GERDA meeting,

LNGS November, 5-7, 2007

$^{dep}GeF_4$ experiment in IChHPS (Nizhny Novgorod)

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General scheme of 76GeO2 production at *Svetlana*

natGe of *6N grade*

↓

natGeF4

↓

76GeF4

↓

76GeF4 → 76GeO2 of *4N grade*

Goals of the experiment

Determination of impurity content in:

- **natGeF_4** produced accordingly to Svetlana' technology
- **depGeF_4 (Ge-76 < 1,0%)**
- **natGeO_2** produced from natGeO_2
- **depGeO_2** produced from depGeO_2

From SVETLANA (the ECP):

- Baloon **№ 001**, filled with **depGeF_4 (Ge-76 < 1,0%, m = 1083,3 g)**
- Baloon **№ 016**, filled with **natGeF_4 (m = 1002,4 g)**

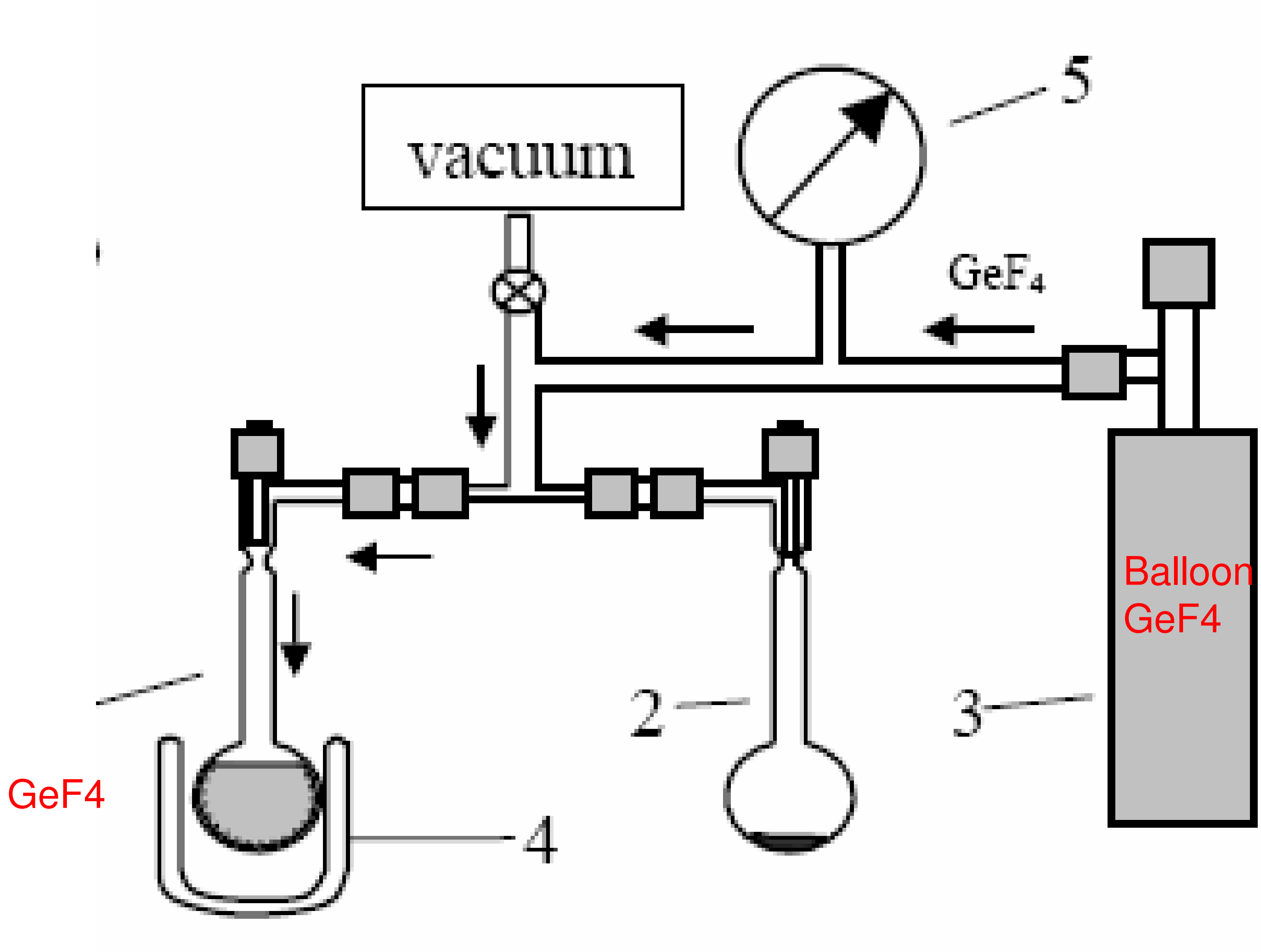
The experiment: general approach

Metals and others dangerous elements (impurities) in gaseous GeF4 are in form of fluorides, oxides and carbides and most probably aggregative state is suspension particles.

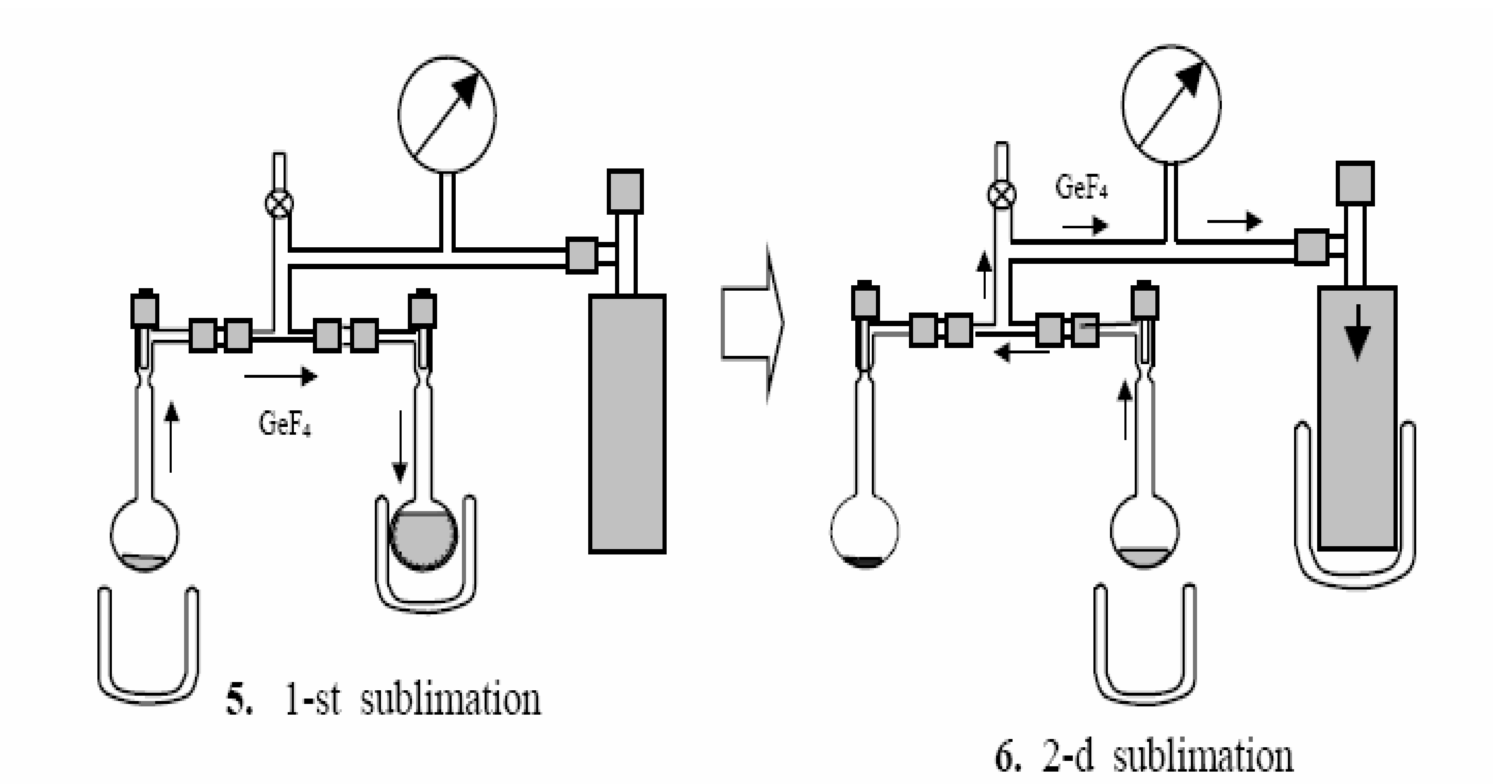
Method concentration of low-volatile impurities (including suspension particles) by GeF4 "matrix" distillation was used.

Impurities concentration on graphite collector (pure graphite powder) and matrix sublimation with very low rate ($\leq 1.10^{-4}$ g/cm^2/sec) following atomic emission analysis of GeF4 were used.

The experiment: filling of ampoule with GeF4



The experiment: sublimation procedure



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Analysis of GeF4 with AES

Element	natGeF_4 ppm	depGeF_4 ppm
Sb	< 0,005	< 0,005
Fe	0,03	0,001
Mg	0,0001	< 0,00006
Mn	0,001	0,0001
Pb	< 0,0005	< 0,0005
Cr	0,005	< 0,0004
Sn	< 0,0002	< 0,0002
Co	< 0,0006	< 0,0006
Ni	0,01	< 0,0006
Al	0,0008	0,0005
Ca	< 0,002	< 0,002
Cu	0,001	0,0006
Cd	< 0,001	< 0,001
Ag	0,0004	0,00008
Ti	< 0,0005	< 0,0005
V	< 0,0006	< 0,0006
Bi	< 0,0001	< 0,0001
Zn	< 0,004	< 0,004

> 6N quality !

Conversion of GeF4 → GeO2 by hydrolysis procedure

$3GeF_4 + 2H_2O = GeO_2 + 2H_2GeF_6$ (1)

$H_2GeF_6 + 6NH_4OH = Ge(OH)_4\downarrow + 6NH_4F + 2H_2O$ (2)

General scheme of hydrolysis:

$\mathbf{3GeF_4 + 2H_2O + 12NH_4OH \rightarrow 3GeO_2 + 12NH_4F + 8H_2O}$

Sample natGeO_2 ~ 20 g

Sample depGeO_2 ~ 23 g

V = 420 mL of water

Ratio H_2O:$GeF_4 \geq 20$:

if the powder serves as sorbent it means a concentration factor k ~ 20

Analysis of GeF_4 and GeO_2

IChHPS, Nizhny Novgorod:

Atomic-emission spectrometry	GeF_4 and GeO_2
Laser mass-spectrometry	GeO_2

IMTHPM RAS (Chernogolovka)

ICP MS	GeO_2

GIREDMET (Moscow)

SS MS	GeO_2

Atomic emission spectroscopy

Impurity concentrates were analyzed by the arc atomic emission method (with spectrograph STE-1):

- direct-current arc of 13 A,
- T exposition of 20 sec,
- intensifying additive is 4% NaCl.

Absolute DL of the method is 10^{-8}-10^{-10} g

Relative DL - 10^{-7}-10^{-9} % mass for sample of 20 g

RMS < 0.6 for concentration of 10^{-6}-10^{-8} % mass

Analysis of GeO_2 with AES

Element	Method			Element	Method		
	Laser	ICP MS	SS MS		Laser	ICP MS	SS MS
Li	-	<0.01	<0.01	Sn	<4	<0.2	<0.1
Be	-	< 0.01	<0.01	Sb	<1	<0.2	<0.05
B	<0.03	<2	0.09	Te	<4	<0.5	<0.4
Na	0.1	<6	<0.05	I	<2	-	<0.05
Mg	-	<1	<0.01	Cs	<2	<0.01	<0.1
Al	0.8	<3	0.1	Ba	<2	<0.4	<0.2
P	?2	<8	6	La	<2	<0.02	<0.1
K	0.4	<7	<0.05	Ce	<2	<0.02	<0.1
Ca	2	17.3	20	Pr	<2	<0.01	<0.05
Sc	<0.2	< 0.2	0.7	Nd	<7	<0.03	<0.2
Ti	<0.3	<1	<0.1	Sm	<8	<0.01	<0.1
V	<0.3	<0.2	<0.05	Eu	<4	<0.004	<0.04
Cr	<0.3	<2	0.04	Gd	<10	<0.01	<0.2
Mn	<0.3	<0.2	0.2	Tb	<2	<0.003	<0.1
Fe	0.9	< 3	0.8	Dy	<9	<0.04	<0.3
Co	<0.4	< 0.04	<0.02	Ho	<3	<0.005	<0.06
Ni	<0.5	< 0.5	0.1	Er	<4	<0.001	<0.04
Cu	1.0	< 0.3	<0.05	Tm	<2	<0.001	<0.05
Zn	0.9	< 0.8	<0.1	Yb	<10	<0.001	<0.2
Ga	<0.6	< 0.5	<0.04	Lu	<3	<0.001	<0.1
As	?10	-	<0.05	Hf	<8	<0.01	<0.2
Se	<1	<1	<0.2	Ta	-	0.25	-
Br	<1	-	<0.1	W	<10	0.2	<0.2
Rb	<1	< 0.02	<0.1	Re	<5	<0.003	<0.1
Sr	<0.9	< 0.2	<0.1	Os	<8	-	<0.4
Y	<0.7	-	<0.1	Ir	<5	<0.001	<0.2
Zr	<2	-	<0.2	Pt	<11	<0.005	<0.2
Nb	<0.8	-	<0.1	Au	<4	<0.05	<0.1
Mo	<0.3	0.11	<0.3	Hg	<13	<0.1	<0.3

Analysis of $^{dep}GeF4$ and $^{dep}GeO2$ with AES and MS

Element	depGeÎ$_2$ ppm				depGeF_4 ppm
	AES ppm	Laser MS	ICP MS	SS MS	AES ppm
Sb	ND	< 4	< 0,2	< 0,1	< 0,005
Fe	< 0,04	0,9	< 3	0.8	0,001
Mg	<0,005	ND	< 1	< 0,01	< 0,00006
Mn	0,005	0,3	< 0,2	0,2	0,0001
Pb	< 0,02	< 8	< 0,08	< 0,3	< 0,0005
Cr	ND	< 0,3	< 2	0.04	< 0,0004
Sn	< 0,02	< 4	< 0,2	< 0,1	< 0,0002
Co	< 0,05	< 0,4	< 0,04	< 0,02	< 0,0006
Ni	< 0,05	< 0,5	< 0,5	0,1	< 0,0006
Al	ND	0,8	< 3	0,1	0,0005
Ca	1,0	2	17,3	20	< 0,002
Cu	<0,003	1,0	< 0,3	< 0,05	0,0006
Cd	ND	< 4	< 0,4	< 0,2	< 0,001
Ag	<= 0,001	< 2	ND	< 0,05	0,00008
Ti	<= 0,04	< 0,3	< 1	< 0,1	< 0,0005
V	ND	< 0,3	< 0,2	< 0,05	< 0,0006
Bi	< 0,01	< 4	< 0,003	< 0,1	< 0,0001
Zn	ND	0,9	< 0,8	< 0,1	< 0,004
Au	< 0,02	< 4	< 0,05	< 0,1	ND
Pt	< 0,03	< 11	< 0,005	< 0,2	ND

Conclusion

Job is not finished!

AES Analysis:

- Content of metals and others dangerous elements in natGeF4 is $10^{-6} - 10^{-8}$ % mass

quality of the material is > 6N!

- Content of Fe, Mg, Mn, Cr, Ni and Cu in depGeF4 is lower compare with natGeF4 because of purification/removal of suspension particles via centrifugation procedure

AES, Laser MS, ICP MS and SS MS:

- Content of "common elements" (impurity) in GeO_2 are higher (for some elements - **few order magnitudes**) compare with GeF4
- These impurities are probably due to pollutions came from laboratory (mainly common light elements → background of analysis.
- Distribution of Al and Ca into the GeO2 samples are not uniform.

Hydrolysis procedure: most probably source of impurities is water which was purified via sub-boiling process. If so, one used water with purity of $< 5 \cdot 10^{-9}$ % mass (taking into account ratio $H_2O:GeF_4 \geq 20$).

INR/IChHPS still have about 0.4 kg of depGeF4 and 0.4 kg of natGeF4

Backup slides

Analysis of GeO2 with AES

Element	natGeO_2 ppm	depGeO_2 ppm
Fe	< 0,04	<0,04
Mg	<0,005	< 0,005
Mn	0,005	0,005
Pb	< 0,02	< 0,02
Sn	< 0,02	< 0,02
Co	< 0,05	< 0,05
Ni	< 0,05	< 0,05
Ca	< 0,2	1,0
Cu	<0,003	<0,003
Ag	<= 0,001	<= 0,001
Ti	<= 0,04	<= 0,04
Bi	< 0,01	< 0,01
Pt	<0,03	<0,03
Au	<0,02	<0,02

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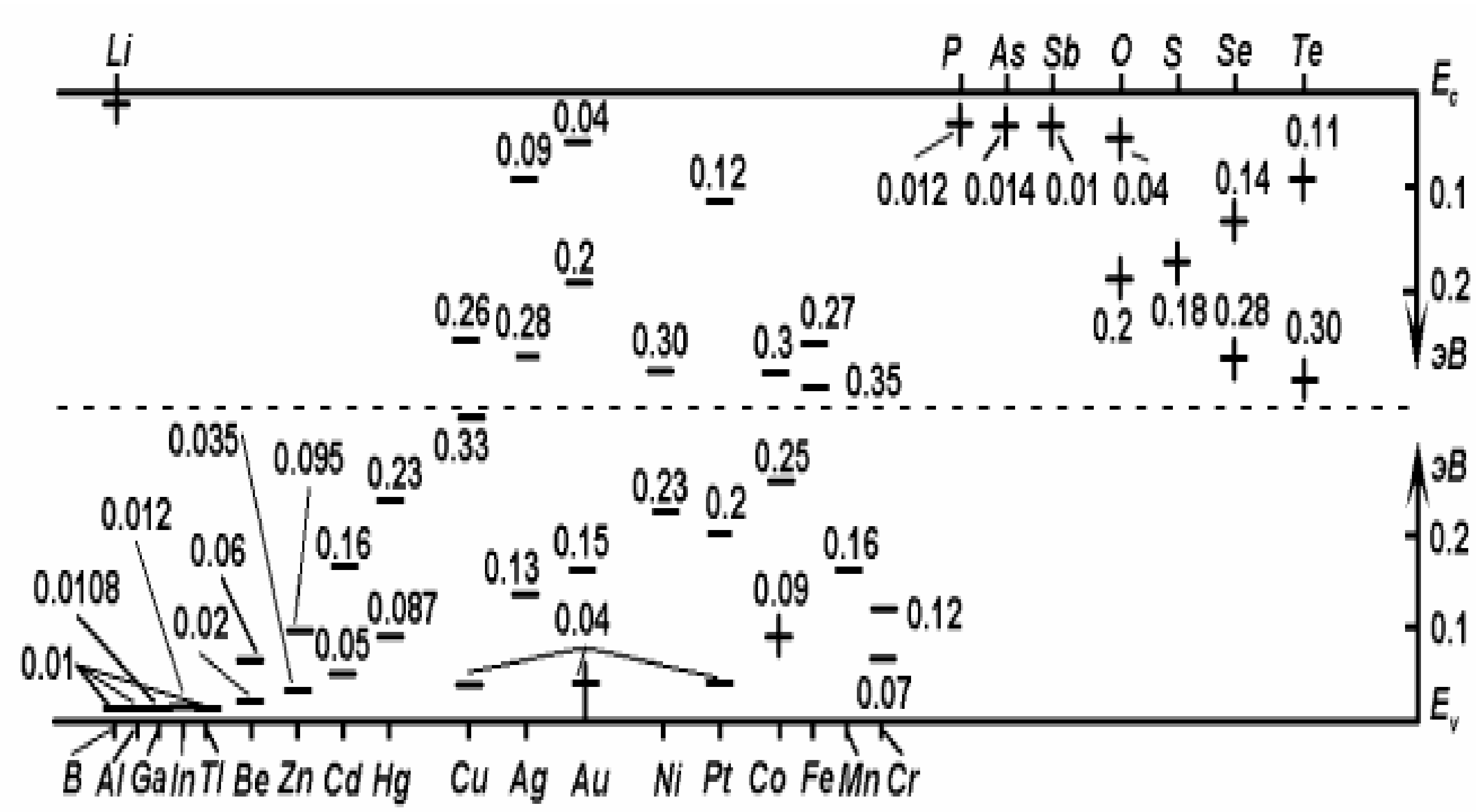
Analysis of GeO2 with Laser MS and ICP MS

Element	Method (ppm)		Element	Method (ppm)	
	Laser MS	ICP MS		Laser MS	ICP MS
Li	-	<0.01	Sn	<4	<0.2
Be	-	< 0.01	Sb	<1	<0.2
B	0.07	<2	Te	<4	<0.5
Na	0.1	<6	I	<2	-
Mg	-	<1	Cs	<2	<0.01
Al	21	<3	Ba	<2	<0.4
P	?2	<8	La	<2	<0.02
K	0.4	<7	Ce	<2	<0.02
Ca	0.9	<8	Pr	<2	<0.01
Sc	<0.2	< 0.2	Nd	<7	<0.03
Ti	<0.3	<1	Sm	<8	<0.01
V	<0.3	<0.2	Eu	<4	<0.004
Cr	<0.3	<2	Gd	<10	<0.01
Mn	<0.3	<0.2	Tb	<2	<0.003
Fe	0.2	< 3	Dy	<9	<0.04
Co	<0.4	< 0.04	Ho	<3	<0.005
Ni	<0.5	< 0.5	Er	<4	<0.001
Cu	0.5	< 0.3	Tm	<2	<0.001
Zn	0.7	< 0.8	Yb	<10	<0.001
Ga	<0.6	< 0.5	Lu	<3	<0.001
As	?10	-	Hf	<9	<0.01
Se	<1	<1	Ta	-	1.75
Br	<1	-	W	<10	0.35
Rb	<1	< 0.02	Re	<5	<0.003
Sr	<0.9	< 0.2	Os	<8	-
Y	<0.7	-	Ir	<5	<0.001
Zr	<1	-	Pt	<11	<0.005
Nb	<0.8	-	Au	<4	<0.05
Mo	<0.3	< 0.06	Hg	<13	<0.1
Ru	<4	-	Tl	<6	<0.0008
Rh	<0.9	< 0.02	Pb	<8.0	<0.08
Pd	<3	< 0.3	Bi	<4	<0.003
Ag	<2	-	Th	<10	<0.007
Cd	<4	<0.4	U	<10	<0.001
In	<1	<0.004			


Li
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0.09
0.12
0.012 0.014 0.01 0.04
0.11
0.14
0.1
0.2
0.26 0.28
0.30
0.3 0.27
0.35
0.2 0.18 0.28 0.30
0.2
эВ
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0.095
0.33
0.23
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0.01
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E_v
B Al Ga In Tl Be Zn Cd Hg Cu Ag Au Ni Pt Co Fe Mn Cr