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POTASSIUM BEARING ROCKS OF UKRAINIAN SHIELD: MASS BALANCE

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Potassium-bearing, mostly two-bifeldspar granites, are widely widespread within Ukrainian Shield. Early published papers have discussed the problem of potassium source for two-feldspar granites which indicate final stages or evolved continental crust formation, with granites of Middle Dnipro and granulites of Dniester-Bug megablocks being taken as typical examples. The conclusion was made that biotites might be a possible source of potassium, which occurrence in the upper layers of lithosphere marks the formation of evolved continental crust. These potassium-rich melts results in formation of two-feldspar granites as well as intensive potassic metasomatism occurred in granulite-gneiss regions. The biotite would be destroyed within instability zone (zone of transition from amphibolite to granulite facies) and, as a result of selective melting of source rocks it (together with rubidium and radiogenic isotope ^{87}Sr) can migrate into melt or fluid, at PT-parameter that do not reach melting conditions. Subduction might be treated as condition (setting) favorable for entering of potassium into granulite rock associations, because it provides sinking of biotite- bearing rocks below granulitic blocks. Granulites are characterterised by low contnets of biotite that is not enough for production (release) of large amounts of potassium. This paper discusses calculation results of mass balance on potassium and strontium, with Middle Dnipro megablock as an example. It is established that for granite selective melts with K_2O > 4% and primary isotope ratio values of two-feldspar granites more than 0,750 to be formed the proportion ratio as 8/1 is enough to be reached between volumes of substratum and two-feldspar granites (parental melt). This value is much less than that established for rocks of Middle Dnipro megablock. Criteria for classification (systematization) of tectonic blocks of Ukrainian Shield are offered.

Keywords: Two-feldspar granites, rubidium-strontium isotope system, mass balance, tectonic block, Ukrainian Shield.

Potassium-bearing rocks, mostly всего two-feldspar granites, are widely abundant within the Ukrainian Shield (USh). It is the formation of large amount of two-feldspar granites indicates the stage of the Earth's crust consolidation. Many varieties of these rocks are described as comprising different structures of Ukrainian Shield [5]. According to Chronostratigraphic Scheme of Ukraine [2] two-feldspar granites are included in composition of Paleoproterozoic: Zhytomyrsky, Osnytsky (Volyn megablock), Khmelnytsky, Berdychivsky, Pobuzhsky (Dniester-Bug megablock), Stavyschensky, Umansky, Gaysinsky, Fhastivsky (Ros-Tykych megablock), Kirovogradsky, Novoukrainsky (Ingulets megablock) and Saltychansky, Anadolsky, Chlebodarivsky (Near Azov megablock) complexes. Archean structures that include these granites are comprised by Mokromoskovsky, Tokivsky, Demurynsky, Slavhorodsky (Middle Dnipro megablock), Tashlyksky (Ingulets megablock) and Tokmaksky (Near Azov megablock) complexes. Two-feldspar varieties form as both large granite massifs which are thousands square kms in area (e.g. Novoukrainsky, Tokivsky, Mokromoskovsky) and small bodies of tens kms in size as well as veins and leucosomes of migmatites. By rough estimation, total area covered by two-feldspar granites does not exceeds 20% of whole area of the Ukrainian Shield. Besides two-feldspar granites gneisses and felsic granulites of Saxonian type, which content of K_2O commonly reaches a few per cents, are also abundant among crystalline basement rocks. Some geological field data indicate metasomatic origin (nature) of these rocks, at any case it is evident for gneisses (biotite and garnet-biotite gneisses of Zelenolivadiska strata) and felsic granulites (geological section outcropped along South Bug river, between Haschuvate village and Zavallia urban village) of Dniester-Bug megablock [3, 6].

Based on widely accepted idea that plagioclase-rich varieties are predominant among Achean felsic rock, the problem of possible source of potassium for formation of two-feldspar granites and origin of potassic (silica-potassic) metasomatism was stated.

Early publications [8, 9] discusses possible source of potassium in two-feldspar granites that marks the final stage of formation of evolved continental crust, with granites of Middle Dnipro and granulite associations of Dniester-Bug megablocks as typical examples. Exactly biotite is the most possible source of potassium which migration into the upper lithospheric layers results in formation of evolved continental crust. It occurs as ether large-scale introduction of granitic melts of two-feldspar granites or silica-potassic metasomatism in granulite-gneiss regions. Bitotite of primary rocks is destroyed within instability zone (PT-conditions of amphibolite to granulite facies transition) and potassium, together with rubidium and radiogenic isotope ^{87}Sr, migrate into partial melt or fluid at PT-parameters below melting conditions. Low content of biotite occurred in granulitic rocks prevents realease large amount of potassium.

Subduction might be treated as setting favorable for potassium to be influxed into granulite associations when biotite-bearing rocks of subducting slab pulled down below granulites. The question arises as to whether potassium amount in substrate is sufficient for two-feldspar granites to be formed? This publication discusses this problem, with rock associations of Middle Dnipro area being taken as an example.

Substrate (parental) rocks of Middle Dnipro area include more than 1% of potassium in average. Diorite gneisses show 1,18 % (0,23 to 1,76) of potassium presence, diorites and quartz diorites have 1,34 % (1,05 to 1,94) of potassium and plagiogranite gneisses are characterized by 1,40 % (0,12 to 2,66) values [11]. Two-feldspar granites commonly are characterized by presence of more than 3,5 % of potassium. Granodiorites and granites of «Tokivsky» or Demurinsky complex (according to Stratigraphic Scheme approved by National Stratigraphic Committee in 2003) include 3,58 % (1,9 to 6,82) of potassium. Tokivsky massif granites show 4,9% (0,4 to 9,36%) and granites of Mokromoskovsky massif do 3,93 % (2,08 to 5,05) of potassium content [11].

It is commonly known that about 50% of K_2O should be extracted (removed) from substratum for granitic melt (two-feldspar granites) to be formed. So, certain proportions between substratum and granite melt should be maintained to reach following potassium content values of two-feldspar granites: 3% - 6:1; 4% - 8 : 1; 5% - 10 : 1; 6% - 12 : 1 and 7% - 14 : 1.

The Earth's crust that reaches 70 km in thickness can include granite shell of about 10 km thick. At standard geothermal gradient (3 °C per 1 km) PT-parameters of granulitic facies will be reached at depths of about 30 km and, than, substratum layer can reach 40 km of its thickness.

At thickness of granite batholithic massifs of about 5 km the value of sabstratum/granite melt ratio might be taken as 8 : 1. Based on early established fact that the area covered by two-feldspar granites reaches 20% of the total area of Middle Dnipro megablock, than proportion between the substratum and partially melted granites is about 40 : 1. Thus based on the real potassium mass balance it is quet natural that primary melts of two-feldspar granites have originated deeply in the Earth's crust, at the level that marks transition from amphibolite to granulitic facies conditions.

The question is whether substratum includes enough rubidium (radioactive isotope ^{87}Rb) responsible for high values of isotopic ratio ^{87}Sr/^{86}Sr (0.725-0.8), that is determined for for two-feldspar granites [8]. It occurs at rather high contents of strontium, 600-1000 ppm established for substratum rocks [11].

Substratum rocks (plagiogranites) of Middle Dnipro area include 140-1245 ppm of Sr and 9-70 ppm of Rb and two-feldspar granites include 60-470 ppm and 35-310 ppm, correspondingly [11]. According to early published data [1, 4] plagiogranites of Dnipropetrovsk complex include 59-1012 ppm of strontium and 57-97 ppm of rubidium. Based on the fact that the essential portion of rubidium and potassium is concentrated in biotite, it can be destroyed within the zone of amphibolite-granulite facies transition and rubidium can migrate into the fluid together with radiogenic isotope ^{87}Sr.

During the 400 Ma period 0,016 gram of ^{87}Sr from 10 gram of Rb and 0,124 of ^{87}Sr from 80 gram of Rb can be formed as a result of radioactive decay. In case of simultaneous extraction of 100 gram of strontium from substratum to each ton of parental 100 (at its minimum content in in two-feldspar granites as 100 ppm), than granites (at reaching condition of isotopic homogenization and 8 : 1 proprotion betwin volumes substratum and two-feldspar granites) will show following primary isotopic ratios $^{87}Sr/^{86}Sr$ - 0,713 in the former and 0,801 in the latter cases. Such a situation we actually observe in many bodies of two-feldspar granites of Middle Dnipro area [8]. In case of extraction of 300 gram of radiogenic isotope ^{87}Sr from substratum (at 300 ppm as maximum amound of Sr in two-feldspar granites 300 ppm) primary $^{87}Sr/^{86}Sr$ ratio will reach only 0,706 value in the former and 0,750 in the latter case.

Thus, based on mass balance values calculated on both potassium and strontium isotopes granite melts

Table 1. **Rb-Sr isotopic system in plagioclases and apatites of Berdychivsky granite and associated gneisses of Upper Bug area, Dniester-Bug megablock**

No.	Field sample	Rock name	Mineral analysed	Content (10^{-6} g/t)		$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$		Age, Ma
				^{87}Rb	^{86}Sr		Measured	Corrected *	
Ivanivka open pit									
1	i-2	Berdychivsky granite	plagioclase	11.534	140.22	0.0813	0.7077	0.7053	2040
2	i-3	Berdychivsky granite	plagioclase	11.743	153.28	0.0757	0.70726	0.70503	2040
3	i-5	Berdychivsky granite	plagioclase	14.446	209.48	0.0682	0.70674	0.70474	2040
4	i-7	Berdychivsky granite	plagioclase	7.409	168.90	0.0434	0.70486	0.70359	2040
5	i-4	Pyroxene gneiss	plagioclase	3.190	167.95	0.0188	0.70308	0.7025	2040
Zhezheliv open pit									
6	Zh-3	Leucosome 1	plagioclase	7.450	110.45	0.0667	0.7064	0.7044	2040
7	Zh-4/1	Leucosome	plagioclase	3.241	124.19	0.0258	0.70602	0.7053	2040
8	Zh-5	Leucosome	plagioclase	6.296	122.65	0.0507	0.70721	0.7057	2040
9	Zh-6	Berdychivsky granite	plagioclase	0.979	137.04	0.0071	0.70885	0.7086	2040
10	VP-9-2	Bi + hyp plagiogneiss	plagioclase	1.091	10.06	0.1072	0.72219	0.7188	2200
11	Zh-4	Pyroxene gneiss	plagioclase	4.548	41.34	0.1088	0.7097	0.7065	2040
Sabariv open pit									
12	P-1/10	Berdychivsky granite	apatite	n/m	n/m	—	0.72094	0.7209	2040
13	P-2	Berdychivsky granite	apatite	n/m	n/m	—	0.74023	0.7402	2040
14	14/13	Pyroxene gneiss	apatite	n/m	n/m	—	0.7314	0.7314	2050

Notes: in tables 1 and 2: n/m — not measured; * — age correction is made on radiogenic $^{87}Sr_r$.

Table 2. **Rb-Sr isotopic system in plagioclases and apatites of granulite association of Upper Bug Area (Dniester-Bug megablock)**

No.	Field sample	Rock name	Mineral analysed	Content (10^{-6} g/t)		$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$		Age, Ma
				^{87}Rb	^{86}Sr		Measured	Corrected *	
Lityn open pit									
1	86/78a	Enderbite	apatite	n/m	n/m	—	0.70808	0.7081	2800
2	196/81	Enderbite	apatite	n/m	n/m	—	0.7068	0.7068	2800
3	40/72-2	Plagiogneiss Px	apatite	n/m	n/m	—	0.70552	0.7055	2800
4	76/73	Plagiogneiss Px	apatite	n/m	n/m	—	0.70657	0.7066	2800
Left bank of Zgar river valley, to the east of Lityn open pit, to the west of Horodyshche city, altitude 290,6									
5	VP-5	OPx plagiogneiss	plagioclase	1.228	65.25	0.0186	0.70407	0.7035	2200
Tyvriv open pit									
6	VP-1	Antiperthite enderbite	plagioclase	9.680	105.2	0.091	0.70523	0.7026	2060
Malynivka open pit									
7	VP-3	Antiperthite enderbite	plagioclase	1.861	82.08	0.0224	0.7042	0.7035	2060
8	VP-3-5	Crystalloschist	plagioclase	3.988	51.39	0.0767	0.70375	0.7016	2010
9	VP-3-1	OPx плагіогнейс	plagioclase	1.781	42.29	0.0416	0.70536	0.7032	3650
Rusanivka open pit, Holoskove village									
10	мар-70	Charnokite	apatite	n/m	n/m	—	0.70568	0.7057	2800
11	128/79	Pyroxene gneiss	apatite	n/m	n/m	—	0.70896	0.7090	2800
Hnivan open pit									
12	VP-2-11	Gt-Bi-Hyp gneiss	plagioclase	4.747	36.56	0.12835	0.7090	0.7050	2200

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with the content of potassium, rubidium and large values of $^{87}Sr/^{86}Sr$ ratio (more than 0,725) is quite possible to be formed.

Some «geologic» conclusions that might be arrived

1. Formation age of two-feldspar granites corresponds to the age of granulitic metamorphism of low crustal rocks, that can be interpreted as the age of tectonic structure consolidation (block, migablock, craton, etc.).

2. Occurrence of 2 (and more) stages of two-feldspar granites formation testify for remobilization processes.

3. Absence of two-feldspar granites in global structures of the Earth's crust is a direct evidence on lack of granulite basement below (at lower crustal level) these structures.

4. Primary isotopic ratio $^{87}Sr/^{86}Sr$ of two-feldspar granites can be used for evaluation of duration (period) of continental crust formation.

The first three conclusion are quite obvious, the fourth one causes actual doubts. If the amount of radiogenic isotope ^{87}Sr accumulated depends, besides constant of radioactive decay, only on duration of decay (presence of biotite), $^{87}Sr/^{86}Sr$ ratio value, which is suggeste to be used for age determinations, additionally depends on value of Rb/Sr ratio.

But, in the case of low variations of the ratio in rocks, that is typical of plagiogranite associations of early Precambrian age, such an assessment is quite appropriate. Results of studying of rubidium- strontium isotope systems in plagioclases and two-feldspar apatites (Berdychiv) of granites of Upper Bug area published in [9] might be taken as an example.

As might be seen from data presented in Table 1 primary $^{87}Sr/^{86}Sr$ ratio of Berdychiv granitoids (Zhezheliv and Ivanivka open pits), except granitoids of Sabariv open pit, does not exceed 0,709. The value of the ratio determined on rocks uncovered by Sabariv open pit exceeds 0,720. Until recently this fact cannot be explained due to the similar age values determined on monazites for granitoids sampled in these open pits, 2,08 and 2,02 Ga [7, 9]. But recent results have shown that the age of granitoids sampled within the two former open pits does not exceed 2,3 Ga [7] whereas garnet-biotite granites uncovered by Sabariv open pit have shown the age of 2.8 Ga (unpublished data). That means that more ancient possibly Archean formations occur as substratum for granites uncovered by Sabariv open. It resulted in more long time of accumulation of radiogenic isotope ^{87}Sr and much higher $^{87}Sr/^{86}Sr$ ratio - more than 0,720 by comparison to 0,704-0,709 established for granites of Zhezheliv and Ivanivka open pits.

Hypersthene bearing two-feldspar granites are characterised by absolutely different isotope values that do not exceed 0,708, irrespectively of presence of Archean, similar to that of charnokitoids of Lityn and Malyn open pits, or Paleoproterozoic zircons, similar to that of Tyvriv open pit (Table 2). This one more evidence of charnokitoids to be treated as restite left after selecting removing of melts parental to two-feldspar granites and fluids enriched in, in case of their complete assimilation by selective melt phases. Low values of primary $^{87}Sr/^{86}Sr$ isotope ratio are also characteristic of granulite rocks of Middle Bug area [10].

Table 3. **Classification scheme of the first rank tectonic structures of Ukrainian Shield**

Blocks (cratons) of Archean age			Blocks (cratons) of Paleoproterozoic age
Archean consolidation	Archean consolidation, remobilized in Paleoproterozoic	Paleoproterozoic consolidation	Paleoproterozoic consolidation
Middle Dnipro	Near Azov	Middle Bug	Volyn, Ingul, Ros-Tykych, Upper Bug + Near Dniester

Table 4. **Duration of formation of a continental crust of Ukrainian Shield by the results of U-Pb dating on zircon and Sm-Nd dating on whole rock**

Megablock	Initial age, Ga	Consolidation age, (two-feldspar granites formation), Ga	Duration of megablock formation
Volyn	2.3	1.96	over 300 Ma
Middle Bug	3.65	1.96	over 1.6 Ma
Ros-Tykych	2.3	1.99	over 300 Ma
Ingul	2.5 ?	2.02	over 400 Ma
Middle Dnipro	3.2	2.70	500 Ma
Near Azov	3.6	2.03	about 1.6 Ga
Upper Bug – Near-Dniester	2.3 ?	2.03	about 300 Ma

Whereas the fact that Tectonic Committee of Ukraine currently discusses the problem of tectonic zonation of Ukrainian Shield, based on above-stated and taking into account geohistorical features of continental crust formation, it is possible to propose criteria for classification (systematization) of tectonic blocks of Ukrainian Shield:

1. Age of supracrustal basement (Archean (Paleo-, Meso-, Neo-), Paleoproterozoic).

2. The age of basement consolidation of the (age of emplacement of two-feldspar granites)

3. Presence (absence) of remobilization (1 or 2 (3) stages of two-feldspar granites formation).

Based on these criteria the first rank blocks of Ukrainian can be classified into (Table 3).

The scheme presented above is in good agreement with duration of formation of first-rank megablocks of Earth's continental crust. Two blocks which rocks of granulitic association – Near Azov and Middle Bug – have been formed during long period of time (more than 1,6 Ga). Near Azov megablock significantly differs in such a way that it was intensively remobilized in Archean that resulted in formation of two-feldspar granites (charnokites) of Tomakovky complex. Middle Bug block and Dniester-Bug megablock as a whole do not show any presence of two-feldspar granites of Archean age. Antiperthitic enderbites of Litinsky complex which age is indicated as 2,8 Ga placed accoring to the Correlation Scheme of NSC [2] should be treated as Paleoproterozoic formations [7, 9]. Middle Dnipro megablock was formed during rather long period of time (about 500 Ma), in comparison to the formation period of Paleoproterozoic megablocks (about 300 Ma) (Table 4).

Conclusions. Two-feldspar granites might be treated as indicators of mature continental crust, on the one hand and, as indirect evidence of the lower Earth's crust that is comprised by rocks metamorphosed at granulite facies conditions, on the other hand. The age of granulite metamorphism coincides with the age of two-feldspar granites that occur in the upper layers of continental crust.

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АДРЕСА

Калийсодержащие породы Украинского щита: баланс вещества

Калийсодержащие породы, прежде всего двуполевошпатовые гранитоиды, достаточно широко распространены на Украинском щите. В опубликованных ранее роботах была обсуждена проблема источника калия двуполевошпатовых гранитоидов, завершающих формирование зрелой континентальной коры на примере гранитоидов Среднего Приднепровья и гранулитовой ассоциации Днестровско-Бугского мегаблока. Было сделано заключение, что

источником калия, массовое поступление которого в верхние горизонты литосферы знаменует формирование зрелой континентальной коры в виде родоначальных гранитоидных расплавов двуполевошпатовых гранитоидов, служит биотит. Биотит в зоне нестабильноси (переход от *PT*-условий амфиболитовой к гранулитовой фации) разлагается и в результате селективного плавления материнских пород, вместе с рубидием и радиогенным изотопом ^{87}Sr переходит в расплав или в флюид если *PT*-параметры не достигают условий плавления. В гранулит-гнейсовых областях кроме мощного гранитоидного магматизма, калий поступает в высокотемпературных флюидах, что приводит к масштабным проявлениям кремнийий-калиевого метасоматоза. Было также показано, что условием поступления калия в породы гранулитовых ассоциаций является субдукция, что обусловлено необходимостью погружения под них биотитсодержащих пород, поскольку содержание биотита в породах гранулитовых ассоциаций низкое и недостаточное для продуцирования необходимого количества калия. В этой публикации, на примере Среднего Приднепровья, сделан расчет баланса вещества по калию и стронцию. Выяснено, что для продуцирования гранитных селективных выплавок с содержанием $K_2O > 4$ % и первичным изотопным отношением в двуполевошпатовых гранитах выше 0,750, достаточным будет соотношение объема субстрата и объема двуполевшпатовых гранитоидов (материнского расплава) как 8 : 1, что значительно меньше реально существующего в Среднеприднепровском мегаблоке. Предложены критерии для классификации (систематизации) тектонических блоков УЩ.
Ключевые слова. двуполевошпатовые граниты, рубидий-стронциевая изотопная система, баланс вещества, тектонический блок, Украинский щит.

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Калійвмісні породи Українського щита: баланс речовини
Калійвмісні породи, насамперед двопольовошпатові гранітоїди, є досить поширеними на Українському щиті. У раніше опублікованих роботах було обговорено проблему джерела калію двопольовошпатових гранітоїдів, які завершують формування зрілої континентальної кори, на прикладі гранітоїдів Середнього Придніпров'я та гранулітової асоціації Дністровсько-Бузького мегаблоку. Зроблено висновок, що джерелом калію, масове надходження якого у верхні шари літосфери знаменує формування зрілої континентальної кори у вигляді родоначальних гранітоїдних розплавів двопольовошпатових гранітоїдів є біотит. Біотит у зоні нестабільності (перехід від *PT*-умов амфіболітової до гранулітової фації) розпадається і в результаті селективного плавлення материнських порід, разом з рубідієм і радіогенних ізотопом ^{87}Sr переходить в розплав, чи у флюїд, у випадку, коли *PTX* параметри не досягають умов плавлення. В грануліт-гнейсових областях окрім потужного гранітоїдного магматизму, калій надходить у високотемпературних флюїдах, що спричиняє масштабні прояви кремній-калієвого метасоматозу. Було також показано, що умовою надходження калію в породи гранулітових асоціацій є субдукція, що обумовлено необхідністю занурення під них біотитвмісних порід, оскільки вміст біотиту в породах гранулітових асоціацій низький і недостатній для продукування потрібної кількості калію. У цій публікації, на прикладі Середнього Придніпров'я, наведено розрахунок балансу речовини за калієм і стронцієм. З'ясовано, що для продукування гранітних селективних виплавок із вмістом $K_2O > 4$ % та первинним ізотопним відношенням у двопольовошпатових гранітах понад 0,750, достатнє відношення між об'ємом субстрату та об'ємом двопольовошпатових гранітоїдів (материнського розплаву) — 8 : 1, що значно менше реального в Середньопридніпровському мегаблоці. Запропоновано критерії для класифікації (систематизації) тектонічної блоків УЩ.
Ключові слова: двопольовошпатові граніти, рубідій-стронцієва ізотопна система, баланс речовини, тектонічний блок, Український щит.

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