Perspectives of the ultra-pure titanium as construction material for future low background experiments

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Current status of the problem

Construction materials characteristics

- Mechanical properties
- Radiopurity figures
- Availability in bulk quantities
- Cosmogenic activation properties
- Price

Candidates in use:

- Copper (electroformed)
- Stainless steel (preselected)

Candidates in limited use:

- Titanium (preselected)
- ??? Other metals and alloys
  (Al, Ni, Zr …..)

WEB resources :

- ILIAS program, European project for the development of the underground science. http://radiopurity.in2p3.fr/
- UK DM project: radioactivity test results http://hepwww.rl.ac.uk/ukdmc/Radioactivity/Index.html
- Low Radioactivity Techniques 2004 — LRT-2004/2006/2010/2013 … workshops
- GOOD SHORT REVIEW: *V. Alvarez, I. Bandac, A. Bettini et al Radiopurity control in the NEXT-100 double beta decay experiment: procedures and initial measurements arXiv:1211.3961v3 [physics.ins-det] 25 Jan 2013*

Driving original facts for our project :

One of the critical (crucial) goal of any low background experiment including DM search is to achieve as low background as possible by decreasing of natural radioactivity of materials which are used for detector construction. So, it means that <u>material selection is extremely important and in some cases critical for an experiment success</u>.

Not too many useful figures for construction materials avaliable, impossible to compare because of absence of "standardized procedures"

(Why ? HPGe is very slow and differs from each other, ICP MS is state of the art technique when we trace impurities below sub-ppb)

.....

The main and only one method which everybody use (say that use) to select (to order) the material is to study samples of stainless steel (or whatever) which supply steel producers from different batches

Why Ti ?

1) It is well known construction material which is widely used in critical applications in such areas as aerospace (mainly), cryogenic, chemistry, medicine, nuclear industries.

2) It was shown before that it could be extremely clean :

LUX was the first experiment which use Ti cryostat

D. S. Akerib et al., Radio-assay of Titanium samples for the LUX Experiment , arXiv:1112.1376 [physics.ins-det].

Who else consider(ed) to use Ti :

LUX/LZ (do stainless steel and Ti design in parallel)

NEXT-100 *V. Alvarez, I. Bandac, A. Bettini et al arXiv:1211.3961v3 [physics.ins-det] 25 Jan 2013*

Dark Side- (after 50)

who else ???? (would appreciate for additional information)

3) The hypothesis was offered that it could be manufactured very clean in big quantities and Russian Ti-industry could be the source of such clean titanium.

The main goal of the "Titanium project"

- to provide DarkSide experiment with ultra-pure construction material in the required quantity thinking about tons-scale detector and above

- to investigate a possibility **to manufacture ultra-pure Ti** and parts from it with the following levels of contaminations:

[fundamental] - 238U < 1 mBq/kg (equivalent to < 0,100 ppb)

[fundamental] - 232Th < 1 mBq/kg (equivalent to < 0,250 ppb)

[less important] - 40K < 1 mBq/kg (equivalent to < 40 ppb)

Steps on the way ….

Step 1. To find a source of ultra pure metal titanium

- To study current titanium-containing products and industrial production cycle(s) being focused on the U/Th contaminations
- To develop if necessary a production cycle which guaranty necessary level of contaminations due to its controllable or, at least, traced migration.
- To develop new or improve existing Ti production plant of the scale match the ultra pure Ti needs.

Step 2. To manufacture necessary parts and whole assembly from ultra pure titanium

To develop procedure and organize mechanical workshop to manufacture the separate parts of a cryostat or the whole cryostat from ultra pure titanium and avoid extra contaminations on this way.

Structure of the World Ti use

- **95% TiO_2 or titanium white**
  - **57% coloring agent for best white colors**
  - **21% plastics**
  - **14% paper**
  - **8% ceramic, catalisators etc.**
  - **<1% - (99,999) fiber optic, microelectronics, pharmacy**

- **5% titanium roll, parts (including Ti-sponge as intermediate product)**
  - **Ti-alloys and non-ferrous alloys with Ti addings - parts for machinery mainly for aerospace industry, nuclear power plants, submarines, medicine, cutting tools etc.**

- **< 1 %**
  - **ferrotitanium in steel production for deoxi and desulphurisation (introduce 0,03-0,2% of Ti in the form of ferrotitanium with Ti 18-25%)**
  - **welding electrodes**

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Consumer Edition - January 2015

Aerospace Edition - September 2014

Medical Edition - March 2014

Industrial Edition - May 2014

Ti-alloys industry trends

"The current effort of main business players is focused on "full breath" of **global titanium supply chain** : feedstock, sponge, master alloys, mill products, part production and scrap.

...

Current state of Ti industry is considered as "unprecedented potential opportunities" due to a record backlog order levels for commercial jets…. Overall, commercial jets represent a demand level of 40 million pounds **(~20kt)** of titanium between now and 2018…. there are over **10,000** large commercial jets in the backlog, with aerospace giants Airbus and Boeing accounting for nearly 94% of the total (one A380 needs ~ 90 t of Ti) "

(TITANIUM USA 2013 Summary International Titanium Association October 6-9, 2013 Las Vegas, Nevada USA)

Russian Ti status

VSMPO-AVISMA **- Boeing - 40%, Airbus - 60%, Embraer –100%**

~35% of world aerospace grade Ti market

Competitors : RTI International, Titanium Metals Corporation & Allegheny Technologies

Very busy and self-sufficient worldwide business

Ti industry R&D activity
(as a reflection of global trends and motivations)

- Development of new Ti processes to reduce Ti self-cost (target is 8 $/kg) to replace up to 10% of stainless steel which self-cost couldn’t be reduced and will only increase

  (Energy consumption efficiency due to less energy for production and less weight of the product (transport systems etc.))

- Depletion (less important) and rice in cost (more important) of mineral resources which makes Ti production less profitable and increase the end product cost.

  (New process for polymetal ores)

- Ti alloys recycling processes development

More than 10 different new technologies of Ti metal production are under development now worldwide

Metal Ti production cycles

Ti slag

TiO2

LiquidTiCl4

Metal – reducing agent

Electrochemical

«Boston University-Solid Oxide Membrane (SOM) Process»

«Avanti Metal» (MIT)

«BHP Billiton Innovation PTY LTD»

«DuPont и Materials & Electrochemical Research Corp.»

«FFC-Cambridge- Process

«Quebec Iron & Titanium Inc.» (QITI)»

Ti powder

Ti parts

Metalothermy

Kroll (Mg) -100% of industry

Molten salts (Mg)
TiRO- Process (Mg)
«Armstrong-процесс (ITP)» (Na)
Flamed (gase phase) (Na)
Mechanochemical nanopowder (ball mill)

Ti sponge

Ti n-powder

Ti parts

Plasmochemical

Ti hydride powder **very clean**

Gas phase Metalothermy with AlClx

Ti powder **very clean**

What are the natural (re)sources of Ti.

Ores:

Ilmenite I (FeO * TiO_2) - 43,7-52,8 % TiO_2

Rutile, Anatase, Brookite 94,2-99,0 % TiO_2

Loparite 38-41 % TiO_2 **(Na,Ce,Ca,Sr,Th)(Ti,Nb,Fe)O_3**

Perovskite 59 % TiO_2

Titano-Magnetite

beaches and alluvial sands - commercial development worldwide but **<20%** of world resources

bedrock deposits in ores belong to the intrusive rock **>80%** of world resources

Natural concentration of U/Th "gabbro" U - $0.6*10^{-4}$ % Th - $1.8*10^{-4}$ % or
"syenite" U – $(4.1\text{-}10.3)*10^{-4}$ % Th – $(7.2\text{-}28.3)*10^{-4}$ %

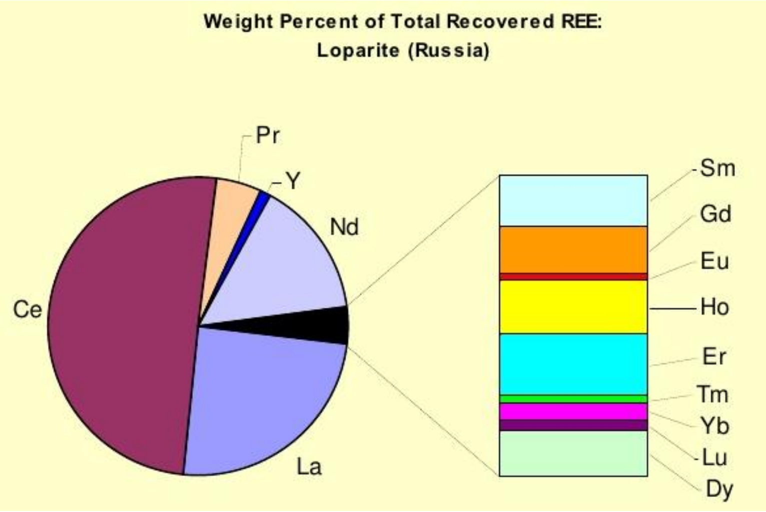
Natural Ti concentrate has natural U/Th radioactivity which depends on the source of the concentrate which is impossible to trace on the stage of Ti metal production

What are the natural sources of Ti.

Ilmenite

Rutile concentrate

Loparite



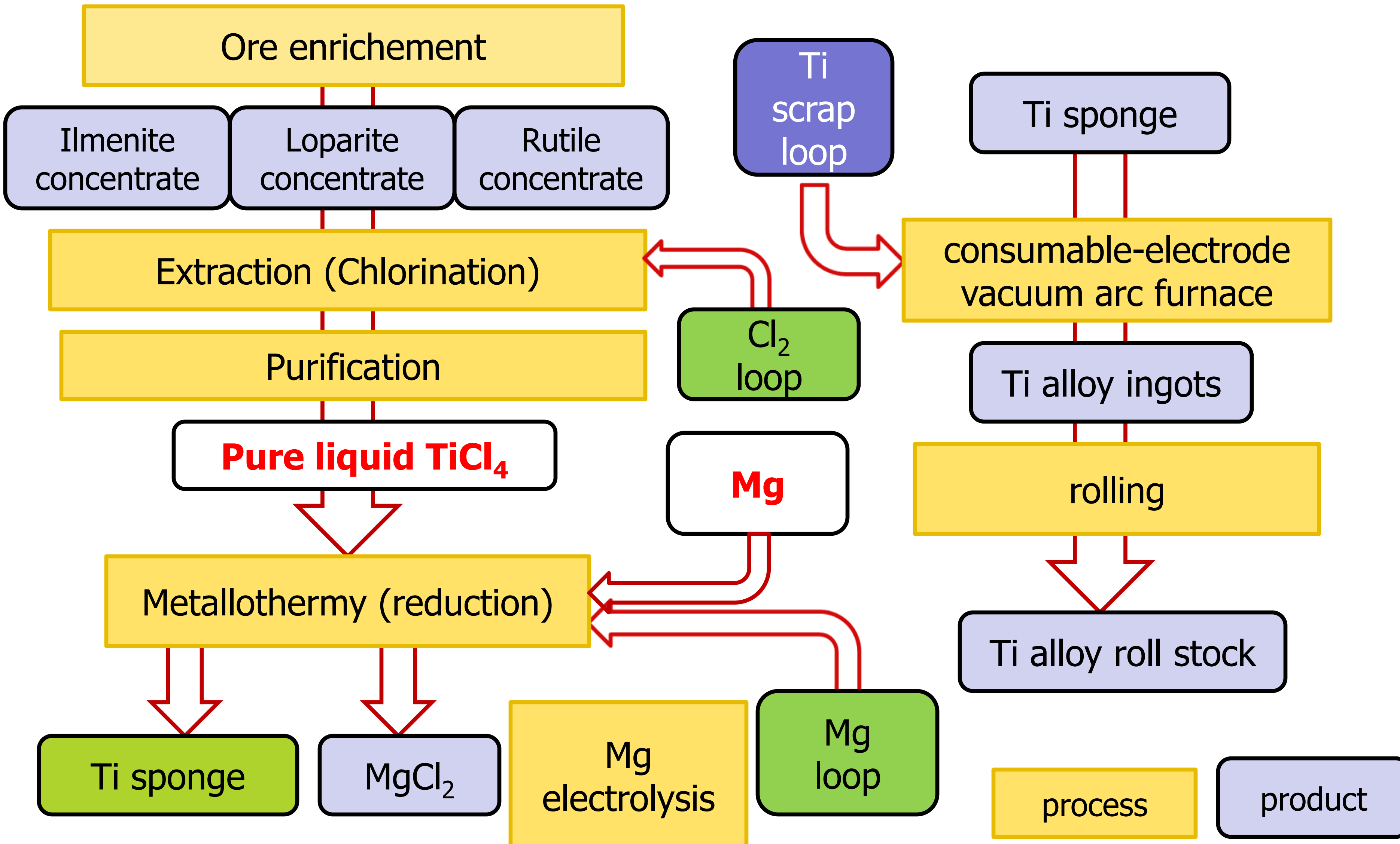
Lovozersky GOK (belongs to SMP), 100% of mineral resources of rare earth and rare metal of Russia

Rare metal - Nb, Ta

<u>Ti as a "side product"</u>

Kroll-based industrial production cycle

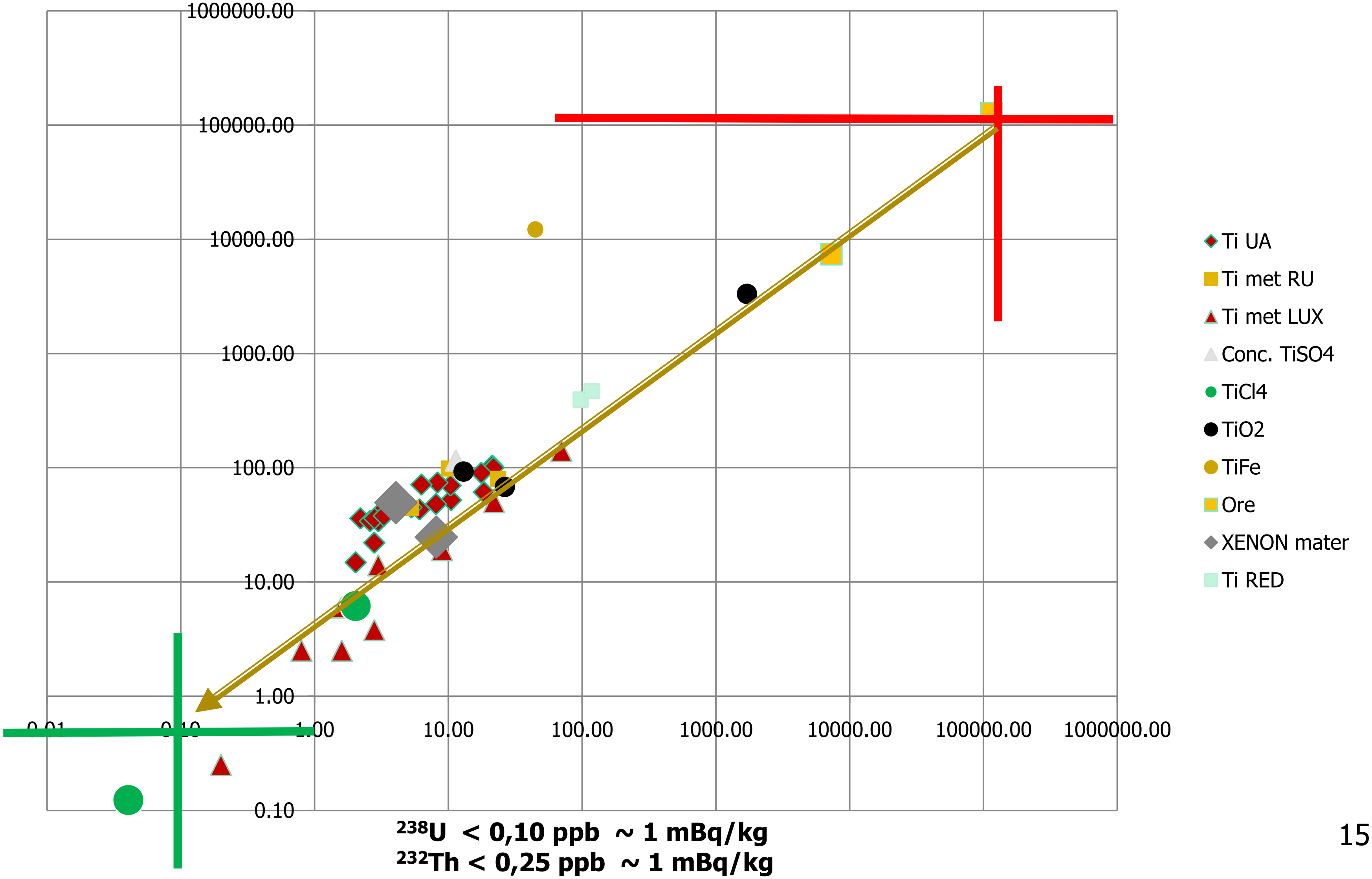
Two simple products are used to produce Ti sponge !!!



First stage results (2012)

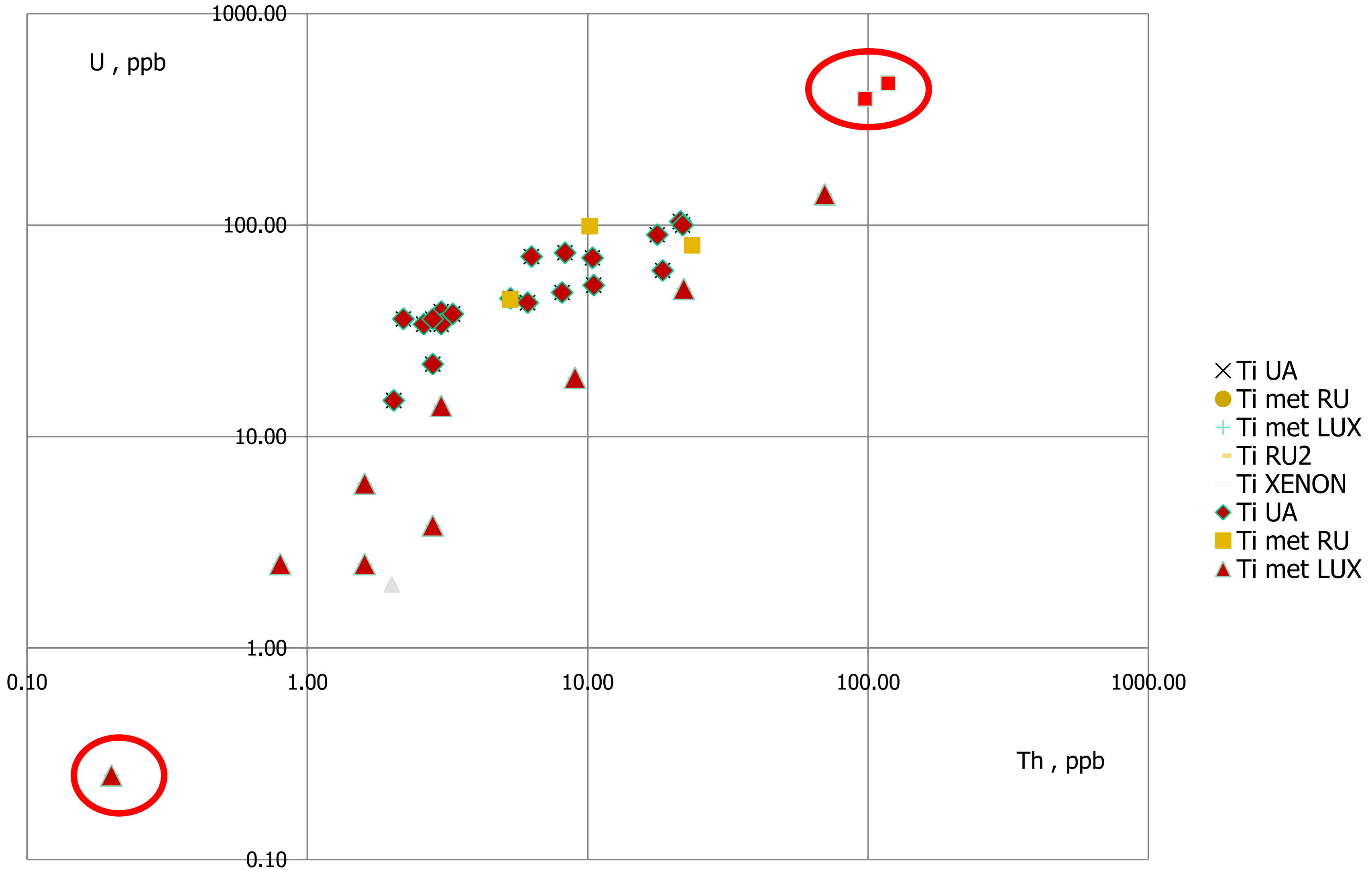
Results from literature and LNGS measurements. Different Ti-containing substances from ore through metal samples to ultrapure $TiCl_4$ for fiber optics (data from supplier spec.).

6 orders of magnitude of U/Th concentration !



^{238}U < 0,10 ppb ~ 1 mBq/kg
^{232}Th < 0,25 ppb ~ 1 mBq/kg

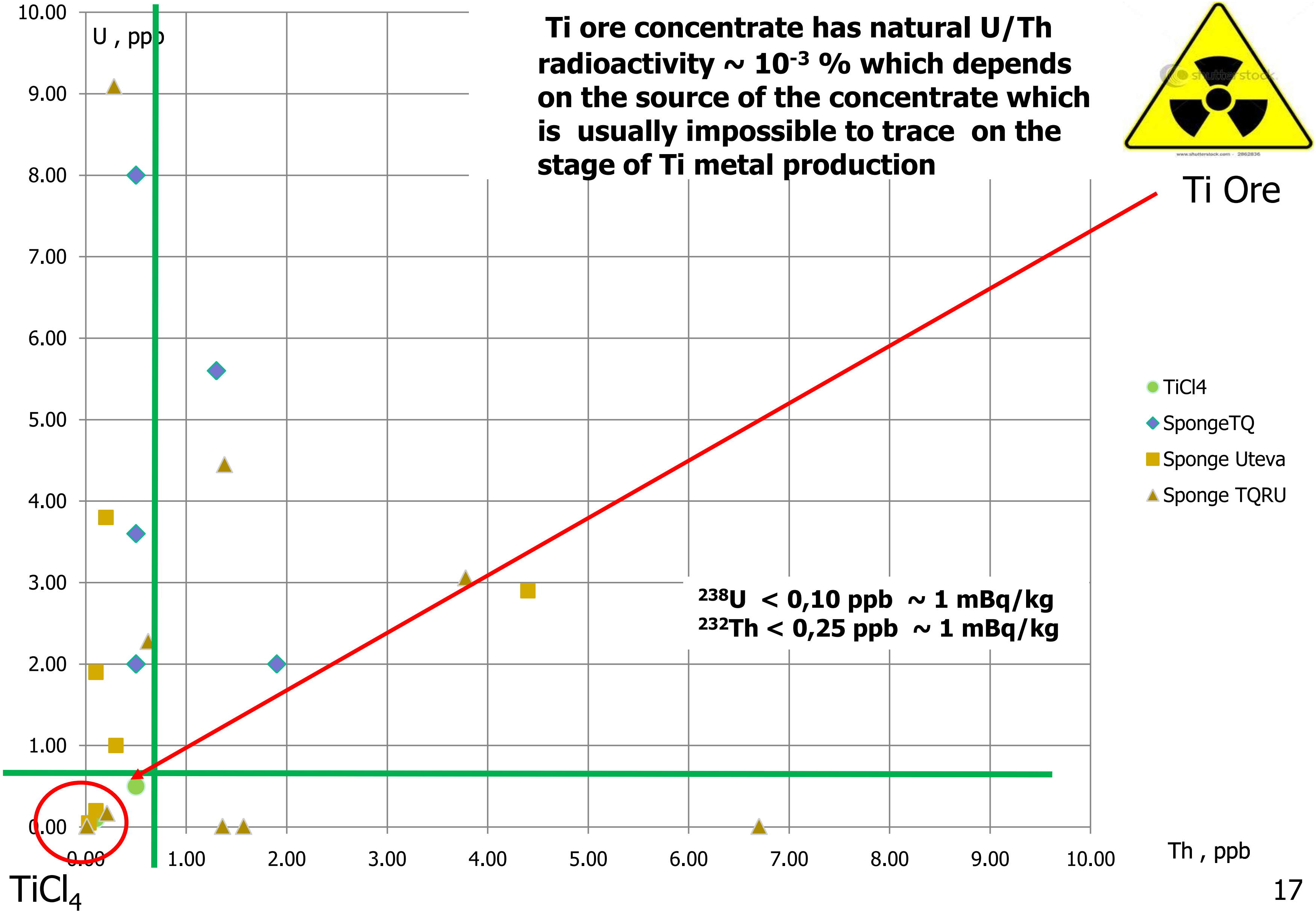
First stage results (2012)
Ti metal samples from different sources U/Th (~4 orders !)



Why it is so widely distributed? Where is the source of U/Th

Second stage results (2013)
TiCl4/Ti sponge samples from different sources- promising analysis results

Ti ore concentrate has natural U/Th radioactivity ~ 10^{-3} % which depends on the source of the concentrate which is usually impossible to trace on the stage of Ti metal production

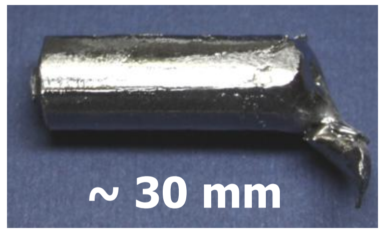


^{238}U < 0,10 ppb ~ 1 mBq/kg
^{232}Th < 0,25 ppb ~ 1 mBq/kg

Ti project roadmap.

Theory of Ti | Ti-sponge | Ti-samples | Ti-ingot/Ti-roll | Ti-parts

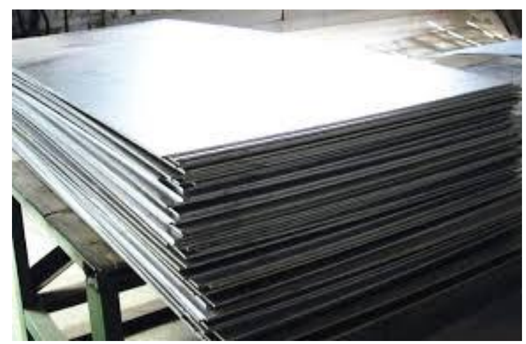
Ti samples study



2012

2013

2014



JSC "Solikamsk Magnesium Plant"

Nonstop operation since 1936
54% of Russian Mg and Mg alloys
100% of Russian rare earth & Nb, Ta

Youngest and most modern (5 years old) Ti-sponge production plant

Solikamsk Magnesium Plant hopefully is unique place all over the World for our "Ti project"

- Produce Mg (knows all about it)
- Produce $TiCl_4$ (as side product with unique original technology)
- Produce Ti sponge (most modern and unique plant in Russia)
- People are flexible and science-oriented

Chief engineer of SMP - Dmitry Melnikov, Alexander Chub, Andry Patrakov, Alexander Dernov, Irina Vaal

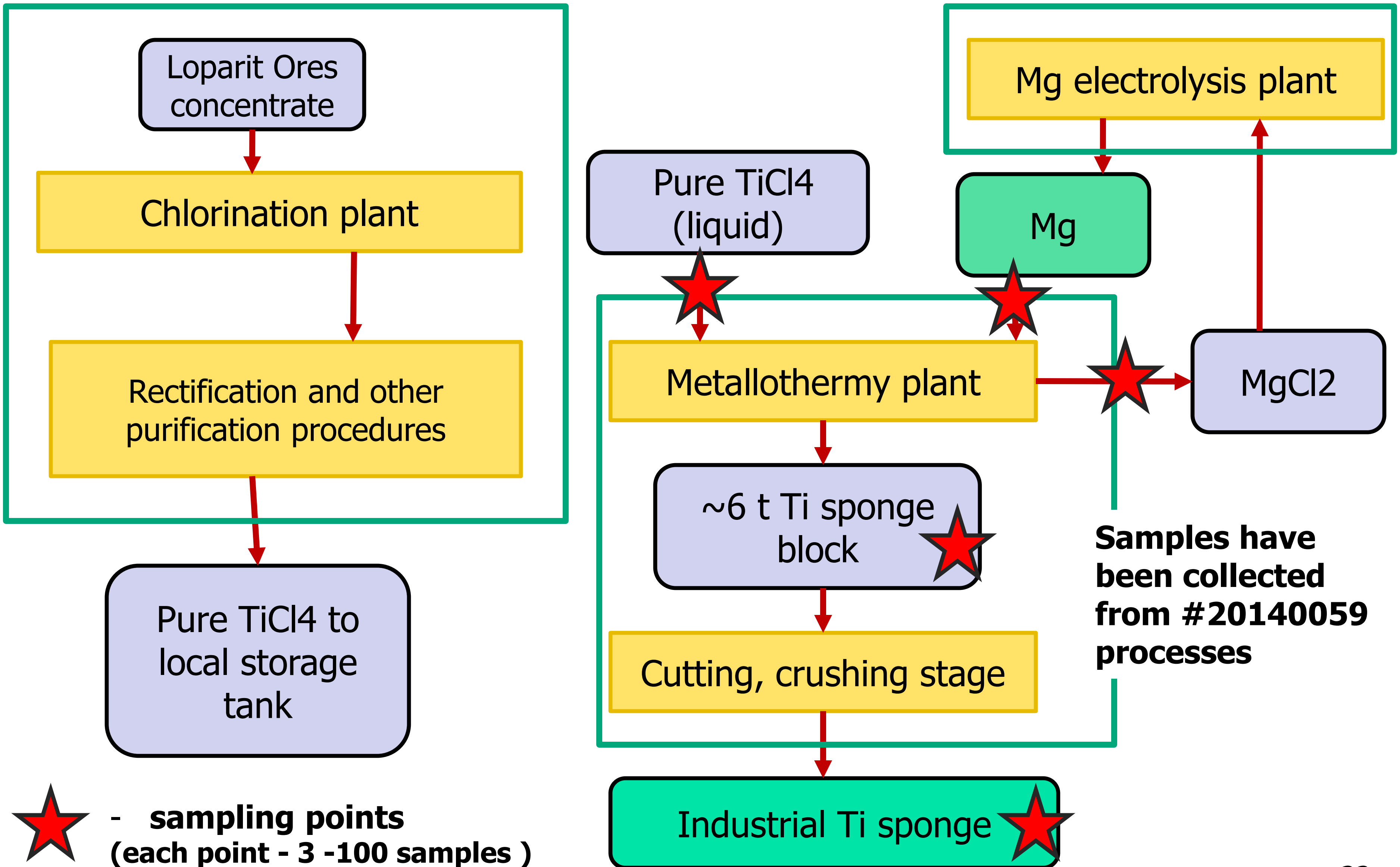
- More or less independent

(possible to negotiate about R&D)

“Ti sponge study program” purposes :

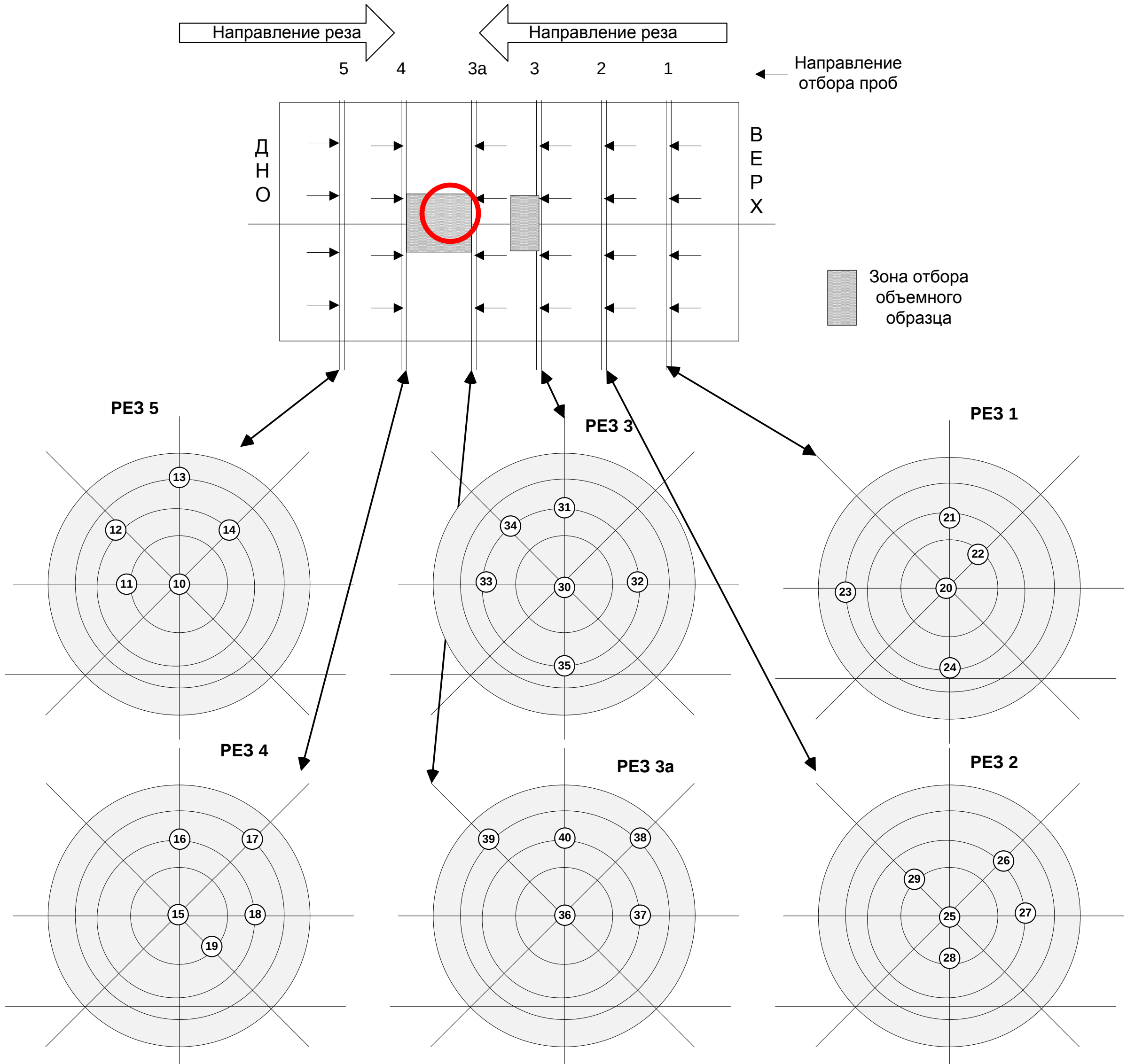
- to determine mass balance of impurities of chemical elements in the titanium sponge with special attention to the U/Th/Pb;
- to study the spatial distribution of chemical impurities (with special attention to the U/Th/Pb) in the block of titanium sponge in order to try to localize the area with acceptable U/Th concentration below 1mBk/kg;
- to explore possible sources of secondary contamination of titanium sponge with uranium and thorium at the stage of cutting of the block to a commercial product

Solikamsk Magnesium Plant Ti sponge production cycle



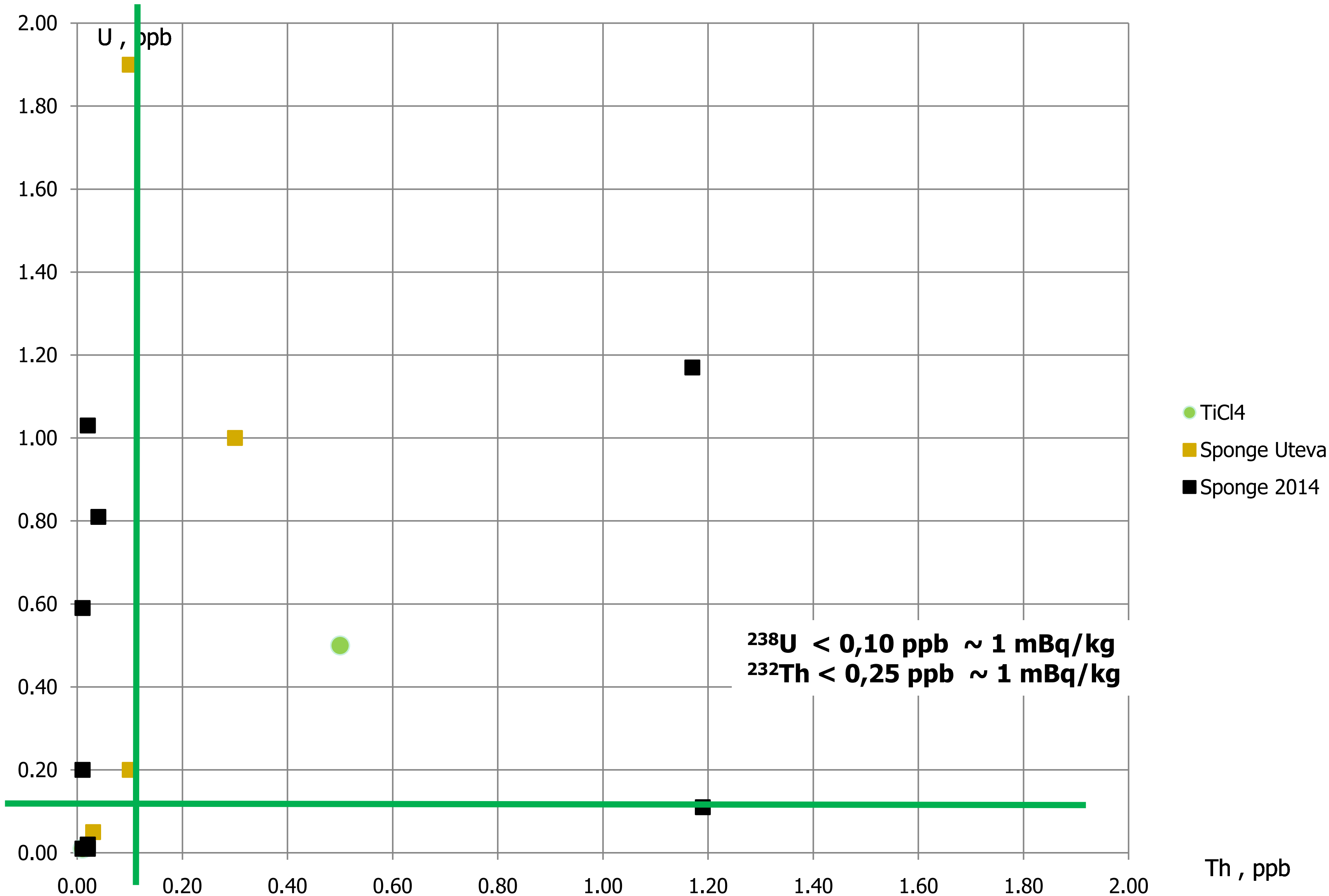
SMP Ti sponge block - 2014 analysis program

#20140059 Ti sponge block ready for cutting (~6 tons)

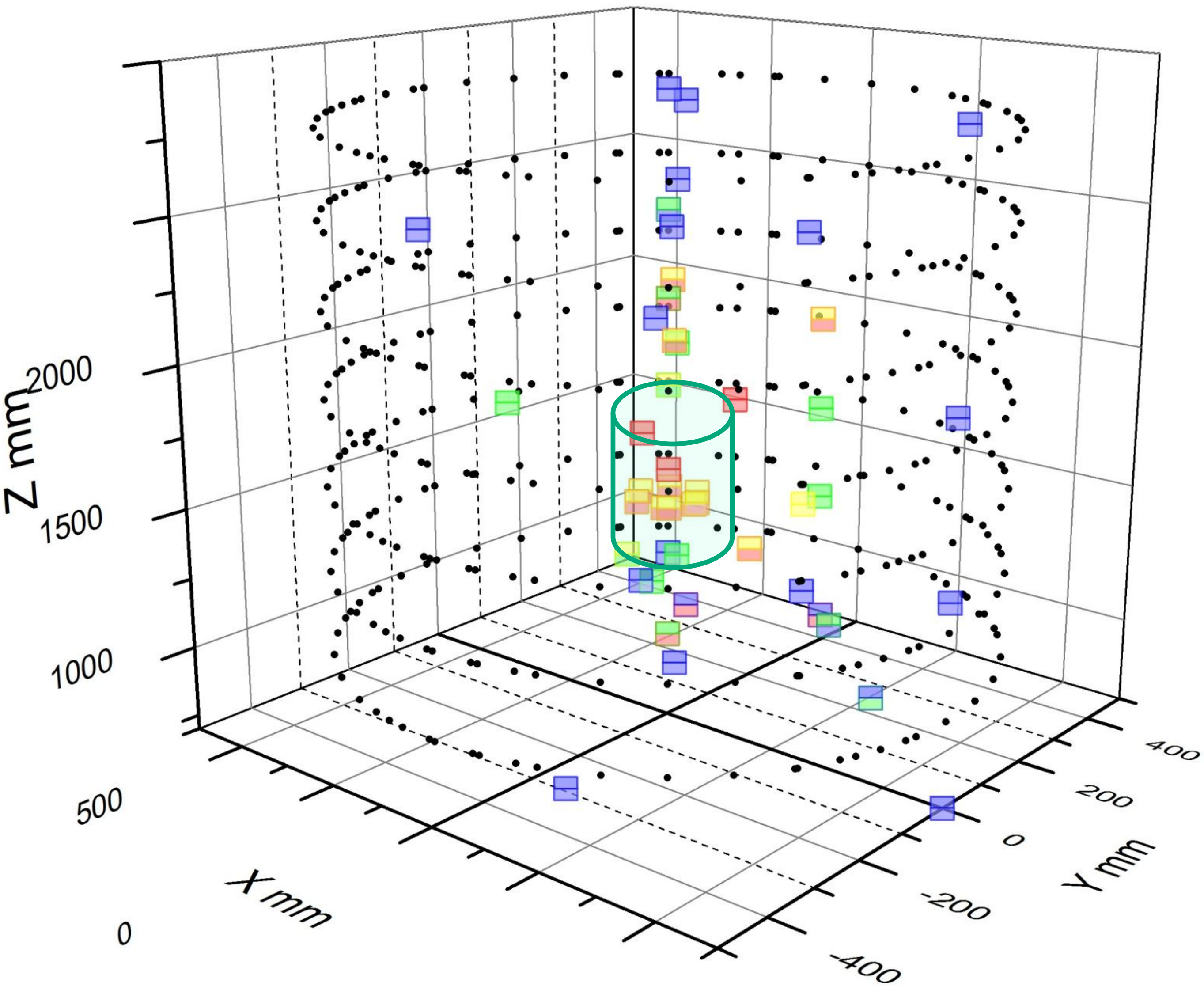


Scheme of Ti sponge block cutting and sampling

Third stage 2014 SMZ TiCl4/Ti sponge - confirmation of the hypothesis – there are clean areas

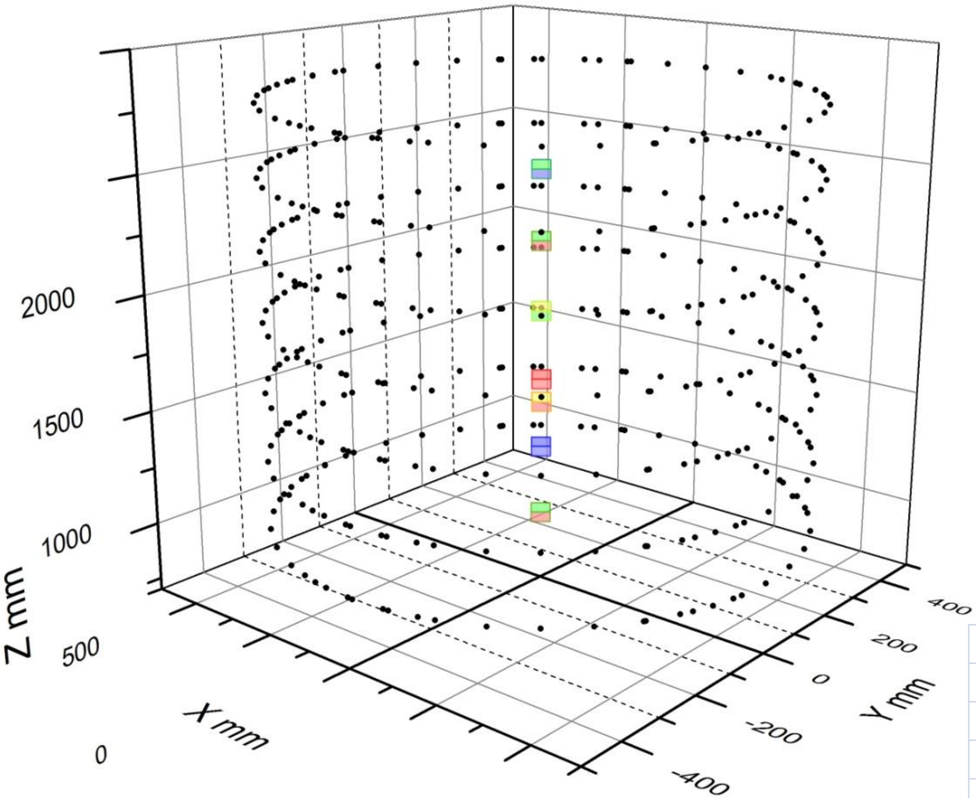


Sponge block. Distribution of U/Th impurities. 3D view of collected samples

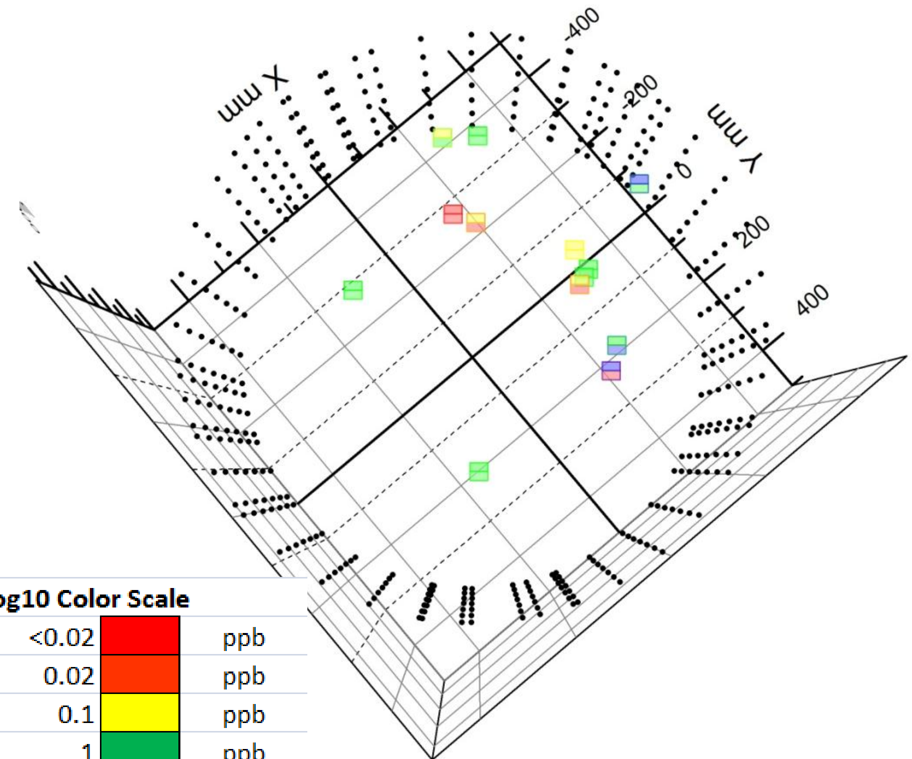


Log10 Color Scale		
<0.02		ppb
0.02		ppb
0.1		ppb
1		ppb
10		ppb
>100		ppb
Th		
U		

Sponge block. Distribution of U/Th impurities.
Other 3D views of collected samples



R=0



Log10 Color Scale		
<0.02		ppb
0.02		ppb
0.1		ppb
1		ppb
10		ppb
>100		ppb
Th		
U		

R>=250 mm

<u>Preliminary results:</u>

-the spatial distribution of impurities is not homogenous (as expected)
- incoming U&Th stay absorbed in the sponge
- there is more clean area in the center

First conclusion from 2012-2014 :
Ultra clean Ti sponge could be produced by Kroll process in bulk quantities if the original materials will be also clean.

BUT !

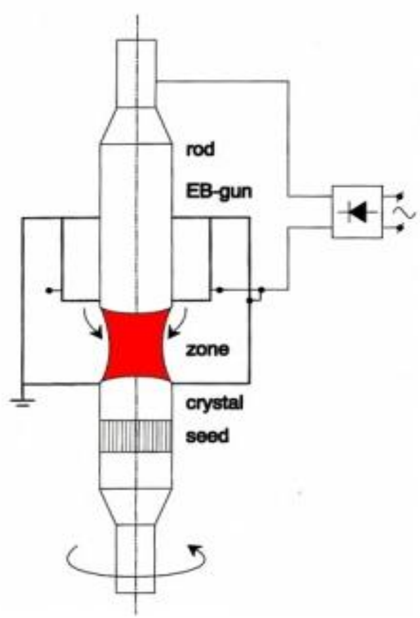
Ti sponge is not a metal Ti

High purity refractory metals – theory, experiment, melting and cleaning facilities in Institute of Solid State Physics, RAS (Chernogolovka, Russia)

(*Vadim Glebovsky, Eugenie Shtinov*)

- Electron beam industrial furnace;
- **Electron-beam furnace ELO 60**
- Vacuum arc furnace I;
- Vacuum induction furnace;
- **Two units of electron-beam zone melting allowing a single crystal of tungsten and molybdenum and titanium with a diameter and a length of 30 to 900 mm**
- **Apparatus for levitation melting in vacuum.**

Electron-beam floating zone melting (EBFZM)



Dross (scoria) samples which are interesting to study for impurities migration

One of Ti ingot received by “creek” vacuum electron beam melting

Iodide Ti ingot partly used to cover chamber to prevent recontamination

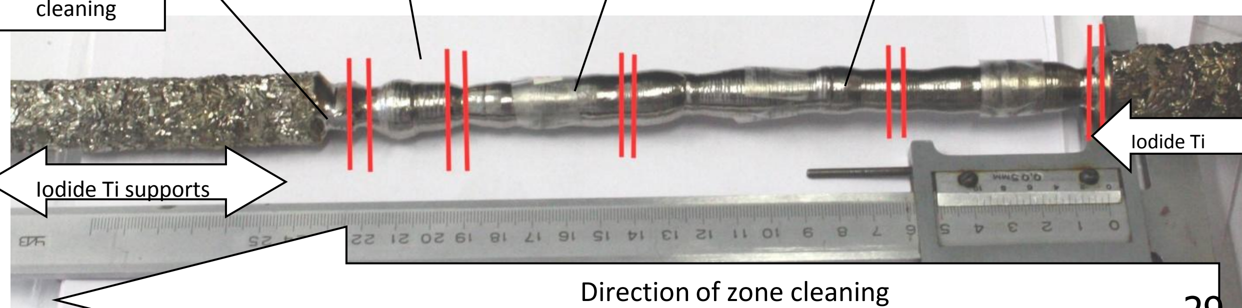
Welded construction from “creek” ingot (at the center) and iodide Ti supports after zone cleaning

One stage zone cleaning

Two stage zone cleaning

Three stage zone cleaning

Original “creek” ingot cleaning



Iodide Ti supports

Iodide Ti

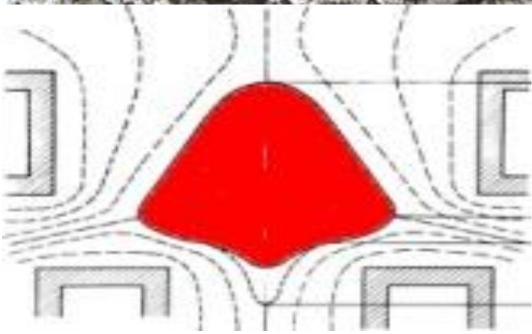
Direction of zone cleaning

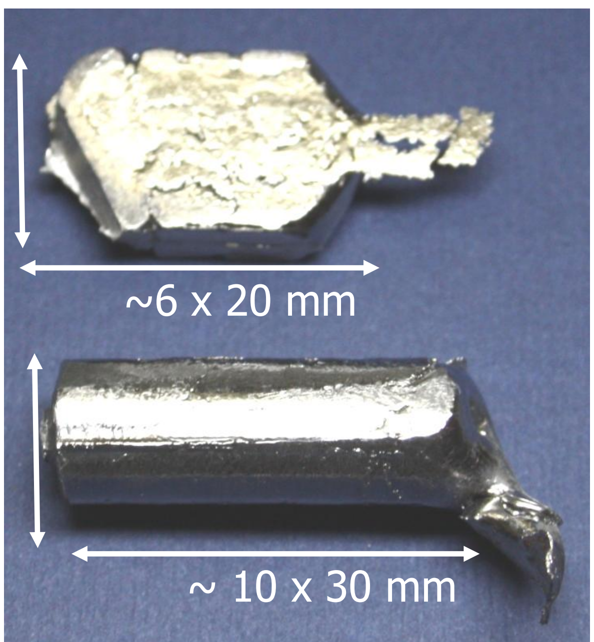
ICP-MS analysis of the EBFZM samples

	Ti 1			Ti 2			Ti 3			Ti 4			Ti 5			Ti 6		
	ppb/ mBq	St_d ppb	St d %	ppb/ mBq	St_d ppb	St d %	ppb/ mBq	St_d ppb	St d %	ppb/ mBq	St_d ppb	St d %	ppb/ mBq	St_d ppb	St d %	ppb/ mBq	St_d ppb	St d %
Th	**<0.13/0.5**			**< 0.10/0.4**			**<0.13/0.5**			**<0.17/0.7**			**<0.07/0.3**			**<0.07/0.3**		
U ?? BAD !	24,85	0,00	0,9	35,09	0,78	2,4	76,43	1,91	2,6	10,33	0,00	0,2	74,32	1,86	2,6	10,28	0,00	0,5

Th is good but the source of U (10^2- 10^3 mBq) is unclear right now !!

High-frequency vacuum levitation melting





$$S = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - x_{cp.}\right)^2}{N-1}}$$

$$\sigma_r = \frac{1}{x_{cp.}}\sqrt{\frac{\sum_{i=1}^{N}\left(x_i - x_{cp.}\right)^2}{N-1}}$$

	Ti_1_cylinder	Ti_2-"boat"		
	ppb/mBq	ppb/mBq	standard deviation ppb	standard deviation %
Th	<0.04/0.2	<0.04/0.2		
U	<0.04/0.5	0,25/3	0,05	20,7

300*300 zone		
ppb/mBq	standard deviation ppb	standard deviation %
0.04/0.2	0,01	28
0,81/10	0,18	22,2

But some other impurities appeared !!

	Ti_1_cylinder	Ti_2-"boat"	300*300 zone
V	7,23E-04	2,76E-04	9,26E-05
Cr	1,36E-02	1,54E-02	3,42E-04
Mn	2,63E-03	2,73E-03	1,66E-04
Fe	1,03E-02	1,66E-02	3,74E-05
Co	1,68E-05	2,89E-05	2,46E-06
Ni	2,02E-02	1,64E-02	1,85E-08
Cu	4,23E-02	2,03E-02	1,50E-03
Zn	1,03E-02	1,01E-02	2,65E-04

%

Second conclusion from 2012-2014 :
Clean sponge could be accurately melted and the impurities stay low

ICP-MS analysis

The total number of processed samples is over 200

- Ti alloy samples from different sources
- Ti-containing substances: dioxides, salts, sponge, MgCl2, TiCl4 etc…

The analyses were performed in parallel at two locations:

1. INFN LNGS chemistry laboratory (*Stefano Nisi, Maria Laura di Vacri*)
2. D. Mendeleev Moscow University of Chemical Technology (*Igor Avetisov, Elena Mozhevitina*)

Two types of analysis for most of samples have been performed:
TotaQuant & Quantitative U/Th analysis

What the next ?

- HPGe analysis of Ti-sponge
- "clean Ti-sponge" experiment with the following e-beam melting
- rolling (vacuum) -> the first sheet (A4 size) of ultra clean Ti for external analysis
- cutting & welding (laser ??) should be carefully studied
  (but stainless steel related experience could be used widely)

The project driving forces:

Lomonosov Moscow State University Skobeltsyn Institute of Nuclear Physics- **“customer” representing DarkSide collaboration and “glue” of the project**

INFN LNGS chemistry laboratory & D. Mendeleev Moscow University of Chemical Technology

– **ICP-MC measurements & “high temperature chemistry” methods**

JSC "Solikamsk Magnesium Plant“ - **interface to Ti industry & experimental setups for studying Ti industrial processes**

Institute of Solid State Physics of RAS (Chernogolovka) - **theory of clean metals, metallurgical unique methods and installations, melting, vacuum rolling**

My acknowledgments for the most critical persons :

Igor Avetisov

Alexander Chub

Vadim Glebovsky

Elena Mozhevitina

Stefano Nisi,

Eugeni Shtinov

Yury Suvorov

Maria Laura di Vacri

Thank you for your attention !