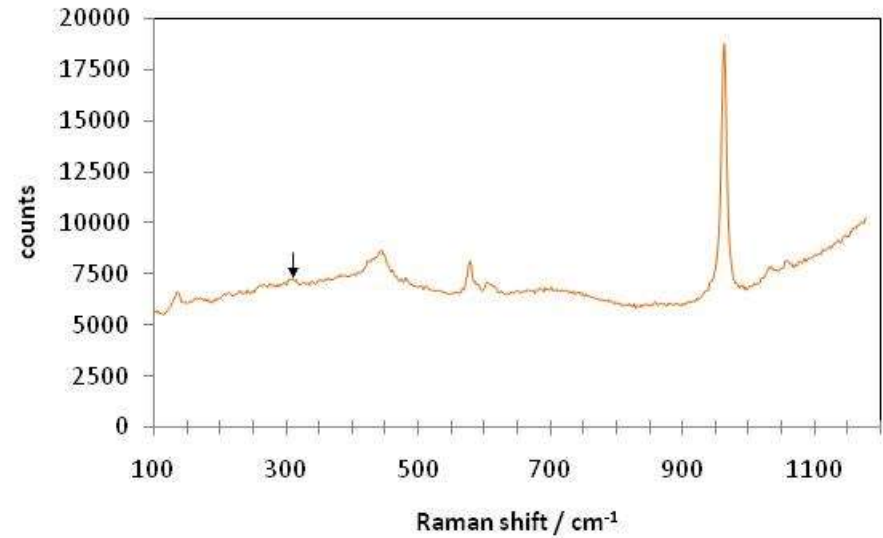
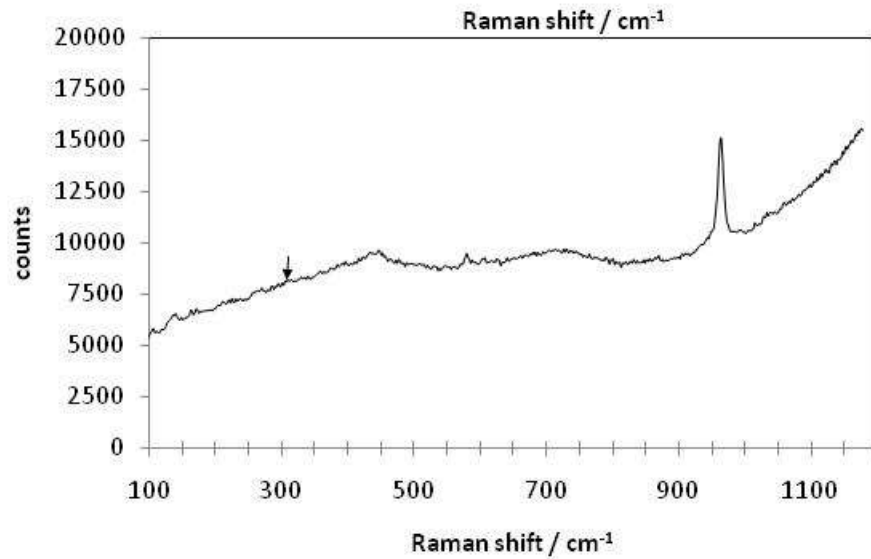
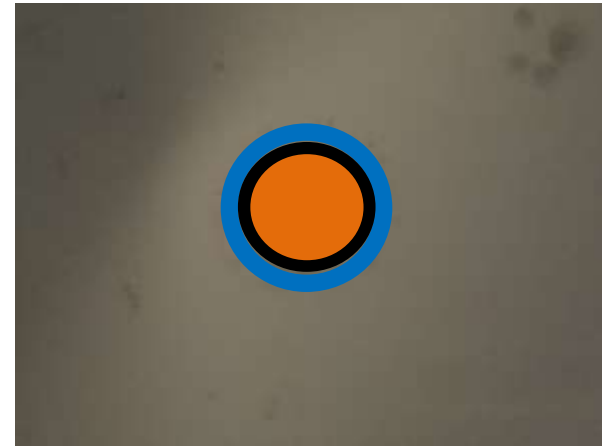
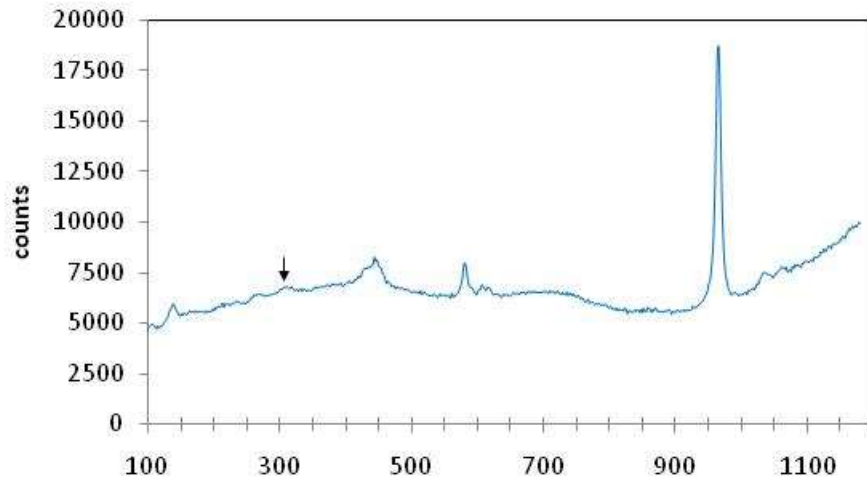
Faisceau électronique || axe c

Faisceau électronique ⊥ axe c

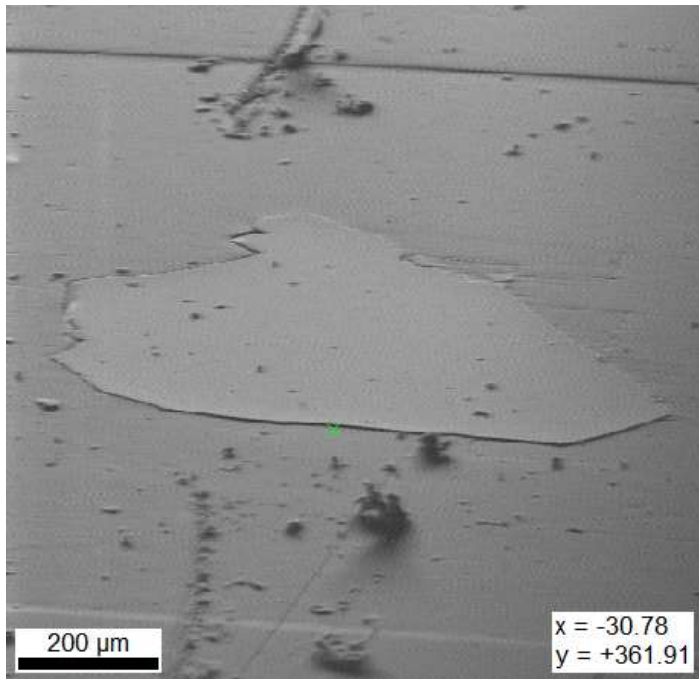
## Etat des échantillons après analyse:



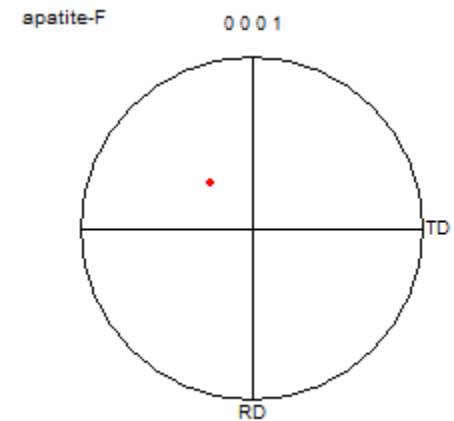
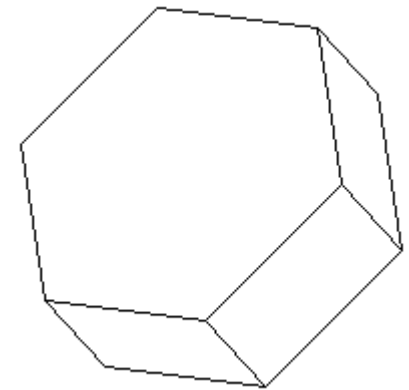
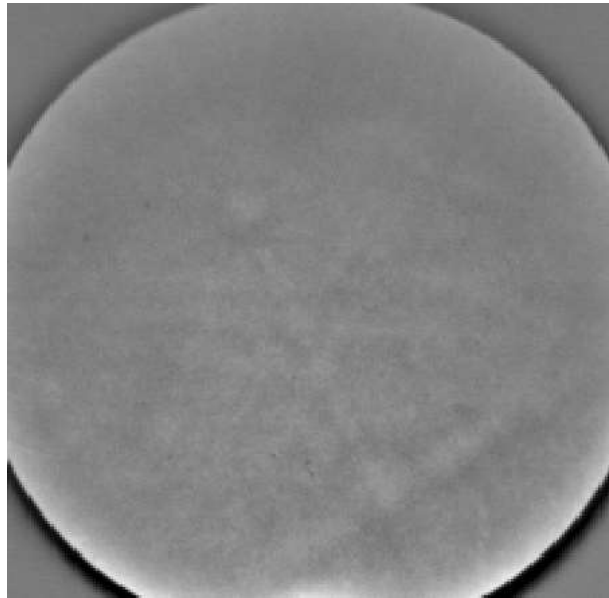
## Que nous suggère le $\mu$ -RAMAN?

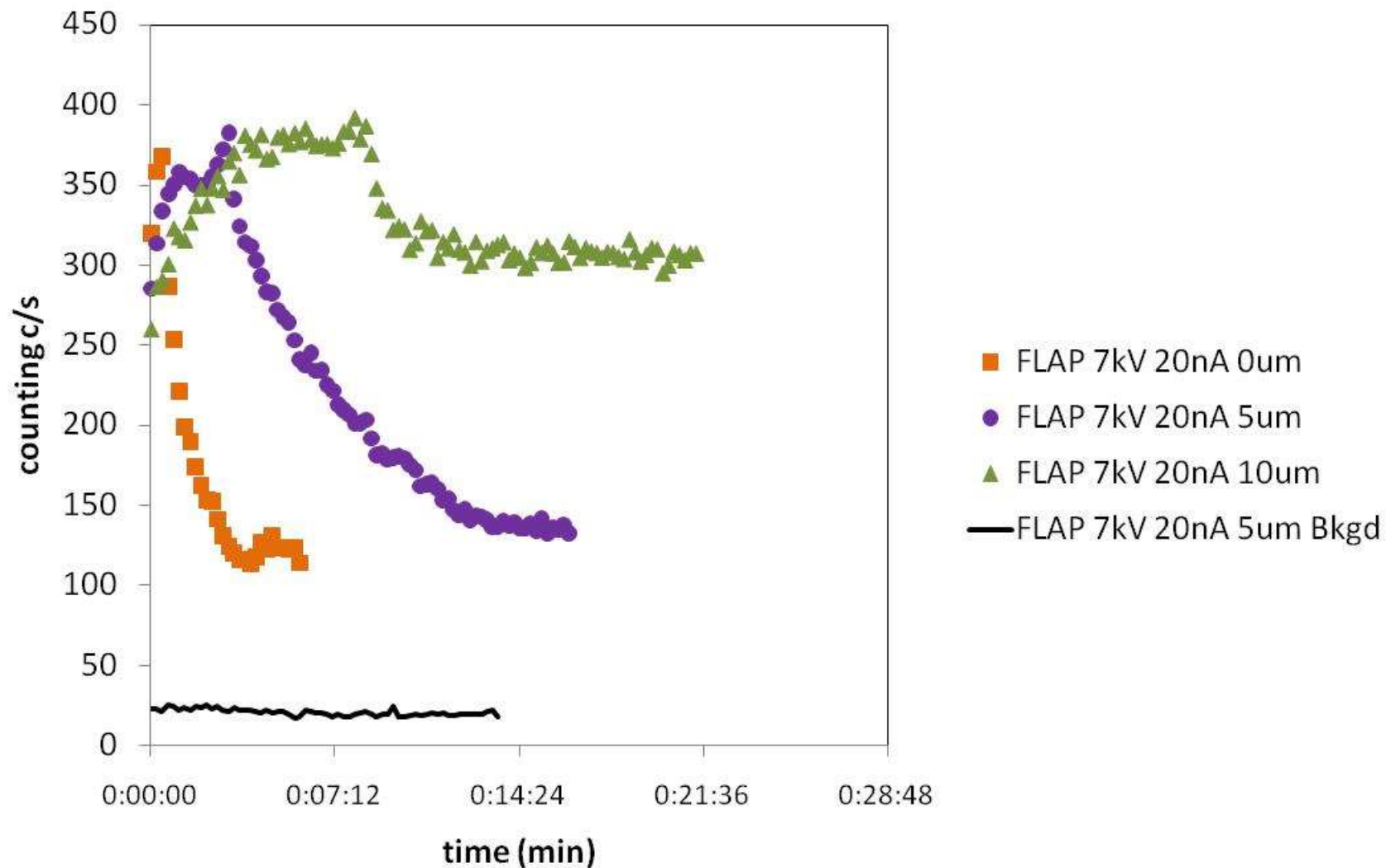


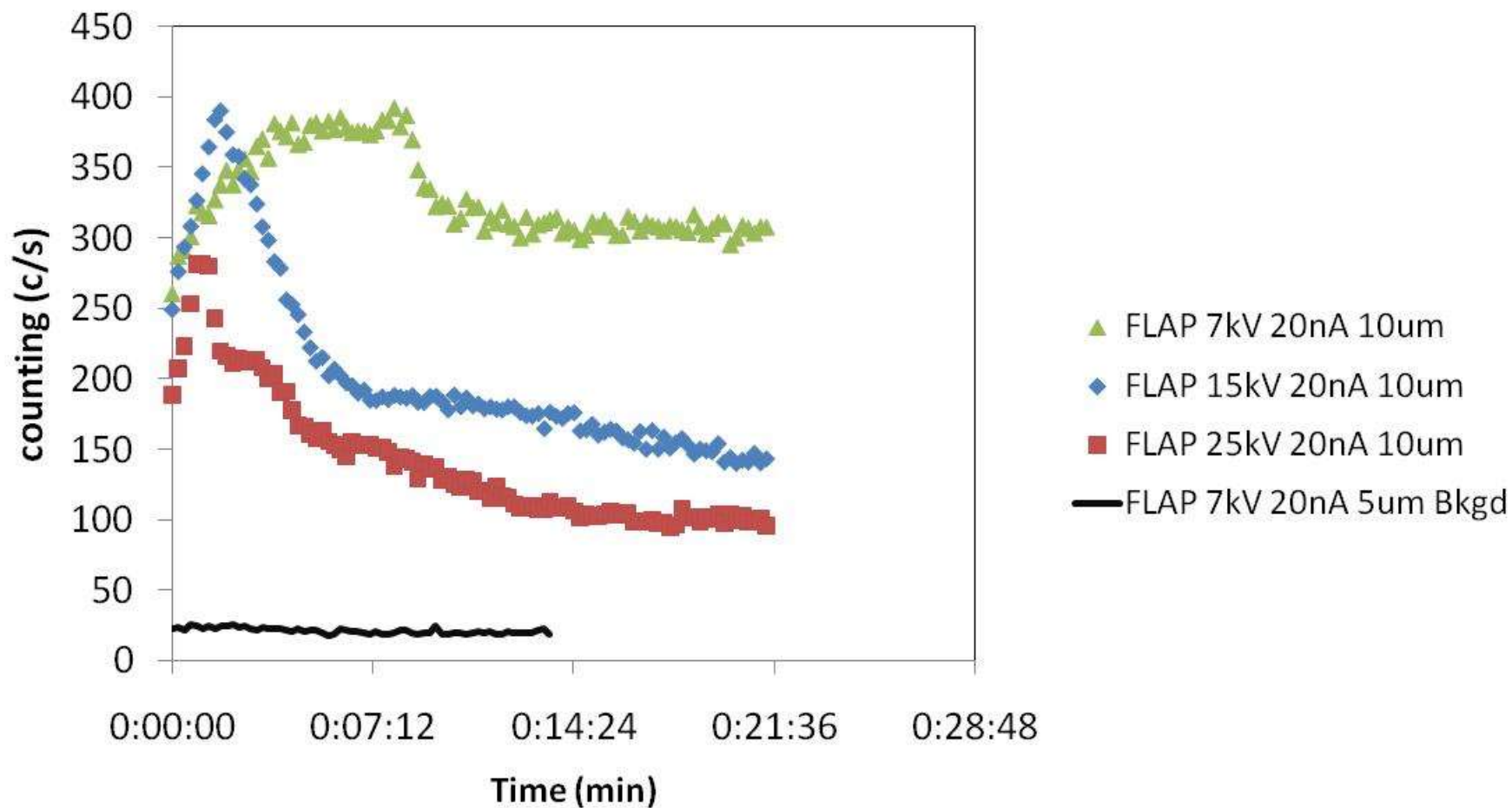
# Apatite Durango



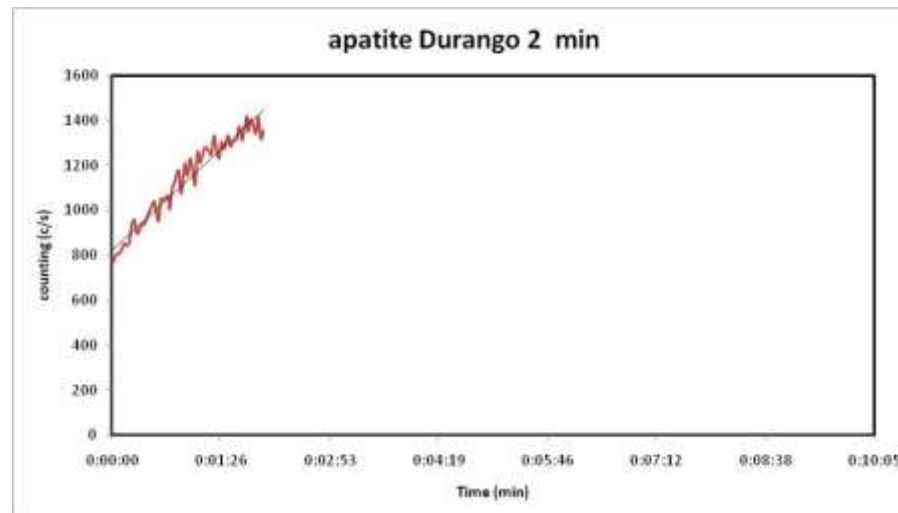
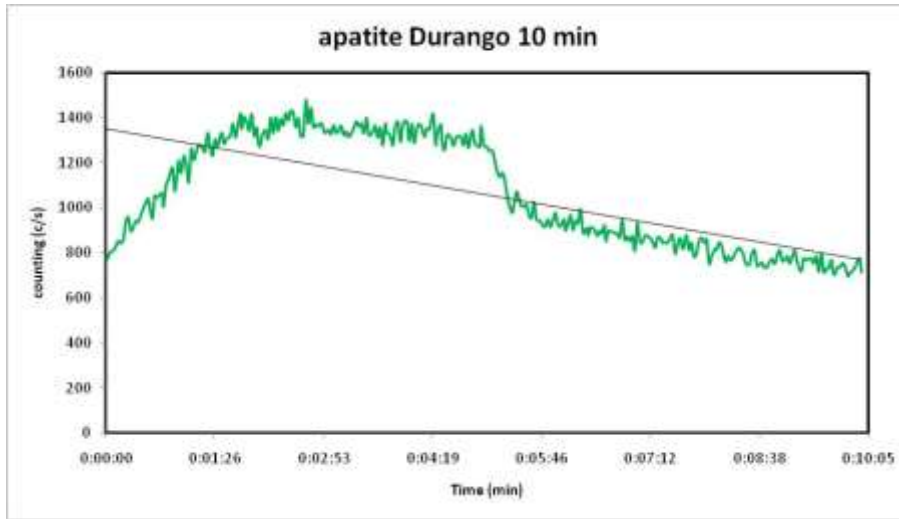
FSD



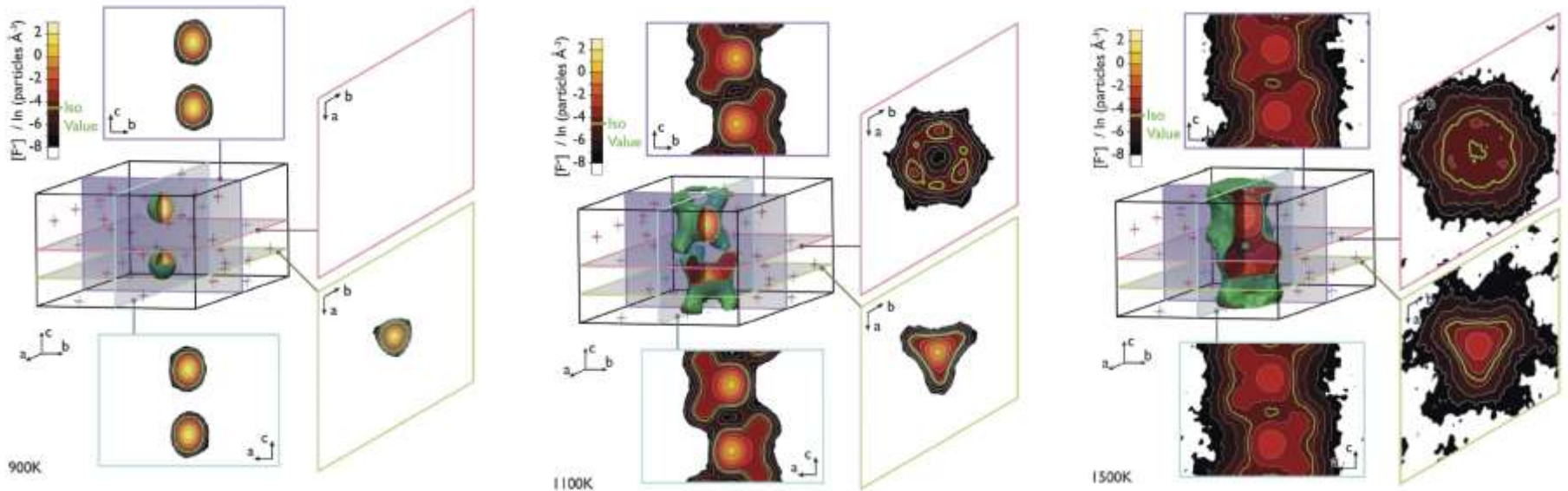




## Fonction de calcul de la teneur en Fluore à « Time = zero »



## Iso-surface pour l'ion F- à différentes températures.



$$\rho: 1.0 \cdot 10^{-2} \text{ particules / \AA}^3$$

Eleanor E. Jay, Michael J. D. Rushton and Robin W. Grimes - Migration of fluorine in fluorapatite – a concerted mechanism - J. Mater. Chem., 2012, 22, 6097



## Conclusions (et conseils!)

- ❑ Les conditions de faisceau (HV, Courant, taille de la sonde) influent sur la migration (vitesse) du Fluor
- ❑ Le micro-Raman suggère que, malgré la variation du signal de F, le minéral irradié reste une apatite et qu'elle contient encore du fluor

Avant de doser le fluor dans une apatite, il faut:

- ✓ choisir de préférence les cristaux orientés perpendiculairement à l'axe c
- ✓ Utiliser un cristal multicouche (PC1/LDE1 2d=60Å)
- ✓ Vérifier la stabilité du fluor dans le témoin (minéral, verre) utilisé pour la calibration

## Perspectives

Déterminer l'influence de l'irradiation sur le dosage des éléments trace

Déterminer la nature de l'évènement lors de l'irradiation



**Merci à vous pour l'attention (et la patience!)**

**et à:**

**Juan Andujar, Arnaud Villaros, Delphine Bruyere, Michel Outrequin**

**Sylvain Janiec, Patricia Benoist-Julliot**