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SiC coatings and Cs diffusion

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Summary

The diffusive release of fission products, such as Ag, I and Cs from TRISO particles at high temperatures has raised concerns regarding safe and economic operation of advanced nuclear reactors. Understanding the mechanisms of Ag, I and Cs diffusion is thus of crucial importance for effective retention of fission products. Two mechanisms, i.e., grain boundary diffusion and vapor or surface diffusion through macroscopic structures such as nano-pores or nano-cracks, remain in debate. Studies about the diffusion of silver and iodine showed a low coefficient of diffusion through the silicon carbide: 3.10-20 m2/s-1 at 1300°C for silver and less than 10-21 m2/s-1 at 1100°C for iodine. However, little information is available on the diffusion behavior of fission products in SiC at temperatures above 1000°C. Friedland et al. conducted a systematic study by ionic implantation through the silicon carbide of elements such as cesium, iodine, silver and strontium. These studies have shown that below 1100°C, the diffusion of these elements is relatively low. No other previous studies have shown a measurable diffusion of iodine below 1000°C. Most previous studies of diffusion have been performed on thin layers of SiC, and the diffused elements were deposited on the SiC layer by vacuum evaporation, or by implantation at room temperature. No study was found on the diffusion of silver, iodine and Cesium through the SiC layer of TRISO particles. In the present work, we purpose to study the diffusion behaviour of silver, iodine and cesium through the SiC layer of TRISO particle.

Approval

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Final Report

D31.21 and D31.31

D31.21 SiC coatings and Ag diffusion

D31.31 SiC coatings and Cs diffusion

Study of silver, caesium and iodine diffusion in SiC-TRISO coated fuel particles

A. Ait Chaou, A. Abdelouas and B. Grambow,

July 2014

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1. Introduction and objective

The diffusive release of fission products, such as Ag, I and Cs from TRISO particles at high temperatures has raised concerns regarding safe and economic operation of advanced nuclear reactors. Understanding the mechanisms of Ag, I and Cs diffusion is thus of crucial importance for effective retention of fission products. Two mechanisms, i.e., grain boundary diffusion and vapor or surface diffusion through macroscopic structures such as nano-pores or nano-cracks, remain in debate.

Fuel elements of modern high-temperature nuclear reactors are encapsulated by CVD-layers which serve as barriers to prevent fission product release. Recent reactor designs generally make use of fuel kernels, which is usually UO_2, surrounded by four successive layers of low-density pyrocarbon, high-density pyrocarbon, silicon carbide and high density pyrocarbon, with silicon carbide being the main barrier for the metallic species. These so-called TRISO particles retain quite effectively most of the important fission products like cesium, iodine and silver. In these fuel particles the silicon carbide coating is the main barrier to limit fission product release into the primary cooling gas circuit. The possibility to operate these reactors to higher temperatures (>1000°C) to increase efficiency is of particular interest. However, few information is available on the silicon carbide retention of fission products at temperatures above 1000°C. A recent study indicates that the spread of cesium through SiC becomes important at temperatures between 1150°C and 1300°C [1].

Studies about the diffusion of silver and iodine showed a low coefficient of diffusion through the silicon carbide [2]: 3.10^{-20} m^2/s^{-1} at 1300°C for silver and less than 10^{-21} m^2/s^{-1} at 1100°C for iodine.

However, little information is available on the diffusion behavior of fission products in SiC at temperatures above 1000°C. Friedland *et al.* conducted a systematic study by ionic implantation through the silicon carbide of elements such as cesium, iodine, silver and strontium [3, 4, 5, 6].

These studies have shown that below 1100°C, the diffusion of these elements is relatively low. No other previous studies have shown a measurable diffusion of iodine below 1000°C [7].

Most previous studies of diffusion have been performed on thin layers of SiC, and the diffused elements were deposited on the SiC layer by vacuum evaporation, or by implantation at room temperature. No study was found on the diffusion of silver, iodine and Cesium through the SiC layer of TRISO particles.

In the present work, we purpose to study the diffusion behaviour of silver, iodine and caesium through the SiC layer of TRISO particle.

2. Materials and methods

The TRISO particles with ZrO_2 kernels were provided by AREVA NP and were mechanically treated to remove the external pyrolytic carbon in order to study the diffusion behavior of silver, iodine and cesium in the SiC layer at high temperature.

2.1.TRISO particles

To study the diffusion through the SiC layer the external pyrolytic carbon was first removed by heat treatment at 1100°C. SEM observation of heat-treated particles showed partial oxidation of SiC. Thus, we decided to mechanically remove the external carbon layer and the results were satisfying (Figures 1 and 2). The kernel composition was analysed to be ZrO_2 (Figure 3).

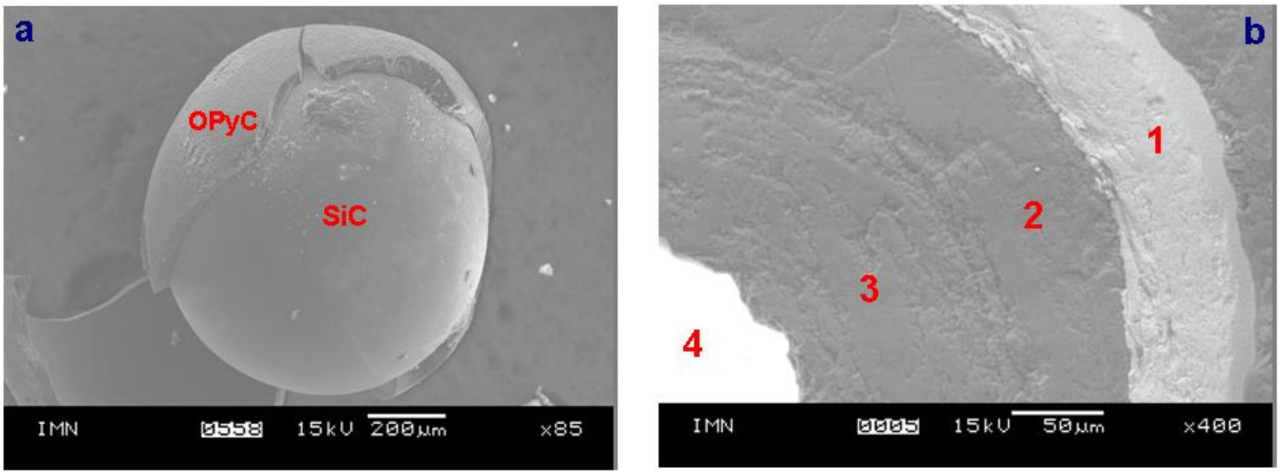


Figure 1: SEM micrograph of TRISO particle showing (a) external pyrolytic carbon and clean SiC layer, (b) a cross-section of a TRISO particle illustrating the tree functional layers and the central core: (1) : SiC, (2) : IPyC, (3) : Buffer Carbon and (4) : ZrO_2 core.

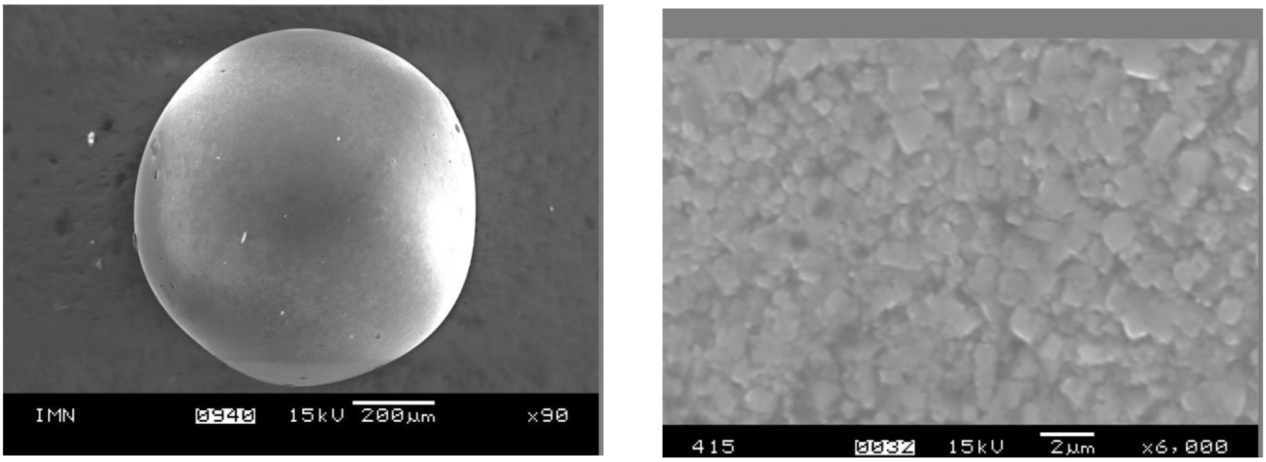


Figure 2: SEM micrograph of TRISO particle showing clean SiC layer. On the right we can see the multigrain structure of SiC.

Table 1: EDX analysis of the TRISO particle surface (SiC layer)

Element	Weight %	Normalized Weight %	Atomic %
Si	66.8	67.3	46.9
O	0.4	0.4	0.5
C	32.1	32.3	52.6

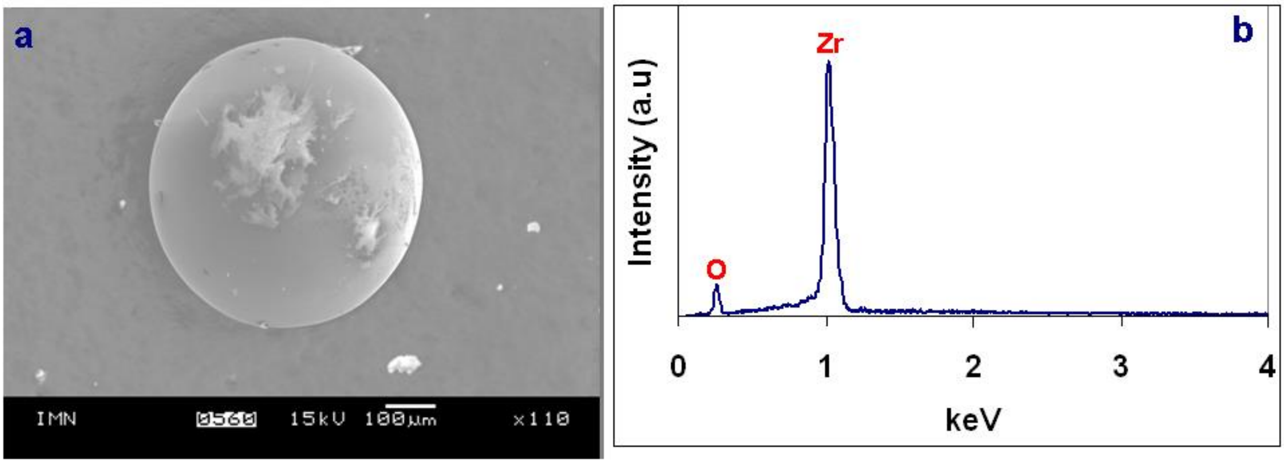


Figure 3: (a) SEM micrograph showing ZrO_2 kernel of TRISO particle with remains of buffer carbon. (b) EDX analysis of the ZrO_2 kernels of a TRISO particle.

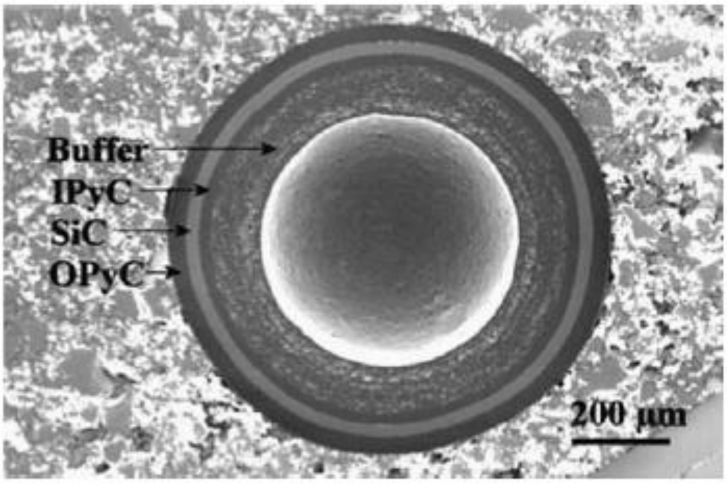


Figure 4: SEM micrograph of TRISO particle showing ZrO_2 kernel with the other layers.

2.2.Diffusion method

The TRISO particles (25 particles) devoid of their carbon layers are introduced into a quartz tube in the presence of diffused elements (sodium iodine (NaI), metallic silver or silver chloride (AgCl) and cesium chloride (CsCl)). The tube is then sealed under vacuum (figure 5) and placed in tubular furnace at different temperatures between 1050 ° C and 1300 ° C for annealing time of 24 to 85 hours.

Table 2: Isochrone diffusion of silver, iodine and caesium at different temperatures

Silver diffusion		**Iodine diffusion**		**Cesium diffusion**	
Sample	**Annealing temperature**	**Sample**	**Annealing temperature**	**Sample**	**Annealing temperature**
25 TRISO + 190 mg of Ag	1180°C	25 TRISO + 45.8 mg of I_2	1080°C		
25 TRISO + 52 mg of Ag	1250°C	25 TRISO + 47.8 mg of I_2	1180°C	25 TRISO + 92.5 mg CsCl	1180°C
25 TRISO + 52 mg of Ag	1300°C	25 TRISO + 49 mg of I_2	1250°C	25 TRISO + 90.8 mg CsCl	1250°C
		16 TRISO + 45 mg of I_2	1050°C	25 TRISO + 91.3 mg CsCl	1300°C
		25 TRISO + 67 mg of NaI	1250°C		
		25 TRISO + 65.2 mg of NaI	1300°C		

Annealing time: 24 to 85 hours

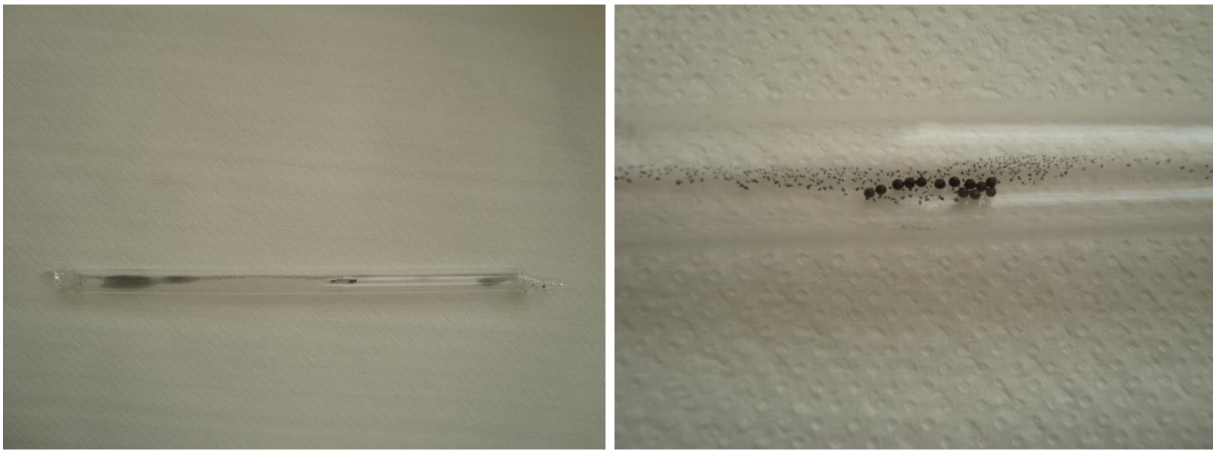


Figure 5: TRISO particles without the external carbon layer with the sodium iodide sealed under vacuum and annealed 24 hours at 1250 °C.

To measure the diffusion profile of iodine, silver and caesium in the SiC layer, the TRISO particles were analysed after diffusion by high resolution ICP-MS, NanoSIMS and nuclear microprobe analysis using the RBS and PIXE techniques. These measures will also determine the diffusion coefficient of these elements at different temperatures.

2.3.Calculation of diffusion profile from the friedland data [8, 9, 10]

Defining the profile width W(t) as the full width at half maximum (FWHM), the following relationship between the final and original widths holds:

$$[W(t)]^2 = 4Dt\ln(2) + [W(0)]^2$$

Where:

W(t) is the diffusion Profile (m)
D is the diffusion coefficient (m^2/s)
t is the time of diffusion (annealing time) at constant temperature (s)
W(0) is the diffusion profile at t = 0 by extrapolating of the curve (m)

Hence the slope of a plot of $[W(t)]^2$ versus annealing time at constant temperature will directly yield the diffusion coefficient D.
The diffusion profile at 1300°C calculated from the data of Friedland *et al.* [8, 9, 10] are given in Table 3

Table 3: Calculation of diffusion profile of silver and iodine in the SiC layer of TRISO particle

Diffusion of Silver In SiC at 1300°C					
W(t) (m)	**$[W(t)]^2$ (m^2)**	**D (m^2/s)**	**t**	**W(0) (m)**	**$[W(0)]^2$ (m^2)**
$1,3\ 10^{-07}$ (135 nm)	$1.8\ 10^{-14}$	$3.0\ 10^{-20}$	24h (86400s)	-	$1.1\ 10^{-14}$
$1,6\ 10^{-07}$ (160 nm)	$2.5\ 10^{-14}$	$3.0\ 10^{-20}$	48h (172800s)	-	$1.1\ 10^{-14}$
$1,8\ 10^{-07}$ (180 nm)	$3.3\ 10^{-14}$	$3.0\ 10^{-20}$	72h (259200s)	-	$1.1\ 10^{-14}$
Diffusion of iodine In SiC at 1300°C					
W(t) (m)	**$[W(t)]^2$ (m^2)**	**D (m^2/s)**	**t (s)**	**W(0) (m)**	**$[W(0)]^2$ (m^2)**
1,3 E-07 (130 nm)	$1.6\ 10^{-14}$	$5.7\ 10^{-20}$	24h (86400s)	-	$2.5\ 10^{-15}$
1,7 E-07 (170 nm)	$3.0\ 10^{-14}$	$5.7\ 10^{-20}$	48h (172800s)	-	$2.5\ 10^{-15}$
2,1 E-07 (210 nm)	$4.4\ 10^{-14}$	$5.7\ 10^{-20}$	72h (259200s)	-	$2.5\ 10^{-15}$

2.4.Calculation from FRESCO-II THEORETICAL BASIS [11, 12]

The transport of mobile fission metals is certainly structure-sensitive and more complex than classical Fickian diffusion and likely a combination of lattice diffusion, grain boundary diffusion, pore diffusion, etc., further complicated by effects like irradiation-enhanced trapping and adsorption. Consequently, any quoted diffusion coefficient should be called an effective diffusion coefficient which implies that the overall migration process is approximately described by Fick's laws [13].
The diffusion coefficient can be calculated using the following formula:

$$D = D_{0,1}.\exp[-Q_1/(R.T)] + D_{0,2}.\exp[-Q_2/(R.T)]$$

D: diffusion coefficient (m^2/s)

Q_1, Q_2: activation Energy (J/mol)

$D_{0,1}$ et $D_{0,2}$: Pre-exponential factor (m^2/s)

R: Gas constant, R= 8.3145 J/(mol.K),

T: Temperature [K].

The data as currently being used in German safety analyses are given in Table 4.

Table 4: Effective diffusion coefficients used in the calculations. Data calculated using THE FRESCO-II CODE from [11, 12]

	Diffusion Coefficient $^{(a)}$ in		
	UO_2	**PyC**	**SiC**
Cesium			
$D_{0,1}$ [m^2/s]	5.6×10^{-8}	6.3×10^{-8}	5.5×10^{-14} × eΓ/5 (b)
Q_1 [kJ/mol]	209	222	125
$D_{0,2}$ [m^2/s]	5.2×10^{-4}	0	1.6×10^{-2}
Q_2 [kJ/mol]	362	-	514
D (m^2/s)			
Silver			
$D_{0,1}$ [m^2/s]	6.7×10^{-9}	5.3×10^{-9}	3.6×10^{-9}
Q_1 [kJ/mol]	165	154	215
$D_{0,2}$ [m^2/s]	0	0	0
Q_2 [kJ/mol]	-	-	-
D (m^2/s)			
Iodine			
$D_{0,1}$ [m^2/s]	1.3×10^{-12}	2.9×10^{-8}	-
Q_1 [kJ/mol]	126	291	-
$D_{0,2}$ [m^2/s]	8.8×10^{-15}	0	-
Q_2 [kJ/mol]	54	-	-
D (m^2/s)			

(a) Effective diffusion coefficient: $D = D_{o,1} \cdot \exp[-Q_1/(R \cdot T)] + D_{o,2} \cdot \exp[-Q_2/(R \cdot T)]$
(b) Γ is the fast neutron fluence in 10^{25} n/m^2, E>0.1MeV

The diffusion data at 1300°C calculated from the data of THE FRESCO-II CODE THEORETICAL BASIS [11, 12] are given in tables 5.

Table 5: Calculation of diffusion data of caesium and silver in the SiC layer of TRISO particle.

Cesium diffusion in SiC

D (m^2/s)	D$_{0,1}$ (m^2/s)	Q$_1$(J/mol)	R (J/mol.K)	T (K)	D$_{0,2}$ (m^2/s)	Q$_2$ (J/mol)
6.1x10^{-19}	8.2x10^{-14}	125000	8.3145	1273	1.6x10^{-02}	514000
1.4x10^{-18}	8.2x10^{-14}	125000	8.3145	1373	1.6x10^{-02}	514000
3.0x10^{-18}	8.2x10^{-14}	125000	8.3145	1473	1.6x10^{-02}	514000
5.9x10^{-18}	8.2x10^{-14}	125000	8.3145	1573	1.6x10^{-02}	514000
1.2x10^{-17}	8.2x10^{-14}	125000	8.3145	1673	1.6x10^{-02}	514000

	W(t) (m)	[W(t)]^2 (m^2)	D (m^2/s)	t (s)	W(0) (m)	[W(0)]^2 (m^2)
At 1300°C						
	1.2x10^{-06}	1.4x10-12	5.9x10^{-18}	86400		0
	1.7x10^{-06}	2.8x10-12	5.9x10^{-18}	172800		0
	2.1x10^{-06}	4.3x10-12	5.9x10^{-18}	259200		0

Silver diffusion in SiC

D (m^2/s)	D$_{0.1}$ (m^2/s)	Q$_1$(J/mol)	R (J/mol.K)	T (K)	D$_{0.2}$ (m^2/s)	Q$_2$ (J/mol)
5.4x10^{-18}	3.6x10^{-09}	215000	8.3145	1273	0	0
2.4x10^{-17}	3.6x10^{-09}	215000	8.3145	1373	0	0
8.6x10^{-17}	3.6x10^{-09}	215000	8.3145	1473	0	0
2.6x10^{-16}	3.6x10^{-09}	215000	8.3145	1573	0	0
7.0x10^{-16}	3.6x10^{-09}	215000	8.3145	1673	0	0

	W(t) (m)	[W(t)]^2 (m^2)	D (m^2/s)	t (s)	W(0) (m)	[W(0)]^2 (m^2)
At 1300°C						
	7.9x10^{-06} (7.9 µm)	6.3x10^{-11}	2.6x10^{-16}	24h (86400 s)		0
	1.1x10^{-05} (11.2 µm)	1.3x10^{-10}	2.6x10^{-16}	48h (172800 s)		0
	1.4x10^{-05} (14.0 µm)	1.9x10^{-10}	2.6x10^{-16}	72h (259200 s)		0

We can note that there is one order of magnitude of difference between the theoretical data calculated from The FRESCO-II CODE THEORETICAL BASIS [11, 12] and the experimental data from Friedland studies [8, 9, 10]. For example, for silver diffusion we obtain theatrically 7.9 µm as profile diffusion at 1300°C after 24 hours of diffusion compared to 135 nm experimentally.

3. Results

3.1. High Resolution ICP-MS

Preliminary analyses were performed by ICP-MS High Resolution.

The apparatus used is a XR Thermo Scientific coupled to a laser ablation device and the analysis Conditions are:

- Laser energy: 80%
- Width ablation: 30µm
- Frequency: 10 Hz
- Rate of ablation: 5µm/s
- Energy in the surface: 0.18-0.19 mJ
- Time of ablation: 1.04 min
- Number of Runs: 100
- Laser trigger at: 15 Runs

Laser ablation analyses are done in time-resolved mode and the background or blank signal is taken while the laser is off. This is followed immediately by turning on the laser and ablating the sample, generating a time-dependent signal (Fig. 6). Reference glass standard (NIST610) is run before and after a sequence of samples. Si29 was used as internal standard for calculating the concentrations.

3.1.1. Analysis of the glass reference standard (NIST610)

The NIST610 glass is used as a standard; it contains many elements of the periodic table at known concentrations. This standard is used to calculate the concentration or percentage of elements in the sample. The NIST610 glass contains silver and silicon but does not contain iodine. Results of silicon 29, silver 107 and iodine 127 analyses are given in figure 6. Si and Ag signals are quite good, while with iodine we have a signal, this is probably originates from interferences with other elements present in the NIST610 standard, which does not contain iodine, or interferences with elements in trace amounts present in the purge gas (helium).

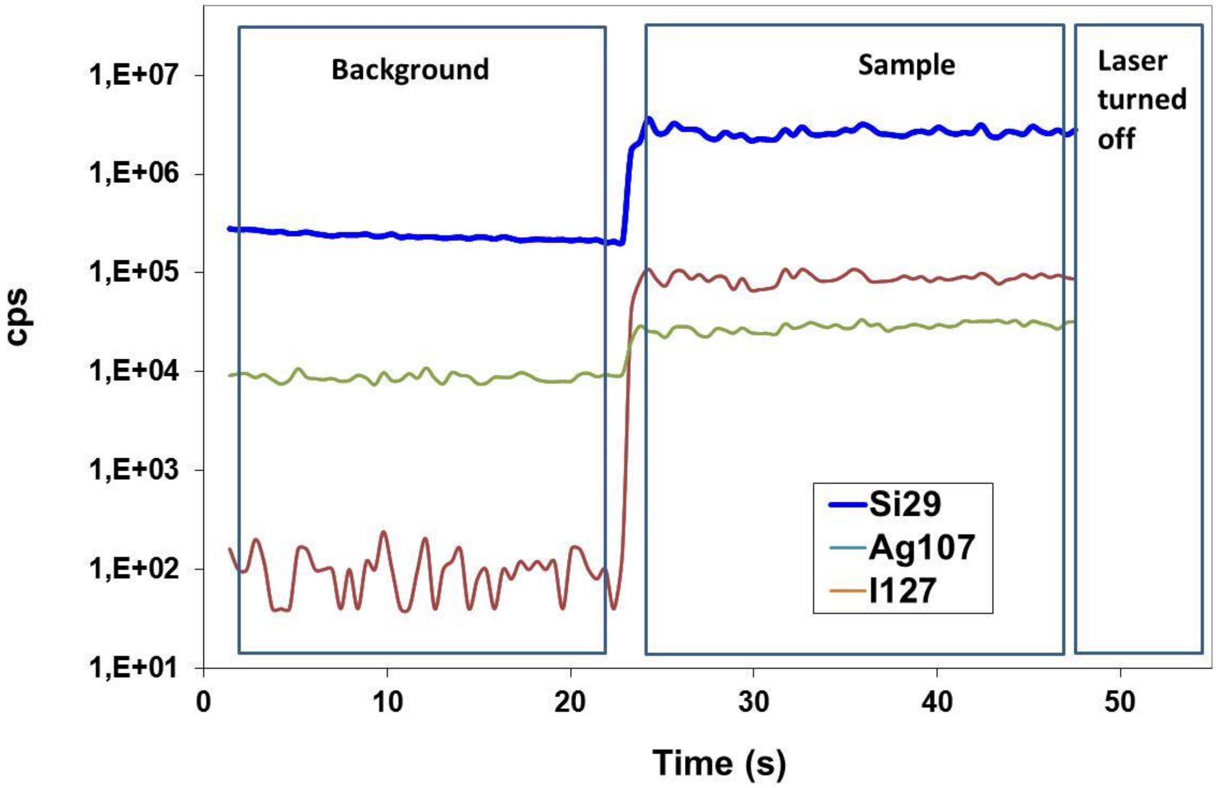


Figure 6: Silicon, silver and iodine analysis in the glass reference standard (NIST610) by laser ablation HR-ICP-MS. Ablation of the sample begins at slice #24. Homogeneity of the glass is revelated by the parallel nature of the time-resolved signals.

3.1.2. Pristine TRISO particles (SiC)

The HR-ICP-MS results of pristine TRISO particle seen in figure 7 are given in figures 8 and 9 for Si, I and Ag analysis. As expected we obtained a signal of Si attributed to SiC and Ag was not detected (figure 9 and table 6). Again, we detected iodine due to interferences or contamination.

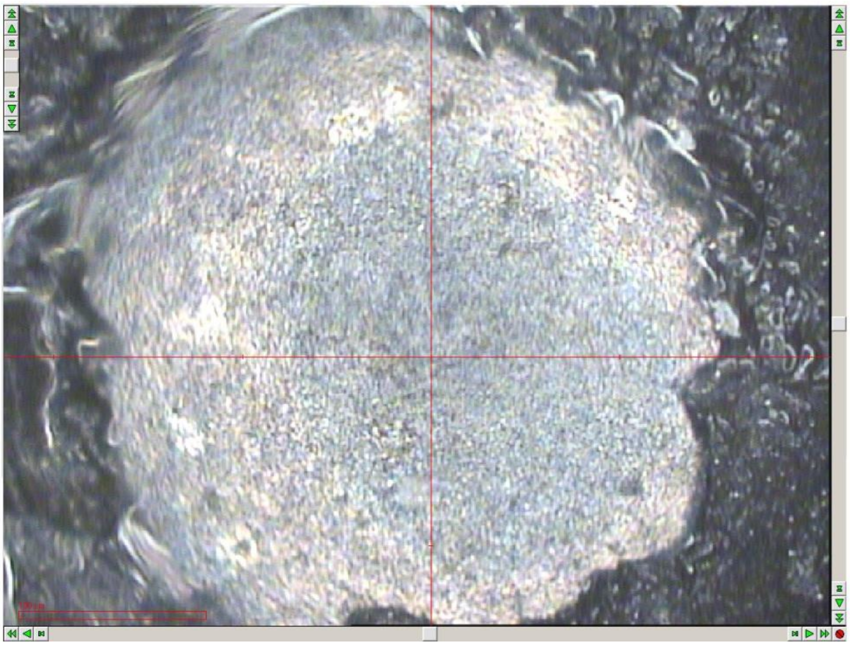


Figure 7: Pristine TRISO particle before the laser ablation HR-ICP-MS.

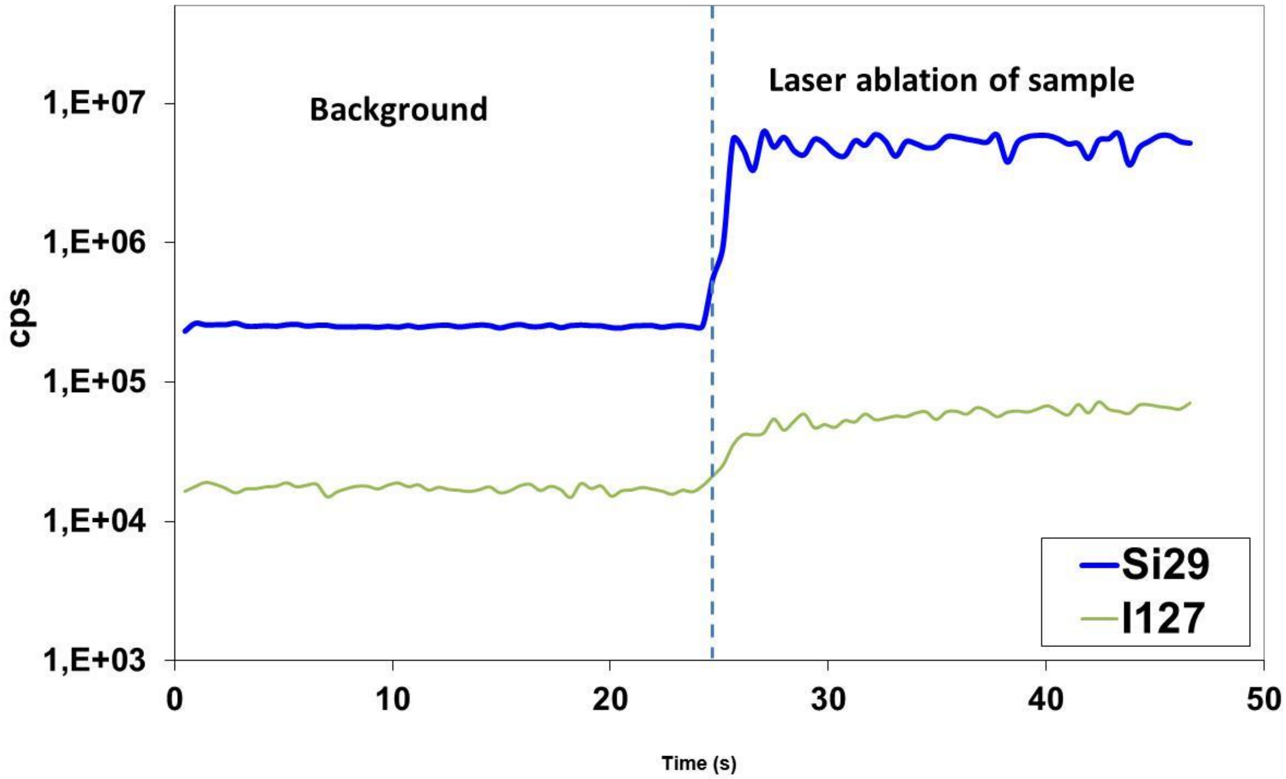


Figure 8: Silicon and iodine analysis in the pristine TRISO particle by laser ablation HR-ICP-MS. Ablation of the sample begins at slice #24.

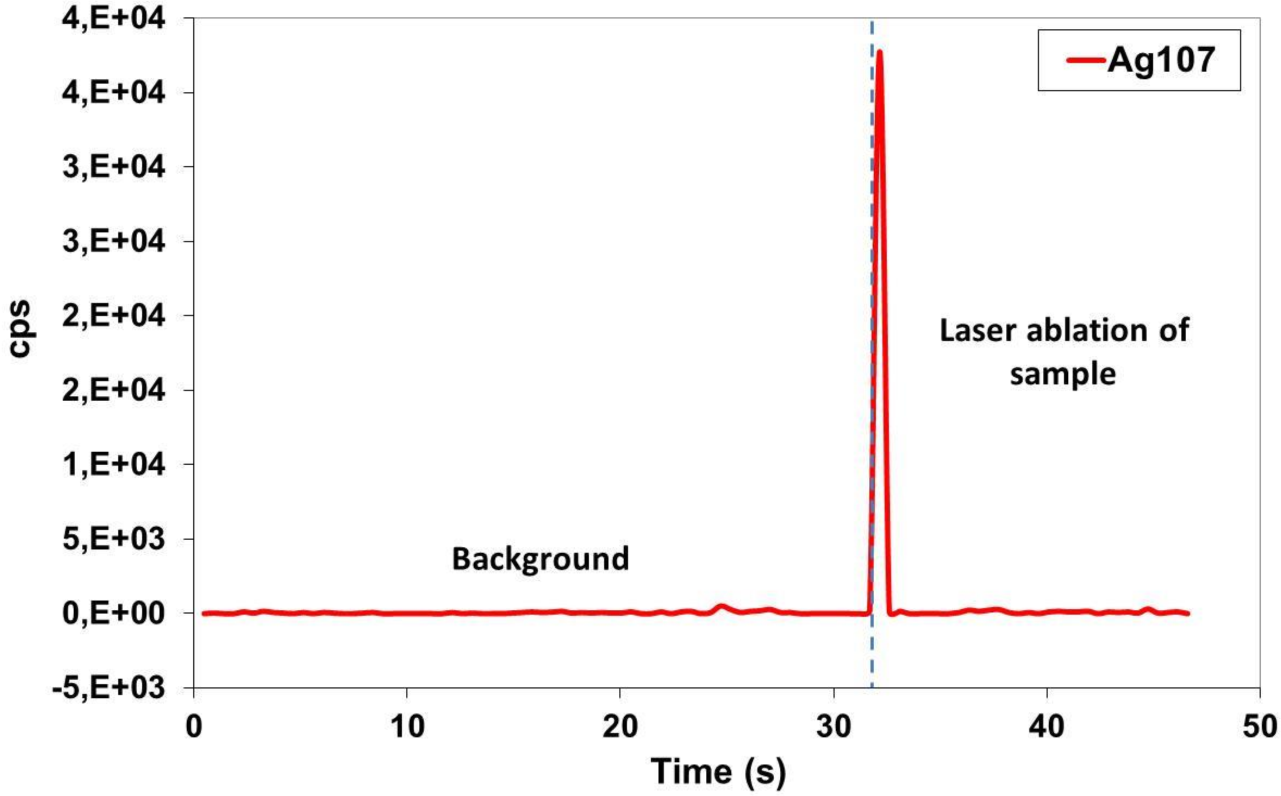


Figure 9: Silver analysis in the pristine TRISO particle by laser ablation HR-ICP-MS in the TRISO particle. Ablation of the sample begins at slice #32. The analysis shows no silver in the pristine particle.

3.1.3. TRISO particle after silver diffusion for 24 hours at 1300°C

Figure 10 shows the TRISO particle annealed 24 hours at 1300°C in the presence of silver and after laser ablations. The results of Si, Ag and I analysis are given in figures 11 and 12. Again iodine was detected (contamination, interference). Silicon from the external SiC layer and silver originating from diffusion in SiC were detected (figure 11 and 12) with a good sensibility. Table 6 show the Si and Ag concentrations in the TRISO particles before and after silver diffusion. As we can see we detect 3 to 6 ppm of silver after the laser ablation at the surface of the particle but with this technique we cannot determine the profile diffusion of silver in the SiC layer.

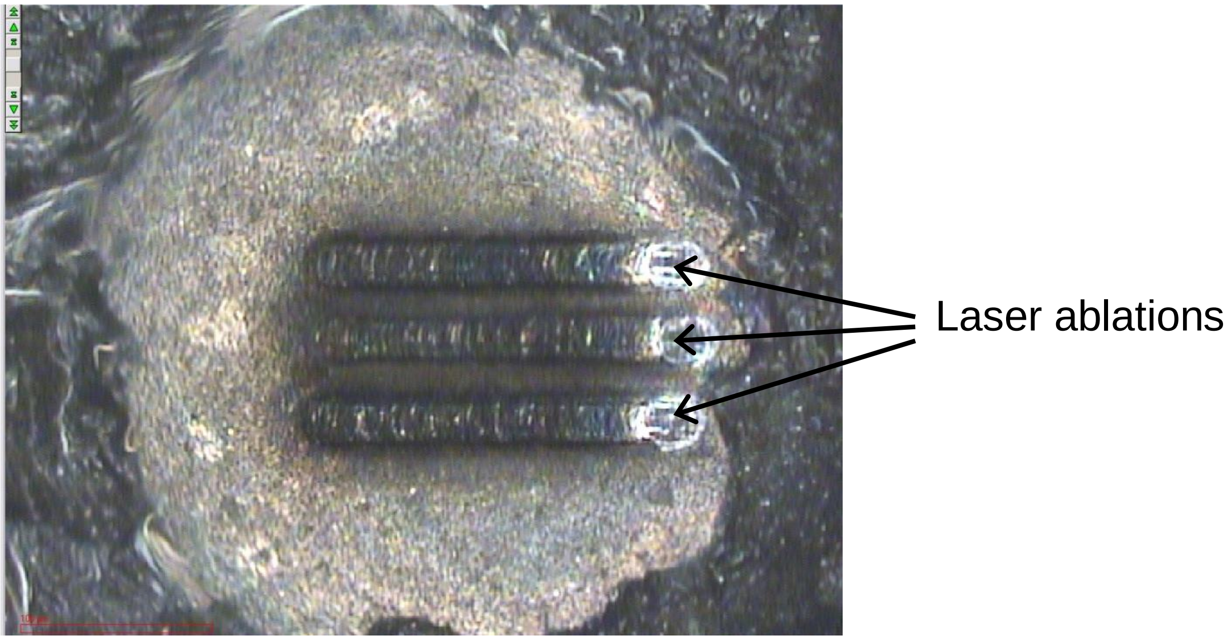


Figure 10: TRISO particle after three laser ablation HR-ICP-MS analyses.

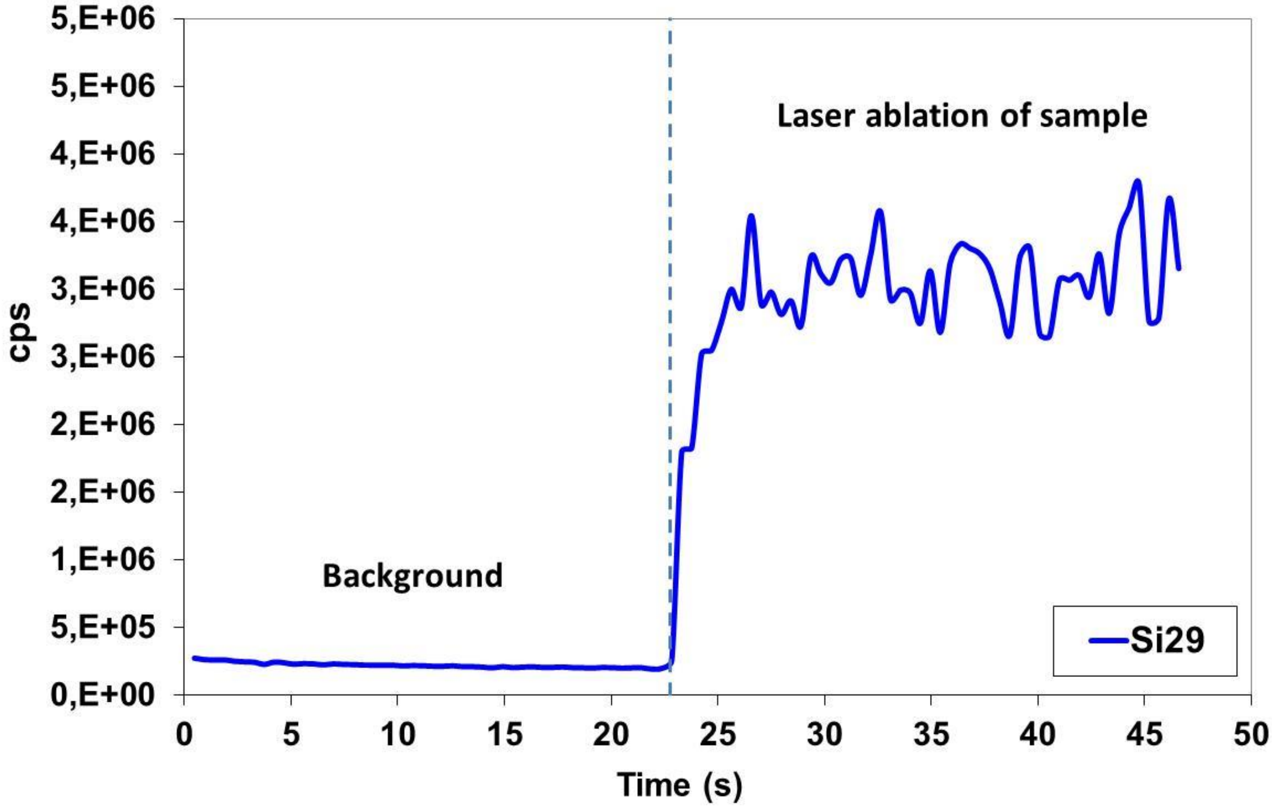


Figure 11: Silicon analysis by laser ablation HR-ICP-MS in the TRISO particle after silver diffusion for 24 hours at 1300°C. Ablation of the sample begins at slice #23.

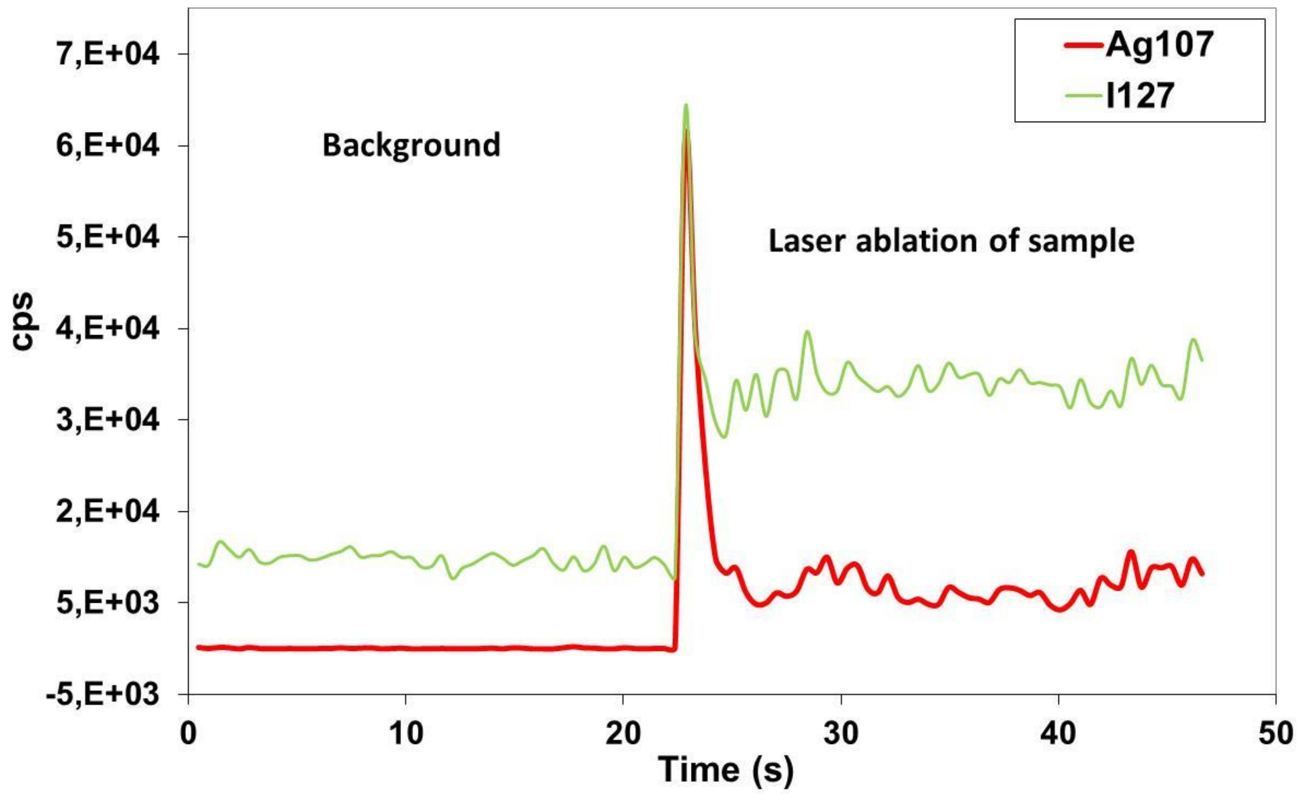


Figure 12: Silver and iodine analysis by laser ablation HR-ICP-MS in the TRISO particle after silver diffusion for 24 hours at 1300°C. Ablation of the sample begins at slice #23.

Table 6: Concentration of silver in the TRISO particles before and after heat treatment at 1300°C in the presence of AgI.

Sample	**Normalized concentrations (ppm)**		
	Si29 (internal standard)	Ag107	I127
Standard NIST610 glass (1)	338000	252.34 ± 7.5	-
Standard NIST610 glass (2)	338000	239 ± 7.1	-
SiC with AgI at 1300°C (1)	70048	2.82 ± 0.16	-
SiC with AgI at 1300°C (2)	70048	6.15 ± 0.36	-
SiC with AgI at 1300°C (3)	70048	4.36 ± 0.26	-
Standard NIST610 glass (3)	338000	239 ± 7.1	-
Pristine TRISO (1)	<LD	<LD	<LD
Pristine TRISO (2)	70048	0.02 ± 0.001	-
Pristine TRISO (3)	70048	0.02 ± 0.001	-
Standard NIST610 glass (4)	338000	239 ± 7.1	-
	LOD (ppm)		
	Si29 (internal standard)	Ag107	I127
Standard NIST610 glass (1)	857.27	0.110	-
Standard NIST610 glass (2)	630.81	0.076	-
SiC with AgI at 1300°C (1)	139.58	0.012	-
SiC with AgI at 1300°C (2)	107.21	0.015	-
SiC with AgI at 1300°C (3)	124.15	0.009	-
Standard NIST610 glass (3)	663.11	0.055	-
Standard NIST610 glass (4)	462.83	0.073	-
Pristine TRISO (1)	-	-1.352	-
Pristine TRISO (2)	30.91	0.007	-
Pristine TRISO (3)	30.91	0.007	-
Standard NIST610 glass (5)	462.83	0.073	-

LOD: Detection limit

3.2. Nano-SIMS analysis

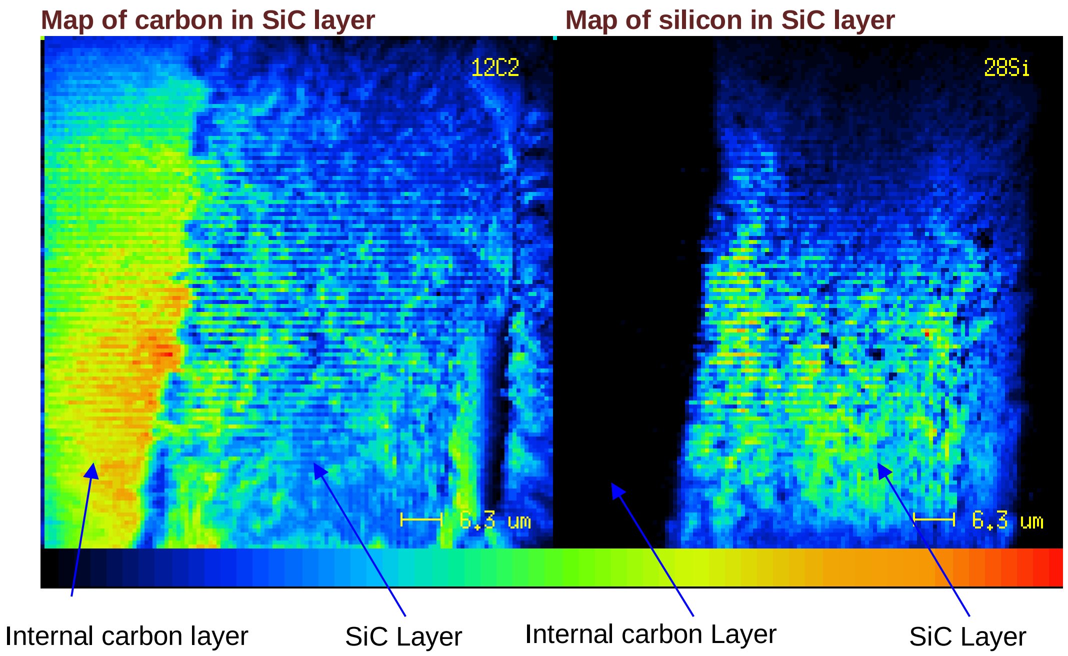
Some Nano-SIMS analyses were performed at the university of Rennes (Microscopy Rennes Imaging Center). The apparatus used was a CAMECA Nano-SIMS 50 Standard. Polished cross sections of TRISO particles were prepared for nano-SIMS observations.

For this study we worked with these parameters:

- Source used: Cs^+
- Energy: 16KV
- Current: 1 to 1.5 pA
- Vacuum: 10^{-10} to 10^{-11} mbar

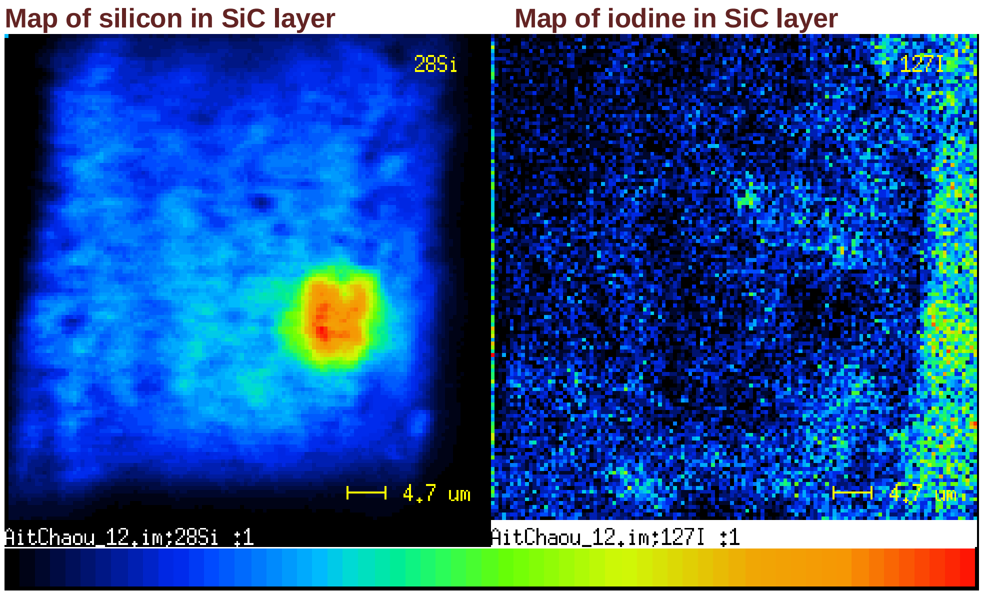
3.2.1. TRISO particle without treatment

The analyses were performed on cross section of pristine and treated TRISO particles. The preliminary results of nano-SIMS analysis are shown in figures 13 and 14 in the form of elemental mapping. The results are difficult to interpret but indicate that no iodine could be detected in the SiC layer.


Map of carbon in SiC layer

Map of silicon in SiC layer

Figure 13: Mapping of silicon and carbon in a pristine TRISO particle.


Map of silicon in SiC layer

Map of iodine in SiC layer

Figure 14: Mapping silicon and iodine in SiC layer of pristine TRISO particle.

3.2.2. TRISO particles with NaI after diffusion at 1300°C for 24H

The preliminary results of nano-SIMS analysis are shown in figures 15 and 16 for C, Si and I. Spots of iodine were detected in SiC but could be explained by some interference as shown in figure 15. Hence, figure 17 shows that, for iodine, we have three peaks between the mass 126 and 127.5. Some peaks may correspond to interferences (molecules with carbon, or elements from the resin coating ....).

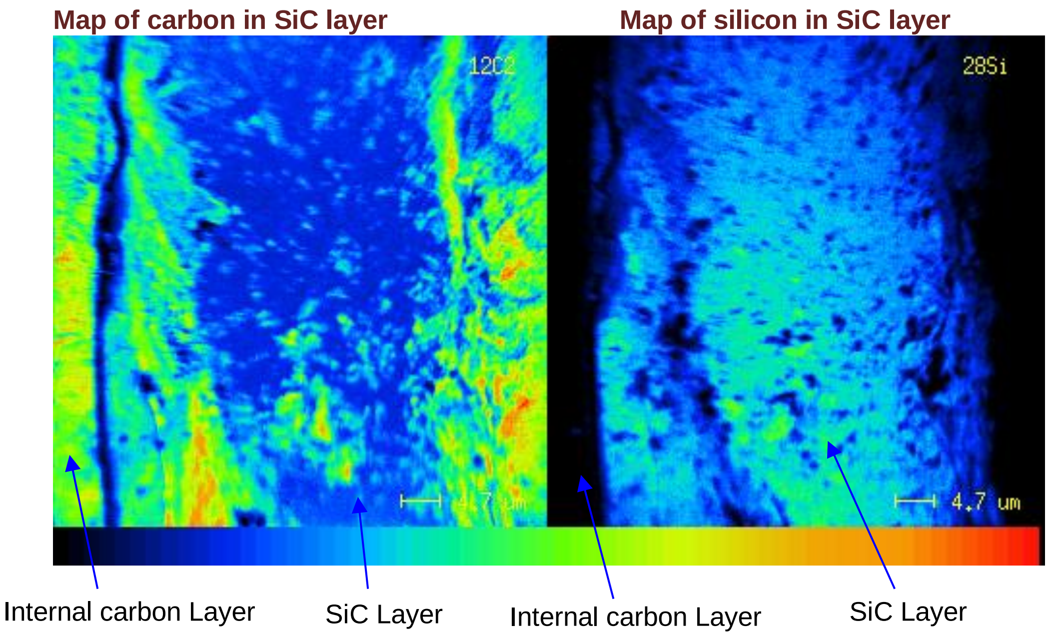


Figure 15: Mapping of silicon and carbon in the TRISO particles after iodine diffusion for 24 hours at 1300°C.

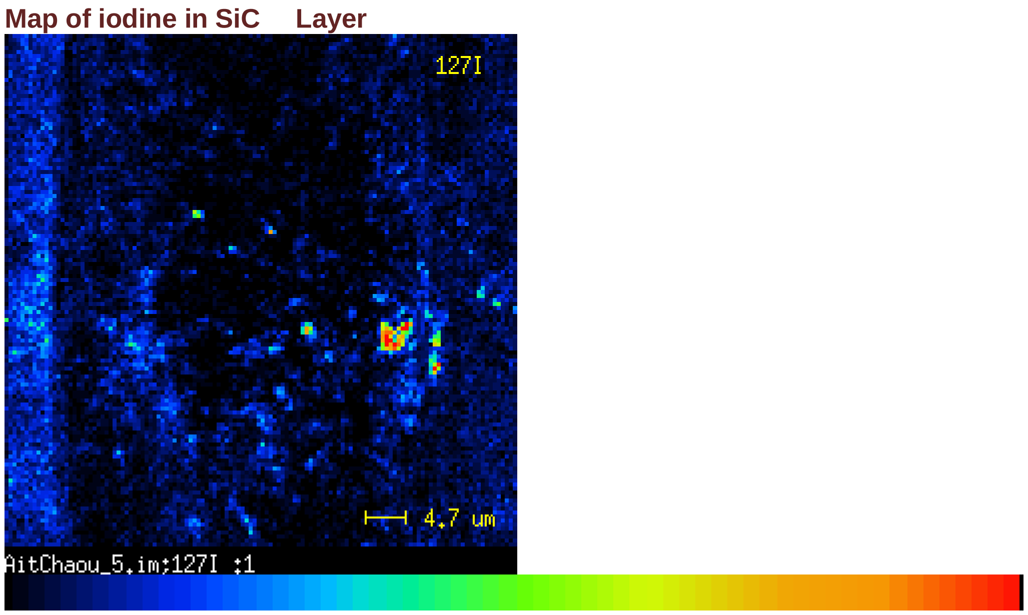


Figure 16: Mapping of iodine in SiC layer after iodine diffusion for 24 hours at 1300°C.

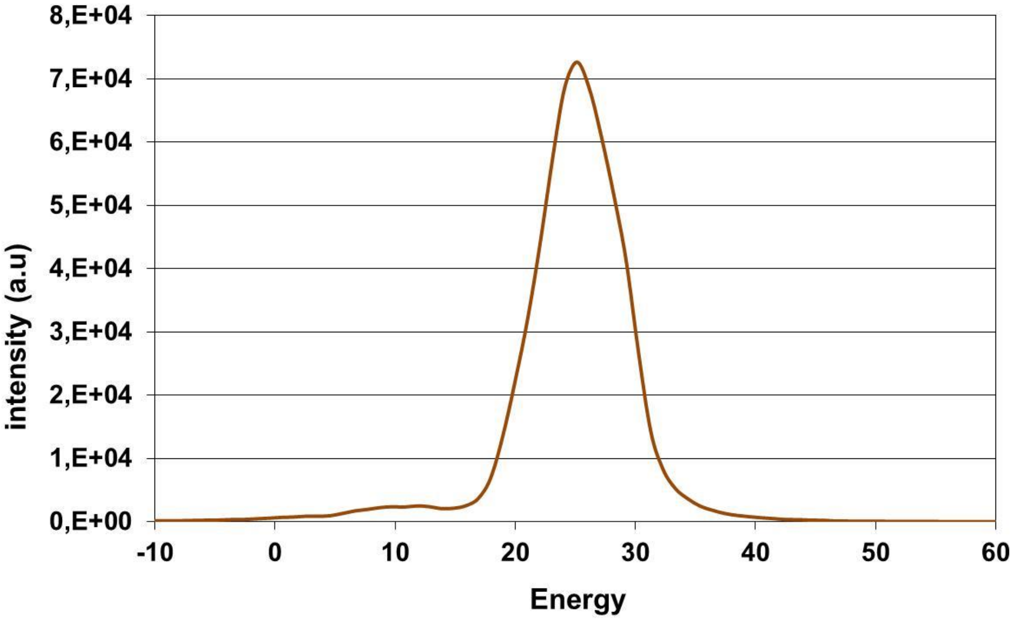


Figure 17: Scan peaks between 126.0 and 127.5 mass

3.2.3. TRISO particles after diffusion of NaI at 1250°C for 24H

Figures 18 and 19 show the SIMS results for a second run of iodine diffusion experiments at 1250°C. Again, spots of iodine were detected on SiC but all these analyses are qualitative (figure 19).

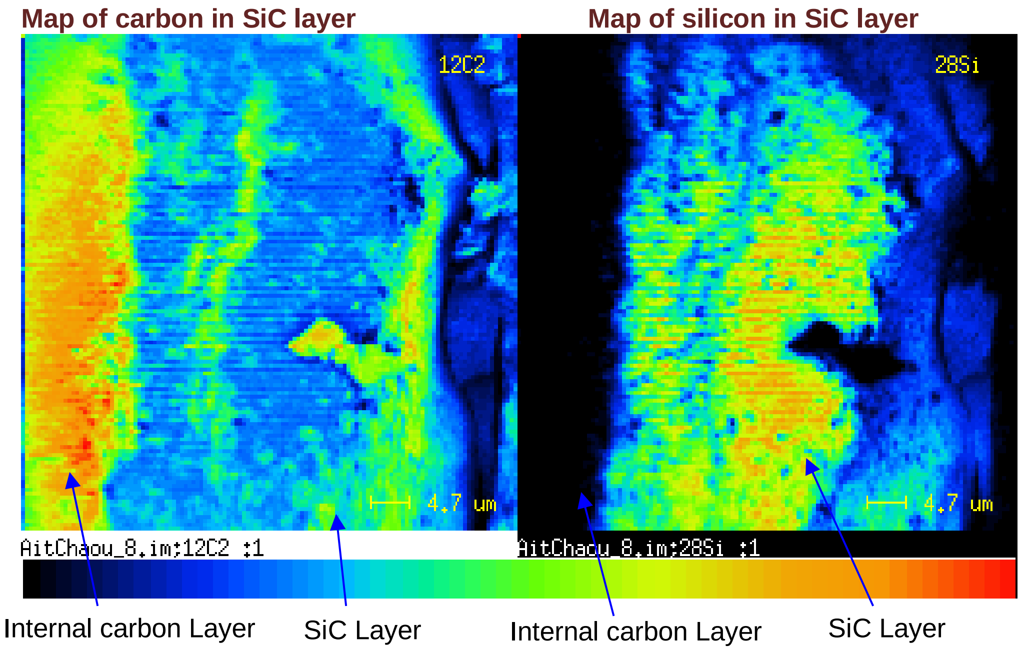


Figure 18: Mapping of silicon and carbon in a TRISO particle after diffusion of iodine 24 hours at 1250°C.

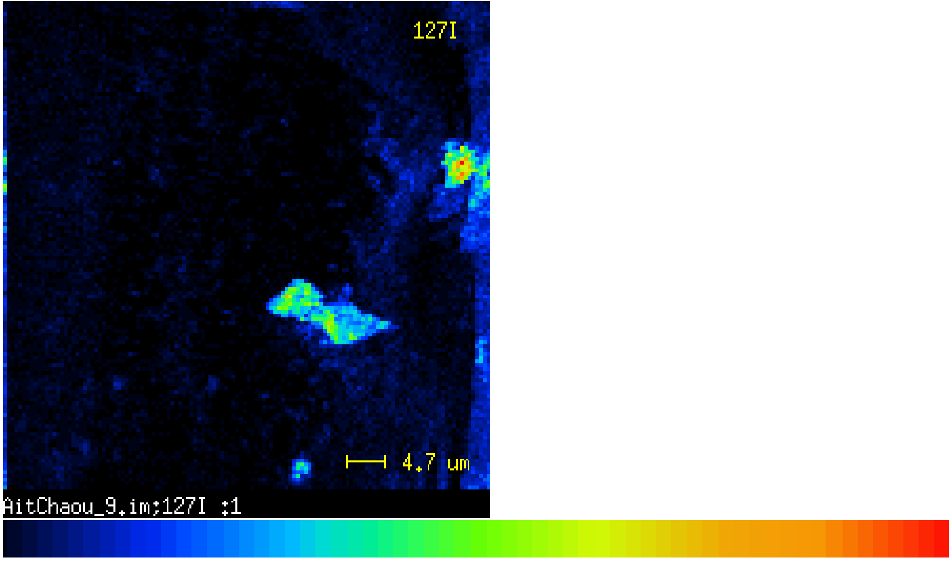
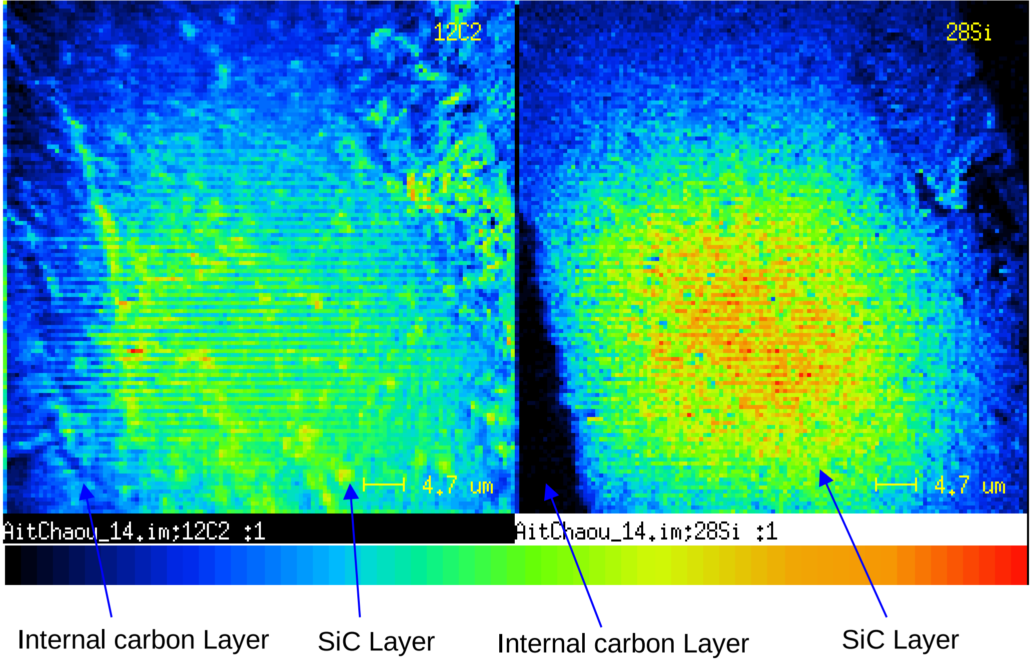

Map of iodine in SiC layer

Figure 19: Mapping of iodine in SiC layer after iodine diffusion for 24 hours at 1250°C.

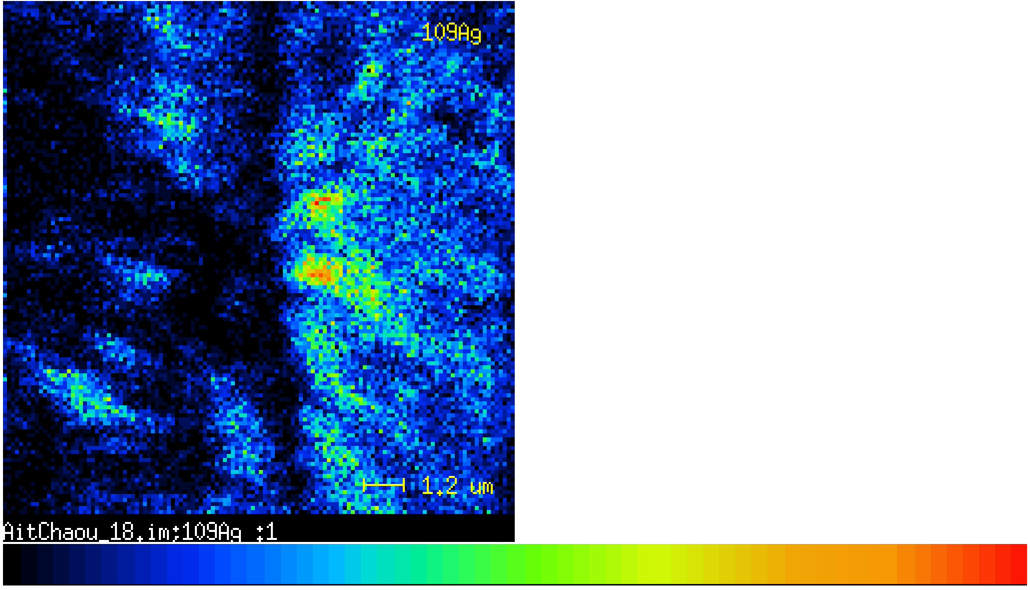
3.2.4. TRISO particles after diffusion of silver at 1300°C for 24H

Figures 20 and 21 show the SIMS results for a silver diffusion experiments at 1300°C. Again, spots of silver were detected on SiC but all these analyses are qualitative.


Map of carbon in SiC layer

Map of silicon in SiC layer

Figure 20: Mapping of silicon and carbon in SiC after diffusion of silver 24 hours at 1300°C.



Map of silver in SiC layer

Figure 21: Mapping of silver in SiC after diffusion of silver for 24 hours at 1300°C.

For these Nano-SIMS analyses, many interferences are detected for silver and iodine. We performed analyses by nuclear microprobe - Rutherford backscattering spectrometry (RBS) in order to obtain the depth profiles.

3.3.Nuclear microprobe analysis - Rutherford backscattering and PIXE analysis

Some RBS analyses were performed in “AIFIRA - Centre d'Études Nucléaires de Bordeaux-Gradignan (CNBG)” and others in “Laboratoire d'Etude des Elements Légers (LEEL) CEA - Gif-sur-Yvette”. The analyses were performed on the cross section of heat-treated TRISO particles. The simulation of the RBS spectra indicated that it was interesting to work at low energy, because the thickness of penetration of elements (I, Ag and Cs) is relatively low (hundreds of nm), working at low energy (below 1 MeV) can in theory improve the RBS signal. In this context, the energy of the beam of Helium ion (He +) was 900 keV.

3.3.1. Methodology

The detection system is composed on two silicon detectors located at 170 ° and 135 ° relative to the beam axis. The detector at 170° is the annular detector (area 150 mm^2, thickness 1000 µm) with a polycarbonate film (2 µm) to filter the RBS signal and select only the signal from heavy elements (I, Cs and Ag). The detector at 135° (area 25 mm^2, thickness 700 µm) provides full RBS signal in order to have a control spectrum.

The experimental analyses showed that the number of counts recorded on the two detectors was not very important in view of the beam intensity (~ nano-Ampere) and the nature of the sample (bulk sample). It will be necessary to review the conditions of analysis and increase ions energy to have a higher production of backscattered particles and therefore have a greater count rate on the detector. Increase the count rate will reduce the acquisition time and improve the sensitivity of the analysis. In the case of cross-sections of TRISO particles, the ideal would be to work with 2 MeV and a beam of 20 microns or 10 microns.

3.3.2. Comments on the data processing and simulations

The first observation is that the RBS spectra do not show the expected form compared to the simulations. Indeed, no characteristic peak relative to diffused element (I, Cs, and Ag) is observed. This is due may be to that analyses are performed on cross-sections of TRISO particles and not on entire particles. The simulation program and processing data take into account the configuration with entire particle (the multi-layer configuration), and in this case the beam will initially interact with the external layer containing the diffused elements and then with the SiC. In the case of cross-section analysis, RBS spectrum is the sum of diffused elements signal and the SiC signal, and this complicates the analyses of the results.

The count rates recorded on both detectors were not very important in view of the intensity of the beam on the sample (~ nano-Ampere) and the nature of the sample analysed (bulk sample). In particular, the counting rate on the annular detector, which is supposed to have the best sensitivity, remained below 40 counts/s, it is too low to expect an analysis within a reasonable time. For the next RBS analysis, it will be necessary to review the conditions of analysis: increase the ions energy to have a higher production of backscattered particles and therefore have a greater count rate on annular detector. Increasing the count rate will reduce the acquisition time and also improve the sensitivity of the analysis. For the cross-sections of TRISO particles, the ideal is to work at 2 MeV with a beam of 20 µm or 10 µm as the count rate recorded. In the case of entire TRISO particles, it is better to work with a beam of 1.5 MeV to reduce the signal from the SiC and to have enough statistics for Ag, I and Cs analysis.

3.3.3. Simulations and experimental spectra

The simulations were performed using the SIMNRA program which is the software generally used for the treatment of RBS spectra. Figure 22 shows the calculated and experimental spectrum of the NaI standard. It is important to note that the shape of simulated spectrum is different to the experimental spectrum.

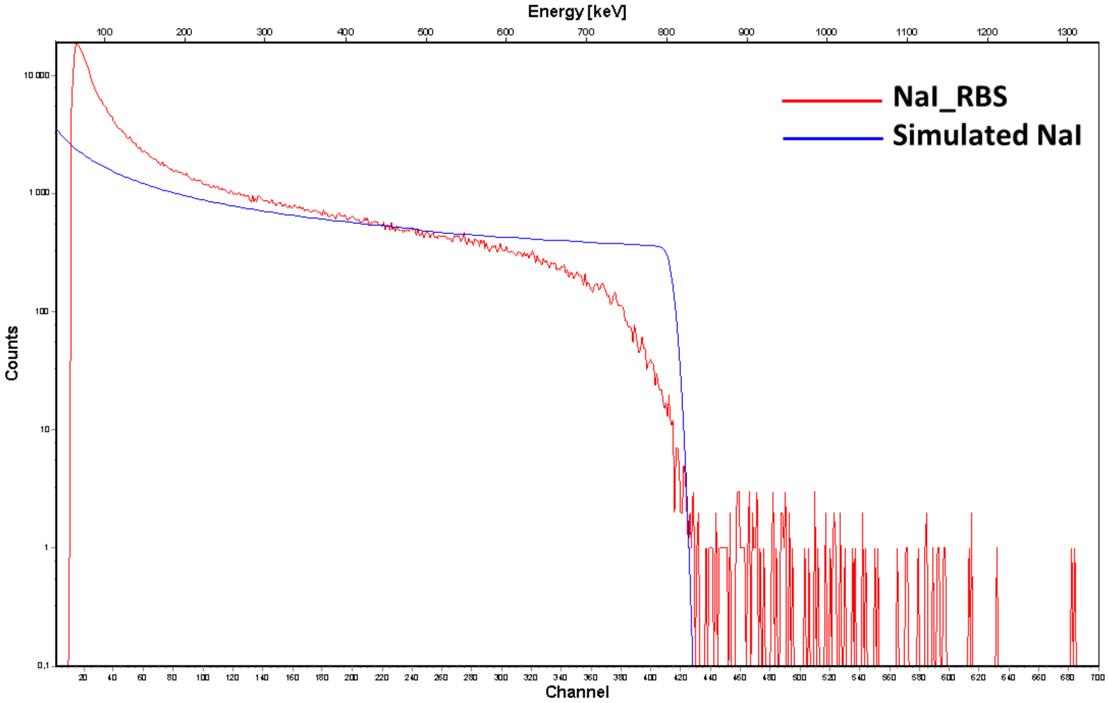


Figure 22: Experimental and simulated spectra of NaI

Figures 23 to 25 correspond to the RBS spectra of different samples (TRISO particles after 24 and 72 hours of treatment at 1300°C in the presence of NaI; TRISO particles after 24 hours of treatment at 1300°C in the presence of CsCl). The simulations show that it is possible to detect the presence of Cs and iodine in the spectrum despite the low acquisition time and the superposition of the signals of the other elements. However, since the solid angle is not known with certainty, it is not possible to know the concentrations of I and Cs but only to compare relative concentrations of these elements in a spectrum compared to others spectrum. These concentrations are reported in Table 7.

Table 7: Iodine and cesium concentrations

Sample	Relative concentration (atomic %)
TRISO_NaI _ 1300°C_72 h	0.0004
TRISO_NaI _ 1300°C_ 24 h	0.0032
TRISO_CsCl _ 1300°C_24 h	0.01

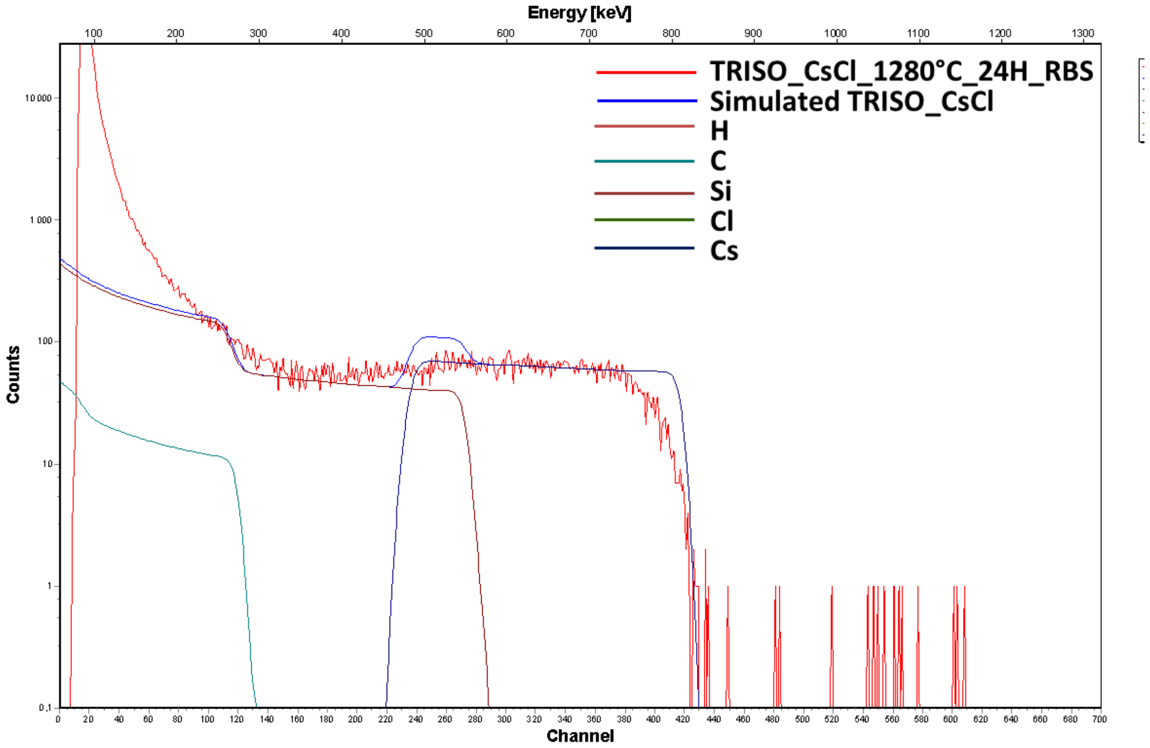


Figure 23: Experimental and simulated spectra of TRISO particle (SiC layer) after heat treatment 24 hours at 1300°C in the presence of CsCl

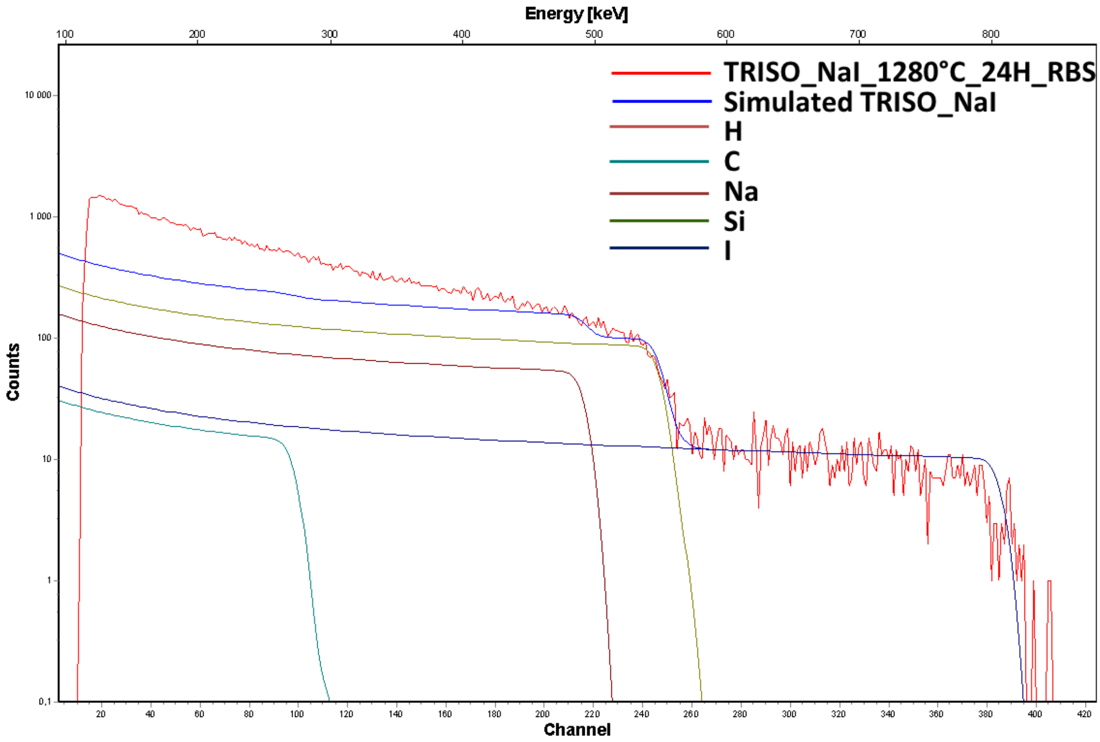


Figure 24: Experimental and simulated spectra of TRISO particle (SiC layer) after heat treatment 24 hours at 1300°C in the presence of NaI

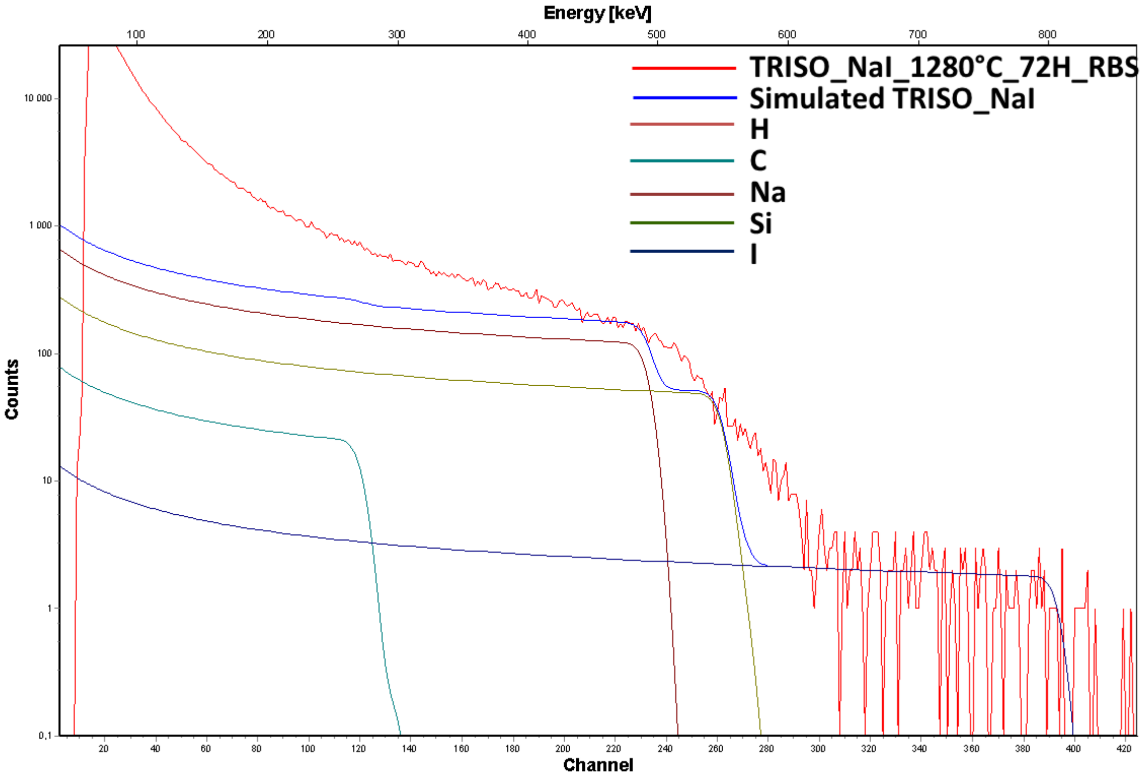


Figure 25: Experimental and simulated spectra of TRISO particle (SiC layer) after heat treatment 72 hours at 1300°C in the presence of NaI

Some PIXE analyses were conducted in Laboratoire d'Etude des Elements Légers (LEEL) CEA - Gif-sur-Yvette" on cross section of TRISO particles after diffusion of iodine (NaI) and silver (AgI) at 1300°C (Figure 26). Mapping of the samples showed no chemical contrast relative to the presence of Ag and I. However, the PIXE analysis of TRISO particle after 85 hours of treatment with AgI at 1300°C showed the presence of Ag peak at the surface of particle and other elements present in the resin (Cl, Zr, C….) (Figure 27).

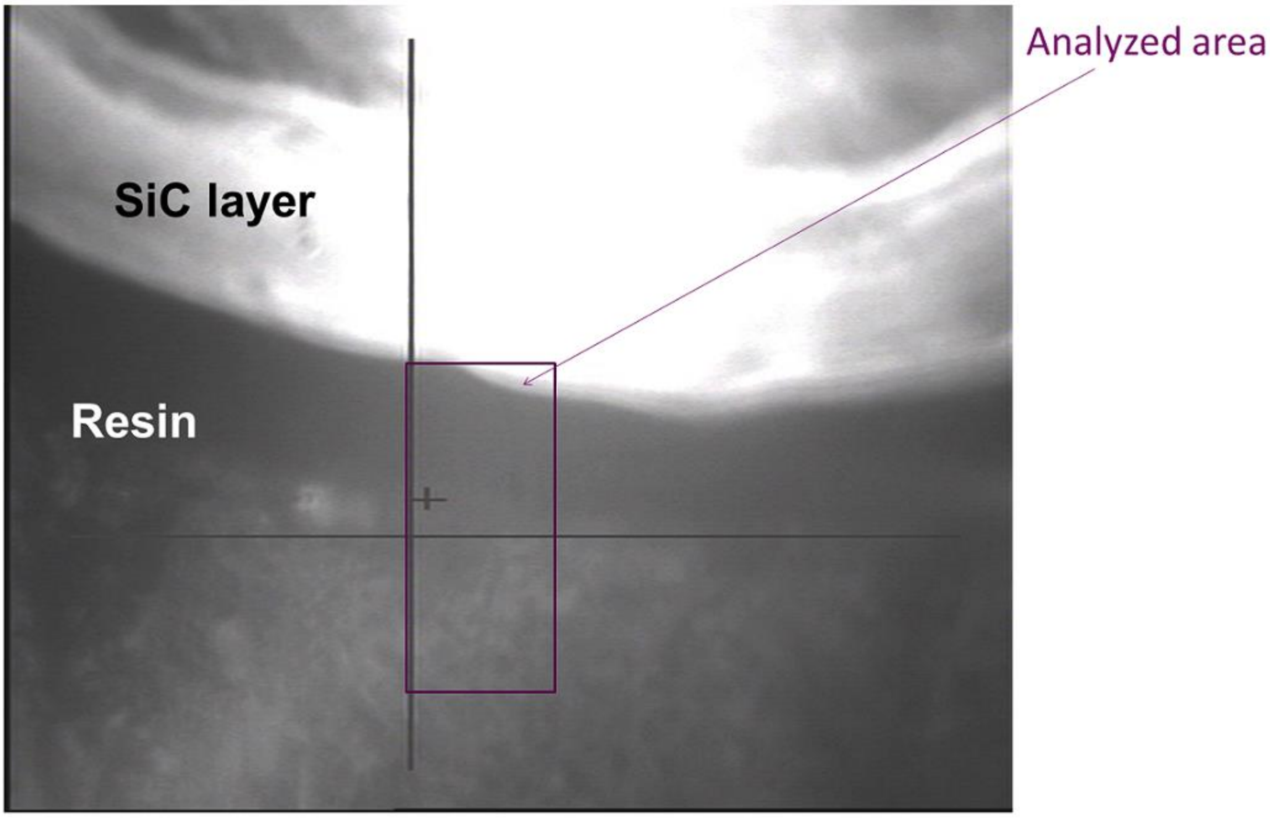


Figure 26: The analysed area in the TRISO particle (SiC layer) after 85 hours of heat treatment at 1300°C in the presence of silver (AgI).

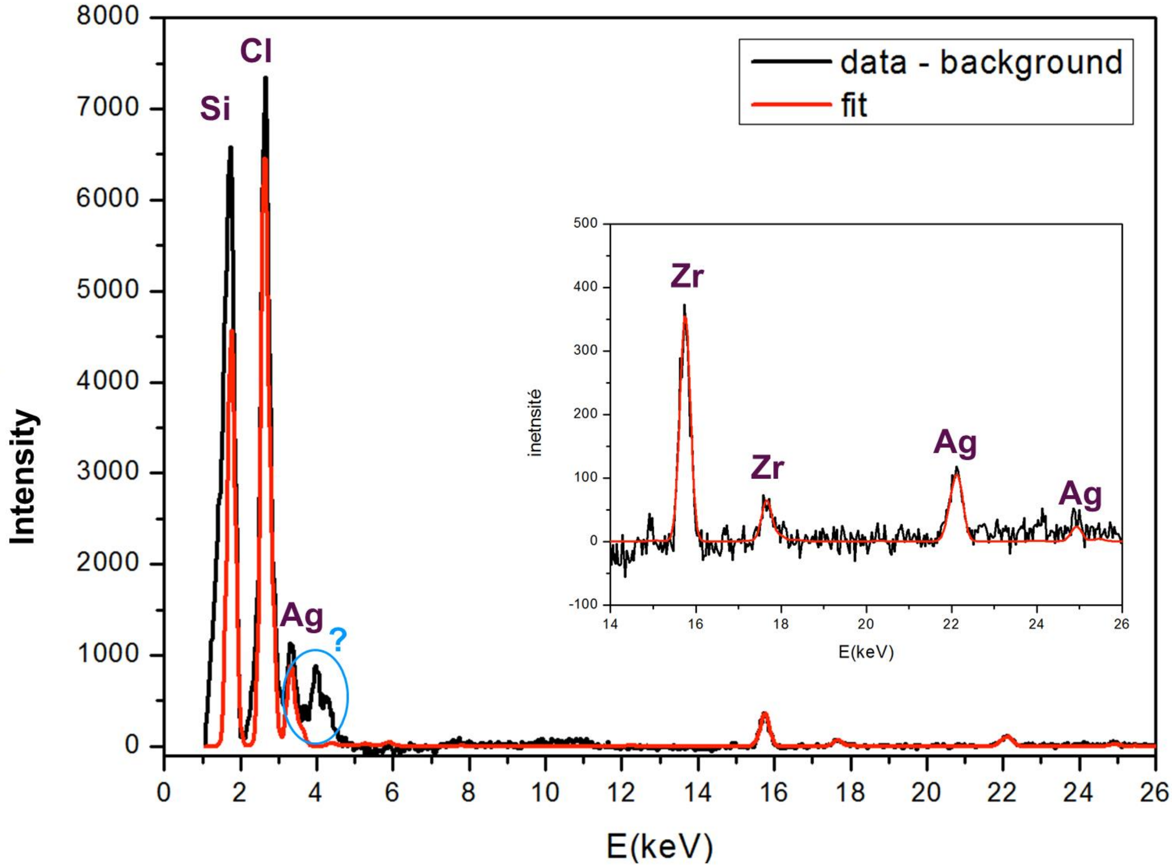


Fig. 27: PIXE spectrum of TRISO particle (SiC layer) after 85 hours of heat treatment at 1300°C in the presence of silver (AgI)

3.3.4. RBS and PIXE analysis with higher energy (2 MeV)

Other RBS and PIXE analyses were conducted in “AIFIRA - Centre d'Études Nucléaires de Bordeaux-Gradignan (CNBG)” with higher beam energy (2 MeV) on the entire and cross section of TRISO particles after diffusion in order to detect an eventual diffusion of silver, caesium and iodine.

3.3.4.1. Standards analyses (pellets of AgI, CsCl and NaI)

a) AgI pellets

The PIXE analyses of standards (AgI, NaI and CsCl) shows that we can detect peaks of Ag, I and Cs. However, the RBS spectra are difficult to interpret. Figure 28 show the PIXE and RBS spectra of AgI pellet. The PIXE spectrum (figure 28-a) shows the presence of peaks of Ag and I. However, the RBS spectrum is difficult to interpret (Figure 28-b).

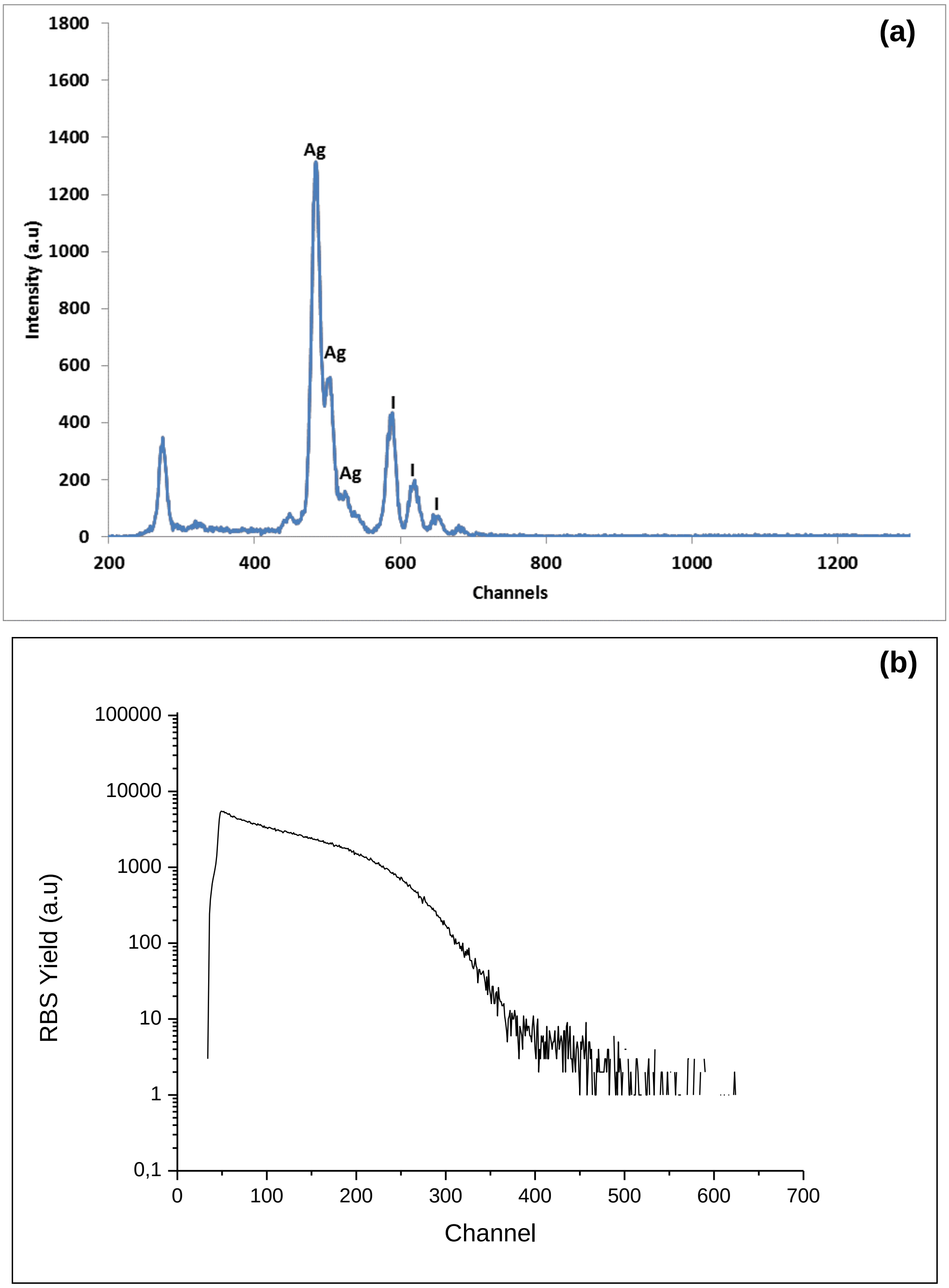


Figure 28: (a) PIXE spectrum and (b) RBS spectrum of AgI pellet.

b) <u>CsCl pellets</u>

Like AgI pellets, the PIXE analysis of CsCl pellets (Figure 29-a) shows the presence of peaks of Cs and Cl but the RBS spectrum shows no presence of caesium.

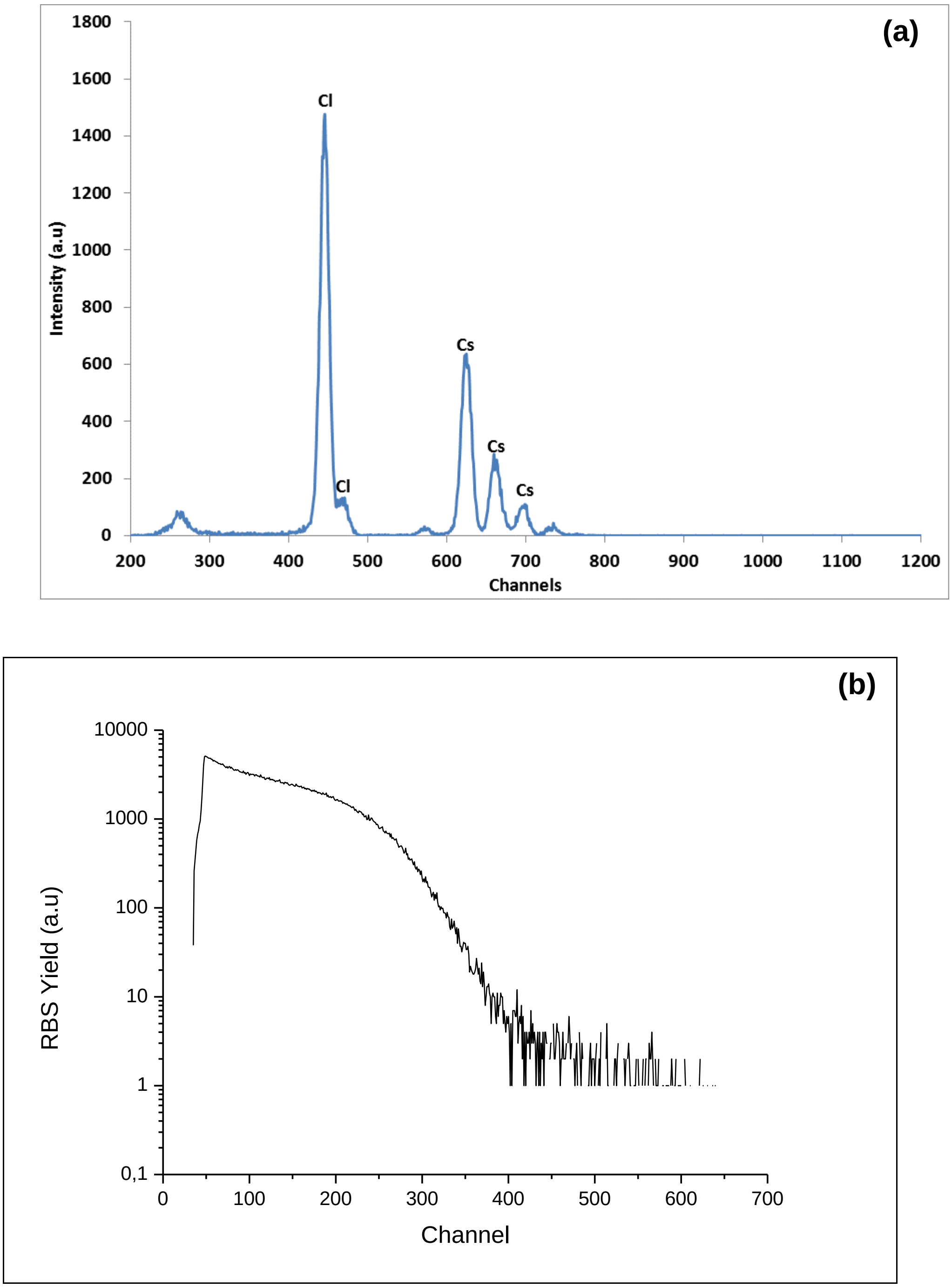


Figure 29: (a) PIXE spectrum and (b) RBS spectrum of CsCl pellet.

c) NaI pellets

For the NaI pellets, it is very difficult to obtain a correct PIXE spectrum despite several analyses of different NaI pellets (Figure 30).

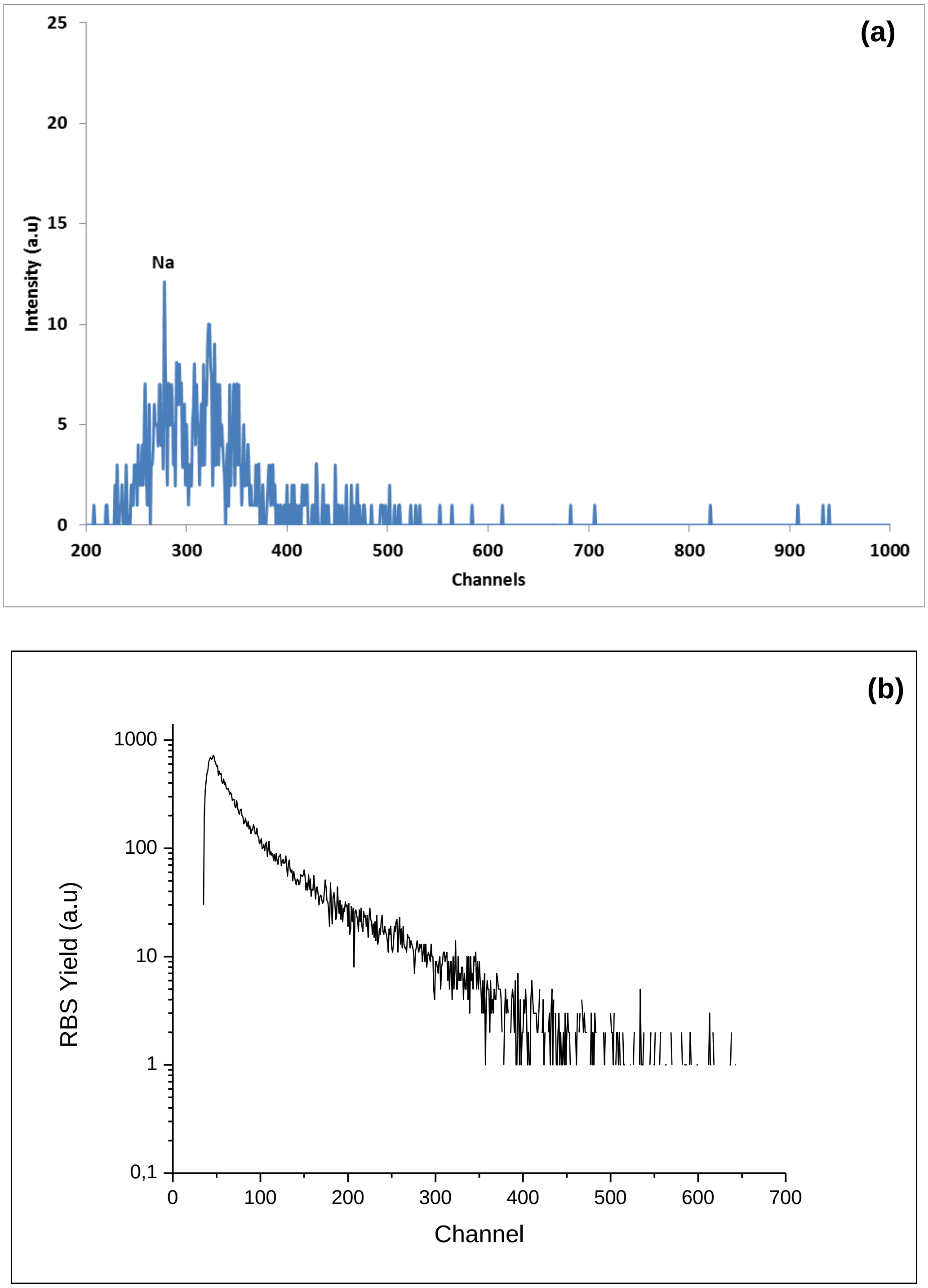


Figure 30: (a) PIXE spectrum and (b) RBS spectrum of NaI pellet.

3.3.4.2.Analysis of entire particles before and after silver, caesium and iodine diffusion

a) Pristine TRISO particles (TRISO particles without any treatment)

The analysis of pristine TRISO particle (SiC) shows the presence of peak of silicon in the PIXE spectrum (figure 31-a). Carbon peaks are not detected in PIXE and RBS because of the lightness of this atom. We detected another peak at lower energies, the position of this peak don't correspond to any element. It is very difficult to obtain a correct RBS spectrum (figure 31-b).

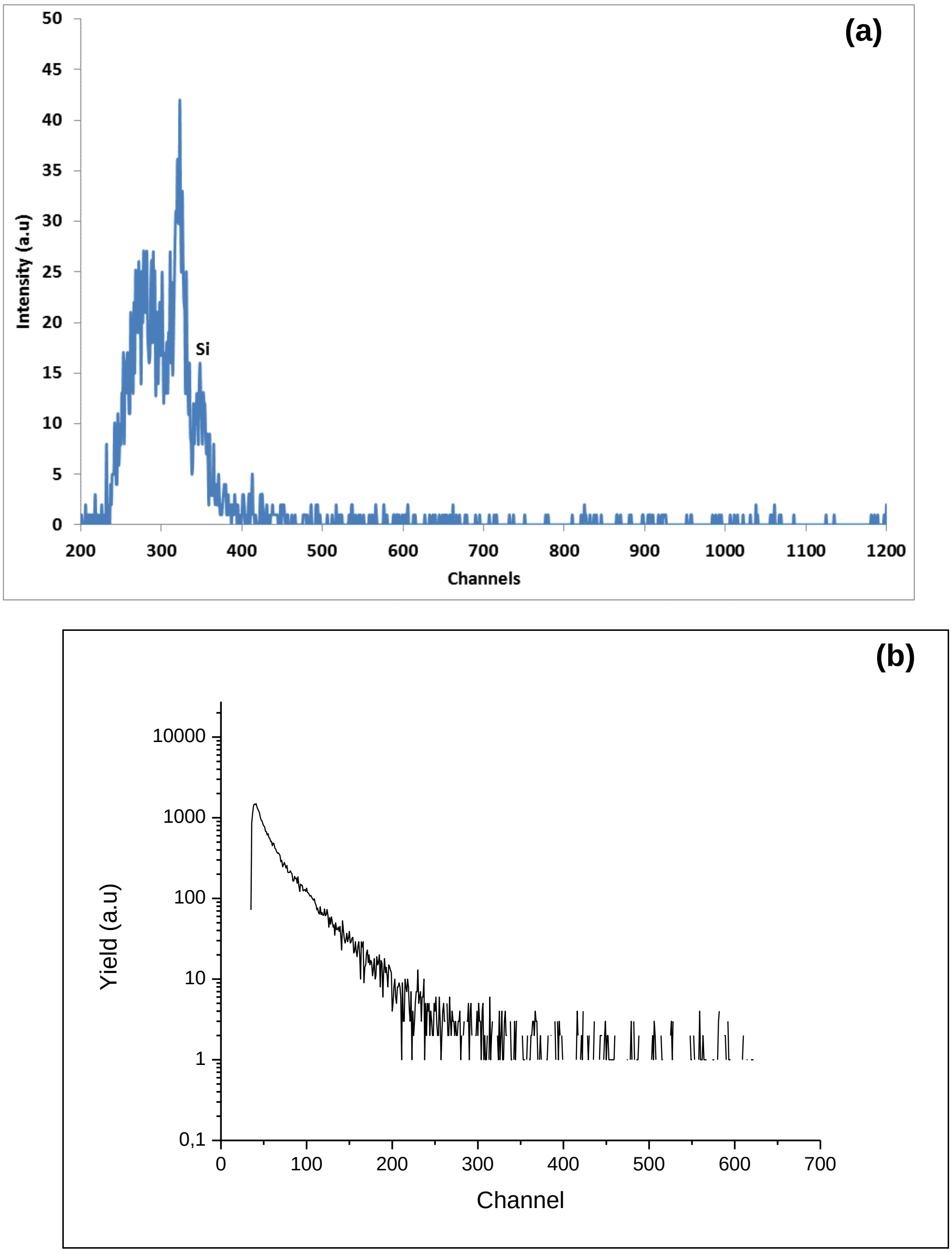


Figure 31: (a) PIXE spectrum and (b) RBS spectrum of Triso particle without treatment.

b) Iodine diffusion

Figure 32 shows the PIXE and the RBS spectra of TRISO particle after 75 hours of diffusion with NaI at 1300°C. We can see peaks of silicon and sodium in the PIXE spectra. In contrast, we did not detect any trace of diffusion of sodium and iodine in the SiC layer by RBS.

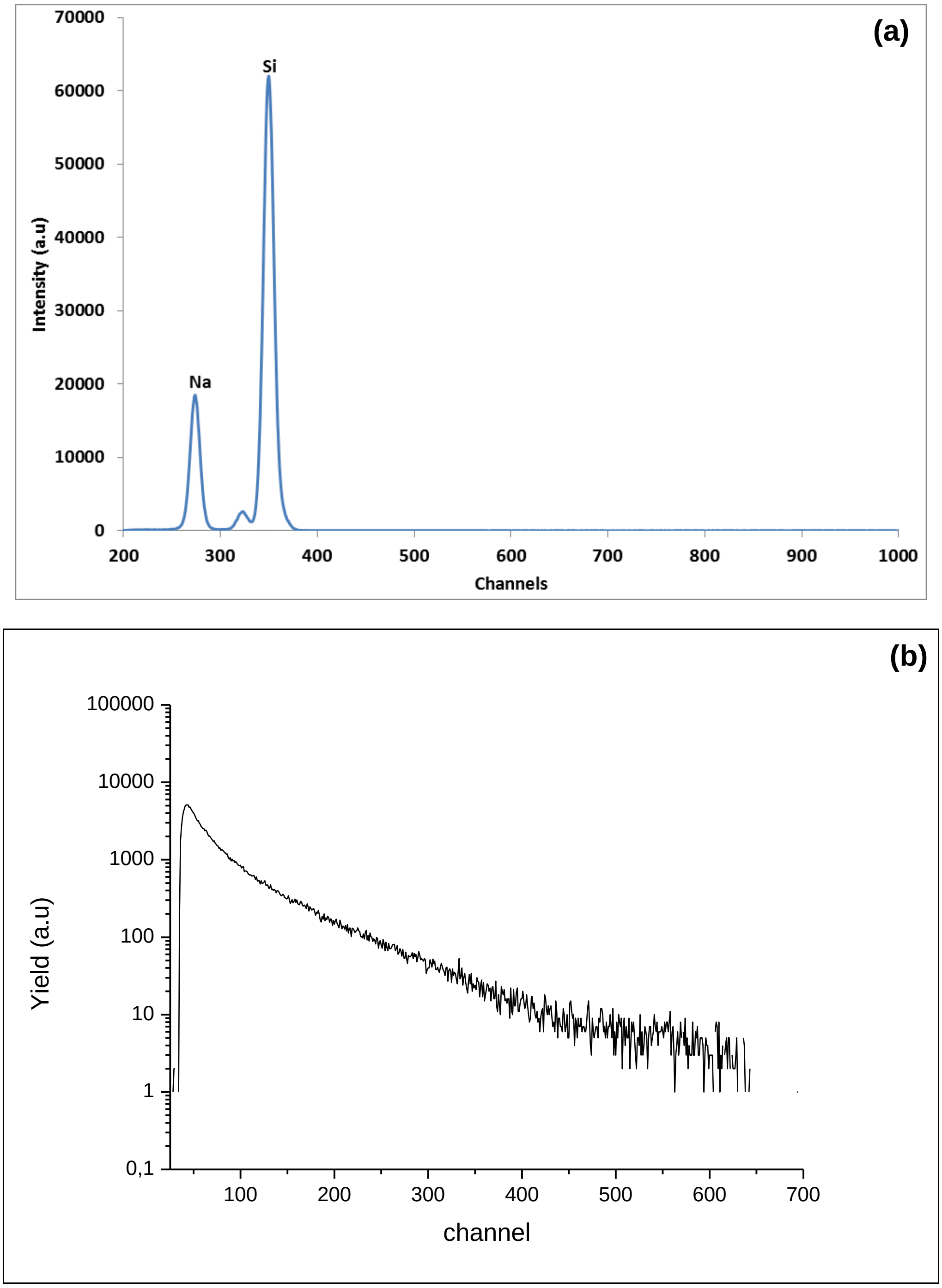


Figure 32: (a) PIXE spectrum and (b) RBS spectrum of TRISO particles after 75 hours of diffusion with NaI at 1300°C.

c) Silver diffusion

Figure 33 shows PIXE and RBS spectra of TRISO particle after 85 hours of diffusion with AgI at 1300°C. Silicon of the SiC layer was detected, but any peak of silver and iodine was detected.

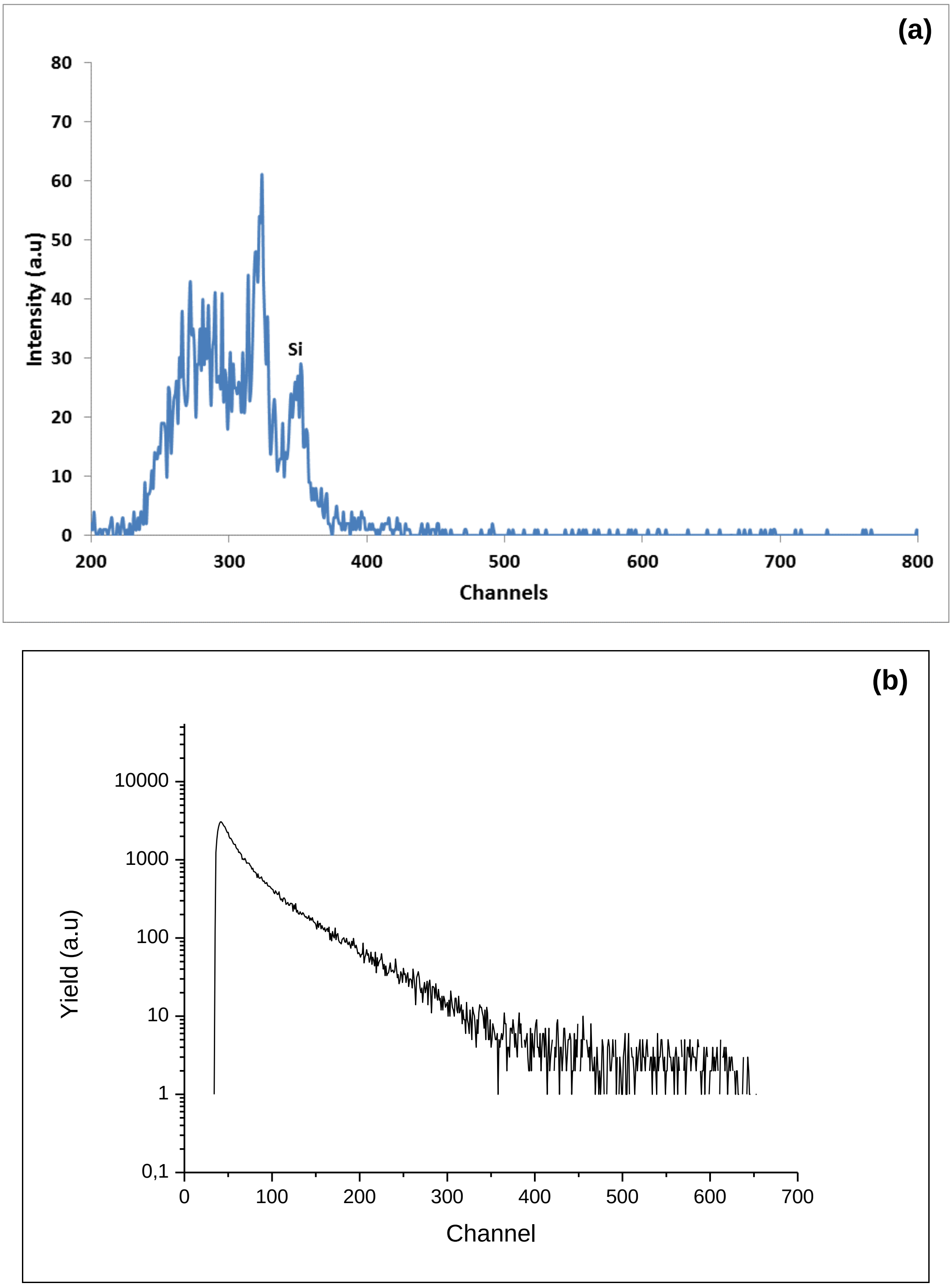


Figure 33: (a) PIXE spectrum and (b) RBS spectrum of TRISO particles after 85 hours of diffusion with AgI at 1300°C.

d) Caesium diffusion

Figure 34 shows PIXE and RBS spectra of TRISO particles after 24 hours of diffusion with CsCl at 1300°C. We detect the peak of silicon in the PIXE spectrum, but any peak corresponding to caesium was observed.

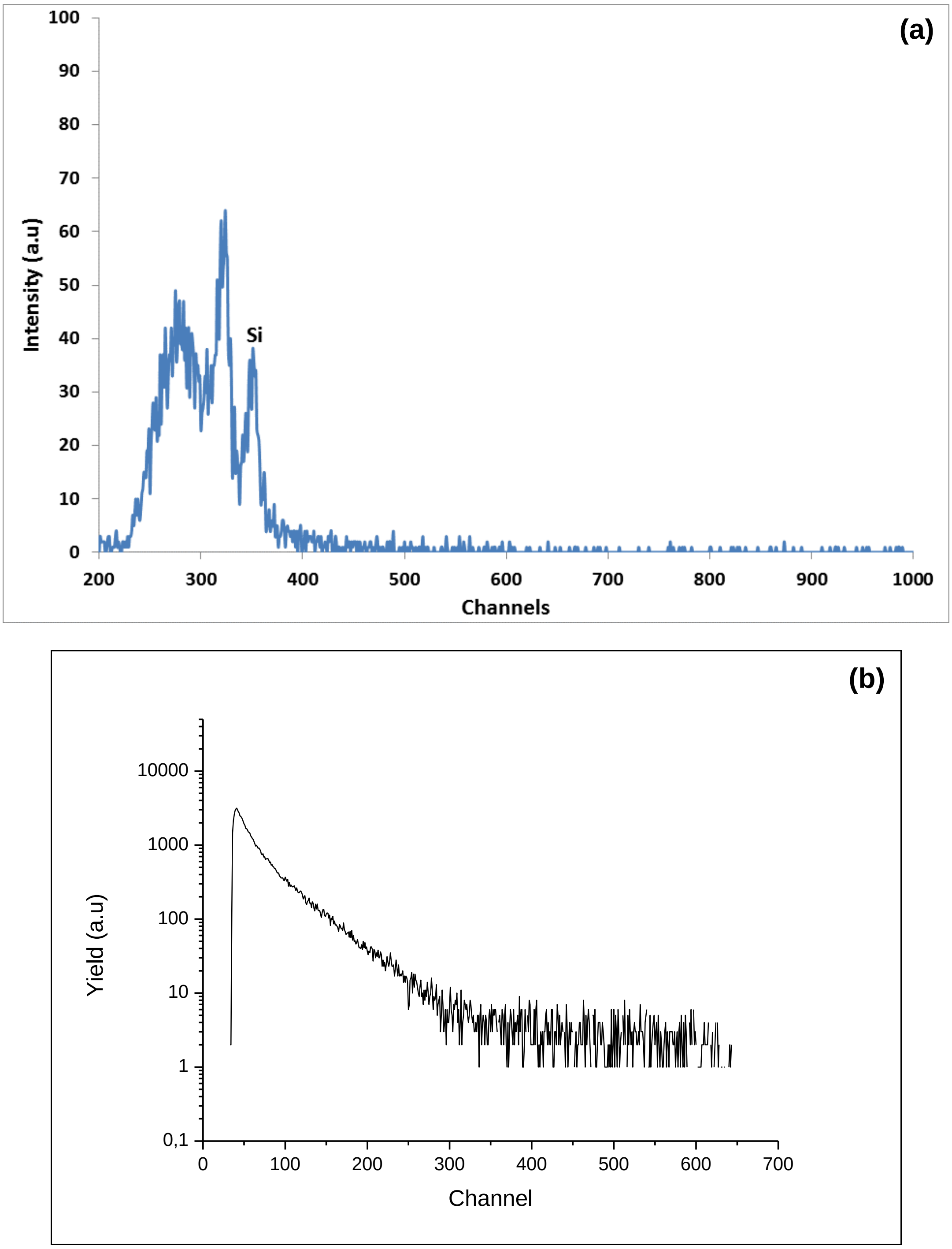
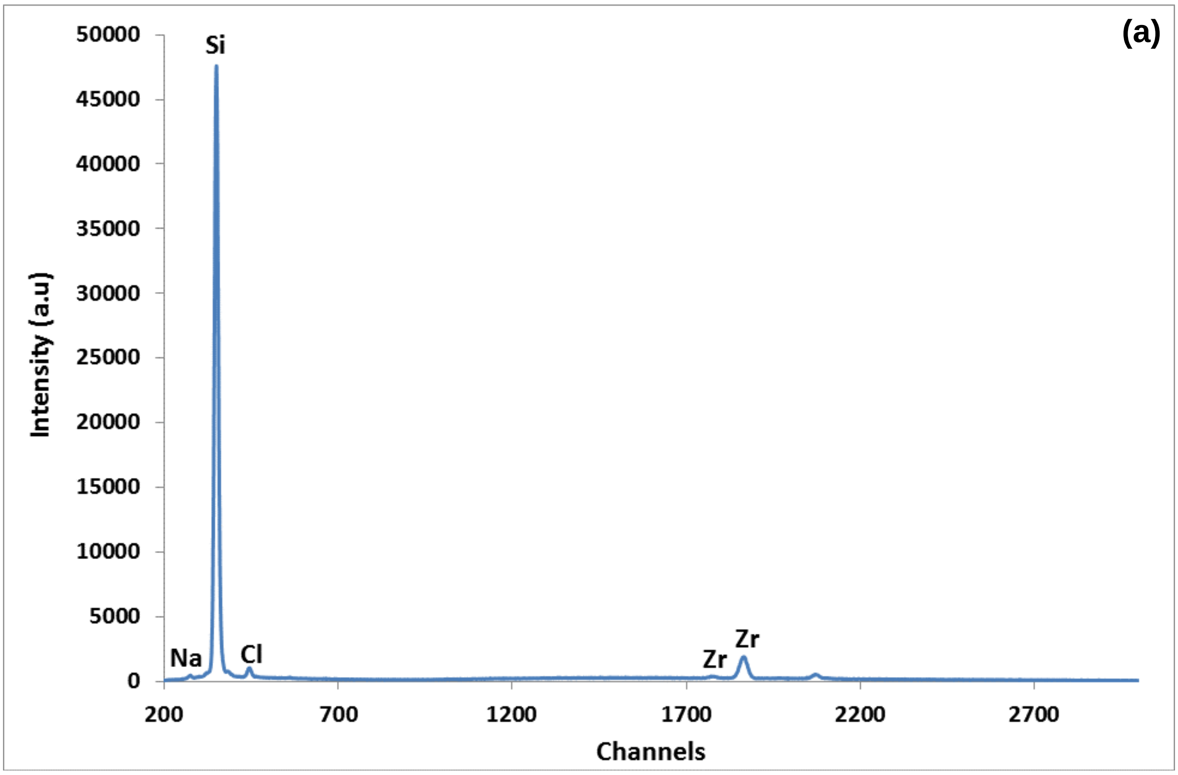


Figure 34: (a) PIXE spectrum and (b) RBS spectrum of TRISO particles after 24 hours of diffusion with CsCl at 1300°C.

3.3.4.3.Analyses of cross section

a) Iodine diffusion

PIXE and RBS spectra of cross section of the TRISO particle after 75 hours of diffusion of NaI at 1300°C is shown in figure 35. As we can see, we detect traces of sodium from NaI diffusion, peaks of zirconium from the kernel of particle (ZrO_2), peak of chlorine from the resin and strong peak of silicon from SiC layer. However, no traces of iodine were detected.



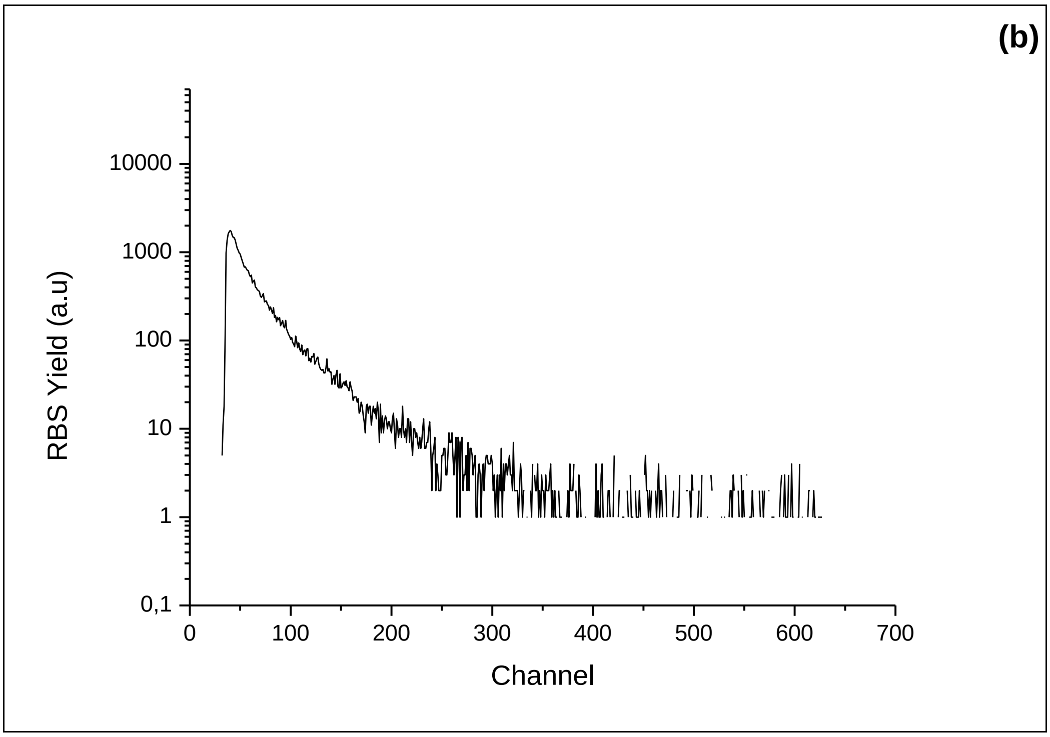


Figure 35: (a) PIXE spectrum and (b) RBS spectrum of cross section of TRISO particles after 75 hours of diffusion with NaI at 1300°C.

b) Silver diffusion

The PIXE analysis of cross section of TRISO particles after 85 hours of diffusion of AgI at 1300°C shows small peaks of silver and iodine (figure 36-a). At lower energy, we observed the peak of silicon. Small amounts of silver and iodine were also detected at the surface of the TRISO particle. Others elements were also observed, Cl from resin and Zr from the kernel of particle introduced with the polishing. RBS spectrum treatment (Figure 36-b) did not provide information on the diffusion profile of Ag and I.

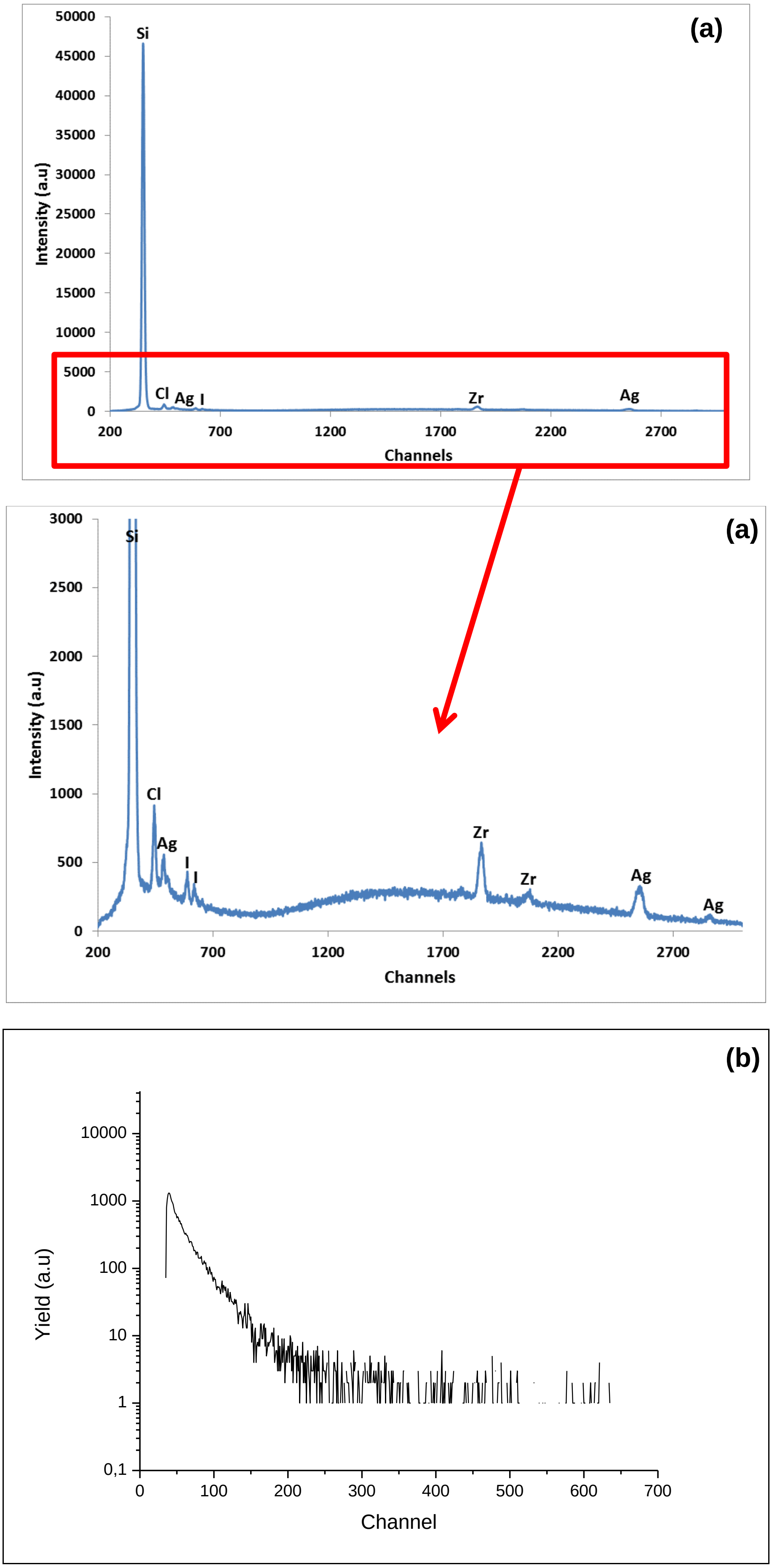


Figure 36: (a) PIXE spectrum and (b) RBS spectrum of cross section of TRISO particles after 85 hours of diffusion with AgI at 1300°C.

c) Caesium diffusion

Figure 37 shows PIXE and RBS spectra of the cross section of TRISO particle after 24 hours of diffusion of CsCl at 1300°C. Silicon (SiC layer), Chlorine (from CsCl) and zirconium (from kernel particle) were detected. peaks of caesium were not detected.

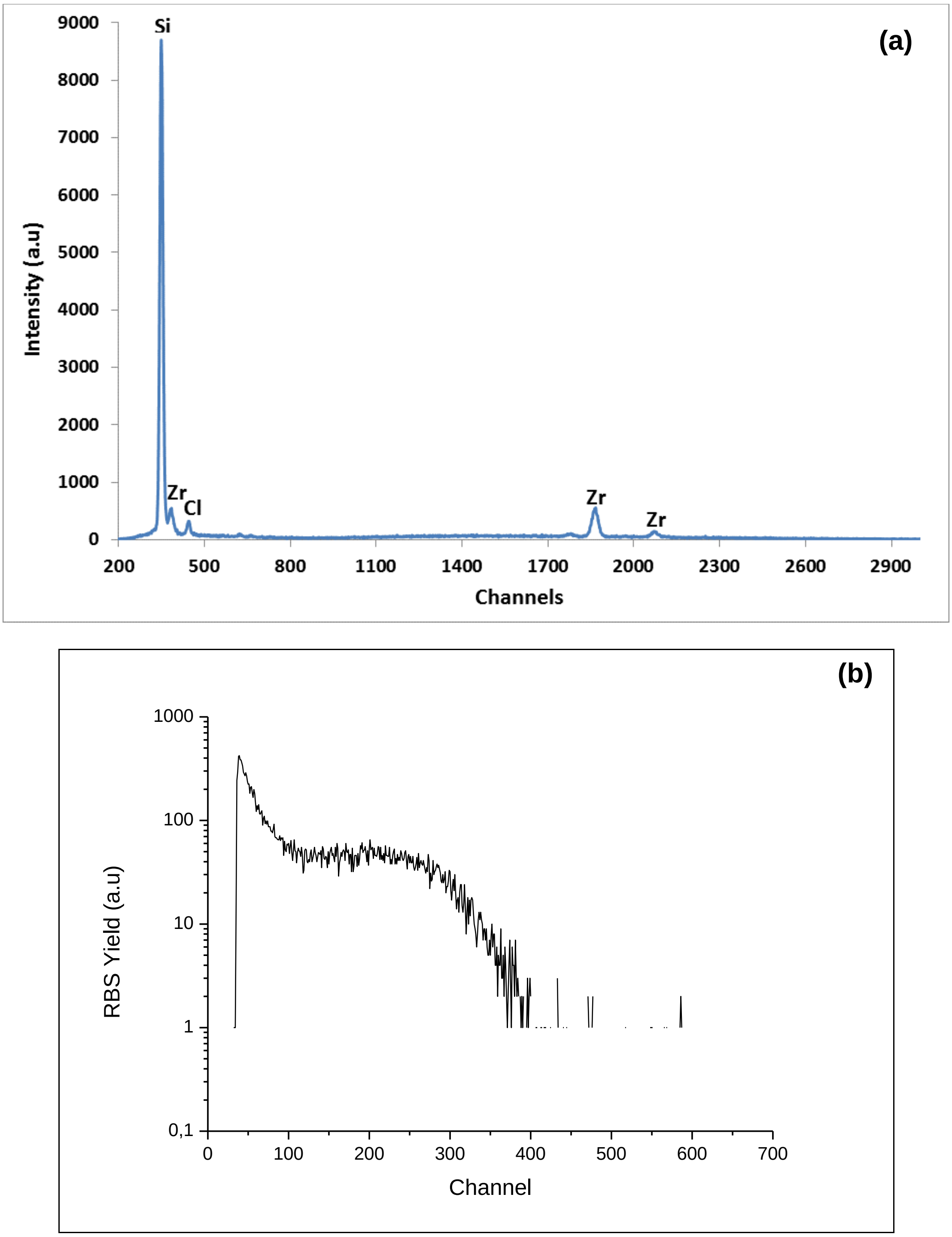


Figure 37: (a) PIXE spectrum and (b) RBS spectrum of cross section of TRISO particles after 24 hours of diffusion with CsCl at 1300°C.

4. Conclusion

The HR-ICP-MS analyses of TRISO particles after heat treatment in the presence of diffusing elements (Ag, Cs and I) showed few ppm of some elements at the surface of the SiC layer. The surface analysis by HR-ICPMS and NanoSIMS of TRISO particles after diffusion showed for the iodine many interferences with the signal of others elements. The PIXE and RBS analysis of entire particle and cross section conducted at lower (900 KeV) and high energy (2 MeV) showed in some cases small peaks of diffusing elements (PIXE spectra) may be only at the surface of particles but the RBS spectra don't show the presence of diffused elements. This is probably due to the very small amount and the very low diffusion of these elements through the SiC layer of TRISO particles.

Acknowledgments

We would like to express our gratitude to Stéphanie Sorieul from AIFIRA - Centre d'Études Nucléaires de Bordeaux - Gradignan (CNBG)" for PIXE and RBS analyses and Suzy Surblé from "Laboratoire d'Etude des Elements Légers (LEEL) CEA - Gif - sur - Yvette" for the PIXE analysis.

5. References

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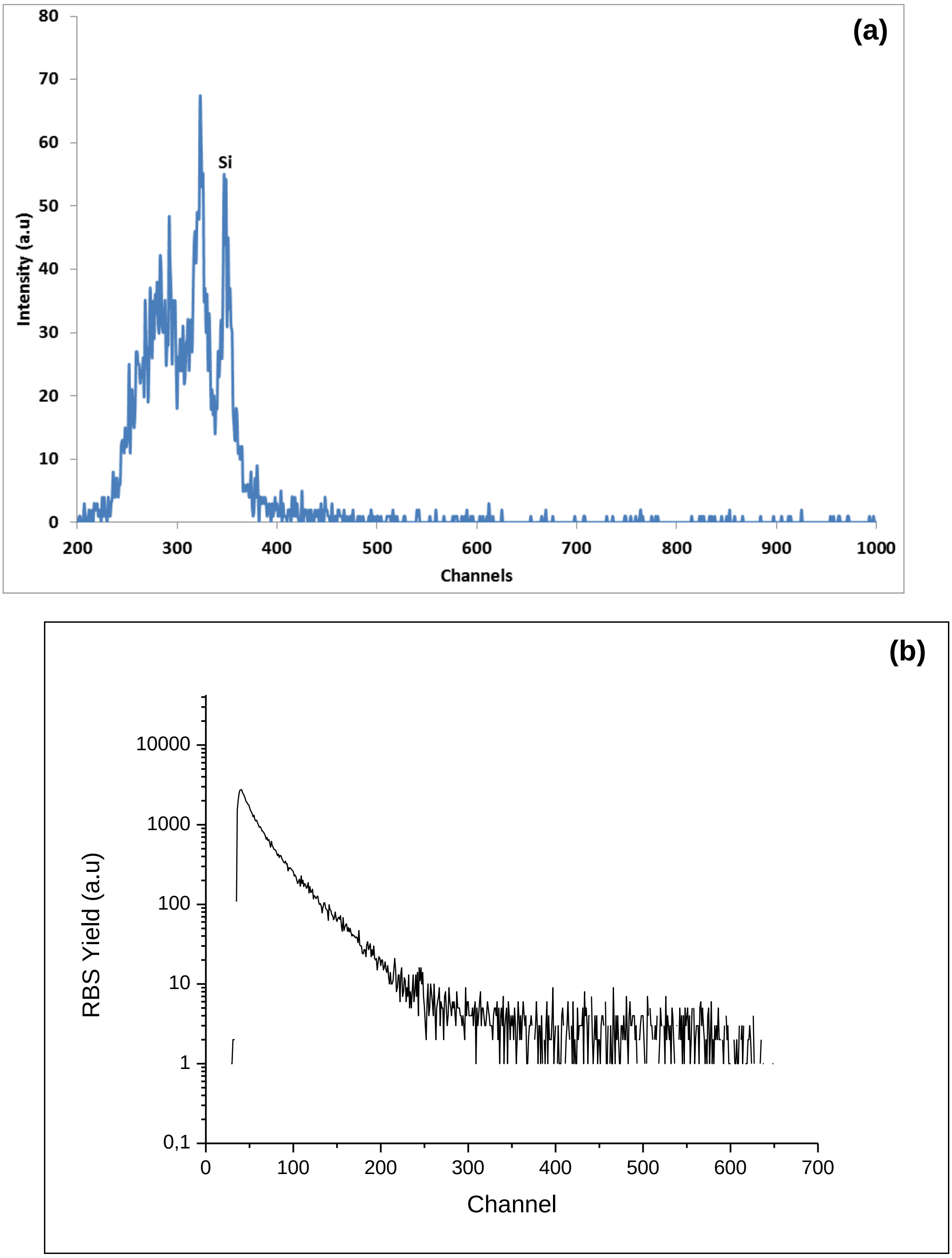
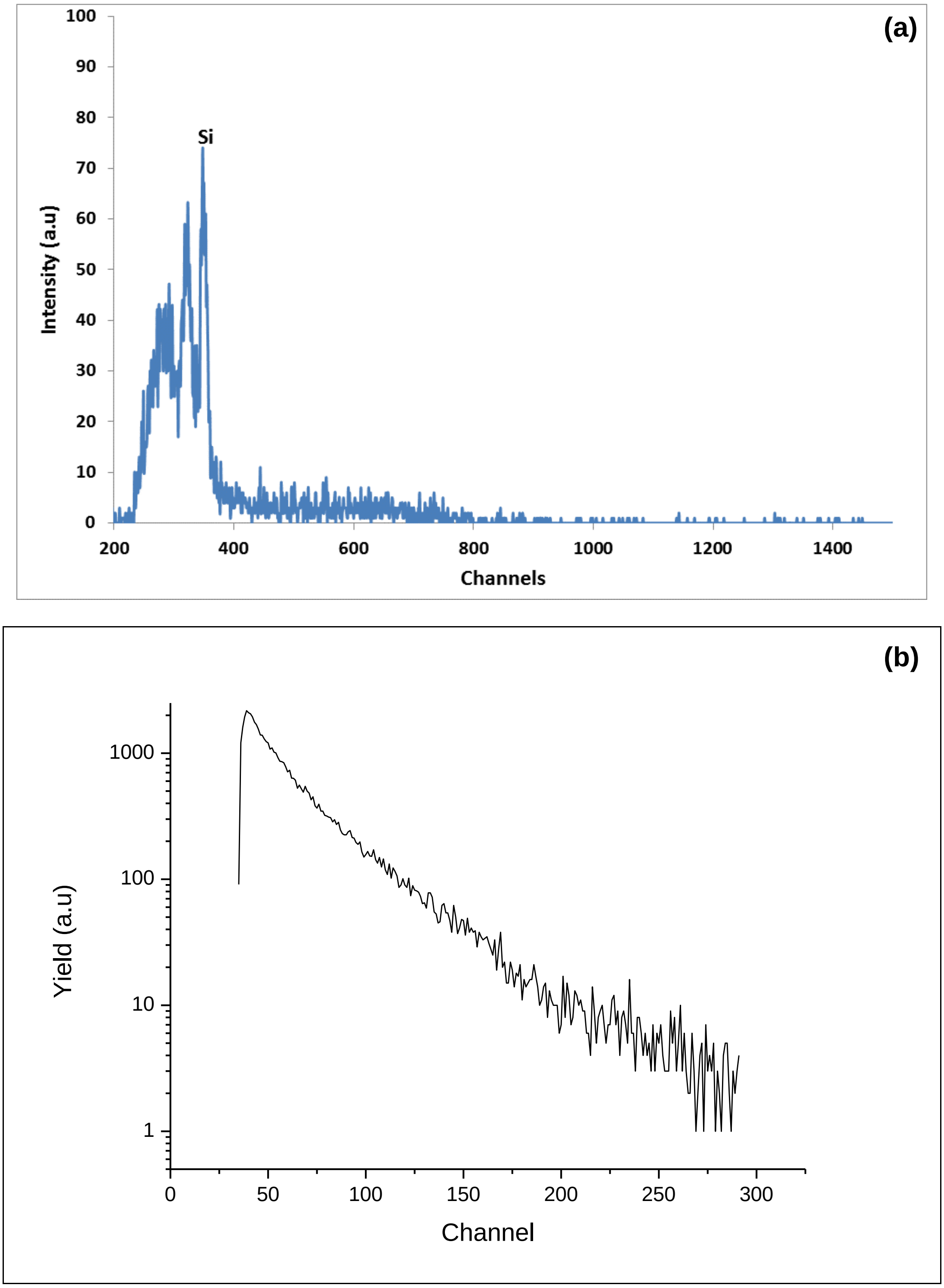
Annex

TRISO particles after 24 hours of diffusion with NaI at 1300°C



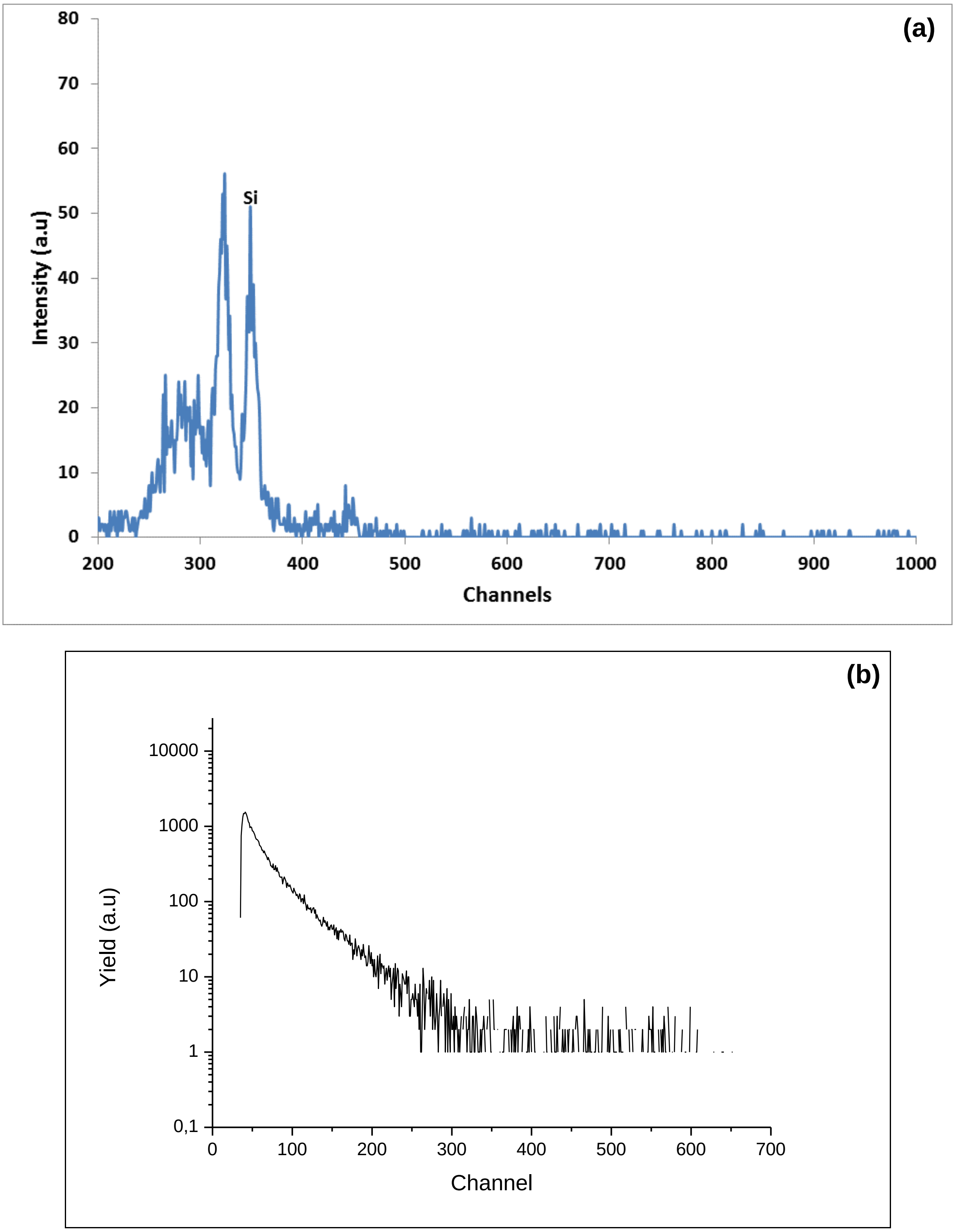
(a) PIXE spectrum and (b) RBS spectrum of TRISO particles after 24 hours of diffusion with NaI at 1300°C.

TRISO particles after 24 hours of diffusion with Ag at 1300°C



(a) PIXE spectrum and (b) RBS spectrum of TRISO particles after 24 hours of diffusion with Ag at 1300°C.

TRISO particles after 24 hours of diffusion with CsCl at 1250°C



(a) PIXE spectrum and (b) RBS spectrum of TRISO particles after 24 hours of diffusion with CsCl at 1250°C.