ESRF	**Experiment title:** **Search for superheavy elements (SHE) by high-energy X-ray fluorescence**	**Experiment number**: HE - 1473
Beamline: ID15A	**Date of experiment**: from: 12. 3. 2003 to: 19. 3. 20003	**Date of report**: 30. 8. 2003
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The natural radioactive decay chains of the nuclei U-238, U-235, and Th-232 found in the earth's crust are normally in radioactive equilibrium. All isotopes of the chain exhibit the same activity despite the enormous difference of their half- lives (and masses) extending e. g. over 20 orders of magnitude for the U-238 chain. In some minerals, these equilibria are disturbed by geochemical processes. Extreme excesses of short lived isotopes (with small masses proportional to their half-lives) are found what can hardly bee explained by chemical processes alone [2,3]. The most dramatic phenomenon is the existence of the short lived Polonium isotopes of the U-238 chain in very old minerals undisturbed since the time of Precambrium (>600 mio. years) [2] without any long lived predecessor. The Po isotopes can be explained as fission fragments of a hypothetical long lived SHE existing in the mineral (e.g. mica) [3]. Two physical methods are proposed to find the SHE in minerals: high energy XRF and mass spectrometry.

We investigated 11 different minerals at beamline ID15A by means of high energy XRF varying the experimental parameters sample–detector distance, filter, and energy (s. table). All samples were irradiated with synchrotron radiation of 208 keV photon energy and - for time reasons - only 4 samples were irradiated additionally with 192 keV exceeding the calculated K-electron binding energies 205.14 keV of element Z=115 and 190.72 keV of element Z=112, respectively [1]. The appropriate Compton edges at 90° scattering angle are about 147 keV and 140 keV.

The distances were chosen beginning with 78.5 cm and were reduced to 40 cm and 16 cm to get a higher geometrical efficiency. Twelve detectors of the ESRF 13-element germanium detector were used, aligned in 3 vertical columns corresponding to 3 slightly different scattering angles near 90°. The data can be viewed individually or numerically resampled and summed up to one spectrum in order to reduce the statistical error.

A typical spectrum is represented in figure (*Zircon, Carolina) showing the elastic line and the Compton peak which is often the strongest and broadest. A gap with the width of the binding energies is seen between the elastic line and the onset of the Compton peak. At lower energies one finds the characteristic lines of the known heavy elements such as Pb, Th, U. Filters of 0.5 mm Pb and additional 4 mm Cu (s. table) were taken in order to suppress the detection of the huge number of photons with lower energies. Mainly the known characteristic lines are reduced. The peak-to background ratio of these lines around 100 keV decreases which we attribute to the photon scattering in the filters. If characteristic lines were to be observed they lied on the high-energy slope of the Compton peak.

The biggest problem for our investigations was the high background between the Compton peak and the elastic peak, e.g. between 147 keV Compton and the 208 keV elastic peak. In this region the K-x-ray peaks of the SHE about Z = 110 until Z = 115 are expected.

At small distances (16 cm) the different scattering angles about 90±4° for the three vertical detector rows play a role. The background in the interesting region between 150 and 200 keV is clearly less, if the angle is >90° (94°).

For this investigation, those minerals were chosen which form the tiny radio centres (inclusions) of the halos especially the enigmatic Polonium halos e.g. in the mineral mica [2]. Additionally, the samples sea salt and Pb-Cu stone were investigated.

1) The minerals Allanite/Orthite from Madagascar and Norway were irradiated with primary photon energies 208 keV and 192 keV (s. table). Only in the spectrum rs484.xls of the Madagascar sample a very small hint of Z = 114 was found, namely, the $K\beta_2$ line 197.5 keV compared to the calculated value 198.0 keV [1]. But, a sure analysis should yield at least two x-ray lines. The line $K\beta_1$ (192.4 keV) was not seen.
Generally, the background increases in all spectra with an edge of about 5 to 9 keV below the primary energy of the synchrotron radiation. This may correspond to the binding energies of Ti (≈5keV) up to Cu (≈9keV). Therefore, one has a better chance to find the highest x-ray lines $K\beta_2$ and $K\beta_1$ in this low background region. These lines are about 2.5 to 8 keV below the binding energy of the SHE [1]. The strongest lines $K\alpha_2$ and $K\alpha_1$ are hidden under the high background.
2) In the minerals Bastnasite and Euxenite no x-ray lines of SHE's were found.
3) In Monazite from Madagascar hints of Z = 115 ($K\beta_2$ and $K\beta_1$) were found at distance 78.5 cm with and without 0.5 mm Pb filters (s spectra rs122.xls and rs184.xls). But, unfortunately, the counting times were rather short (3.75 h and 2.25 h).
4) The sample Pb-Cu-stone, a fraction from the Pb-ore processing, yielded all the 10 sum peaks from pileup of the 4 Pb x-ray lines (72.8, 74.97, 84.94 and 87.36 keV) in the region 145 –174 keV. But no x-ray line of a SHE could be detected.
5) The sea salt sample produced no SHE x-ray line.
6) The mineral Xenotime from Madagascar gave faint lines of Z = 115 at the distance 78.5 cm: $K\beta_2$ (203 keV) and $K\beta_1$ (197 keV) in the spectrum rs187.xls and only $K\beta_2$ in the spectrum rs125.xls.
7) The mineral Yttrotitanite/Sphene from Norway yielded $K\beta_2$ and $K\beta_1$ lines of the elements Z = 113 and Z = 115 only at long distance (78.5 cm) compared with the calculated x-ray lines [1]. The counting times should be longer.
8) Zircon was often identified as the mineral of the radio inclusions in mica that shows normal Uranium-halos and also Polonium-halos [2a,b]. The lines found in the spectra of Zircon from Carolina (190 and 195 keV) fit best the calculated XRF- energies $K\beta_2$ and $K\beta_1$ (187.8 and 193.3 keV) of element Z=113. Theoretically, the element Z=114 should be more probable.
The Zircon spectra of minerals from Norway and Colorado show no XRF lines.

These very first investigations at the excellent ESRF facility are very promising. However, they are only hints for the characteristic lines of the SHE. In order to trace an element for sure, statistics has to be increased dramatically and several characteristic lines have to be observed simultaneously. Once, a whole pattern is found, experimental parameters have to be changed systematically in order to ensure its reality. Therefore we conclude it is worthwhile to continue this kind of search for SHE in the minerals mentioned.

[1] Th. A. Carlson and C.W. Nestor: Calculation of K and L X-rays for elements of Z=95 to 130. At. Data Nucl. Data Tables19 (1977)153-173.
[2] a) G.H. Henderson and F.W. Sparks: A quantitative study of pleochroic haloes IV., New types of haloes, Proc. Roy. Soc. of London/A 173(1939)238.
b) R.V.Gentry: Radioactive Halos, Ann. Rev. Nucl. Sci. 23(1973)347.
c) N.Feather: The unsolved problem of the Po-haloes in Precambrian biotite and other old minerals, Communications Roy. Soc. of Edinburgh 11(1978) 147.

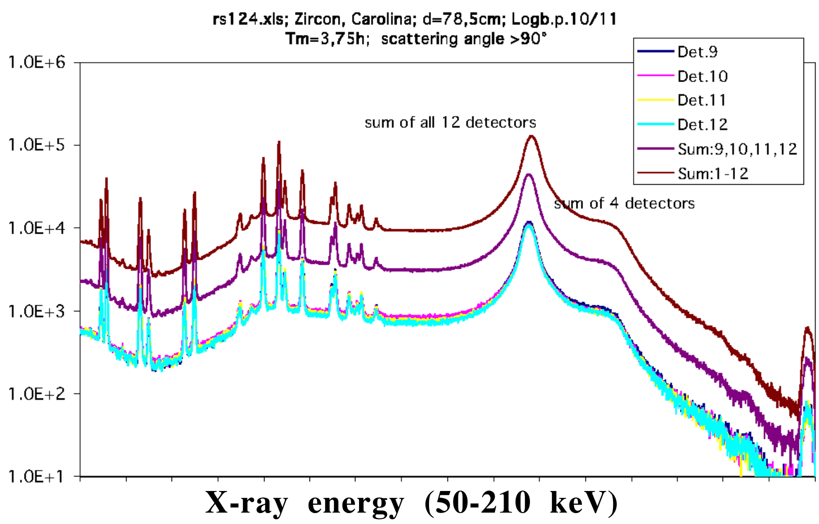

Figure: Typical spectrum showing the elastic peak to the left (208 keV). The main intensity is the Compton background peaking at 148 keV. Characteristic lines for the known heavier elements are seen at the low-energy-end of the spectrum.

Survey over the XRF measurements at beamline ID15 A at ESRF in Grenoble 12 March until 19 march 2003

Each sample is located in a washer fixed between plastic films during exposure of high energy synchrontron radiation

Sample Provenance	**approximate composition plus admixtures**	**density g/ccm**	Spectrum No.	**Log book**	**radiation** energy [KeV]	**Filter**	**distance** sample -det.	**measuring time** Tm	**remarks** possible SHE K-lines
Allanite, Orthite	(Ca,Ce)2(Al,Fe3+)3(SiO4)3(OH)	3.3 - 4.2	rs484.xls	p.28 and p. 33	208 KeV	0.5mm Pb +	16 cm	4.75 h	Z=114 (only Kβ2)
Tsarartra, Madagascar	REE,Y,Th,U,Na,K,Mg,Sr,Mn,Ti,Pb etc					4mm Cu			
Ce-rich			rs558.xls	p. 29 and p.33	**192** KeV	0.5mm Pb +	16 cm	4.75 h	...
						4mm Cu			
Allanite, Orthite,			rs485.xls	p.28 and p. 33	208 KeV	0.5mm Pb +	16 cm	4.5 h	...
Flekkefjord,Norway						4mm Cu			
			rs559.xls	p.29 and p.33	**192** KeV	0.5mm Pb +	16 cm	4.75 h	...
						4mm Cu			
Bastnasite	Ce[F/CO3]	4.9 - 5.2	rs399.xls	p. 26	208 KeV	0.5mm Pb +	16 cm	5.25 h	...
Ambrositra, Madagascar						4mm Cu			
Euxenite	(Y,Er,Ce,U,Pb,Ca) -	variable	rs291.xls	p.20/21	208 KeV	0.5mm Pb	16 cm	5.25 h	...
Itrongay, Madagscar	- [(Nb,Ta,Ti)2(O,OH)6]		rs400.xls	p.26	208 KeV	0.5mm Pb +	16 cm	5.25 h	...
	(together with Zircon)					4mm Cu			
Monazite XLS	Ce[PO4]	4.8 - 5.5	rs122.xls	p. 11	208 KeV	no filter	78.5cm	3.75h	Z=115: Kβ2, Kβ1
Madagascar	REE,Th,Ca,Si etc		rs184.xls	p. 12	208 KeV	0.5mm Pb	78.5 cm	2.25h	Z=115: Kβ2, Kβ1
			rs217.xls	p. 17	208 KeV	0.5mm Pb	40 cm	3.25h	...
			rs276.xls	p. 19	208 KeV	0.5mm Pb	40 cm	10596 s	...
			rs290.xls	p. 21	208 KeV	0.5mm Pb	16cm	5.25 h	beam size = 2x3 mm
Pb-Cu-Stone	Pb, Cu etc	≈3	rs293.xls	p. 20 - 23	208 KeV	0,5 mm Pb	16 cm	5.0 h	all sum peaks of lead
	from Pb-ore processing	(cast density)							(especially for angle>90°)
Sea salt	freeze dried (40g/l)	...	rs487.xls	p. 28 u.33	208 KeV	0.5mm Pb +	16 cm	4.5 h	...
Pacific Ocean	many elements								
Sample VA13-1			rs561.xls;	p.28/29	**192** KeV	0.5mm Pb +	16 cm	4.5 h	...
						4 mm Cu			
Xenotime	Y[PO4]	4.4- 5.1	rs125.xls	p.10/11	208 KeV	no filter	78.5 cm	3.75 h	Z=115: only Kβ2
Madagascar	REE, Th, U, Zr, Sn,Si,S		rs187.xls	p.12	208 KeV	0.5mm Pb	78.5 cm	2.0 h	Z=115: Kβ1, Kβ2
			rs220.xls	p.17	208 KeV	0.5mm Pb	40 cm	3.25 h	...
Yttrotitanite/Sphene	Ca,Ti,SiO5 with Y-content	3.3 - 3.6	rs123.xls	p.10	208 KeV	no filter	78.5 cm	4.0 h	Z=115: Kβ1, Kβ2
Toedestrand, Norway	Fe,Mn,Mg,Al,Cr,Zr,Nb, REE etc		rs185.xls	p.12	208 KeV	0.5 mm Pb	78.5 cm	2.0 h	Z=115:..;Z=113: Kβ1, Kβ2
			rs218.xls	p.17	208 KeV	0.5mm Pb	40 cm	3.25 h	...
			rs486.xls	p.28	208KeV	0.5mm Pb	16 cm	4.5 h	...
						4 mm Cu			
			rs560.xls	p.29	**192** KeV	0.5mm Pb	16 cm	4.75 h	...
						4 mm Cu			
Zircon	ZrSiO4	4.3 - 4.8	rs124.xls	p.10/11	208 KeV	no filter	78.5 cm	3.75 h	Z=113: Kβ1, Kβ2
Carolina	Hf,Y,REE,P,Nb,Ta,Th,Al,U,Fe,Ca	...	rs186.xls	p.12	208 KeV	0.5 mm Pb	78.5 cm	2.0 h	Z=113: Kβ1, Kβ3
			rs219.xls	p.17	208KeV	0.5 mm Pb	40 cm	3.25 h	...
Zircon			rs292.xls	p. 20-22	208KeV	0.5 mm Pb	16 cm	5.0 h	...
Norway			rs401.xls	p.26	208KeV	0.5 mm Pb +	16 cm	5.25 h	...
Tjötting near Larvik			...			4mm Cu			
Zircon: Cyrtolite			rs402.xls	p.26	208KeV	0,5mm Pb +	16 cm	5.0 H	...
Jefferson, Colorado	(radioactively changed)					4mm Cu			