Applications of low-background gamma spectrometry techniques to sign the geographical origin of food-products

Motivations

The natural radioactivity ($^{238}U/^{232}Th$ chains, ^{40}K) is present everywhere with a more or less high activity depending on the nature of the soils (granitic, clayey, limestone…).

→ the low-background gamma spectroscopy is a very powerful technique in others disciplines to measure the activity of these radioelements

Examples at the Bordeaux university

- in archeology: dating techniques by thermoluminescence need to measure with high accuracy the level of gamma radioactivity of $^{238}U/^{232}Th$ and ^{40}K in the soils

- in oceanography: dating technique for water needs to know the $^{228}Ra/^{226}Ra$ ratio in many sites to understand the sea water fluxes

→ with low-background gamma spectroscopy: reduction of the volume of water to be collected from 500 l down to 30 l and gain of time acquisition

Also in Bordeaux: the DGCCRF laboratory, a food and drug french government agency

How to be sure that what is written on a food-product is correct or not?

The main activity of the DGCCRF in Bordeaux is the wine and also others local food-products which are protected by a quality control label

➡ economical problem

Is it possible to determine the geographical origin of some food-products using the low-background gamma radioactivity technique?

- wines from Bordeaux (see Philippe Hubert's talk)
- french atlantic salts (Ré, Guérande, Noirmoutier…)
- prunes from Agen

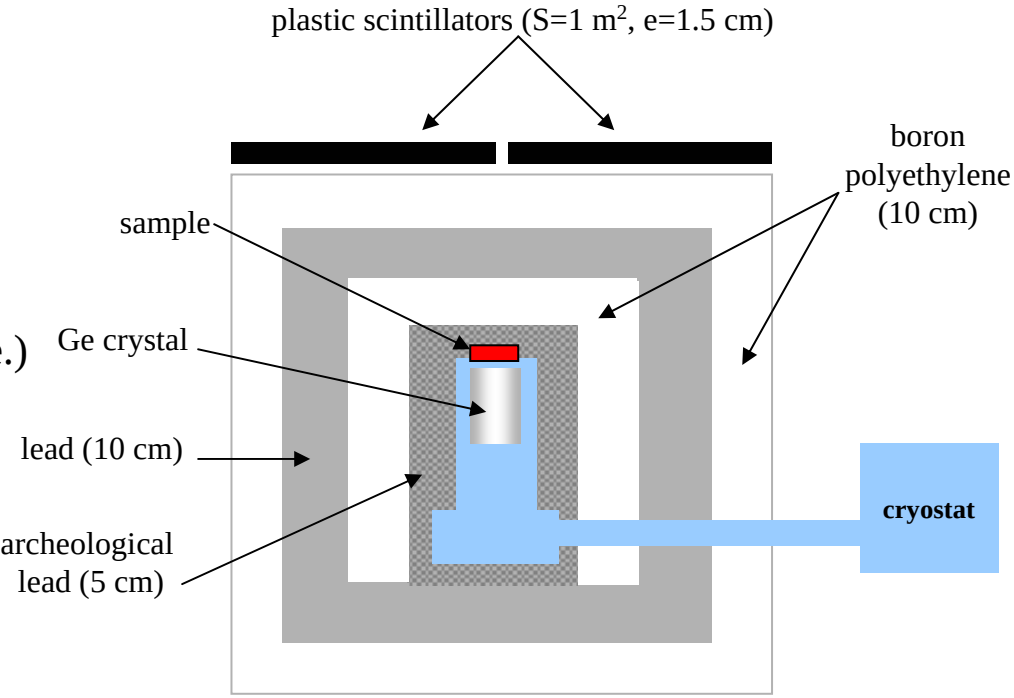
Low-background Ge spectrometers in Bordeaux at the sea level

Ge spectrometers available:

- 2 coaxial-type Ge detectors (100 cm^3)
- 2 well-type Ge detectors (300 cm^3)

Reduction of background:

- at the basement of a 5-floor building (6 m w.e.)
- active shielding for cosmic rays
- passive shielding for natural radioactivity



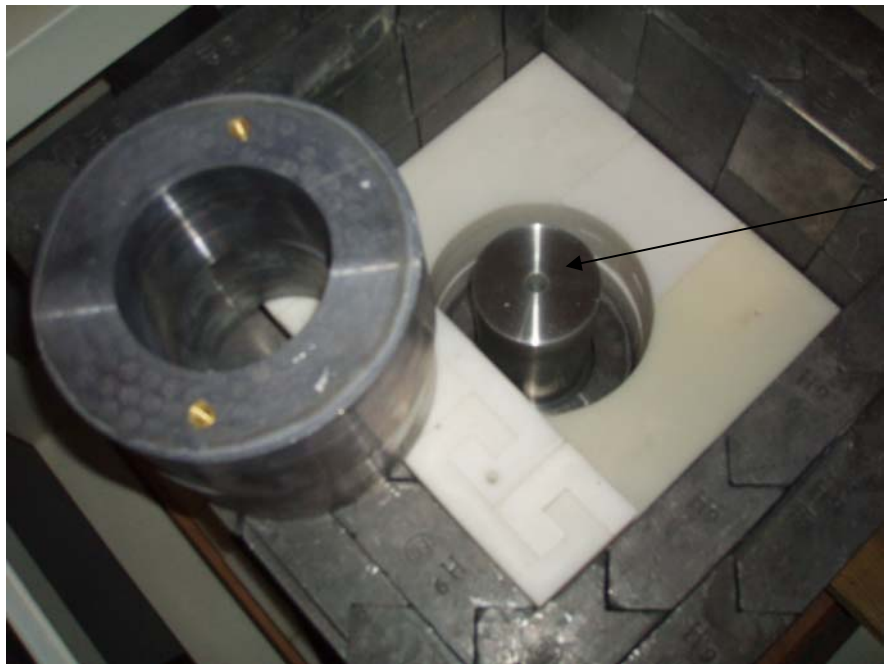
Background counting rate 30-3000 keV:

- 5 counts/mn for the 100 cm^3 Ge detector
- 10 counts/mn for the 300 cm^3 Ge detector

allows to reach sensitivities of few mBq/kg depending on the nature of the sample

sample of salt

coaxial-type Ge

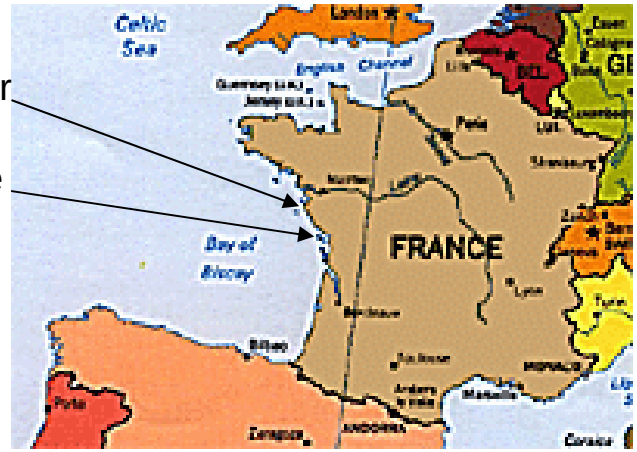


well-type Ge

First example: marine salts

Guérande
Noirmoutier

Ré



Economical context:

french atlantic salts (Ré, Guérande, Noirmoutier) are protected by a quality control label

Question from the DGCCRF laboratory:

How to discriminate between french atlantic salts and others salts (mine, Mediterranean, Spain, Portugal…)?

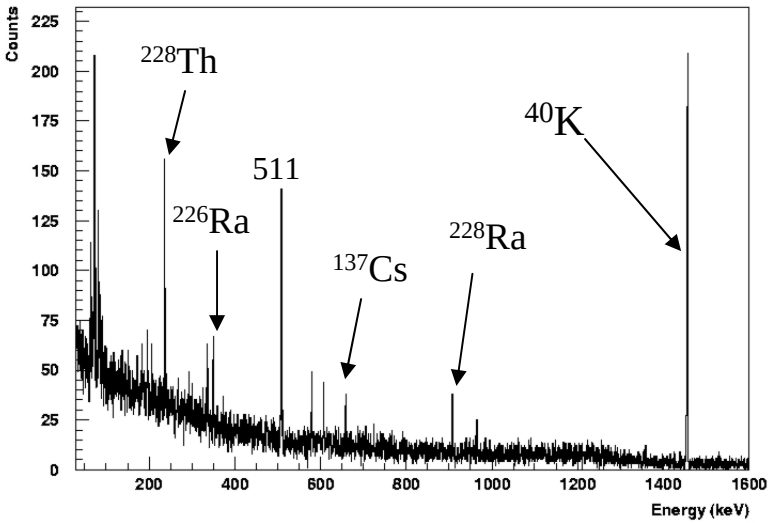
Analysis of the mineral elements (Na, K, Ca, Mg…) done by the DGCCRF lab.

➡ No enough informations to discriminate between all the salts!

Could gamma radioactivity measurements bring complementary informations?

Gamma radioactivity in marine salts

French atlantic salt from the island of Ré

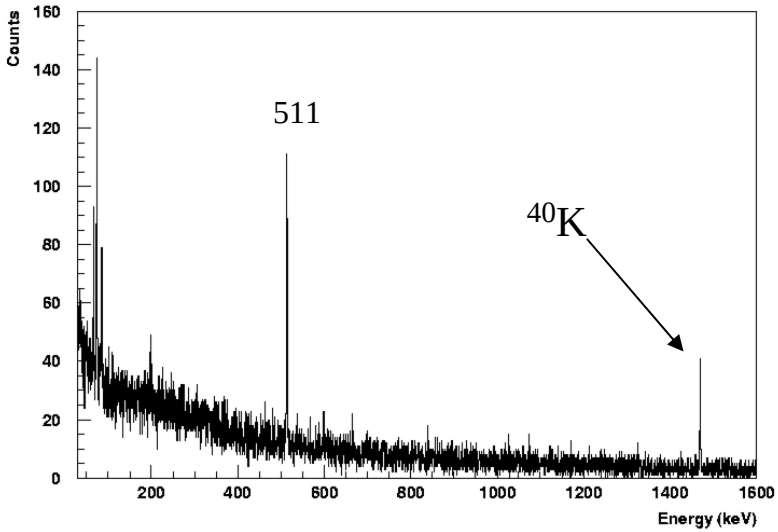


- Typical mass sample: 80 g in a ϕ=7 cm, h=2 cm box
- Measure with the 100 cm^3 Ge detector
- Acquisition time: few days

In the french atlantic salt:

- ^{40}K activity: ~40 Bq/kg
- ^{226}Ra, ^{228}Ra, ^{228}Th: ~500 mBq/kg
- traces of ^{137}Cs: ~70 mBq/kg

Marine salt from Spain

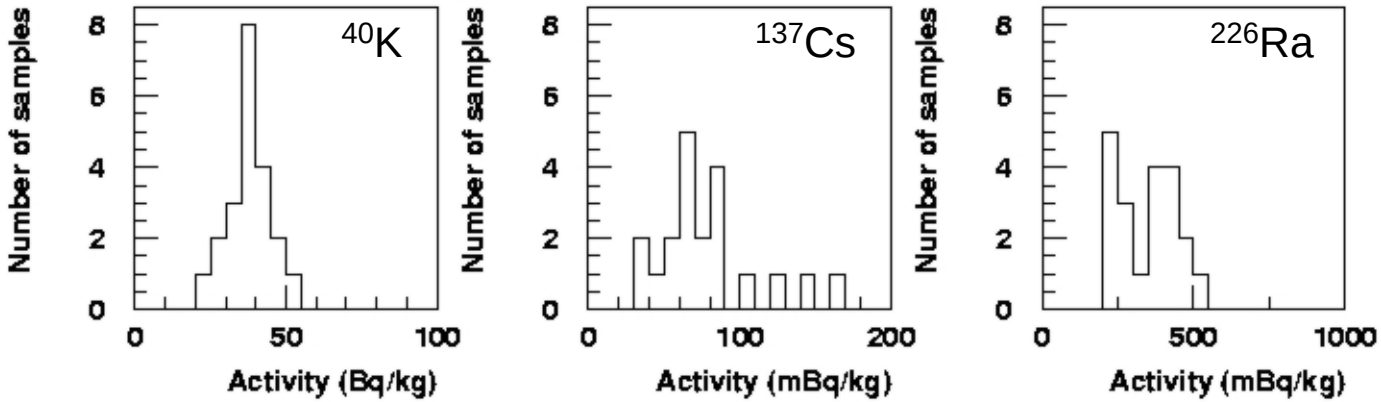


In the spanish atlantic salt:

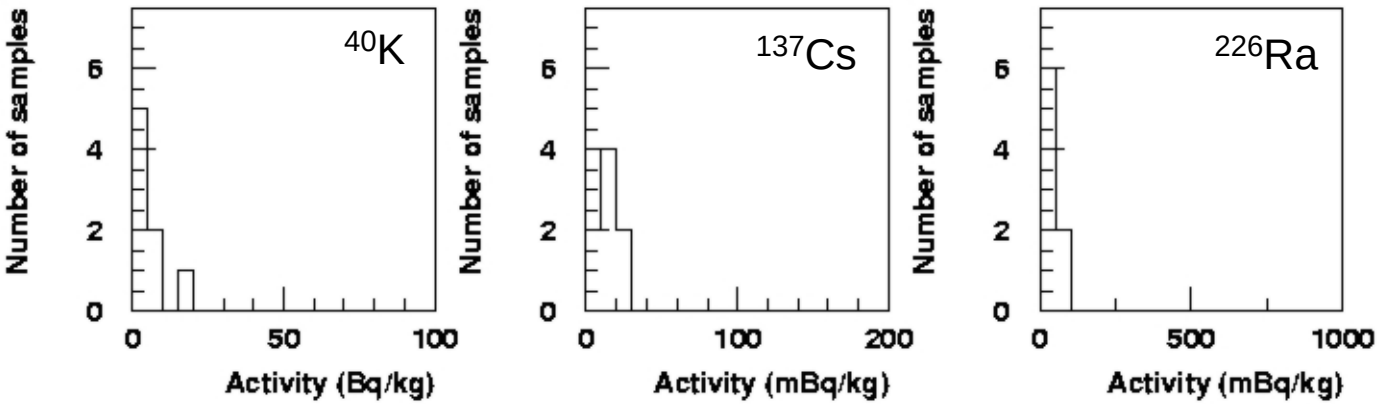
- ^{40}K activity: ~5 Bq/kg
- only upper limits for ^{226}Ra, ^{228}Ra, ^{228}Th and ^{137}Cs

Activity distribution in marine salts

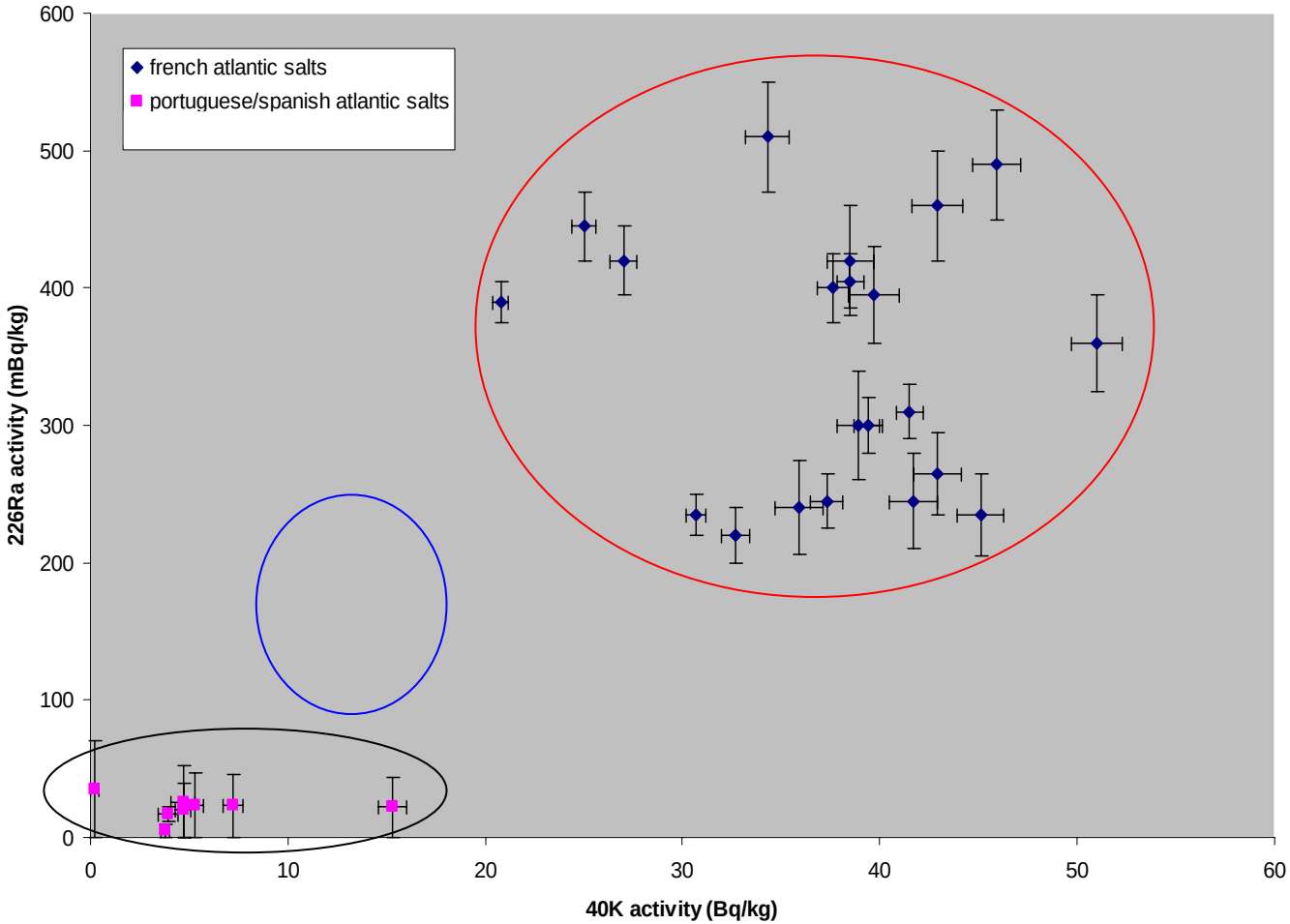
French atlantic salts (Ré, Guérande, Noirmoutier): 21 samples



Spanish/Portuguese atlantic salts: 8 samples



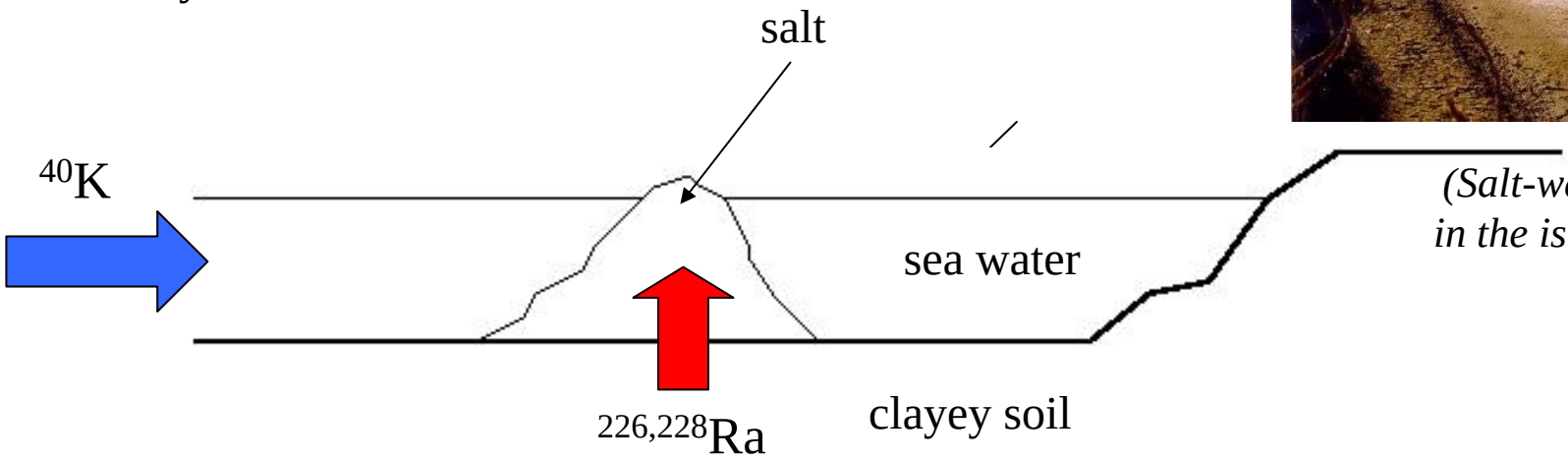
Gamma radioactivity in marine salts



Possible origins of the radioactivity in the salts

In sea water:

- 0.4 g/l for K^+ ions gives 13 Bq/l of ^{40}K: enough to explain the level of ^{40}K activity
- 1 or 2 mBq/l of ^{226}Ra: not enough to explain the level of ^{226}Ra activity



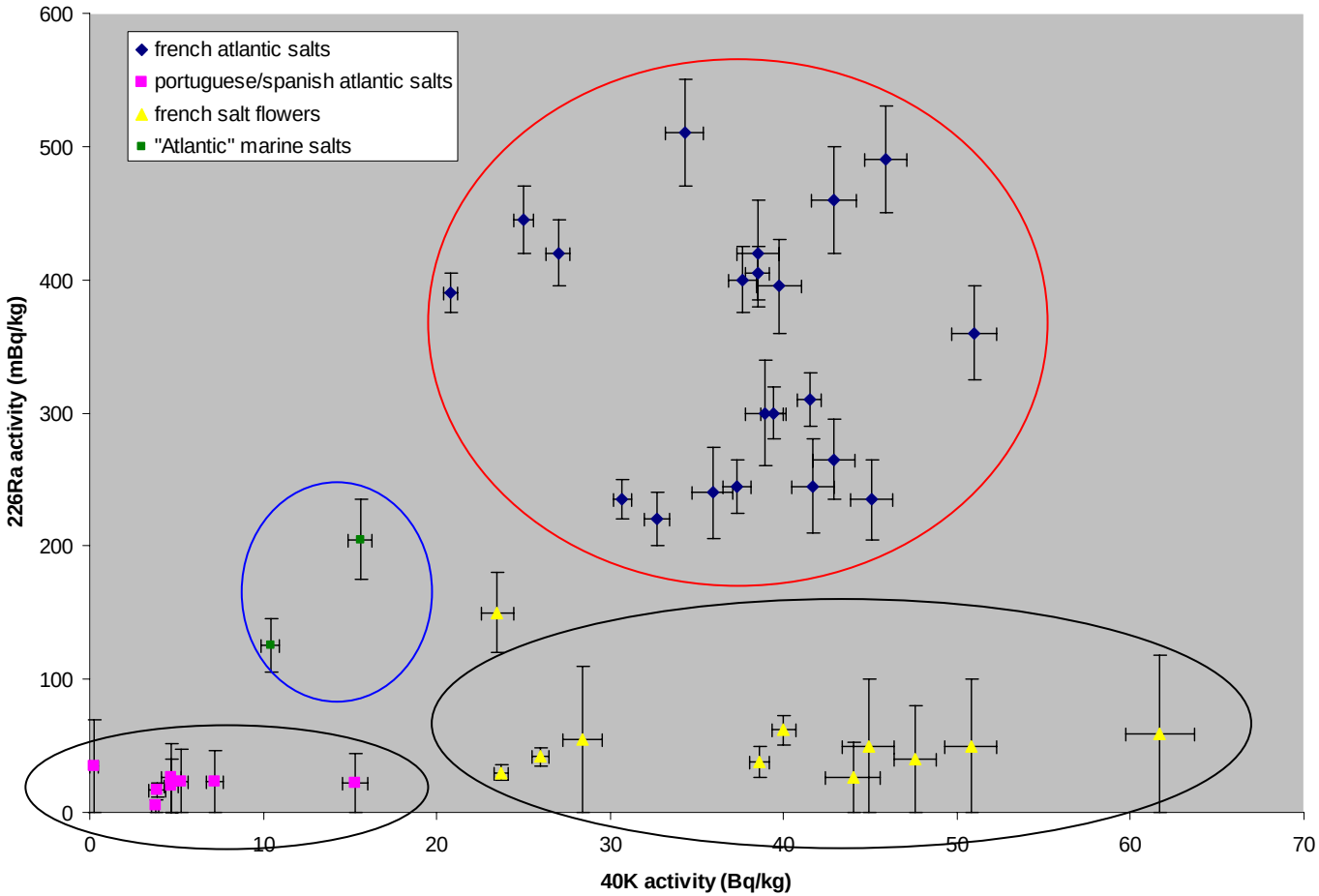
(Salt-water fields in the island of Ré)

presence of radium isotopes in salts due to diffusion of $^{226,228}Ra$ from the soil to the salt

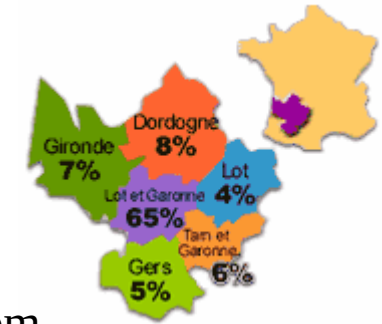
possible difference of level of radioactivity in clay from France to Portugal

In marine salts: « salt flowers » are most expensive and better taste for cooking

This salt is collected at the surface of the salt-marine fields



Second example: prunes from Agen



Economical context: prunes from Agen has also a quality control label from the european commission called IGP (Protected Geographical Identification)

Problem: prunes from Argentina, Chile or California can be sold as « Pruneaux d'Agen » because they belong to the same variety of plum tree called « Prune d'Ente »

Previous studies done by DGCCRF lab:

- analysis of the form of prunes cores
- chemical analysis
- analysis of the mineral elements (K, Ca, Mg, P, Na) by atomic absorption spectrometry

→ gives a separation at a level confidence of 90%

Could gamma radioactivity measurements bring complementary informations?

Preparation of the samples

Preparation of prunes without cores

↓

crushing

↓

drying to remove the humidity

↓

Mineralisation
(heating up to 550°C)

↓

2 or 3 g of ashes

↓

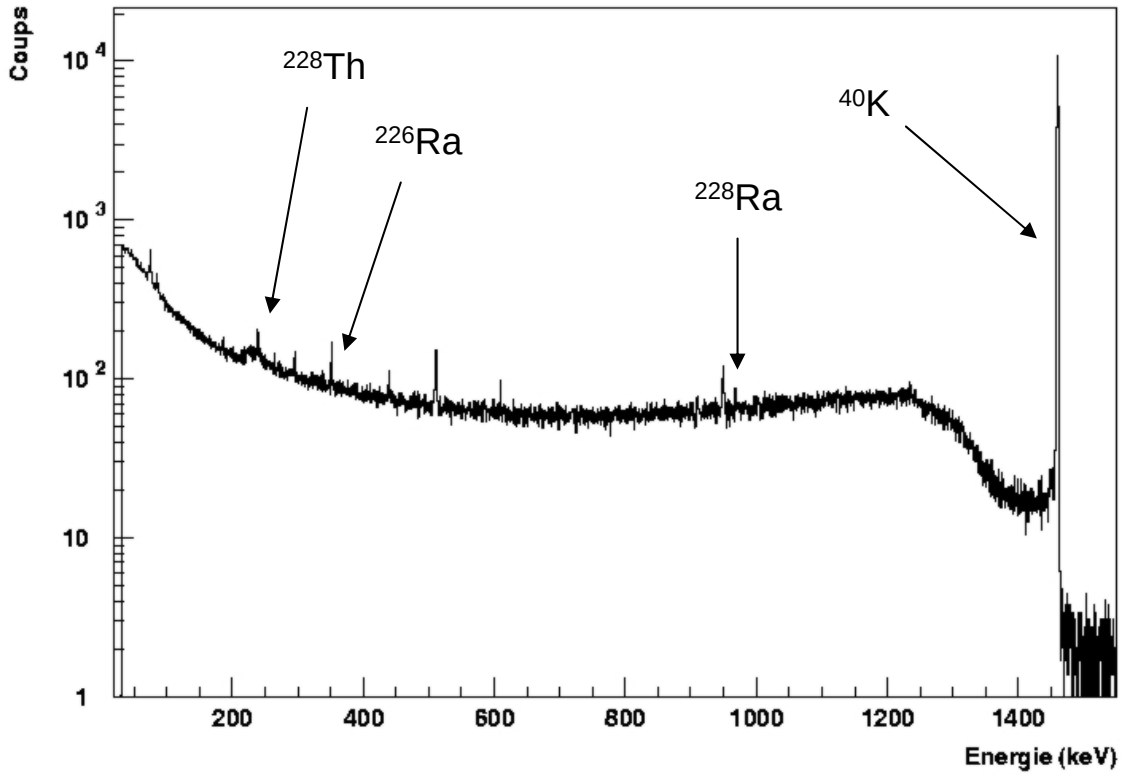
Put in a closed tube of 4 cm^3
for the well-type Ge detector

→

Waiting for 2-3 weeks to reach the secular equilibrium due to radon emanation

Gamma radioactivity in prunes

Sample of prunes from Agen : 6-7 days for a typical acquisition time

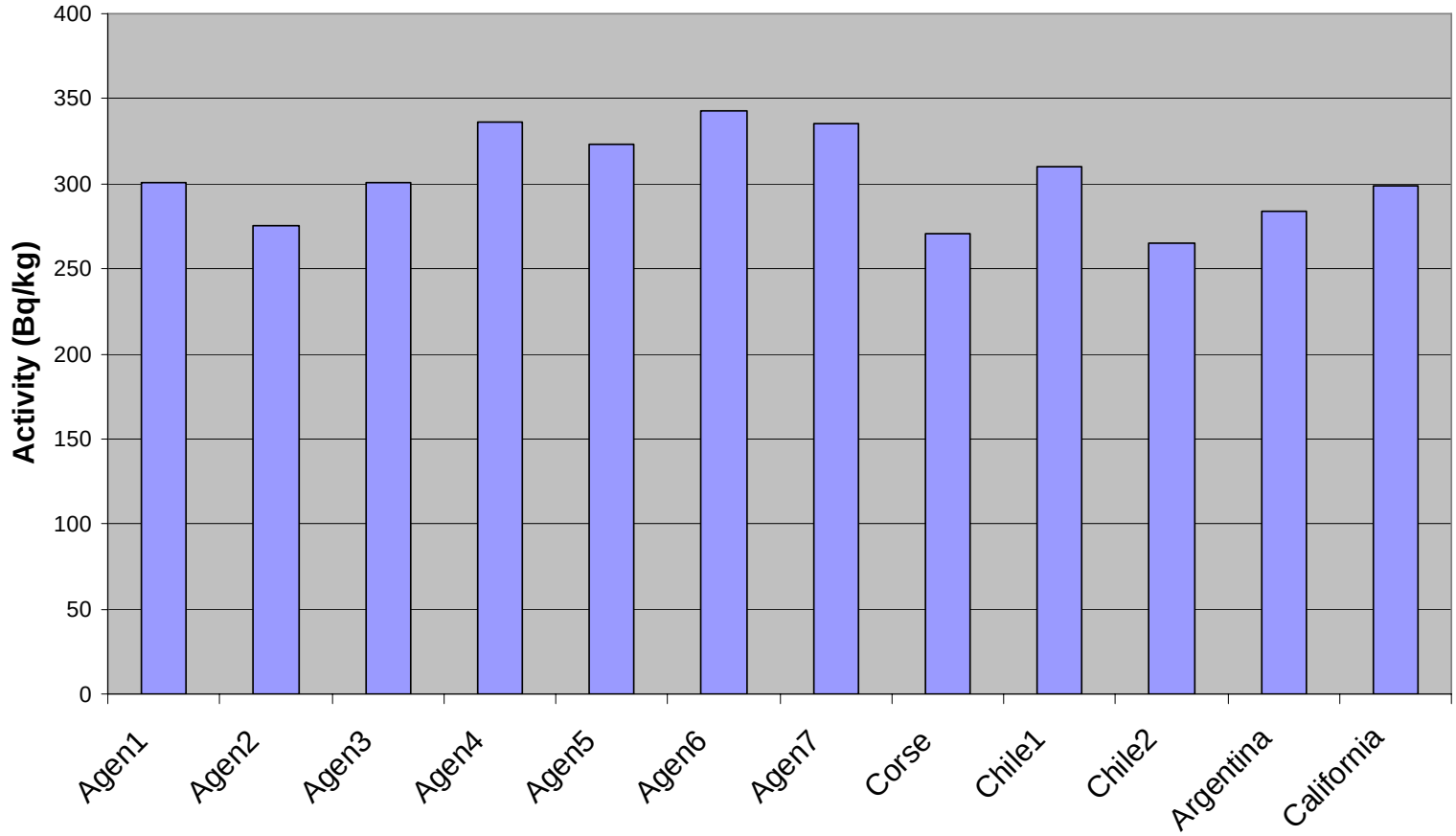


- high ^{40}K activity (300 Bq/kg!!) ➡ huge background due to Compton scattering and Bremmstrahlung effect

- traces of ^{226,228}Ra and ^{228}Th : ~80 mBq/kg (3 or 4 order of magnitude less than ^{40}K activity)

- also traces of ^{137}Cs in few samples only from Agen (10-20 mBq/kg)

^{40}K activity



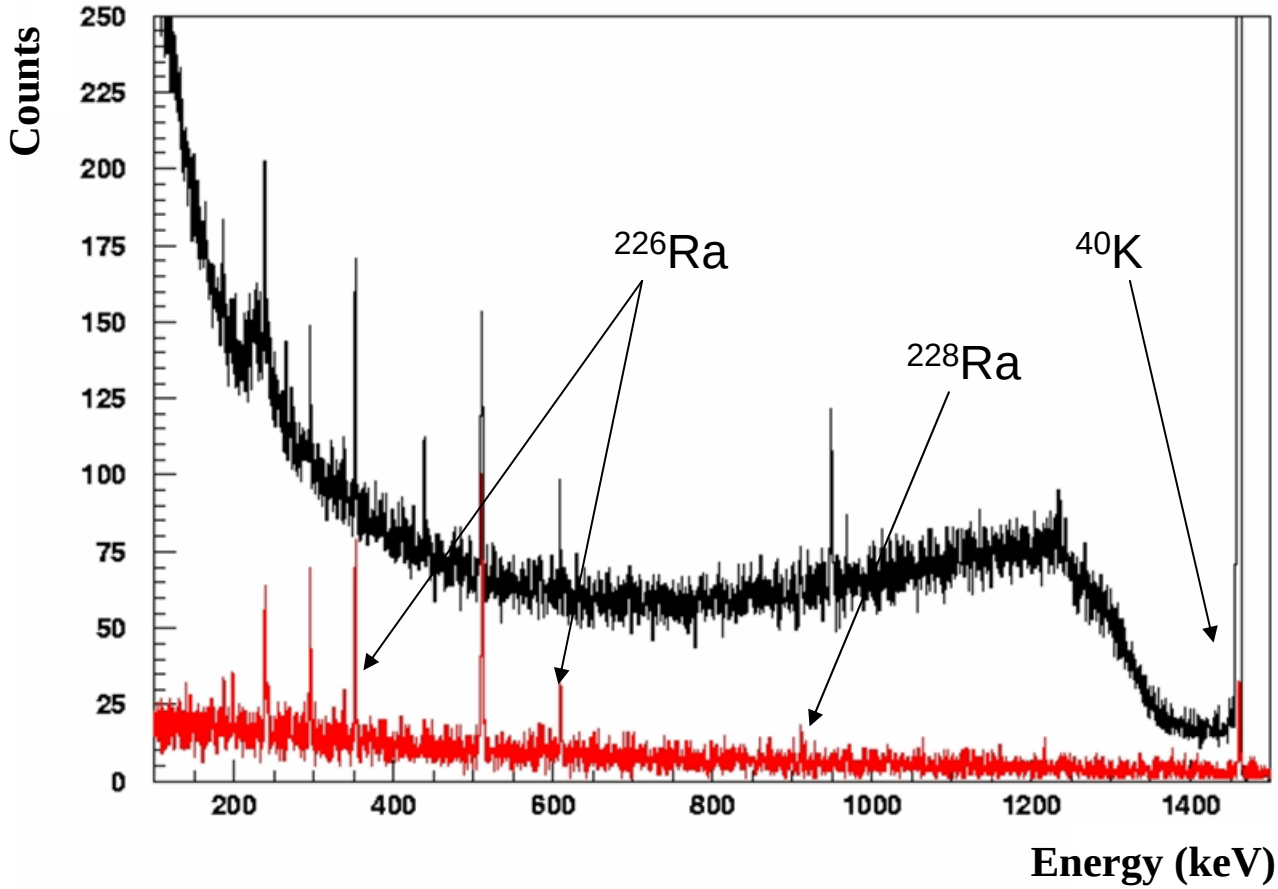
Activity around 300 Bq/kg for all prunes from Agen, Corsica, Chile, Argentina, California

^{40}K not characteristic of the geographical origin

has to be removed to improve the sensibility of the radium measurement

Extraction of the Ra isotopes by radiochemistry

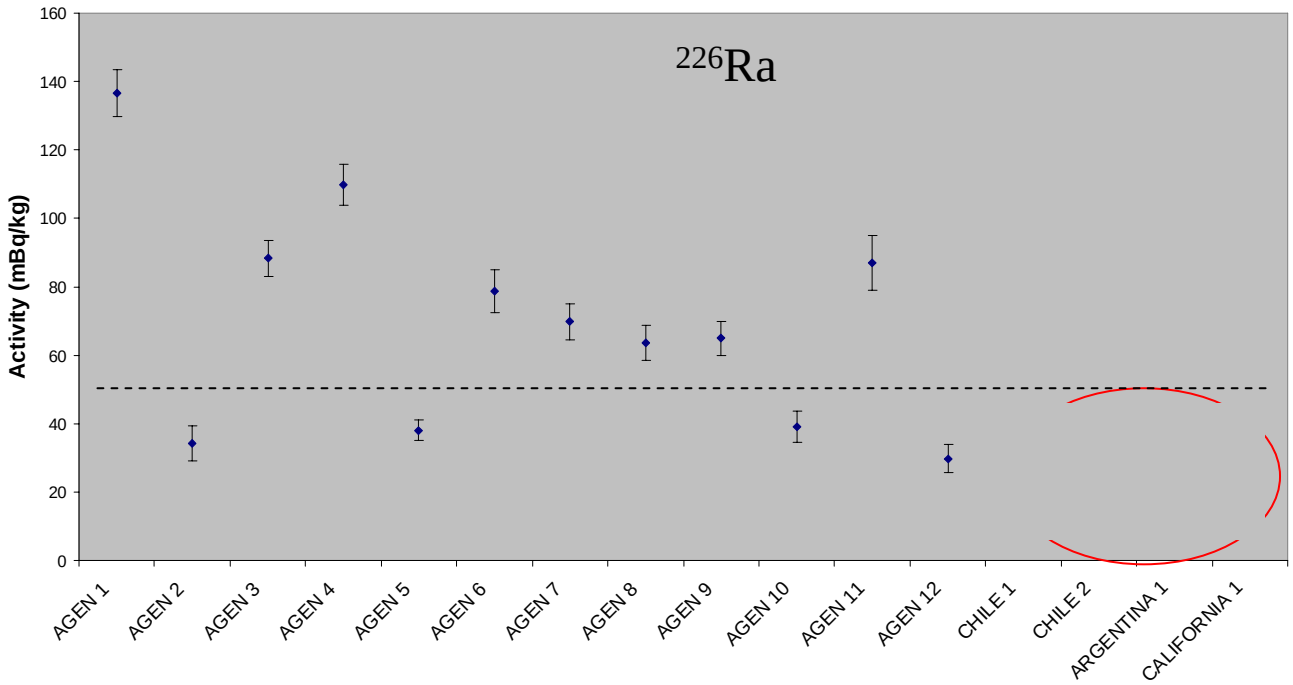
Black spectrum normalized to the red one (after radiochemistry): ~2 days of time acquisition



➡ reduction of ^{40}K activity from 300 Bq/kg to ~0.5 Bq/kg: gain of factor 500

➡ precipitation of radium isotopes with a ~90% chemistry efficiency

^{226}Ra activity distribution after radiochemistry



Prunes from Agen: ^{226}Ra activity distribution between 30 and 140 mBq/kg

Prunes from others countries: ^{226}Ra activity distribution between 20 and 40 mBq/kg

4 samples of Agen prunes cannot be discriminate from others prunes

Summary

Marine salts:

discrimination of the geographical origin seems to work thanks to variations of ^{40}K and ^{226}Ra activity and also presence of ^{137}Cs in the french atlantic coast

➡ specificity of radioactivity measurements for salt flowers: only way to discriminate them

Prunes:

- Radiochemistry performed to extract radium isotopes and removed ^{40}K

  ➡ successful: diminution of the ^{40}K activity by a factor 500 and gain in sensitivity
- No clear separation between prunes from Agen and other prunes

  ➡ low-background gamma spectroscopy doesn't work in that case to discriminate between different geographical origins

Such kind of measurements could be also investigated for coffee or cocoa beans in collaboration with the DGCCRF laboratory

For future environmental measurements, a special set-up with an anti-Compton detector could reduce the huge background due the Compton scattering of the 1460 keV gamma ray from ^{40}K without using complex radiochemistry

Possibility of dating prunes?