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PREFACE

This volume contains the conferences program and abstracts prepared by the authors. The authors and participants are most warmly welcome at Maria Curie-Skłodowska University (UMCS) in Lublin, Poland.

Present conference on Dating of minerals and Rocks XIII joined for the second time Bio-Geo conference, according to postulates expressed in previous conferences on Dating to include the use of stable isotopes in bio-geochemical studies.

This joined conference is organized in the 100th Birthday of Włodzimierz Żuk, professor of UMCS, who constructed the first mass spectrometer in Poland. It is worth to remain that the first all-Polish dating conference was organized at UMCS in the frame-work of celebration of 50th anniversary of UMCS in October 1994. At that time the only invited speaker was professor Jan Burchart from the Institute of Geological Sciences PAN, Warsaw. He was talking on advantages and drawbacks of the K-Ar method. During this conference we have a great opportunity to provide for all the participants excellent monograph entitled Isotopic Record of the Earth Past (in Polish) authored by Prof. Burchart and Dr. Jan Kral from Slovakia.

The Organizing Committee wish to express sincere thanks for help in organization and financial support of this conference to the Lublin Division of the Polish Physical Society.

Sincerely Yours,

Yours sincerely,

Prof. dr hab. Stanisław Hałas
Dr Tomasz Pieńkos
Dr eng. Miłosz A. Huber

13th Geochronological Conference "Dating of Minerals and Rocks XII"
2st International Conference on Biology and Earth Sciences "Bio-Geo"
UMCS, Lublin, 20-21.10.2016

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Mass Spectrometry Laboratory, Maria Curie-Skłodowska University in Lublin
Earth Science and Spatial Management Faculty, Maria Curie-Skłodowska University in Lublin
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Prof. dr hab. Mieczysław Budzyński, director of Physics Institute in Lublin, UMCS

PROGRAM OF CONFERENCES

Hour	Speaker	Hour
Thursday 20.10.2016. Part I „DATING” **The Institute of Physics UMCS, room 613, 1 Maria Curie –Skłodowska sq.**		
14:35	Registration	
14:50	Opening ceremony	
15:10-15:40	**Michał Banaś**	From MS20 to NU Noblesse: a short story of K-Ar dating in Kraków
15:40-16:10	**Zbigniew Czupyt**	SHRIMP IIe/MC ion microprobe
16:10-16:50	**Sylwia Kowalska,** Stanisław Hałas, Artur Wójtowicz, Claus Wemmer	Methodological aspects of K-Ar dating in application to sedimentary basins thermal history reconstruction
16:50	**Prof. dr hab. Jan Burchart**	Promotion of the monograph “Izotopowy zapis przeszłości Ziemi” diuring the cofee break
Hall of Physics, 1st floor, (in the framework of the Polish Physical Society Meeting)		
17:15-18:00	**Monika Kusiak**, Dunkley D.J., Lyon I., Wirth R., Whitehouse M.J., Wilde S.A.	How far we can get with high-spatial resolution geochronology for U-Pb dating of ancient rocks
18:00-18:40	**Daniel J. Dunkley**, M. A. Kusiak, Y. Hiroi, K. Tani, D. E. Harlov & K. Shiraishi	Fluids attack the citadel of zircon: some case studies
19:30	**Conference Dinner**	**Husar Hotel Restaurant, Ul. Spadochroniarzy 9**
Piątek 21.10.2016. Part II „BIO-GEO” **Room 613, 1 Maria Curie –Skłodowska sq.**		
10:15-11:00	**Sándor Kele**	Clumped isotopes
11:00-11:40	**Stanisław Hałas**, Tomasz Pieńkos	Towards determination of multiple sulfur isotope fractionation
11:40-12:00	Coffe Break	
12:00-12:40	**Zdzislaw Migaszewski** , Agnieszka Gałuszka	Stable S and O isotopes in the Wiśniówka acid mine drainage water bodies (Holy Cross Moutains, Poland)

12:40-13:20	**Adrian Pacek**, Tomasz Pieńkos, Stanisław Hałas	A novel ion source for TIMS (used in ^{7}Li/^{6}Li and ^{39}K/^{41}K ratios)
13:20-14:00	**Miłosz Huber**, Tamara B. Bayanova, Stanisław Hałas, Emilia Reszczyńska , Lesia Lata, Sebastian Skupinski	Sulfur isotopy geochemistry of basic and ultrabasic complexes of the Kola Peninsula
14:00-15:00 Coffe Break and Poster Session		
15:00 Honorable Run of the δ^{33}S- δ^{34}S Mass-Spectrometer and lunch.		

Posters index

Author	Poster Title
Fedorowicz S., Łanczont M. , Bogucki A., Standzikowski K., Mroczek P., Kusiak J.	Interlaboratory luminescencje dating of meso-pleistocene loesses from Wołyń and Podole: methodical aspects
Huber M., Bayanova T.B. , Hałas S., Reszczyńska M., Lata L. , Skupinski S.	3,7 Ga metamorphosed gneisses from Murmansk, preliminary geochemistry and isotopic data.
Kusiak M.A., Dunkley D.J.1,, Sałacińska A., Whitehouse M.J., Wilde S.A.	Igneous protolites of the Uivak gneiss, preliminary data from the Saglek Block, Northern Labrador
Hałas S., Pieńkos T., Pelc A., Wójtowicz A.	Determination of d^{33}S and d^{34}S on SO$_2$ gas using negative/positive ion mass spectrometry
Huber M., Lata L.	Environmental and pollution characteristics of the Lublin roughcast
Karpinski T.M., Huber M., Lata L.	Environmental and pollution characteristic of plants samples from Karkonosze region, S Poland.
Pieńkos T., Hałas S., Pelc A., Wójtowicz A.	A dual inlet and triple collector mass spectrometer for analysis of ^{33}S/^{32}S and ^{34}S/^{32}S isotope ratios
Huber M., Lata L.	Environmental moss characteristics from Middle Roztocze (Tomaszów area)
Ciszak A.	Fluorination line for extracting of oxygen from minerals

FROM MS20 TO NU NOBLESSE: A SHORT STORY OF K-Ar DATING IN KRAKÓW

Michał Banaś

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The Laboratory for K-Ar Dating in Kraków was established in the period 1999-2002 based on the hardware of the CNRS from Strasbourg (Figure 1). The reactor, power supply, controller and control the spectrometer cold fingers were made at the Maria Curie-Skłodowska University in Lublin (Figures 2 and 3).

In 2011, the Institute of Geological Sciences PAS received a grant from the National Fund for New Technologies for the purchase of modern equipment for the laboratory. It was selected the company's offer NU Instruments "Noblesse 2.1" (Figure 4). A line for gas extraction and purification of the samples was carried out in Warsaw ITR (Figure 5). The construction of the laboratory was completed in 2014.

Fig. 1.

Fig. 2.

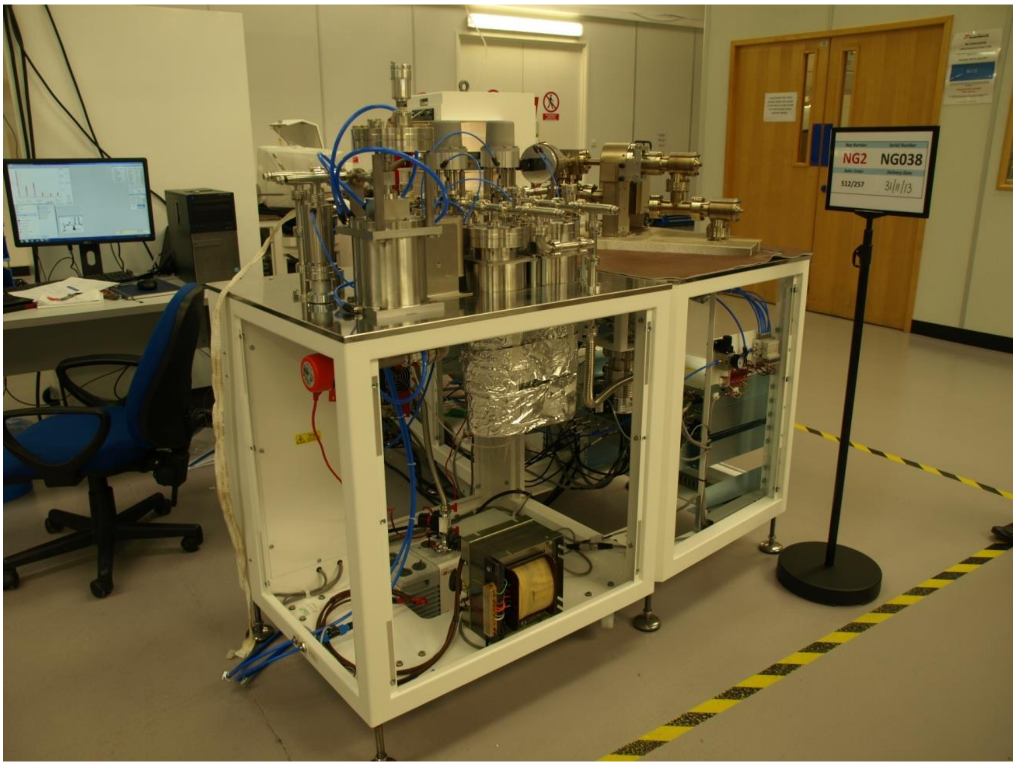
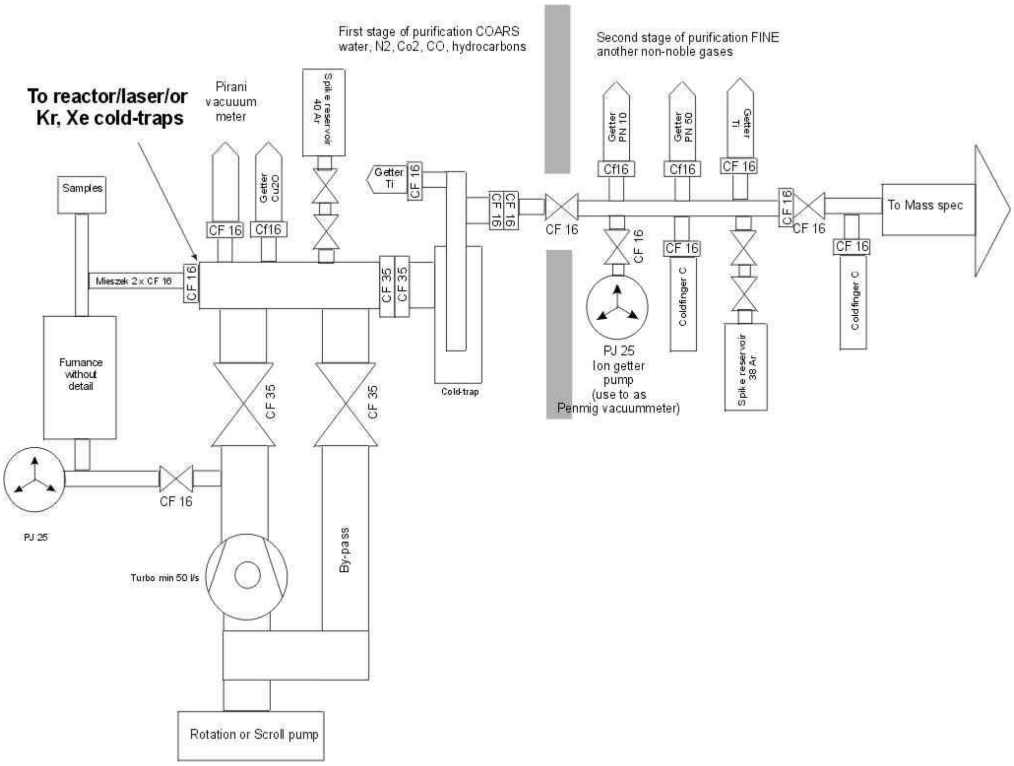


Fig. 3.

Fig. 4.


First stage of purification COARS
water, N2, Co2, CO, hydrocarbons
Second stage of purification FINE
another non-noble gases
To reactor/laser/or
Kr, Xe cold-traps
Pirani
vacuuum
meter
Spike reservoir
40 Ar
Getter
Cu2O
Samples
CF 16
Cf16
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Ti
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Furnance
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CF 35
Cold-trap
CF 16
PJ 25
Turbo min 50 l/s
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Coldfinger C
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Fig. 5.

SHRIMP IIE/MC ION MICROPROBE

Zbigniew Jan Czupyt

Micro-area Analysis Laboratory, Ion microprobe section Polish Geological Institute - National Research Institute, 4 Rakowiecka St., 00-975 Warsaw; e-mail: zczu@pgi.gov.pl

SHRIMP IIe/MC (Sensitive High Resolution Ion MicroProbe) is a Secondary Ion Mass Spectrometer (SIMS) that is capable to in situ isotopic and chemical surface analyses of solid targets [3-5,12-15] A high-energy beam of primary ions is focused onto a small area (from 5 to 30 µm diameter) on the surface of the target. The ion bombardment sputters atoms and molecules from the sample. These secondary ions are gathered using electrostatic lenses and transferred to a mass spectrometer, in which they are separated according to their relative masses. SHRIMP IIe has high mass resolution which is achieved by the use of a double-focusing mass spectrometer, simultaneous energy and mass refocusing, with a very large turning radius, magnet radius is 1000 mm and electrostatic analyzer radius is 1272 mm. That is why instrument has a beam line over 7 m long and weighs more than 14 tones [18].

The SHRIMP has the high secondary ion transmission necessary to detect trace elements [2, 17] while maintaining the high mass resolution required to resolve the many molecular interferences that result from chemically complex minerals. The operation at high transmission with a mass resolution sufficient to distinguish MREE from LREE oxides, and Pb from Hf dioxides makes the SHRIMP ideal for low level trace element analyses of geologic materials and U-Th-Pb geochronology [11]. It can be used for routine measurement of the isotopic composition of, for example, Pb, U, Th, O, S, C, Mg, Ca, Ti, B, Li, Si and Cr, and the abundances of most elements in the periodic table in geological, cosmochemical, experimental, or industrial samples.

The SHRIMP IIe/MC has a multicollector which allows subpermil (>0.2 ‰) resolution for isotopic ratios of C, O, S, and other geologically interesting elements [18]. The use of charge mode electrometers allows the minor isotopes of ^{36}S, ^{17}O, and ^{13}C in carbonate to be measured using a Faraday cup instead of an electron multiplier, even though the count rate is only a few hundred thousand cps in most cases. The use of high-sensitivity hall probes instead of NMR allows for multiple isotopic systems (O, S in sulfates; O, C in carbonates) to be analyzed in a single analytical spot via field switching. Stable isotope geochemistry examines the change of the isotopic composition of an element (H, Li, B, C, N, O, S) produced by chemical or physical processes. SHRIMP measurement of S isotopes has been used to understand mineral growth mechanisms and genesis, follow changes in fluid compositions and to constrain the conditions under which rocks and ore deposits form [6].

For isotopically uniform electrical insulators such as zircon, SHRIMP IIe/MC demonstrated capability to produce replicate oxygen isotopic analyses over a period of several hours that have a standard deviation of better than 0.2 per mill. SHRIMP IIe/MC main use is U-Pb geochronology. It provides rapid, reliable dating of micron-scale domains in U-bearing trace minerals at the 1-2% level. The current technique comprises a measurement of Pb isotopes, U, Th, and uranium oxide species which are used to calibrate the relative ionization efficiency of U and Pb. SHRIMP analyses are advantageous in that the fine spatial resolution (in range 20 μm) allows targeting of subgrain domains in mineral grains with complex growth histories, avoiding inclusions or metamict domains [18]. When temporal precision higher than 1% is required, the SHRIMP IIe/MC can be used to screen zircon grains for lead loss, inherited cores, or other problems that may inhibit or complicate TIMS analysis.

The small analytical volume (~1000 cubic microns) allows minimal sample consumption [10]. This allows for later whole-grain dissolution, combined U - Pb - Th- dating, or the use of multiple in situ techniques on the same sample, such as SHRIMP IIe U-Pb geochronology, SHRIMP IIe/MC oxygen isotope analysis, and then laser ICPMS Hf isotopic analysis. SHRIMP IIe has been used for the U-Pb geochronology of minerals such as zircon, titanite, monazite and xenotime. [1, 5, 7-9, 14, 16-17].

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METHODOLOGICAL ASPECTS OF K-Ar DATING IN APPLICATION TO SEDIMENTARY BASINS THERMAL HISTORY RECONSTRUCTION

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K-Ar dating of maximum diagenesis is widely used in geology for thermal history reconstruction in sedimentary basins. Various research centers give different sizes measurement error, which should be taken for the results. Usually the reported measurement bias responds only to standard operating procedure of an individual laboratory. The aim of the present study was to find out what the real error should be taken into account as the real error when interpreting geological K-Ar dating results. For this purpose an interlaboratory comparison with the participation of four well-known laboratories was organized. Three of them are performing measurements by K-Ar method and one by Ar-Ar method with the use of the capsule technique specially adapted for very fine clay materials. Following scientists took part in the interlaboratory comparison: Prof. Stanislaw Hałas and Dr. Artur Wojtowicz from the University in Lublin (K-Ar), Dr. Klaus Wemmer of the University of Göttingen (K-Ar), Dr. Yakov Kapusta from ACTLAB laboratory in Canada (K-Ar) and Dr. Chris Hall of the University of Michigan in the USA (Ar-Ar).

The research material consisted of Silurian and Ordovician bentonites from different boreholes drilled by PGNiG S.A. during hydrocarbon exploration. Interlaboratory comparison was carried out on three samples. From each sample four different grain fractions <0.02, 0.02-0.05, 0.05-0.2 and 0.2-2 μm were separated at the Institute of Geological Sciences in Krakow. Samples were splited by quartering, encrypted and sent to the laboratories participating in the comparison.

The determination of the radiogenic argon content in the Mass Spectrometry Laboratory (UMCS Lublin) was made by use of internal spike method on the modified MS-10 mass spectrometer. Aliquots from about 40 mg to about 50 mg have been made. Each sample was melted in the double-vacuum crucible of the argon extraction-purification line in temperature of 1150°C. Pure 38Ar (produced by the Institute for Inorganic and Physical Chemistry, University of Bern) was used as spike. Atmospheric argon content was determined by measuring an 36Ar peak in the mass spectrum. After every measurement cycle blank cycle was performed (at temperature of about 1200°C) to check if all argon had been extracted from the sample. For K-Ar age calculation the decay constants $\lambda e = 0.581\cdot 10\text{-}10$, $\lambda b = 4.962\cdot 10\text{-}10$, 40K/K=0.01167% [1] were used. Uncertainty in K-Ar age was calculated from the extended error propagation formula [2]. The age calculation was made with the use of K content measured by ACTLAB laboratory.

Based on the results of interlaboratory comparison, it is clearly visible that the most difficulties arise from the determination of potassium as for this element greater dispersion of results was achieved - Fig.1. The results of K-Ar and Ar-Ar dating, summarized in Table 1, show that dating of diagenetic age is possible for a fraction less than 0.2 µm. All laboratories obtained very similar results for the three finest fractions. The faction 0.2-2 µm gave distinctly older ages, which proves an admixture of detrital material. This observation is also confirmed by further studies carried out simultaneously for several bentonite samples from other boreholes. Comparison of the results achieved from laboratories taking part in the research clearly indicates that the actual measurement errors range up to +/- 10 Ma. Significantly younger ages obtained with the Ar-Ar method confirm the large influence of the Ar escape effect from the very fine grained samples, the so called “recoil effect" [3] .

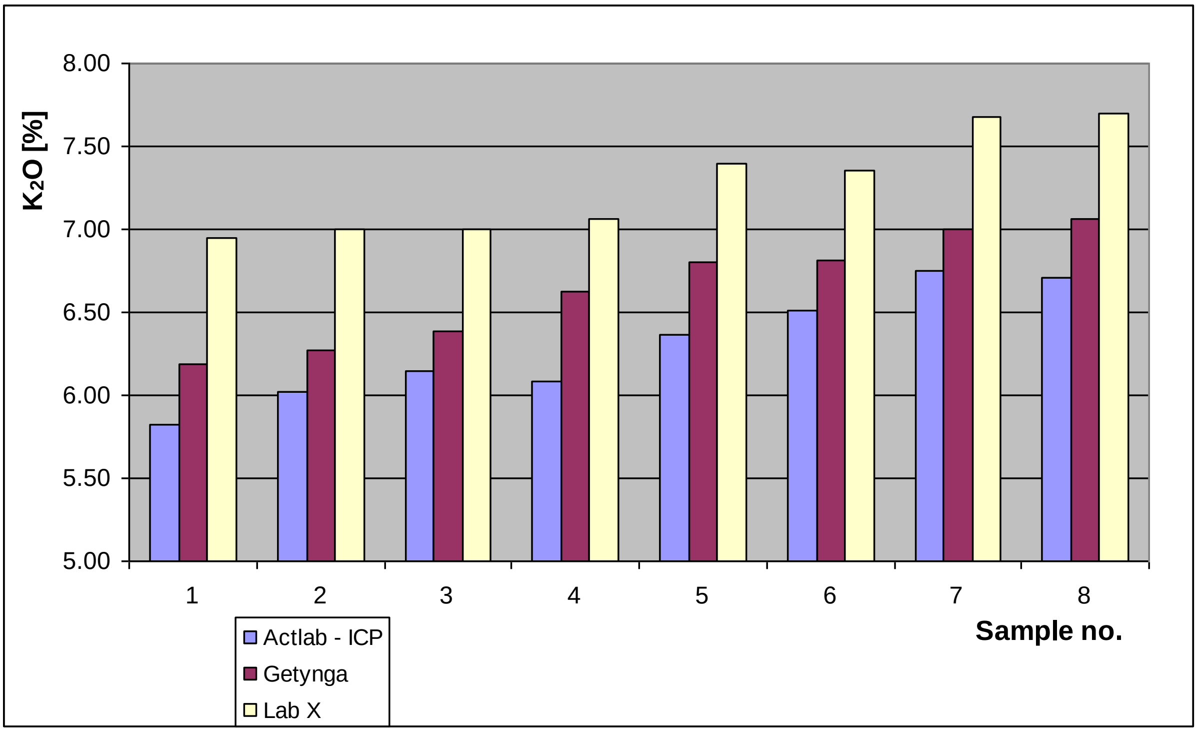

Fig.

Fig. 1. The results of interlaboratory comparison – determination of K content.

Tab 1. The results of interlaboratory comparison - K-Ar and Ar-Ar dating.

Sample	Grain size [µm]	K-Ar [Ma]			Ar-Ar
		Lublin	Getynga	Actlab	Michigen
1	<0,02	362	349	367	290
	0,05-0,02	354	348		282
	0,2-0,05	357	351		296
	0,2-2	384	356	387	319
2	<0,02	372	365		
	0,05-0,02	363	359		
	0,2-0,05	368	364		
	0,2-2	387	380		
3	<0,02	190			147
	0,05-0,02	196			
	0,2-0,05	212			
	0,2-2	272			

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HOW FAR WE CAN GET WITH HIGH-SPATIAL RESOLUTION GEOCHRONOLOGY FOR U-PB DATING OF ANCIENT ROCKS

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U-Pb dating of zircon ($ZrSiO_4$) is arguably the most versatile geochronological age dating technique, due to the ability of zircon to survive through the entirety of Earth history and for the internal check of reliability provided by concordance between the ^{238}U-^{206}Pb ($\tau_{1/2}$~4.5Gyrs) and the ^{235}U-^{207}Pb ($\tau_{1/2}$~0.7Gyrs) chronometers. The greatest innovation was the ability to analyse in-situ on the tens-of-micron scale, which has allowed us to differentiate and date multiple stages of mineral growth. Zircon U-Pb isotopic analyses commonly yield discordant data in which ^{206}Pb/^{238}U ages are younger than ^{207}Pb/^{206}Pb ages due to Pb loss or analysis of mixtures of zircon of different ages. Such disturbed data commonly lie along a discordia line on the concordia (^{206}Pb/^{238}U versus ^{207}Pb/^{235}U) diagram, which can yield meaningful ages from the upper and lower intercepts with the Concordia curve. More difficult to explain is the situation where zircon data are reversely discordant (ie. ^{206}Pb/^{238}U ages are older than ^{207}Pb/^{206}Pb ages). Much research is currently being undertaken to understand these effects (Kusiak et al., 2013 a,b). It has been discovered that in zircons from the Napier Complex in East Antarctica, radiogenic Pb was mobilised during high-grade metamorphism to form metallic Pb nanospheres (Kusiak et al., 2015), typically 20-35nm in diameter.

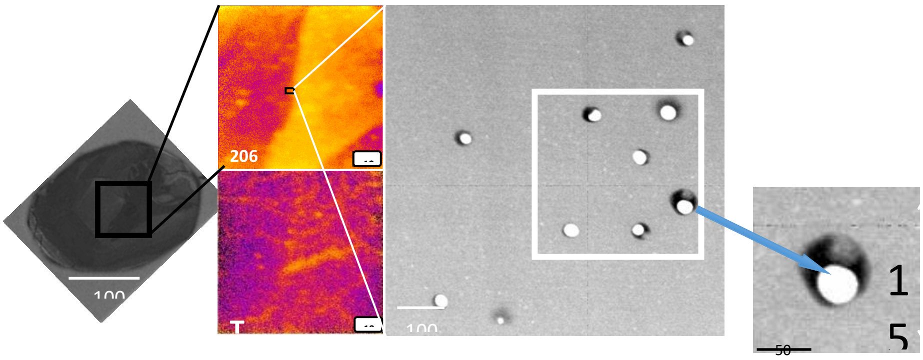

Fig. 1. Zircon grain in back-scattered electron image (left), ion image masp of ^{206}Pb and ^{48}Ti showing inhomogeneous distribution of selected isotopes, transmission electron microscope images showing Pb nanospheres together with Si-Al phase.

Since the spheres are on the nanometer scale, conventional SIMS analysis, with an analytical spot size of ca. 15-20µm, can sample variable quantities of the spheres during sputtering and so yield scattered apparent ^{207}Pb/^{206}Pb ages within a single analysis. We measured ^{207}Pb/^{206}Pb in individual Pb nanospheres using the NanoSIMS at the University of Manchester (UK), with an O$^-$ primary beam from a conventional duoplasmatron producing a 100nm wide spot, and on the NanoSIMS of the University de Pau (France), with a Hyperion O$^-$ primary source producing a spot size of 50nm. The spacing between individual Pb nanospheres is generally greater than 100nm and therefore ^{207}Pb/^{206}Pb can be defined for individual nanospheres. Depth profiling and 3-D reconstructions of sputtered volumes reveal how the nanospheres are spatially related to one another. A range in ^{207}Pb/^{206}Pb of 0.1 to 0.6 in nanospheres was obtained from different zircons. Modelling of Pb isotope behaviour on this scale shows how such extreme ^{207}Pb/^{206}Pb isotopic heterogeneity on a 100nm scale within the zircon can arise and be preserved throughout the subsequent history of the zircon, allowing for a more accurate reconstruction of its true history.

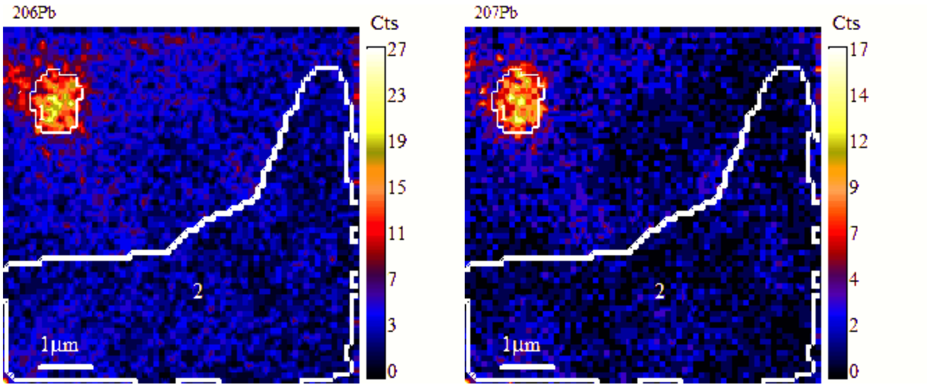

Fig. 2. NanoSIMS images of Pb distribution in the area of 7um in zircon.

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FLUIDS ATTACK THE CITADEL OF ZIRCON: SOME CASE STUDIES

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Zircon is an accessory mineral that can preserve within a single crystal multiple records of growth and modification during geological events. In such complex crystals, isotopic analysis must be done on micron-scale domains, chosen from interpreted images of polished grain sections provided by scanning electron microscopy. This is especially the case in rocks produced during high-grade metamorphism, where zircon interacts with other minerals, and with hydrothermal fluid and anatectic melt phases. Such interactions are conventionally viewed as dual stage dissolution and growth processes, producing grains with relict cores and overgrowth rims. However, modification of zircon during metamorphism also involves chemical re-equilibration via solid-state processes, either through recrystallization or via coupled dissolution-reprecipitation, especially in the presence of fluid phases. Zircon textures typical of solid-state modification by hydrous fluids are recognised from experiment [1] and low/mod-T metamorphic environments, as a result of multiple processes [2]. Diffusion-reaction (DR), involving partial decomposition of metamict zircon by Ca-Cl-bearing or other hydrous fluids, can be diagnosed from Ca enrichment, lowered backscattered electron response, and preservation of primary structures. Coupled dissolution-reprecipitation (CDP), involving re-equilibration of zircon with fluid or melt, can be diagnosed from reaction fronts with modified U, Th, Y and/or HREE contents, plus pores and inclusions rich in elements ejected from primary zircon (e.g., xenotime, thorite, uraninite). At high temperatures (>700°C), modification can be mediated by hydrous fluids or anatectic melts, but their specific roles can be ambiguous; especially in migmatites, where both agents are likely to be involved.

Here, three case studies are presented for which the role of fluids can be demonstrated, to help establish links between reaction textures and agents.

CASE 1: The Karkonosze Pluton of Silesia, Poland, contains magmatic phases produced by the interaction of evolving S-type granitic magmas with batches of lamprophyric magma. Zircon in microgranular magmatic enclaves are the product of magma hybridization, being unusually U and Th-rich, and show further interaction with fluids by alteration along Ca-enriched reaction (DR) fronts and subsequent repair and re-equilibration through CDP processes, into pristine zircon with pores and inclusions of xenotime, thorite and other phases. Such zircons record both ca. 315Ma magmatic growth and ca. 305Ma re-equilibration, the latter recording the time at which late deuteric fluids released by magma crystallization interacted with the pluton and country rocks [3].

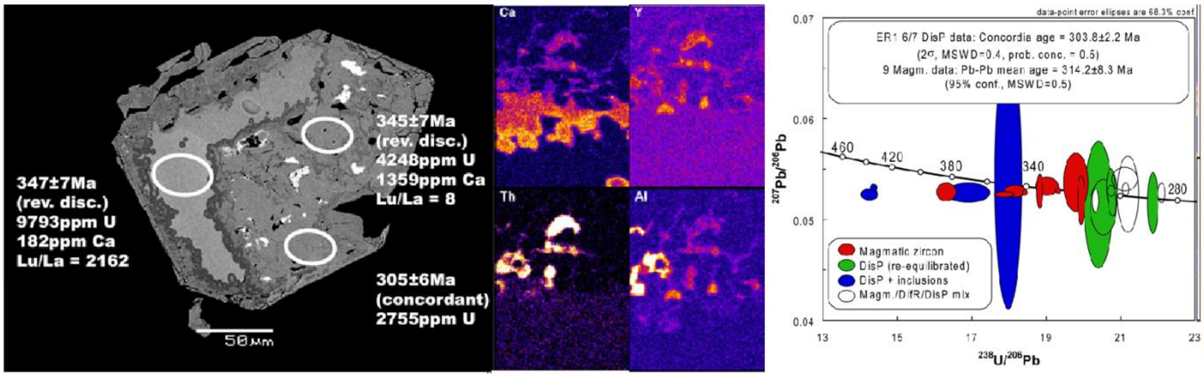

Fig.1. Backscattered electron image of zircon (left) from a microgranular magmatic enclave, Karkonosze Pluton, with spot analyses by Sensitive High-Resolution Ion Microprobe (SHRIMP). Centre: element maps from a 30x50 micron area on the same grain, by field emission electron microprobe. Right: Age data from SHRIMO spot analyses of magmatic (red), altered (blue) and re-equilibrated (green) domains of zircon. After Kusiak et al. (2009).

CASE 2: At Skallevikshalsen in East Antarctica, granulite-grade dolomitic marbles contain relics of ca. 630Ma felsic dykes scapolitised by Cl-rich brines. U-rich magmatic zircon was re-equilibrated by CDP, as demonstrated by the presence of lobate domains depleted in U, with inclusions of uraninite). Decomposition of metamict zircon can also be observed along fronts of Ca enrichment which erode the original magmatic zircon. U-Pb dating resolves two discrete episodes of fluid activity during high-T metamorphism, at ca. 590 and ca. 540Ma, the latter being confirmed by ages from uraninite released from zircon during the process [4].

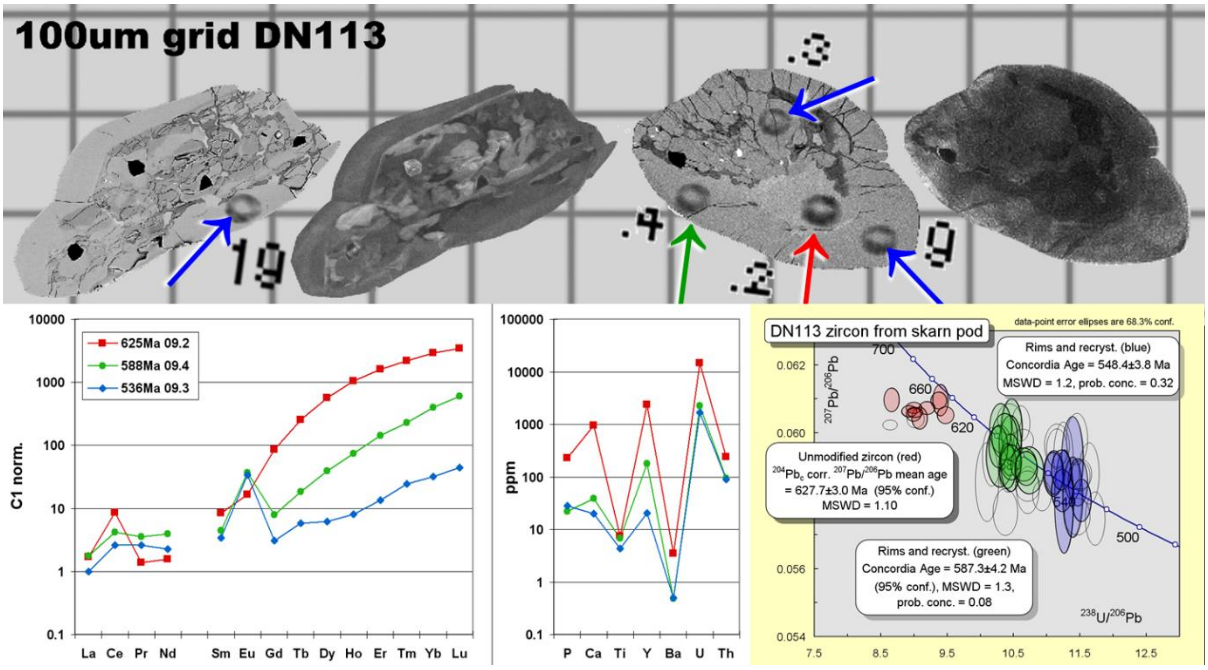

Fig.2. Backscattered electron and cathodoluminescence (CL) images of zircon (top) from skarnified pod in dolomarble, Skallevikshalsen, East Antarctica, with spot analyses by SHRIMP. Below: REE (left), other element (centre) and U-Pb isotopic data (right) plots for SHRIMP spot analyses on magmatic (red), 1st stage metasomatic (green) and 2nd stage metasomatic (blue) domains of zircon.

CASE 3: Godzilla Mullion, a Miocene oceanic core complex on the edge of the Philippine Sea Plate, includes Fe-Ti gabbros that were hydrated at and below 800°C, through the injection of seawater along deeply penetrating faults that also exhumed oceanic lithosphere. Metamorphosed gabbros and felsic melt veins both contain zircon crystals with Th+U+Y-rich cores, which were modified by CDP processes into zircon with abundant pores and inclusions of xenotime, thorianite, britholite and apatite. Re-equilibrated, lower U+Th zircon is younger than unmodified zircon by less than 1m.y. DR textures are absent, as expected for non-metamict zircon, demonstrating that neither low-grade alteration nor metamictisation is required to initiate CDP [5].

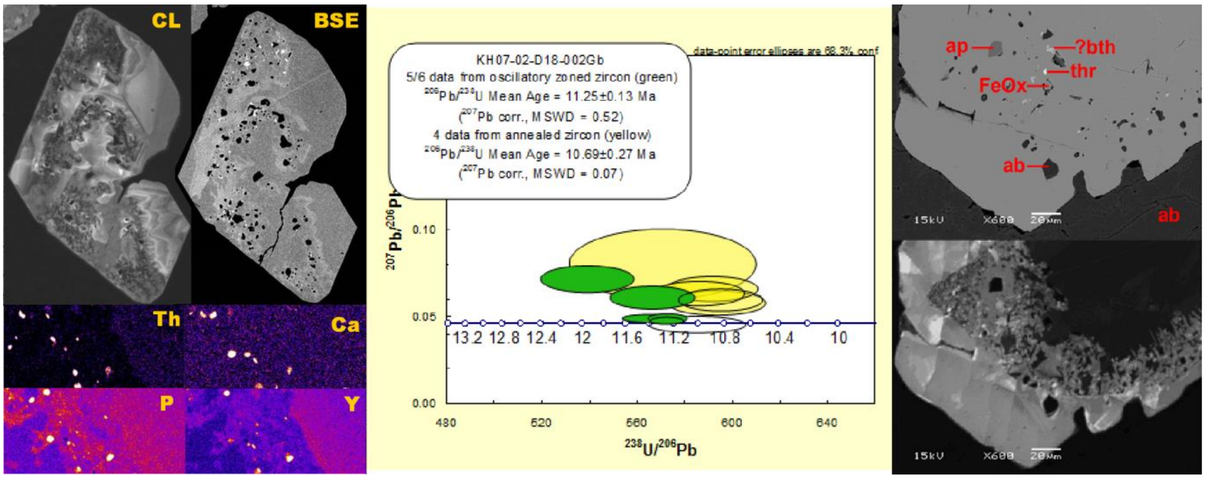

Fig.3. Backscattered electron and CL images of zircon (left) from metagabbro, Godzilla Mullion. Below left: element maps from a 30x100 micron area on the same grain, by field emission electron microprobe. Right: Backscattered electron and CL images of zircon from felsic vein cutting metagabbro. Centre: SHRIMP age data from magmatic (green), and re-equilibrated (yellow) domains of zircon. Modified after Tani et al. (2011).

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CLUMPED ISOTOPES: THEORY, CALIBRATIONS AND APPLICATIONS

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Introduction, history, theoretical base

Clumped isotope geochemistry is a new and dynamically developing research field of geochemistry, which concerns with the state of ordering of rare isotopes in natural minerals. This short review briefly introduces the reader to the principles of this method, reviewing the current state of the art including theoretical basis, calibrations and applications. Clumped isotopes or multiply-substituted isotopologues are isotopologues that contain two or more rare isotopes (e.g. ^{13}C and ^{18}O) in one molecule and they have unique thermodynamic properties (e.g. bond vibration frequencies, zero point energies, near-infra-red absorption spectra [1] (**Table 1**). They were discussed by the early works of [2] and [3] but until the end of the 80’s they were not studied due to their extremely low abundances (i.e. lack of proper instrumentation) and lack of appropriate theoretical framework. Their study started at Caltech (California Institute of Technology, Pasadena, California) in the early 2000s by John Eiler and his team. [4] showed that clumped isotopes have unique thermodynamic properties, which can be used to answer long-standing questions of geochemistry.

Table 1. Stochastic abundances of the twelve isotopologues of CO_2 [1].

Mass	Isotopologue	Relative abundance
44	$^{12}C^{16}O_2$	98.40%
45	$^{13}C^{16}O_2$	1.11%
	$^{12}C^{17}O^{16}O$	748 ppm
46	$^{12}C^{18}O^{16}O$	0.40%
	$^{13}C^{17}O^{16}O$	8.4 ppm
	$^{12}C^{17}O_2$	0.142 ppm
47	$^{13}C^{18}O^{16}O$	44.4 ppm
	$^{12}C^{17}O^{18}O$	1.50 ppm
	$^{13}C^{17}O_2$	1.60 ppb
48	$^{12}C^{18}O_2$	3.96 ppm
	$^{13}C^{17}O^{18}O$	16.8 ppb
49	$^{13}C^{18}O_2$	44.5 ppb

Clumped isotopes are reported by the Δ_{47} parameter, which describes the preference of two heavy (rare) isotopes (e.g. ^{13}C and ^{18}O) to bind to each other. The Δ_{47} variable was defined by [4] and [5] as the difference in per mil (‰) between the measured 47/44 ratio of the sample and the 47/44 ratio expected for the same sample if its stable carbon and oxygen isotopes were randomly distributed among all isotopologues (i.e. in case of stochastic distribution) [6]:

$$\Delta_{47}(‰) = \left[\left(\frac{R^{47}}{R^{47*}} - 1\right) - \left(\frac{R^{46}}{R^{46*}} - 1\right) - \left(\frac{R^{45}}{R^{45*}} - 1\right)\right] \times 1000$$

where R^i is the abundance of the minor isotopologues relative to the most abundant isotopologue with mass 44, and the expected stochastic ratios R^{i*} are calculated based on the measured abundance of ^{13}C and ^{18}O in the sample. A more detailed description of the calculation of the Δ_{47} variable can be found in [1].

Instrumentation is a key issue in clumped isotope analyses as the measurements require extremely good precision and reproducibility. Instruments with faraday collectors allowing the simultaneous measurement of masses 44 to 49 are needed. A commonly used instrument is the Thermo Fisher Scientific MAT 253 Isotope Ratio Mass Spectrometer, which can be coupled to a KIEL IV Carbonate Device as at ETH Zürich [7, 8] allowing automated analyses from relatively small samples (2-3 mg). The Nu Perspective IS mass spectrometer is specially configured to make precise clumped isotope measurements with exceptional sensitivity and linearity (e.g. at UCLA, Rice University). There are other mass spectrometers as the MIRA (Multi-Isotope Ratio Analyser) at University of East Anglia, which is specifically configured for analysis of CO_2 isotopologues. However, there are still challenges in clumped isotope geochemistry as: 1) the method needs relatively large sample size (2-8 mg); 2) analyses are time-consuming; 3) extremely good precision and reproducibility is needed; 4) similarly to stable isotopes, disequilibrium processes can affect the clumped isotope data; 5) there is discrepancy between the published temperature calibrations.

Applications

The method is used in several research fields of geology, including palaeoclimatology, palaeoceanography, atmospheric research, reservoir geology, geomorphology, structural geology, diagenesis, biogeochemistry, low temperature metamorphic processes, meteorite research, etc.. Due to continuous developments, the number of applications is still significantly increasing. The method has already been applied to a number of materials and questions in geology, for example to soil carbonates [9, 10], dolomites [11, 12, 13], apatites [14], speleothems and cryogenic cave carbonates [15, 16, 17], travertines [18], land snails [19], brachiopods [20], foraminifera [21], meteorites [22] and studies on diagenesis and low grade metamorphism [23]. However, the use of clumped isotopes is not restricted only to CO_2 and gasses like CH_4 [24], O_2 [25], N_2 [26] can be also studied with the method.

Paleothermometry

In geoscience, one of the most important application of clumped isotopes is paleothermometry. The main problem of the conventional carbonate-water paleothermometry is that it requires knowledge of the oxygen isotope composition of the water from which the carbonate precipitated. However, using the clumped isotope thermometer, the temperature of the carbonate precipitating fluids can be determined with high precision (±2 °C), based on solely the clumped isotope value (Δ_{47}) of carbonates, as it is based on homogeneous equilibrium (where only components of a single phase is involved in the isotope exchange process) and independent of the $\Delta\ ^{18}O$ and $\Delta\ ^{13}C$ values of the solution [1].

The theoretical basis of the clumped isotope paleothermometer is the proportionality between observed excess abundance of $^{13}C^{18}O$-bonds in carbonate relative to its stochastic distribution and the carbonate precipitation temperature. Clumping of heavy isotopes (e.g.$^{13}C^{18}O$-bonds) relative to stochastic distribution increases with decreasing temperature and vica versa. In practice this means that the Δ_{47} parameter is low at high temperatures (e.g. the Δ_{47} of CO_2 is 0‰, when the gas is heated to 1000 °C), high at low temperatures and it is about 0.7‰ for carbonates forming at Earth surface conditions [6]. The blocking or closure temperature of the method is around 250-300 °C where the solid-state exchange ceases [27].

Calibrations

The first calibration of the clumped isotope thermometer was obtained by laboratory precipitation experiments [6] in the 1-50 °C temperature range, which was followed by several studies on biogenic carbonates (brachiopods, mollusks, foraminifera) and inorganic carbonates (travertines, diagenetic calcites, pedogenic carbonates, dolomites, etc.). However, discrepancy between the published calibration curves hamper the use of the clumped isotope thermometer. It was suggested that the different phosphoric acid reaction temperatures for the conversion of sample carbonate to CO_2 may be one of the main causes of discrepancies [28], but there are arguments against this idea [29].

Because laboratory calibrations are challenging, naturally precipitated carbonates are an important source of calibration materials for both the oxygen isotope and clumped isotope fractionation, provided that temperature and conditions of carbonate precipitation are well known. Most calibrations based on natural samples are limited to temperatures below 45 °C, while experimental calibrations can cover wide (e.g. 25-250 °C, [30]) temperature range.

The study of active travertine depositing hot spring systems as well as tufa precipitating karstic springs are important in understanding the dominant controls on the carbonate-water oxygen isotope fractionation and on the clumped isotope thermometer. [18] proposed a travertine-based calibration of the clumped isotope thermometer, which is based on recently forming calcitic and aragonitic vent and pool travertines, including tufa and cave deposits (Fig. 1). The main advantages of the travertine-based calibration are: (1) Travertines grow over a wide (6-95 °C) temperature range; (2) the temperature, pH, and chemistry of the depositing water and deposition rate can be measured in the field; (3) these carbonates represent mainly inorganic deposits and show no biological vital effect; (4) they can form different polymorphs of calcium carbonate (calcite, aragonite). The travertine-based T- Δ_{47} relationship is [18]:

$$\Delta_{47} = (0.044 \pm 0.005 \times 10^{6}) / T^{2} + (0.205 \pm 0.047) \qquad R^{2} = 0.96$$

Tufa samples and three biogenic samples (bivalve, brachiopod, eggshell) fit well within the error of the regression, supporting the validity of the travertine calibration also for tufa formed in karstic environments and for biogenic carbonates. This calibration is the most robust available calibration from naturally precipitated inorganic carbonates and it suggests that pH, mineralogy, precipitation rate have no or only minor effects on the Δ_{47}–signal of carbonates [18]. Using the travertine-based, empirically determined calcite–water oxygen isotope fractionation factor, the Δ^{18}O values of the travertine and tufa depositing waters can be calculated with more confidence.

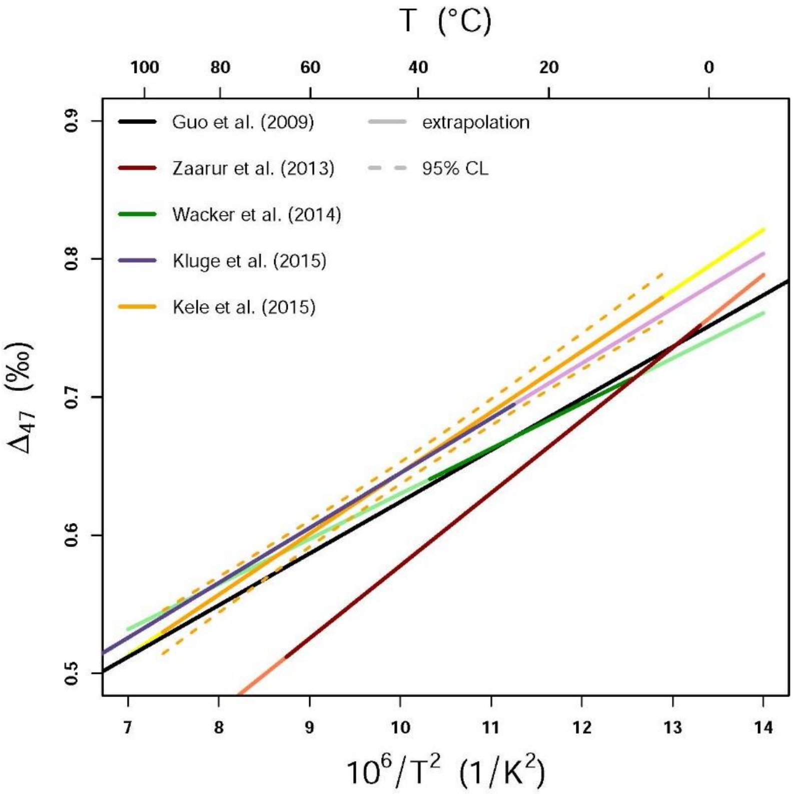

Fig.1. Comparison of recently published calibration curves of the clumped isotope thermometer.

The travertine calibration was successfully used for dolomites [12] and gastropods [31] as well proving its usefulness for other type of carbonates. Newest studies [13] seems to confirm this hypothesis suggesting that an universal Δ_{47} –T may exists across all carbonate-bearing mineral phases.

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TOWARDS DETERMINATION OF MULTIPLE SULFUR ISOTOPE FRACTIONATION

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The principal motivation of this study is to apply SO_2 gas in the multiple isotope analysis (i.e. simultaneous analysis of sulfur isotope ratios: $^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}S/^{32}S$) of sulfur rather than SF_6 gas. The first one can by easily prepared from sulfides [7] and sulfates [4] whilst the second requires the use of a fluorination line [3, 6] and a mass spectrometer with enhanced resolving power to resolve isotope peaks $^{33}SF_5^-$ from $^{32}SF_5^-$ (masses 128 and 127).

This lecture summarizes the main achievements obtained in our Mass Spectrometry Laboratory with analysis of electronegative gases such as SF_6, SiF_4, SO_2, CH_3Cl, CO_2, CO, O_2 etc. Previously described negative ion source bases on the thermal emission from hot metal surface [5]. However, that type source is useful for analysis of the negative ions like SF_5^-, Cl^-, Br^-, which are formed by low energy (~0 eV) electron attachment.

In the patent application [2] we have described a new ion source which can be applied for analysis of gases requiring much higher electron energy for their generation, of order of ~10 eV. Yet in our preliminary experiments we have demonstrated useful mass spectra of SO^- and S^- ions obtained from SO_2 gas for sulfur isotope analysis [1].

Figure 1. Overall view on the 60° magnetic sector mass spectrometer. The dual inlet system is installed at the front panel. The ion source is on the right side and the collector assembly on the left of the flight tube. The recording of mass spectra and the analysis of isotope ratios are computer controlled.

The new ion source differs from the Nier type ion one that the electron beam is replaced by a filament for a strong electron emission inside the ionization chamber. The former ion repeller inside the chamber is kept on positive potential with respect to the filament. This significantly enhances generation both of negative and positive ions in the space along the filament which is immersed in a uniform magnetic field (5-10 mT) with its vector directed along the filament. The magnetic field is produced by a small external electromagnet. The ions generated inside the ionizer chamber are extracted in usual way by an electrostatic lens. It was demonstrated recently that sulfur isotope analysis is more accurate on positive S^+ ions because the ion currents are larger at least by two orders of magnitude.

The analyzed gas is admitted to the ionizer through separate capillaries connected to the pneumatically operated changeover valve as described by Halas (1979). The overall view of the mass spectrometer is shown in Fig. 1.

We thank to Dr. Keith Hackley for donation of old mass spectrometer to UMCS, on the basis of which we were able to develop the new instrument.

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STABLE S AND O ISOTOPES IN THE WIŚNIÓWKA ACID MINE DRAINAGE WATER BODIES (HOLY CROSS MOUNTAINS, POLAND)

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Acid Mine Drainage (AMD) is typically produced by weathering processes of pyrite, marcasite (FeS_2) and other iron-bearing sulfides, which are induced by mining, mineral processing or other human activity. In contrast, Acid Rock Drainage (ARD) occurs in oxidizing surficial environments when unmined sulfide ore deposits or mineralized rock formations are exposed by geologic processes. Sometimes a collective term Acid Mine_Drainage (AMD) or Acid Drainage (AD) is used when describing both naturally- and anthropogenically-induced processes. The AMD waters are characterized by the following properties:

- Low pH (1.5 – 4.0),
- Increased metal(loid) concentrations (0.1 – 500 mg/L);
- High sulfate concentrations (500 – 10,000 mg/L);
- Low concentrations of dissolved oxygen (<5 mg/L),
- Increased suspended solids.

The AMD formation is initiated by oxidation of pyrite and marcasite (FeS_2) or other iron-bearing minerals, including arsenopyrite (FeAsS) and chalcopyrite ($CuFeS_2$), according to the following simplified reactions:

FeS_2 (pyrite) + $3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ (1)

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ (2)

The reaction (2) is more effective in generation of hydrogen ion involving ferric iron as an oxidant. Subsequently, ferrous iron undergoes oxidation to ferric iron (reaction 3) which in turn either hydrolyzes and precipitates in the form of $Fe(OH)_3$ (reaction 4) or oxidizes pyrite (reaction 2):

$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$ (3)

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+$ (4)

Geochemical studies of AMD waters in the Wiśniówka mining area (Fig. 1), including stable S, O and H isotope determinations, have been carried out since 2005 [1,2,3]. The principal objective of these and ongoing studies is to: (i) better understand oxidation processes, (ii) apply characteristic S and O isotope profiles to pinpoint rock mining and processing operations, (iii) assess a potential impact of AMD waters on the neighboring surface water systems and farmer's wells.

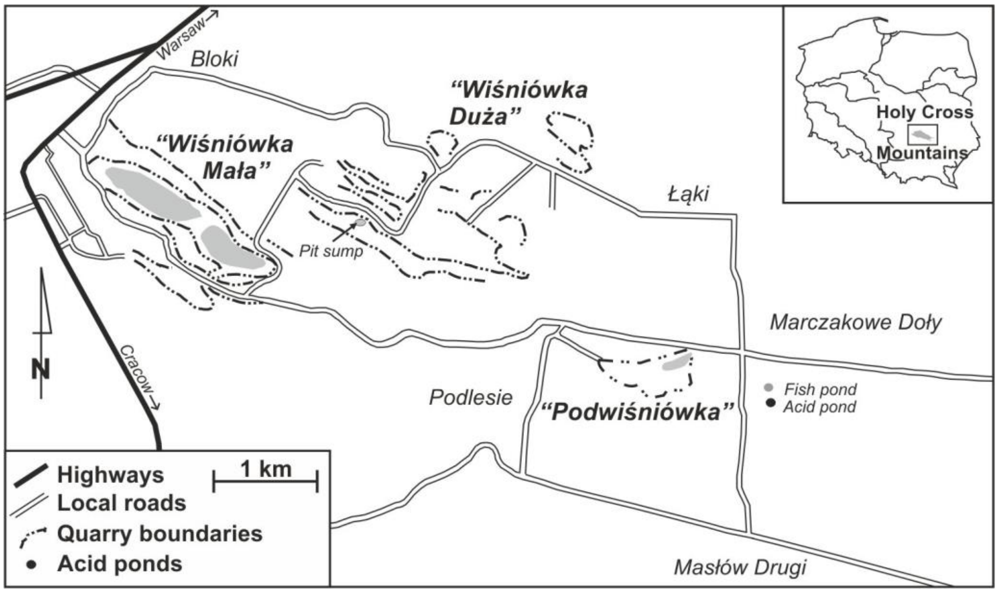

Fig. 1. Localization of acid water bodies in the Wiśniówka area

The stable S and O ratios of these acid water bodies indicate that the principal source of dissolved sulfates is the oxidation of pyrite. This is evidenced by the presence of negative δ^{34}S-SO$_4$ values, which in the Podwiśniówka area are relatively close to the δ^{34}S-FeS$_2$ values. Both the former non-existent pit pond [1] and the present acid pit lake (ongoing study) showed similar δ^{34}S-SO$_4$ signatures: mean of –15.6±1.5‰ and –15.1±0.3 ‰, respectively. By comparison, the mean δ^{34}S-FeS$_2$ value is –25.4±2.5‰. This isotope shift toward less negative δ^{34}S-SO$_4$ values is induced by bacterial (dissimilatory) reduction of dissolved sulfate combined with the release of isotopically lighter H_2S, and presumably with subordinate mineralization of carbon-bonded sulfur compounds.

The previous and present geochemical studies have revealed no relationship between the old and new Podwiśniówka water bodies and the Marczakowe Doły acid and fish ponds, which is also documented by different chemistry of these waters [3]. Of the three farmer's wells examined, only the one located near the Marczakowe Doły fish pond (Fig. 1) reveals a negative δ^{34}S-SO$_4$ value (–12.8‰) as opposed to the others located in two villages of Masłów Drugi and Łąki (+6.4 and +7.5‰). Moreover, these three farmer's wells exhibit different δ^{18}O-SO$_4$ values, i.e. the farmer's well near the Marczakowe Doły fish pond (–2.1‰) vs. the remaining two wells (+1.8‰ and –0.9‰), respectively.

The preliminary study shows that the Wiśniówka Duża pit sump water is enriched in a ^{34}S isotope compared to the Podwiśniówka acid water bodies. The δ^{34}S-SO$_4$ value varies in the range of –11.7 to –10.4‰. This may suggest the other generation of pyrite mineralization. However, this issue needs further studying.

Acknowledgements

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IMPROVED TRIPLE-FILAMENT ION SOURCE FOR TIMS USED IN ^{7}Li/^{6}Li AND ^{39}K/^{41}K RATIOS DETERMINATIONS

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Lithium and potassium belong to the first group of the Periodic Table. Their ionization energy is relatively low, what makes lithium and potassium atoms easily ionizable in the contact with a hot metal surface of high electronic work function. This is the reason why Thermal Ionization Mass Spectrometry (TIMS) is convenient method for precise analysis of Li and K isotope ratios. However one should be aware that there are two essential difficulties in TIMS analysis: mass fractionation effect and cross contamination. The first one can be overcome by usage of high-mass compounds as a loading form to ion source (e.g. phosphate, [1]), but the second one has been an unsolved problem so far.

Our improved triple filament ion source (Fig. 1) is equipped with two evaporation filaments (rhenium) and one ionization filament (platinum/iridium) located parallel between them in front of the extraction slit.

Figure 1. Triple filament ion source of TIMS with wide ionization filament (Pt/Ir) between evaporation filaments (Rh).

The ion source enable independent control of the temperature at which the sample evaporates and of the temperature at which ionization occurs to get stable ion current beam. Because of high work function of platinum, the ionization filament does not require very high temperatures to serve as ionizer. In order to improve ion source efficiency, we have reconstructed the ion optics systems (Fig. 2). As a result the ion source produces a stable and high intensity ion beams that allows to analyze of nanogram quantities of lithium or potassium.

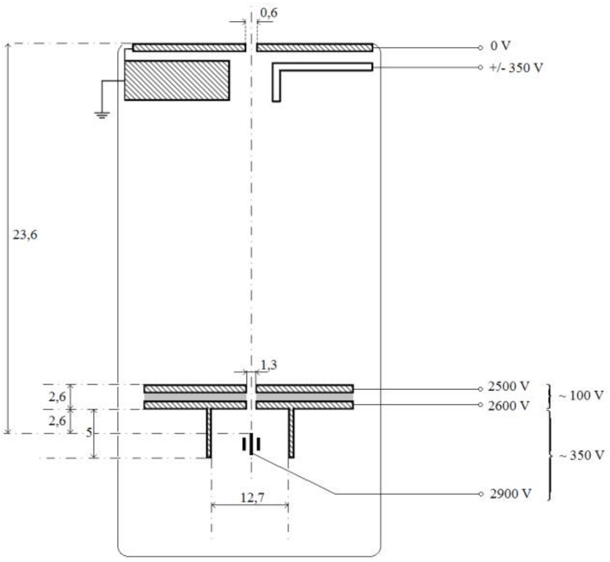

Figure 2. Schematic diagram of improved triple filament ion source of TIMS. Distances are given in millimeters.

The most important original invention is to use a new concept of ionizing filament i.e. platinum filament which is wide enough to prevent *cross contamination* of isotopically different samples loaded on two separate evaporators. Thus different samples can be measured one after another alternately without venting the mass spectrometer chamber. The results of measurements of two extremely different potassium samples are shown in Fig. 3. One is natural sample with R = 13.59 and the second is ^{41}K spike with R = 0.0522, where R is the isotopic ratio R = ^{39}K / ^{41}K. The analysis was conducted for over 100 minutes, however no symptoms of *cross contamination* for at least 5 hours of alternate analysis were noticed.

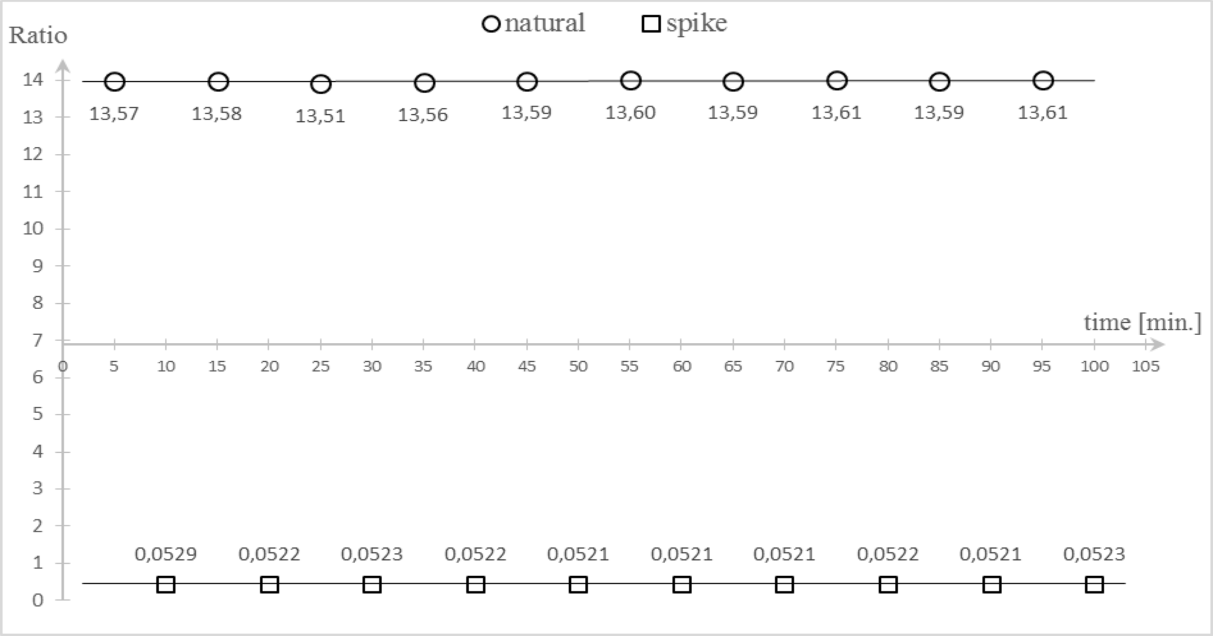

Figure 3. The results of measurements of the isotopic ratio of two extremely different potassium samples loaded at the same time on different evaporators. The measurements was conducted alternately without venting spectrometer chamber.

Mass spectra corresponding to the measurement of natural sample and ^{41}K spike sample discussed above are shown in figures 4 and 5, respectively.

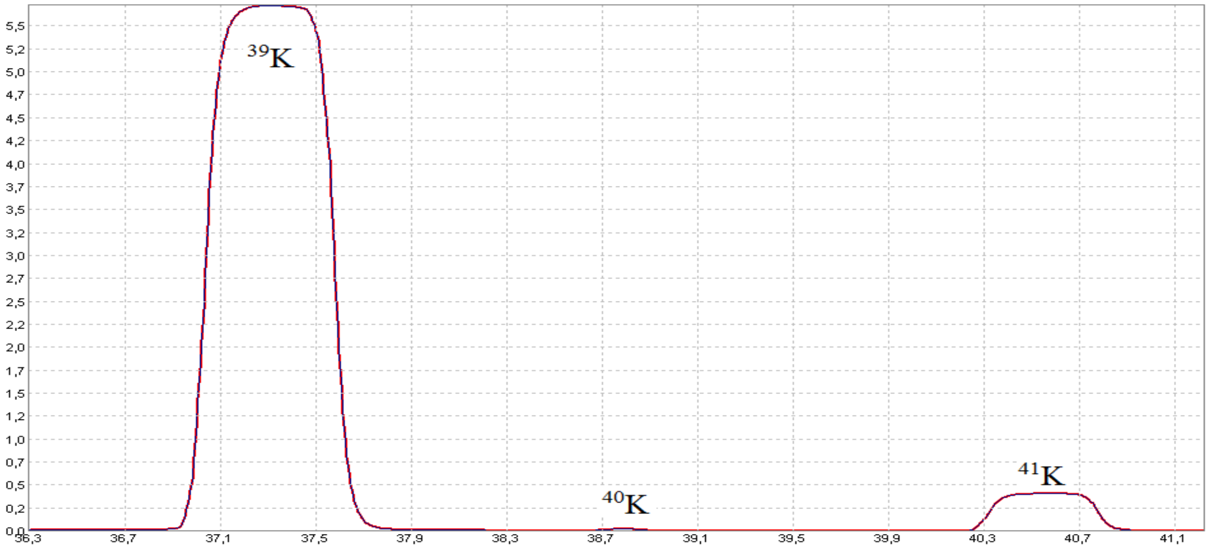

Figure 4. Mass spectrum of K natural with visible trace of ^{40}K peak.

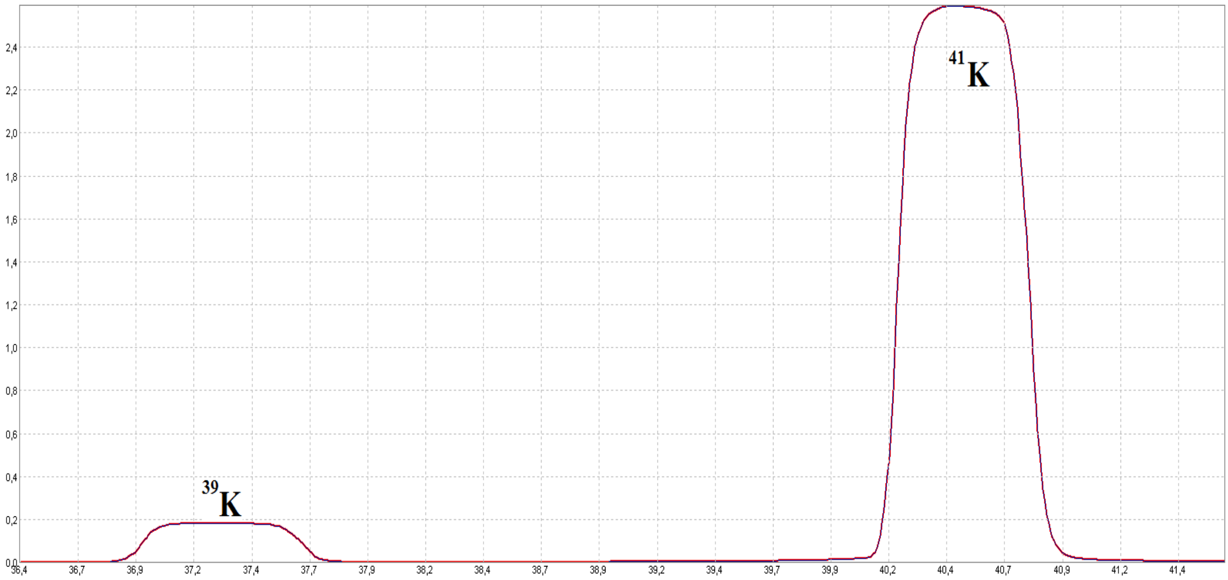

Figure 5. Mass spectrum of ^{41}K spike.

In this approach Li or K are loaded onto evaporation filaments in form of phosphate. Consequently *mass fractionation effect* is reduced by the evaporation of relatively heavy molecular species of phosphate [4]. Phosphate molecules dissociate and ionize at the ionization filament predominantly to the Li^+ or K^+ ions, where electric field directs them to the analyzer chamber of the mass spectrometer. Minimizing of *mass fractionation effect* is extremely important in the case of lithium – very light element. The values of δ^7Li for the natural samples are determined with achieved reproducibility about a few permil or better. Illustrative mass spectrum of Li is shown in Fig. 6. Numerical simulations of the ion beam forming in the ion source are shown in Fig. 7.

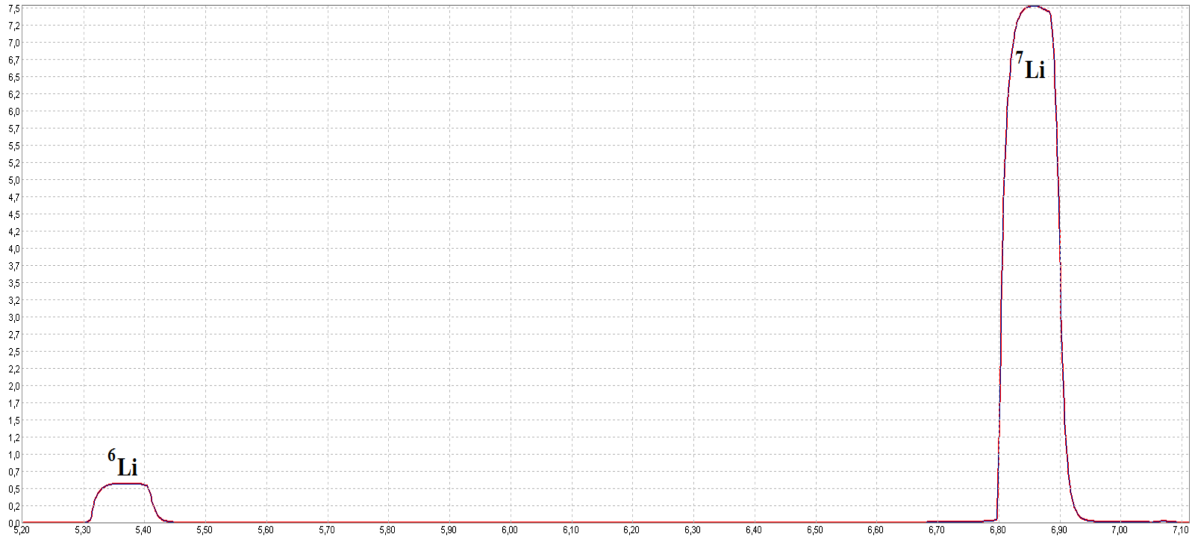

Figure 6. Mass spectrum of Li.

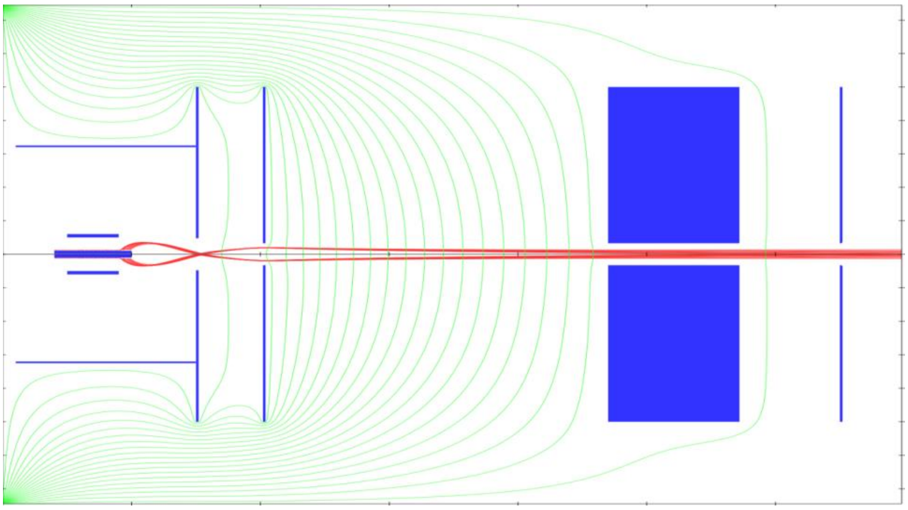

Figure 7. Numerical simulations of the ion trajectories along the ion source. The blue objects are the electrodes whist the green lines indicate cross-sections of the equipotential surfaces.

This relatively cheap method of lithium and potassium isotope determination requires neither complicated chemical preparation of the investigated samples, nor large quantities of material. In fact this is one of the simplest methods, although in comparison to ICP-MS is quite time consuming. We have demonstrated that our new ion source allows to measure the isotope ratio of potassium with accuracy of half permil or better. High sensitivity of such analysis is confirmed by the presence of the peak ^{40}K in potassium spectrum. Possibility of alternate sample-standard analysis may lead to detect the variability of potassium isotopic ratio in natural samples, which has never been found so far.

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MICROANALYSIS OF PGE MINERALS IN MONCHEGORSK PLUTON, KOLA PENINSULA, BALTIC SHIELD

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The selected samples of sulfide ore from mafic intrusion from the central part of Kola Peninsula were performed using a microanalysis with stable sulfur isotopes and XRF analysis. The sulfide samples were selected from the main ore-bearing rocks of the layered Monchetundra intrusion. The analyzed sulfides formed several generations of mineralization in the above mentioned fields associated with primary and hydrothermal stage of formation of the deposits. Isotopic studies confirm a few consecutive stages of mineralization, which already was particularly well described in the case of sulfides from Fiodoro-Pansky deposit. These data were compared with the results of Sm-Nd dating of sulfide mineralization. This is due to the processes of their formation and also imposed factors metamorphic and hydrothermal processes occurring in these rocks. The results of geochemical and geochronological studies indicate a complementarity in the context of determining the mineralization stages. In these rocks was found a PGE phases like kotulskite, maslovite and sperylite. The gabbroanorthosite (2925 ± 7 Ma) earlier demonstrated zones of sulphide mineralization with increased Pt and Pd concentrations [5-10]. According to Bayanova et al. [1-5] the ore-bearing intrusions formed earlier in the Kola belt (Fedorov-Pana and other intrusions, 2530-2450 Ma) and at some later stage in the Fenno- Karelian belt (2450-2400 Ma). These rocks have massive structure and granoblastic texture with plagioclase, varies from bytownite to labradorite and mafic minerals represented by amphibole and epidote. Accessory minerals are represented by zircon, titanite, apatite, and Ti-magnetite. The collected samples of rocks were analyzed using an optical microscope Leica DM2500P and scanning electron microscope Hitachi SU6600 with EDS at the Department of Geology and Lithosphere Protection (UMCS, Lublin, Poland). Inclusion of platinum arsenide (sperrylite,PtAs2) and others PGE phases has been found in the samples with accompanied sulphides. The stable isotope analysis δ^{34}S from selected sulfide phases was made in Institute of Physics (UMCS), Lublin, on a dual inlet and triple collector mass-spectrometer. Studied sulphides in the rock massif Monchegorsk indicate high volatility isotopic resulting from the coexistence of several generations of sulphides. These minerals form the structure disintegrating, the sulfur contamination of fluids with different backgrounds which makes it difficult separations and causes large scatter of test results of the same samples of rocks. In general, these analyses to demonstrate the following characteristics of samples: Multiple injection ultrabasic magma in the growing cold rocks which contributes to a certain oscillation of sulfur isotopes of the primary sulphide phases, multi-stage mineralization (magmatic, secondary magmatic, hydrothermal, epigenetic) -what is associated sulphides processes metamorphism of sulfides scale and numerous regional tectonic processes sulfide scale meson micro sulphides rocks of sulphides also creating structures disintegration contributing to the contamination of sulfur isotopes. PGE examined phases are located in zones of hydrothermal disintegration and, therefore, are associated with significantly subsequent processes to the original rock forming a background in which there was a sulfide ore mineralization and mineralization of PGE.

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INTERLABORATORY LUMINESCENCJE DATING OF MESO-PLEISTOCENE LOESSES FROM WOŁYŃ AND PODOLE: METHODICAL ASPECTS

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W zachodniej części Ukrainy, występuje zwarta i miąższa pokrywa lessowa. Do kluczowych profili na tym obszarze należą Wołoczysk, Korsziw, Bojanice usytuowane w odległości od siebie od 70 do 150 km. Profile te odgrywają ważną rolę w stratygrafii środkowego i górnego plejstocenu w Europie Środkowej i dlatego wytypowano je do szczegółowych datowań luminescencyjnych. Wykonano je w 3 polskich laboratoriach (Gdańsk, Lublin, Gliwice). Daty były wykonane metodami luminescencyjnymi: termoluminescencyjną (TL), optycznie stymulowanej luminescencji (OSL) – technikami SAR oraz post IR IRSL. Wykorzystano różne rodzaje i frakcje ziaren, najgrubsze kwarcowe: 90–125 µm (SAR OSL w Gliwicach) i 80-100 µm (TL w Gdańsku), polimineralne frakcje o wielkości: 45-65 µm (SAR OSL w Lublinie), 45-56 µm (post-IR IRSL w Lublinie) 4-11 µm (post- IR IRSL w Gliwicach). Szczególnie cenne z punktu widzenia porównań są daty uzyskane dla próbek pobranych z tych samych miejsc i wykonane przez wszystkie 3 laboratoria, jak było w przypadku profili Korsziw i Wołoczysk. Dodatkowo dla Wołoczyska uzyskano wyniki dla różnych frakcji ziaren polimineralnych najnowszą metodą post-IR IRSL.

Ramy czasowe formowania sekwencji lessowo-glebowej zostały skorelowane ze stadiami izotopowo-tlenowymi (MIS). Są one dla obszaru Ukrainy następujące: less L2 tworzył się od 210 do140 ka, gleba interglacjalna S1 – od 140 do75 ka, less L1 – od 75 do kilkunastu ka. W obrębie lessu zarówno L2 jak i L1 wyodrębnione zostały mniejsze jednostki stratygraficzne dotyczące gleb interstadialnych.

W profilu Wołoczysk (Wyżyna Podolska) badano część sekwencji osadów obejmujących dwie jednostki lessowe (L2 i L1) rozdzielone pedokomleksem horochiw (S1). Młodszy less L1 rozdziela interstadialną gleba dubno (MIS3), a w obrębie jego części górnej występuję inicjalny poziom krasyliw (MIS2). W 2010 r. pobrano 13 próbek na datowanie: Gdańsk i Lublin (13 dat TL), Lublin (13 dat SAR OSL), Gliwice (9 dat SAR OSL). W roku 2014 wykonano dodatkowo dla tych samych próbek daty metodą post IR IRSL (Lublin – 6, Gliwice - 12). Łącznie dla 13 próbek uzyskano 53 daty.

W profilu Korsziw (Wyżyna Wołyńska) pełna sekwencja lessowo-glebowa obejmuje warstwy korelowane z okresem MIS8-2. Wiek luminescencyjny oznaczono dla lessu L2 z poziomem interstadialnej tarnopolskiej gleby, pedokompleksu horochiw (S1), oraz lessu L1 z śródlessowymi poziomami glebowymi niższej rangi gleb dubno (MIS3) oraz riwne i krasyliw (MIS2). W 2010 r. pobrano 31 próbek (31 dat TL – Gdańsk, 28 dat TL – Lublin, 20 dat SAR OSL – Gliwice). Łącznie dla 31 próbek uzyskano 79 dat.

W profilu Bojanice (zachodnia części Wyżyny Wołyńskiej), badano osady reprezentujące okres MIS6-MIS2 z podobnym układem warstw lessowych i glebowych jak w Korszewie. Próbki do datowań pobrano w latach 2007 (14 dat TL – Gdańsk) i 2009 (20 dat TL – Lublin).

Duża liczba (166) wykonanych dat luminescencyjnych daje dobrą podstawę do wniosków metodycznych i stratygraficznych:

1. Generalnie daty TL są starsze od pozostałych;

2. Daty OSL są wyraźnie niedoszacowane dla osadów najstarszych;
3. Wszystkie daty gliwickie i lubelskie dla SAR OSL są zaniżone w stosunku do przedziałów wyznaczonych przedziałami MIS z wyjątkiem subjednostek lessowych i glebowych w obrębie L1;
4. Żadna zastosowana metoda badawcza nie umożliwiła uzyskania w całości poprawnych dat w odniesieniu do ram czasowych wyznaczonych przez MIS. To samo stwierdzenie należy odnieść do różnej rodzajów i wielkości ziaren.
5. Zamiana dużych ziaren kwarcowych 90–125 μm na polimineralne ziarna 4-11 μm to krok w dobrym kierunku. Powoduje on powiększenie dat OSL i zbliżenie się do przedziału czasowego wyznaczonego przez MIS 4-5.
6. Najstarsze daty TL dobrze wyznaczają początek depozycji lessu L2 (około 200 ka);
7. Daty uzyskane dla pedocompleksu horochiw (S1) są również zaniżone. Skrajne daty wskazują, że czas jego tworzenia wynosi około 70 tysięcy lat, co jest zgodne z czasem wyznaczonym przez MIS5;
8. Subjednostki dubno (MIS3), riwne (MIS2) i najmłodszy krasyliw wyróżnione w obrębie L1 dobrze odpowiadają ramom czasowym wyznaczonym przez MIS;
9. Daty TL gleby dubno z profilu Bojanice mieszczą się w przedziale 45-50 tysięcy lat i odpowiadają czasowo dacie gleby interstadialnej glinde w Europie Zachodniej;
10. Data uzyskana w spągowej części gleba dubno w Korszewie była porównywalna do daty uzyskanej w profilu Bojanice;
11. Data uzyskana z próbki pobranej ze stropowej części profilu gleby dubno w Korszewie uzyskała wiek około 24 tysięcy lat. Najprawdopodobniej daty potwierdzają dwudzielność tego poziomu, wykazaną w wielu ukraińskich profilach;
12. Daty inicjalnego poziomu krasyliw wskazują, że ostatni jego formowania w minionym glacjale miał miejsce kilkanaście tysięcy lat temu;

Nie znaleziono dotąd takiej metody ani techniki badawczej która byłaby niezawodna w datowaniu luminescencyjnym i dawała w pełni satysfakcjonujące wyniki, zgodne z rozpoznaniem przyrodniczym. Należy w dalszym ciągu poszukiwać nowych sposobów, pamiętając o tym że procesami sedymentacji w przeszłości sterowały skomplikowane warunki klimatyczno-środowiskowe, które trudno odtworzyć we wszystkich aspektach ich złożoności, a które miały pośrednio wpływ na proces wybielania datowanych ziaren.

3.7 GA METAMORPHITE BLOCK FROM MURMANSK: MINERALOGICAL CHARACTERISTICS

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The complex of crystalline rocks are located in the city of Murmansk. It is classified by researchers of the oldest Kolska series [1,7,9,16-18], which are in the vicinity of contact with Murmansk Block deposits. Studied parametamphites were dated on age of 3.7 Ga, using U-Pb method (unpublished of the Bayanova data 2015), what makes these rocks among the oldest in the Baltic Shield and on Earth. It is a complex of rocks that have multiple metamorphism which have numerous intrusive and ultrametamorphic processes [15].

These rocks are the subject of petrological-geochemical analyzes in order to demonstrate their complex history and interesting mineralization associated with a number of subsequent secondary processes recorded in those rocks. The samples were collected in the study area shown in Figure 1. These preparations were examined using an optical Leica DM2500P microscope with transmitted and reflected light and then tests were performed using a scanning electron microscope Hitachi SU6600 with an EDS attachment. These studies were carried out in the Geology and Lithosphere Protection Department at the Earth Sciences and Spatial Management Faculty at Maria Curie-Sklodowska University (UMCS). In addition, a study was made of rock with a mass spectroscope at the Institute of Physics, UMCS, in order to determine the composition of stable isotopes of sulfur in sulphide selected samples. Selected preparations were also investigated using powder XRD analysis in Geological Institute of the Jagiellonian University in Kraków. In addition, selected samples were examined by ICP-MS in the Department of Soil Science and Soil Protection (UMCS).

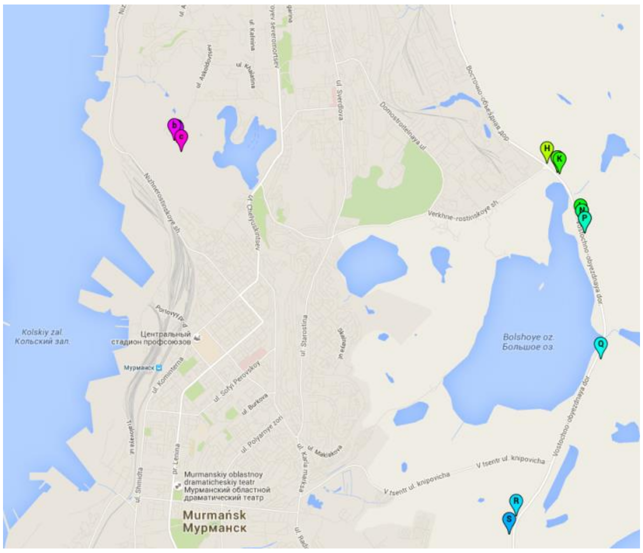

Fig 1. Sketch map with the localization of sampling points in Murmansk region.

Examined rock samples contain mainly garnet-mica gneisses with plagioclases, quartz sometimes sillimanite and a range of accessory minerals. Samples of particular interest have signatures of secondary processes. Recognized garnets constitute solid solutions composed of different individual particles, which may be associated with crystallization under different conditions. Current plurality of phases such as pyroxenes, amphiboles, micas point to processes replacing mafic minerals by various stages of metamorphic rocks. Particularly interesting are the Accessory minerals which can distinguish various types of sulfides including pyrite, galenite and barite as well as several generations of apatite. In the rocks are both ordinary and apatite minerals rich in elements of the cerium. The latter indicate that cross-contamination of fluids probably associated with hydrothermal processes, accompanied by numerous alkaline intrusions associated in the region of rocks [10-14. 2-6,8]. In these rocks they are also recognized numerous kinematic processes of a disjunctive and partly plastic tectonic. Underlined are the structures spindle-blasts, and interference zones and lubricating microflecsural highlighted by staurolite and micas. These structures are present mainly in the areas of fault ruptures associated Kola region overwhelmed that during the formation probably had an impact on the surrounding rocks. The evidence of these processes and presence of numerous veins intersecting these rocks indicates the advanced processes of mobility in the region during its extensive history of existence.

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IGNEOUS PROTOLITHS OF THE UIVAK GNEISS, PRELIMINARY DATA FROM THE SAGLEK BLOCK, NORTHERN LABRADOR

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The Saglek block in northern Labrador is part of the Nain Province, which forms the westernmost part of the North Atlantic Craton (Fig.1). It is one of the few regions on Earth where early Archean crust is preserved. It is bound by the Paleoproterozoic Torngat Orogen to the west and, before break-up, was contiguous with the early Archean Amîtsoq gneisses of eastern Greenland.

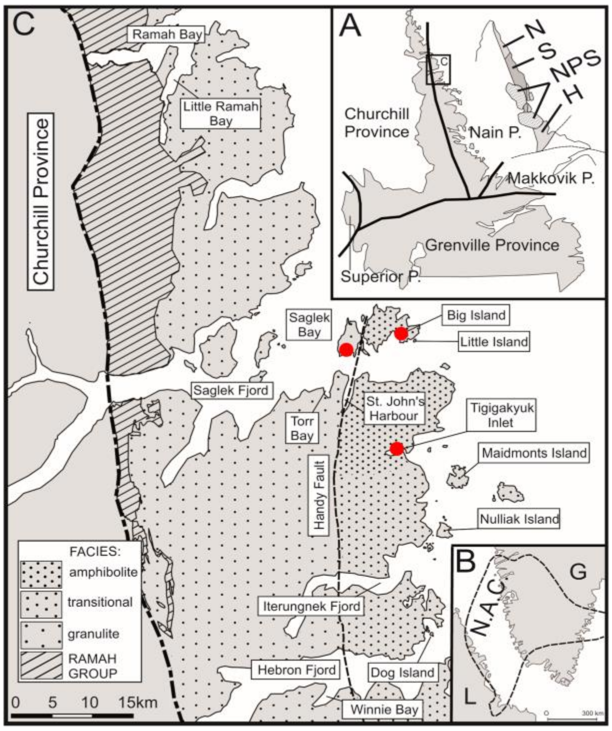

Fig.1. Sample locations – Saglek Block, Nain Province (Labrador Peninsula). Red circles – samples localities.

The block comprises gneisses regionally metamorphosed to granulite-facies at *ca.* 2.74 Ga and/or amphibolite-facies at *ca.* 2.70 Ga [1]. Outcrop is dominated by two suites of metaigneous gneisses: the Uivak I suite (>3.6 Ga), comprising fine to medium-grained tonalite-trondhjemite -granodiorite (TTG) gneisses, and the less extensive Uivak II augen gneiss (ca. 3.4 Ga), consisting of Fe-rich porphyritic granodiorite and diorite [2, 3].

The Uivak suites are tectonically juxtaposed and interlayered with supracrustal assemblages, along with several generations of felsic pegmatite. Based on the zircon dating, the presence of enclaves or tectonic intercalations of pre-Uivak I felsic crust have been proposed, such as the monzonitic ca. 3.95 Ga Nanok Gneiss [4] and the tonalitic ca. 3.9 Ga Iqaluk Gneiss [5].

Samples of Uivak gneiss were collected and examined from various localities around the Saglek block (Fig.1). Intrusive relationships were observable in the Uivak gneiss in low-medium strain domains in the field, including at Tigigakyuk Inlet, where the Nanok gneiss was first 'identified'.

Preliminary U-Pb isotopic dating of zircon from three samples, two possible candidates for Nanok gneiss (Fig.2A&B) and a metapelitic gneiss (Fig. 2C), was done by ion microprobe at the John de Laeter Centre, Curtin University (Perth, Australia) and the Natural History Museum (Stockholm, Sweden).

Fig.2. Samples analysed in this study: (A) Tigigakyuk Inlet, sample L1440, felsic orthogneiss; (B) Big Island, sample L1443, felsic orthogneiss; (C) Shuldham Island, sample L1450,

Concordant age data obtained from zircon cores with characteristic igneous growth zoning fall within the interval 3.67-3.76 Ga (Fig. 3A, B, D), consistent with age estimates for the protoliths of Uivak I gneiss by Schiøtte et al. [7], rather than the older 'Nanok' gneiss. Monazite grains from the metapelite yield metamorphic age of 2.71 Ga (Fig.3C). Older ages comparable to those found by Krogh & Kamo [1] (3.81 Ga and 3.99 Ga) and Collerson [3] (3.91Ga) were not obtained.

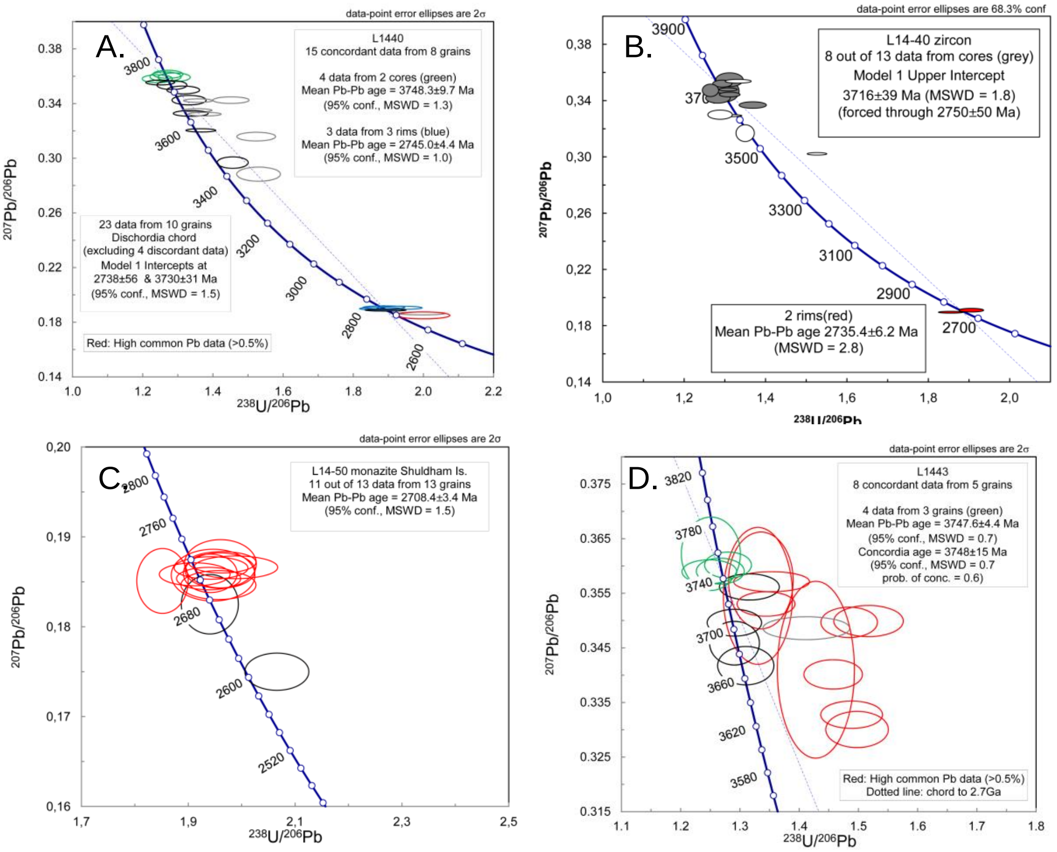

Fig.3. SHRIMP monazite (A) & (C) and zircon (B)& (D) ages for gneisses and metamorphic schist.

The granodioritic to tonalitic compositions of the orthogneiss samples (L1440, L1443) and mineralogy (mostly plagioclase and quartz, with minor K-feldspar and biotite, and accessory zircon and apatite) are consistent with published descriptions of Uivak I Gneiss [3]. Although the lack of older data does not eliminate the possibility of the existence of an older 'Nanok' gneiss, it supports interpretations that the older ages are from inherited zircon in younger Eoarchean protoliths.

This research is conducted thanks to the grant for MAK by a Polish National Science Centre; NCN (nr 2014/15/B/ST10/04245) and funds to MJW from the Knut and Alice Wallenberg Foundation and the Swedish Research Council. Field work was carried out with the permission and support of Parks Canada and the Nunatsiavut Government.

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ENVIRONMENTAL AND POLLUTION CHARACTERISTICS OF THE LUBLIN ROUGHCAST

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Lublin, are the county town of the middle ages. The first houses built in this place already in the early Middle Ages [2-6]. During the Renaissance falls flourishing city, which is shown in the numerous monuments including churches and laity. In later centuries, particularly during the partitions Lublin becomes a provincial town, and in the twentieth century recover again the importance of the regional town and passes a number of changes[1]. This significantly improves the use of stone in the architectural details. At the time of socialism in Lublin housed various manufacturing plants, most of which did not withstand political changes. In Lublin, there are numerous examples of the use of diverse stone in the details of architecture and these rocks respond differently to destructive factors related to human activity. Sampled within the old city were subjected to observation of corrosion. For this purpose, we performed field studies involving the making observations architectural details that helped distinguish several types of corrosion and lesions associated with human activity (figure 1). Collected samples walls were observed with an optical microscope Leica DM2500P reflected light. Further tests were carried out in the micro using a scanning electron microscope of Hitachi SU6600 snap EDS under low vacuum. These studies were performed in the Department of Geology and Protection of Lithosphere UMTS. Analysed samples were tested for the presence of metals emissions related to the use of methods of ICP-MS and ASA in the Department of Soil Science and Soil Protection UMCS.

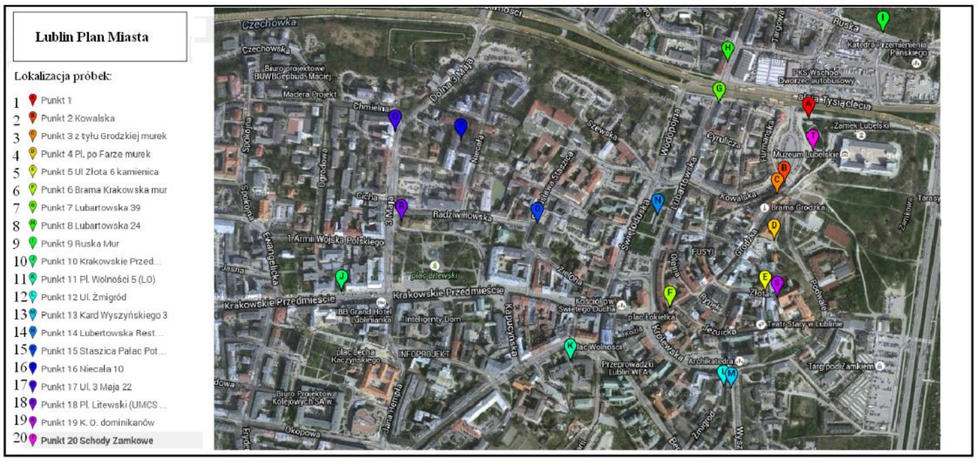

Fig 1. The sketch (from Google maps) of the centre of Lublin with samples localization.

The chemical composition of the roughcasts samples showed a present of some metals such as lead, chromium and other. It is also present a carbonate, sulfate precipitates and mosses . There are a processes of destruction in some houses. It is also present in some samples a dissolved compounds (enrichment Mn, Fe) and crystallization slots plaster. In the center of city is also present a carbonates (in these houses is a carbon heating), Some metallic additions are corresponded with roof corrosion processes (eg. The Cracow Gate, which has a roof made of copper plates). In conclusion, the largest source of pollution in Lublin are localized on the main streets and close proximity in to the city center.

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ENVIRONMENTAL AND POLLUTION CHARACTERISTIC OF PLANTS SAMPLES FROM KARKONOSZE REGION, S POLAND ROUGHCAST

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Sudeten are located in the south-western part of the largest Polish acting within the limits of our country area where outcrop igneous and metamorphic. They represent a larger portion of the Bohemian Massif [2,3,8,5]. These formations are often uneven-aged rocks in contact with each other in a tectonic which is associated with mosaic nature of these mountains. There are exposed rocks of multistage rocks from Precambrian in Sowiogórski terrain, Śnieżnik Massif and Izera Massif gneisses [1,8], to the youngest cells of Neogene–volcanic rocks [8]. These mountains are built mostly of rock folded in Hercynian orogeny, rejuvenated block the movements of Alpine [1,2,3]. Relevant to this discussion is the intrusion of granitoide rocks of the Karkonosze Mountains, breaking into a metamorphic gneiss of Izera and complex rock Leszczyniec units built with hornfelses, schists and amphibolites, with the subsequent processes he has contributed to the mineralization in these mountains [6,7]. Rock samples were taken in the Karkonosze Mountains, in the vicinity of the Sowia Valley, Skalny Stół, Śnieżka Valley Łomniczka, area of Szklarska Poreba and Karpacz in 2015 with the knowledge and consent of the authorities of the Karkonosze Mountains National Park. Preparations were made of rocks and dry up mosses collected in the course of fieldwork. These samples were examined using a Leica DM2500P polarizing microscope in transmitted and reflected light and then the micro involving scanning electron microscope Hitachi SU6600. Rock samples were tested in addition to the participation of X-ray fluorescence spectrometer Epsilon 5 XRF PANalytical. Comp plant were reviewed by ICP-OAS. Microscopic and spectroscopic studies were performed in the Department of Geology and protection of the Lithosphere in the Faculty of Earth Sciences and Spatial UMCS. The samples investigated by ICP-OAS examined in the Department of Soil Science and Soil Protection UMCS. Results of analyses have been developed using Microsoft Excel and Surfer. Examined samples of bedrock have some variation characteristic of igneous and metamorphic rocks. Particularly interesting is the mineralization of metals, which is represented by a variety of ore minerals. They can penetrate into the soil and the plants further contributing to the accumulation. The investigated plants show relatively low metal content, and the small quantities of iron, titanium and manganese. It is also associated with a relatively contaminated area which are Sudety. Some of Zn, Ni, Cu may be related to rock ore mineralization, as noted only in a two important things arsenic. Karkonosze Mountains is an area with very interesting geological structure and sculpture associated with numerous geological processes and windy. Occurring within the study sites rocks are mainly granitoids, metamorphic rocks cover Karkonosze granite such as gneiss, schist, hornfelses. These rocks have relatively similar to each other mineral and chemical composition, differing only and additions of accessory and ore minerals. The area of the Karkonosze Mountains is the Karkonosze National Park, which is a protected zone. The result is that in the area of the Karkonosze Mountains industry is very limited. This affects the quality of the air. Environmental conditions and the quality of the substrate contribute to the contamination studied mosses. These, however, are relatively small. Any admixture of metals are closely connected with the geological substrate.

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A DUAL INLET AND TRIPLE COLLECTOR MASS SPECTROMETER FOR ANALYSIS OF $^{33}S/^{32}S$ AND $^{34}S/^{32}S$ ISOTOPE RATIOS

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This poster summarizes the properties of recently developed instrument for isotope analysis of $^{33}S/^{32}S$ and $^{34}S/^{32}S$ isotope ratios on SO_2 gas in the Mass Spectrometry Laboratory [1,2]. So far such triple-isotope analysis was possible only on SF_6 which is difficult to prepare quantitatively from natural samples. The new possibility offers a newly designed ion source which generate sufficiently strong ion currents of isotope species ^{32}S, ^{33}S and ^{34}S in the negative as well as in positive mode. The ion currents of the positive isotope species are detected by three Faraday cups and high-ohm resistors with resistances of 1, 100 and 10 giga-ohms, respectively. The triple collector assembly is shown in Fig.1, it is installed on a rotatable CF 63 flange. The resolving slits are located in the focal plane.

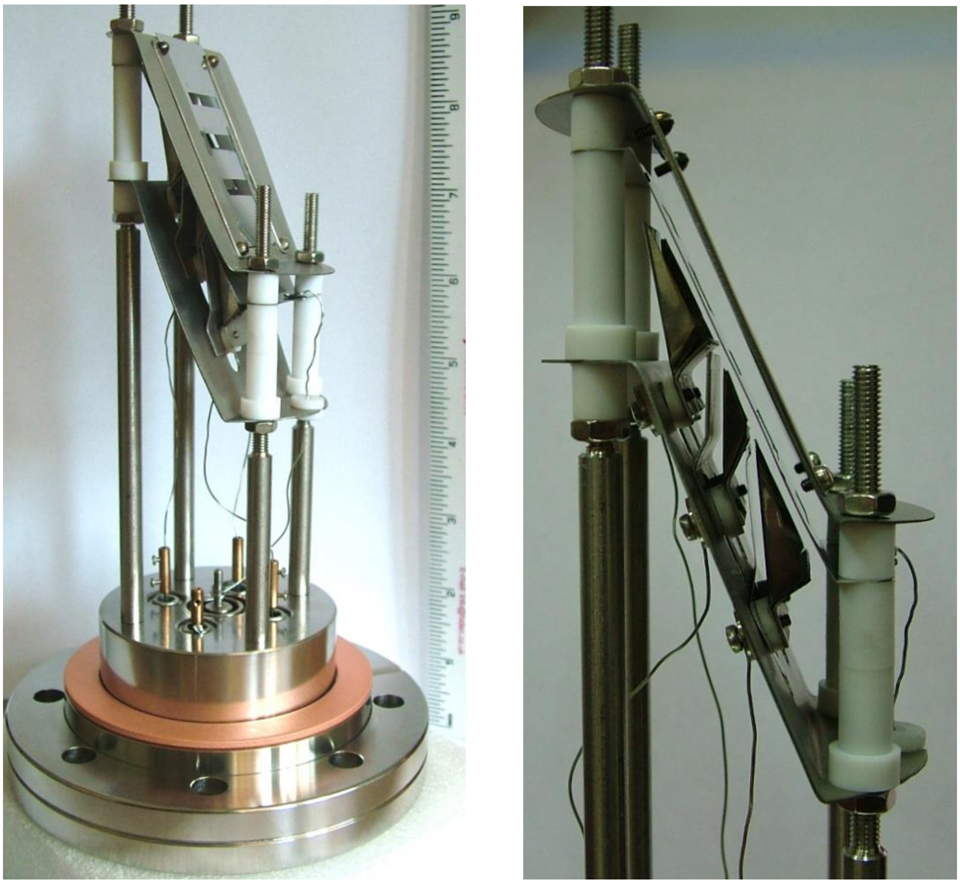

Fig. 1. Triple collector assembly for collection of 32, 33 and 34 ion beams installed on rotatable CF 63 flange.

It is important to have SO_2 samples well purified from volatiles which eliminates O_2 interference at mass 32 peak. The UHV in the flight tube of mass spectrometer should be free of water molecules

(H_2O, HO and O ions), otherwise the interference at mass 33 may occur from SH ions. When these conditions are fulfilled, then the observed respective peak ratios are close to $^{32}S/^{34}S = 22.5$ and $^{34}S/^{33}S = 5.6$ for laboratory working standard.

A great advantage of the isotope analysis on S^+ instead of SO^+ or SO_2^+ is that there is no need to keep constant oxygen isotopic composition in the SO_2 gas. Usually sulfide and sulfate samples have different oxygen, but it doesn't matter in the case of analysis in S^+.

The achieved precision (1σ) on positive ion beams was 0.03‰ and 0.01‰ for $\delta^{33}S$ and $\delta^{34}S$, respectively. The details of the design of the ion source, vacuum system and electronic controllers are presented in the poster.

We thank to Dr. Keith Hackley for donation of old mass spectrometer to UMCS, on the basis of which we were able to develop the new instrument.

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ENVIRONMENTAL MOSS CHARACTERISTICS FROM MIDDLE ROZTOCZE (TOMASZÓW AREA)

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In the spring of 2016 years they have been carried out field work within Middle Roztocze covering cities such as Susiec, Nowiny, Ulów, Kunki, Krasnobród, Huta Różaniecka. Roztocze is a strip of hills, which are located in an arc between Upland Lublin and Sandomierz Basin. In the course of its formation (mainly in the Mesozoic and Neogene, as called. Climactic part of the Metacarpathian Embankment) it was initially subjected to movements subsidention then elevating movements of Alpine orogeny in the form of a block of a framework [3, 10, 12, 13, 15]. Carrying mites was held evenly dividing the entire area into individual blocks [2, 4, 11]. In the ground mites are therefore chalk cliffs (mostly marl and bedrock Late Cretaceous –mastricht, [9]) and on the rocks arrears rocks included in the Neogene. Neogene is represented by sands and sandstones and organodetritic limestones and reef, which were at that time deposited during marine transgression in Baden and Sarmat [1, 7, 11]. The youngest link marine sedimentation and land are numerous sandstones and found the petrified tree trunks that had been created in conditions resembling the current wetland cypress forests in brahical environment [1, 4,5,6, 8,11,14]. In later periods followed by erosion that removed a large part of the Miocene deposits especially in the middle Roztoczu [1,11].

Examined rock samples show a typical variety of this area. They are both the chalk cliffs, Neogene and Pleistocene. The latter are associated with the formation of the covers of origin glacial and periglacial where there have to redeposition crumbs older songs sedimentary rocks and crystalline and aeolian sediment formed in the periglacial conditions. Demonstrated a number of admixtures of chlorine, sulfur, potassium and other elements resulting from surface surveys in the micro may indicate a dust adsorbed on these plants. It can be that its origin is associated with fertilizers which are commonly used in the agricultural area. They found a small metal content in the analyzed samples were the lowest among all examined in this study sample which indicates a very clean environment prevailing in the mite. Small quantities of Zn and Pb detrital limestones of the Miocene (as As, Ti) may be associated with the activity of hydrothermal processes that accompanied hauling metacarpathian blocks shaft at the time of the formation of hills mites. Small quantities of manganese and iron noted Krasnobrod of mosses are characteristic of the rocks contained in the substrate in which these metals are common. Some dopant elements found on the surface of these products may be associated with intensive livestock farming in this region. Moss samples examined by means of ICP - OAS metal content, have a relatively high degree of purity of all the analyzed samples in this study. This is due to the lack of industry in the vicinity of the study and a low background metal found in rocks of the substrate.

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FLUORINATION LINE FOR EXTRACTING OF OXYGEN FROM MINERALS

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Linia fluorynacyjna (pierwotnie nazwana linią krzemianową) została skonstruowana przez prof. S. Savina z CASE w Cleveland, USA. W wyniku porozumienia prof. J. Środonia i prof. S. Savina linia ta została sprowadzona do Polski do Instytutu Nauk Geologicznych PAN w Warszawie a następnie przekazana do Zakładu Spektrometrii Mas w Instytucie Fizyki Uniwersytetu Marii Curie-Skłodowskiej w Lublinie. Linia fluorynacyjna z pewnymi modyfikacjami została przeze mnie złożona pod kierownictwem i z pomocą prof. dr hab. S. Hałasa i jest gotowa do pierwszych testów.

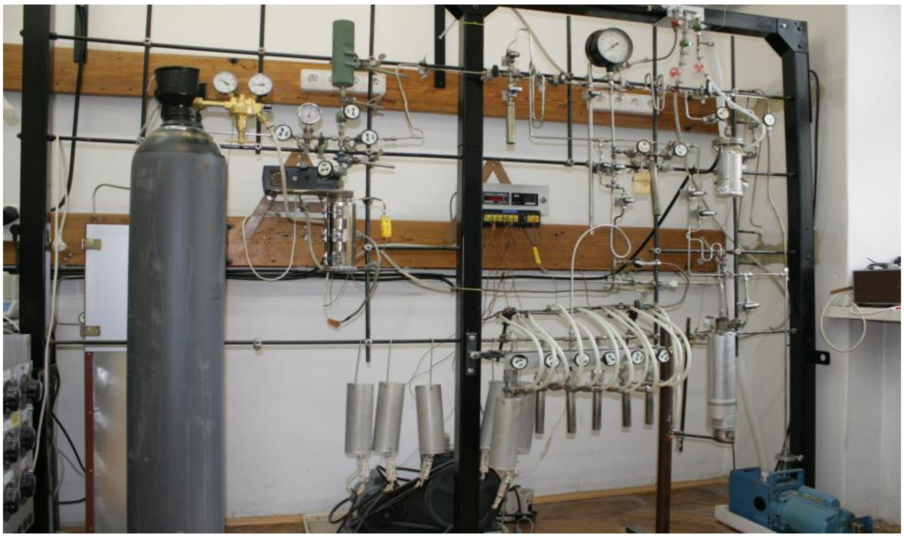

Fig 1. Linia fluorynacyjna

Zasadniczą rolą linii fluorynacyjnej jest ekstrakcja tlenu w postaci cząsteczkowej O_2 z minerałów zawierających w swoim składzie tlen takich jak krzemiany, tlenki, fosforany i woda. W związku z tym linia z krzemianowej zmieniła swoją nazwę na linię fluorynacyjną. Proces ekstrakcji tlenu polega na ogólnej reakcji:

$$M_2SiO_4 + 4F_2 \rightarrow 2MF_2 + SiF_4 + 2O_2$$

Próbka minerału ogrzewana jest w obecności czystego fluoru F_2 w temperaturze 450 - 750 °C w kolbie niklowej. Otrzymany w wyniku tej reakcji tlen poddawany jest analizie izotopowej na spektrometrze mas. Analiza izotopowa na gazie O_2 pozwala na określenie pełnego składu izotopowego ^{16}O, ^{17}O oraz ^{18}O. Dzięki analizie izotopów tlenu można określić genezę złóż mineralnych, temperaturę wody, w której wytrącała się krzemionka lub wzrastały kryształy kwarcu a także odtworzyć zmiany klimatyczne na Ziemi.

Outline of Professor Włodzimierz Żuk (1916 – 1981) life

Sylwetka Profesora Włodzimierza Żuka (1916 – 1981)

Stanisław Hałas

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Profesor Włodzimierz Żuk urodził się 29.IX.1916 w Klimowiczach (obecnie teren Białorusi). Jego ojciec wykładał matematykę w Seminarium Nauczycielskim w Siedlcach, matka pracowała jako nauczycielka. W okresie I wojny światowej rodzina przemieszczona została w głąb Rosji. Włodzimierz Żuk w Siedlcach ukończył 4 klasy Gimnazjum im. Żółkiewskiego, następnie 4 klasy ukończył w Gimnazjum im. Zamoyskiego w Lublinie. Po maturze odbył służbę wojskową przez 1 rok w Wołyńskiej Szkole Podchorążych Rezerwy Artylerii we Włodzimierzu Wołyńskim. Następnie studiował fizykę na Uniwersytecie Warszawskim w latach 1936-1939. Magisterium uzyskał już po wojnie na UW, w roku 1946 na podstawie badań z fosforescencji kryształów u prof. Stefana Pieńkowskiego. Bardzo szybko, bo już w 1949 r. Włodzimierz Żuk zdobył stopień doktora nauk matematyczno-przyrodniczych na podstawie pracy dotyczącej zjawisk jonizacyjnych w spektrometrze masowym.

W czasie kampanii wrześniowej 1939 r. Włodzimierz Żuk walczył w armii gen. Kleeberga, uczestnicząc w słynnej bitwie pod Kockiem. Okres okupacji przebył w okolicach Białej Podlaskiej. Natychmiast po wyzwoleniu Lubelszczyzny, bo już 1 września 1944 r. rozpoczął pracę, najpierw w Liceum Chemicznym w Lublinie, a od listopada także na Uniwersytecie Marii Curie-Skłodowskiej. Przez pierwsze dwa lata pracował na obydwu etatach, potem tylko na Uniwersytecie, gdzie przez niemal 37 lat zajmował się fizyką eksperymentalną, przy czym prawie cały czas fizyką jądrową.

Na początku swojej kariery W. Żuk był asystentem prof. Jana Blatona i prof. Stanisława Ziemeckiego. W bardzo szybkim tempie przebył dalsze szczeble kariery uniwersyteckiej pełniąc kolejno funkcje adiunkta, zastępcy profesora, docenta, profesora nadzwyczajnego (1960). W roku 1967 został mianowany profesorem zwyczajnym. Chociaż od 1944 r. przez cały czas W. Żuk związany był z UMCS, to jednak pracował równolegle na etatach poza Uniwersytetem: w Liceum Chemicznym (1944–1946), w Zakładzie Fizyki Cząstek Elementarnych w Warszawie jako kierownik Laboratorium Neutronowego przy budowie pierwszego reaktora (1954–1955), w Instytucie Badań Jądrowych w Świerku (1955–1961), w Wyższej Oficerskiej Szkole Lotniczej w Dęblinie. Wykładał także fizykę w byłej Filii UMCS w Zamościu.

Prof. Żuk wcześnie nawiązał kontakty naukowe z zagranicą, pierwsze już w listopadzie 1944 r. z Uniwersytetem im. Łomonosowa w Moskwie. W latach 1946–1947 trzy razy wyjeżdżał na do Berlina, gdzie wspólnie z prof. Stanisławem Ziemeckim dokonał zakupu aparatury naukowej dla potrzeb UMCS oraz dla innych ośrodków w Kraju. W kolejnych latach nawiązał kontakty z Vinca Institute of Nuclear Sciences w Belgradzie (Jugosławia), z Uniwersytetem Lajosa Kossutha w Debreczynie, Zjednoczonym Instytutem Badań Jądrowych w Dubnej (ZSSR) oraz instytutami naukowymi w NRD, Szwecji i Danii. Z licznych wyjazdów zagranicznych profesora wymieńmy te, które dla rozwoju fizyki jądrowej na UMCS miały szczególne znaczenie: w 1957 r. - półroczny staż naukowy w Instytucie Nobla w Sztokholmie, w 1961 r. - 9-miesięczny pobyt na Uniwersytecie w Uppsali, w 1968 r. - w Instytucie Oersteda w Kopenhadze.

Zagraniczne staże pogłębiły jego wiedzę w tej dziedzinie i skłoniły do intensywnych prac nad budową aparatury spektroskopii jądrowej, spektrometrów beta i gamma oraz aparatury do pomiaru korelacji kątowych gamma-gamma i e-gamma. Profesor Żuk kierował pracami grupy lubelskich naukowców w Zjednoczonym Instytucie Badań Jądrowych w Dubnej inicjując szereg badań dotyczących wyznaczania wartości spinów stanów wzbudzonych i multipolowości przejść gamma w jądrach pierwiastków ziem rzadkich.

Nawiązane wcześniej kontakty naukowe były stale przez prof. Żuka odświeżane, a także nawiązywane nowe na międzynarodowych konferencjach naukowych, w których brał czynny udział.

Prace naukowe prof. Żuka i jego zespołu w zakresie elektromagnetycznej separacji izotopów, spektrometrii mas i spektroskopii jądrowej spotykały się z dużym uznaniem fizyków polskich i zagranicznych. Główny kierunek badań naukowych, którym jest nadal uprawiana w Lublinie spektrometria mas, rozwinął prof. Żuk na początku swojej pracy naukowej. W 1949 r. zbudował pierwszy w Polsce spektrometr mas. Również jako pierwszy w Polsce zastosował zbudowany pod jego kierunkiem elektromagnetyczny separator izotopów do implantacji jonów do półprzewodników. Jest autorem monografii „Spektrometria masowa” (PWN 1956) a także redaktorem i zarazem autorem większości rozdziałów monografii „Spektrometria mas i elektromagnetyczna separacja jonów” (PWN 1980). Bibliografia prac profesora liczy 205 pozycji (Wojnarowicz 1980, Biblioteka Główna UMCS). Wiele prac zostało opublikowanych czasopismach zagranicznych i w materiałach konferencji międzynarodowych.

Prof. Żuk był od r. 1970 kierownikiem Zakładu Fizyki Jądrowej w Instytucie Fizyki. W przeszłości pełnił wiele funkcji administracyjnych na Uniwersytecie: od 1956 r. pełnił funkcję kierownika Katedry Fizyki Doświadczalnej, w latach 1960–1962 był dziekanem Wydziału Mat-Fiz-Chem, zaś w latach 1962–1968 prorektorem do spraw nauki.

Był wychowawcą dwóch pokoleń fizyków – wykształcił ponad 300 magistrów, przeprowadził 19 przewodów doktorskich i kilka habilitacyjnych. Dla pracowników zakładu prof. Żuk był nie tylko autorytetem naukowym, lecz również opiekunem i wychowawcą. Wymagający i krytyczny, gdy chodzi o sprawy naukowe, jednocześnie z ogromną życzliwością pomagał w rozwiązywaniu trudności zarówno naukowych, jak i życiowych. Codzienny kontakt z nim bardzo ułatwiała jego bezpośredniość i szczerość.

Zmarł nagle w pełni sił twórczych 13 stycznia 1981 r. Obszerny życiorys prof. Włodzimierza Żuka opublikowali jego byli współpracownicy – prof. dr hab. Dariusz Mączka i dr Janusz Zinkiewicz (1982), *Postępy Fizyki*, tom 33, 273-297.

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