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Occurrence of wolfram, copper, cobalt and gold mineralization in the area of the Argentine Islands (West Antarctica)

Abstract. **Objective.** The objective of our research was to search for manifestations of ore mineralization on the Roca and Cruls islands in the Argentine Islands, West Antarctica. **Methods.** Samples of rocks with the manifestation of ore mineralization were taken in the field routes. Silicate analysis of the rocks was carried out using the wet chemistry method in M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the National Academy of Sciences of Ukraine (IGMOF of NAS of Ukraine). The X-ray diffraction analysis of samples was carried out using a DRON-2 diffractometer, with copper radiation ($Cu_{K\alpha}$ = 1.54178 Å). The samples were surveyed in the 4—65° 2θ interval of angles, with a scan step of 0.1 degr. / min. For mineral diagnostics, the catalog of reference samples of the PDF-2 database (International Diffraction Data Center, ICDD) 2003. The chemical composition of minerals was examined using a JXA-733 X-ray microanalyzer (Jeol, Japan) using wave and energy-dispersion spectrometers. Contents of trace elements in the rocks were determined using the ICP-MS and quantitative spectral analysis methods. The validity of analyses was checked by means of determination of international and Russian reference samples GSP-2, VM, SGD-1A, ST-1. Concentration measuring errors were 3 to 5 wt. % for most elements. The quantitative spectrum analysis was carried out in IGMOF of NAS of Ukraine. Petrographic studies of rock sections were carried out using a MIN-8 polarized-light microscope. **Results.** Wolfram, copper, zinc, and lead were found in the minor intrusion of lamprophyres in the Andes complex granodiorites, on a small island of the Roca Islands. This semi-ring-shaped minor intrusion up to 0.5 m thick rooted in the not yet crystallized granodiorite intrusion. The dip angle of the minor intrusion is about 70°. It showed tungsten (28.7 g/t), copper (445 g/t), zinc (207 g/t), and lead (123 g/t) mineralization. In the eastern part of one of the Cruls Islands, a steep (dip azimuth NW 345°, angle 82°) tectonic zone up to 10 m wide was studied. Three metasomatic belts, one of which is up to 0.5 m thick, are associated with this zone. Metasomatites include pyrite-plagioclase rocks, epidosites and pyrite-epidote rocks, which have been formed due to hydrothermal and metasomatic changes of granodioritic tectonic breccia. The occurrence of cobalt (800 g/t), copper (200 g/t) and gold (up to 0.3 g/t) has been discovered. In these metasomatites, magnetite, pyrite, copper pyrite and pyrrhotite are available. Cobalt is present as magnetitic and pyritic impurities. **Conclusions.** During geological surveys in 2010 and 2012 the mineralization of wolfram, copper, lead, cobalt and gold was first discovered. The ore mineralization of such genesis was previously unknown in this area. The data obtained allow clarifying of perspectives of exploration activities in West Antarctica.

Keywords: Argentine Islands, dike, breccia of granodiorites, metasomatites, mineralization point, wolfram, copper, cobalt, gold.

INTRODUCTION

As of the moment, ore mineralization in the region of the Argentine Islands is very inadequately investigated.

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Quartz-molibdenitic, quartz-magnetitic and quartz-pyritic ore channels have been discovered in Andean complex granodiorite intrusions (Hawkes et al., 1981). These explorers came to a conclusion that only the root of the porphyry copper system had not been eroded. In Andean complex gabbroid intrusions, magnetite, ilmenite and sulfidic ore mineralizations have been described. A conclusion has been made

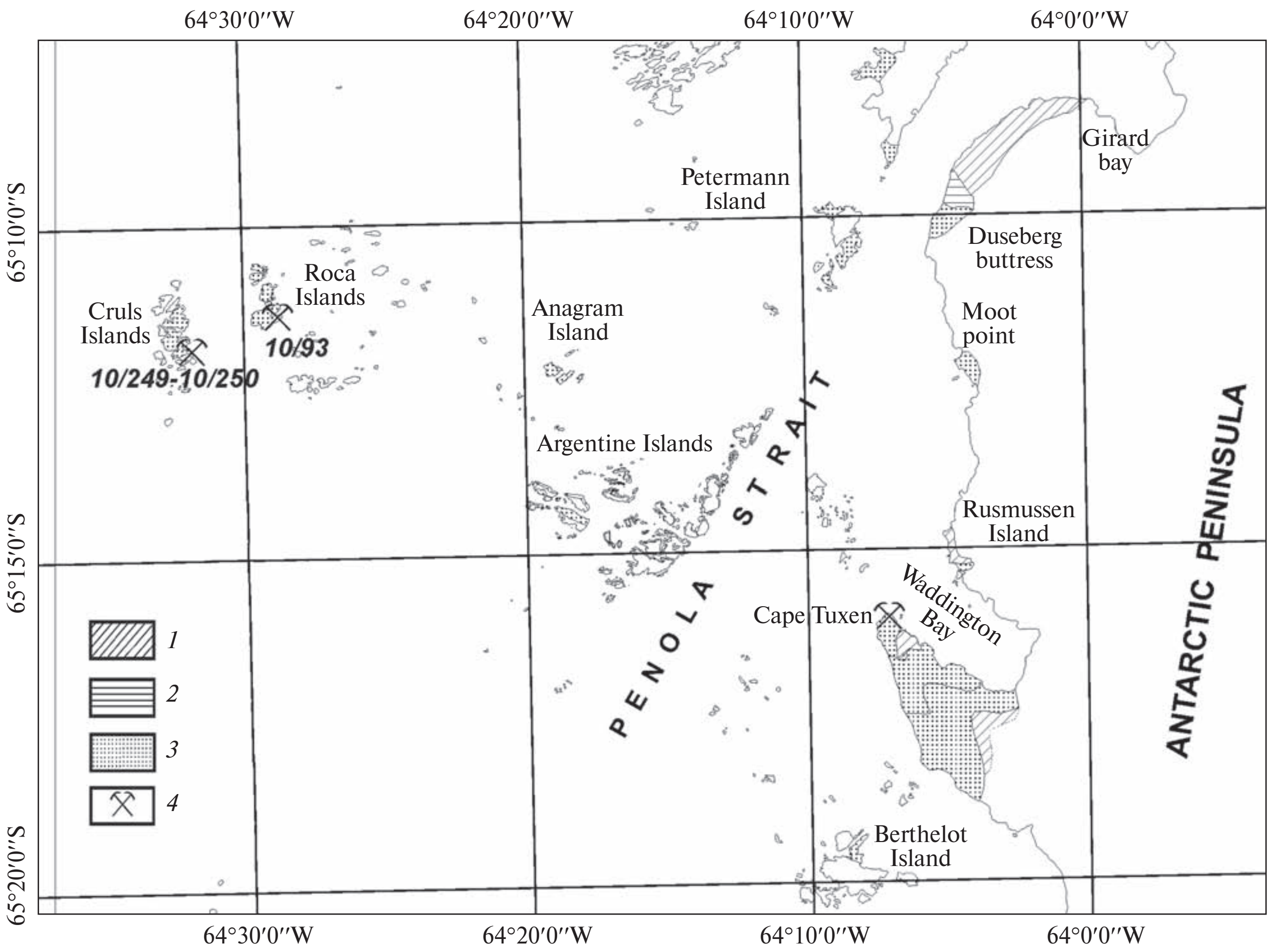

Fig. 1. Schematic geological map of the Argentine Islands area (Bakhmutov et al., 2013) with lamprophyre sampling locations on Roca Islands and metasomatite sampling locations on Cruls Islands. *1* — basalts, andesites, acid volcanites (Upper-Jurassic volcanic group); *2* — tuffaceous rocks (Upper-Jurassic volcanic group); *3* — gabbro, diorites, granodiorites (Andean complex); *4* — sampling locations

regarding their connection to residual Fe-Ti cumulate rocks of gabbroid and later gabbro-pegmatite intrusions. There, elevated concentrations of V, Cr, Co, Cu have been found. In pyrite, Co content is up to 3.5%. It has been determined that vein quartz in the Andean intrusive complex granodiorites (Barchans Islands, West Antarctica) grew in heavy-pitch pure quartz pockets, where a temperature drop, which is required for massive quartz dissolution and crystallization of transparent faceted crystals in vein centers, was reached. The connection of quartz producing fluids and postmagmatic processes (hydrothermal stage) in the granodiorite intrusions has been justified (Naumko et al., 2018).

During geological and geochemical surveys, in 2010 and 2012, new occurrences of wolfram, copper, zinc and lead have been discovered in a lamprophyric dike on Roca Islands, as well as occurrences of cobalt, copper and gold on Cruls Islands. Results of these surveys are shown herein (Fig. 1).

METHODS

Silicate rock analyses were carried out in the Institute of Geochemistry, Mineralogy and Ore Formation of the National Academy of Sciences of Ukraine (IGMOF of the NAS of Ukraine).

The X-ray diffraction analysis of samples was carried out using a DRON-2 diffractometer, with copper radiation ($Cu_{K\alpha}$ = 1.54178 Å). The samples were surveyed in the 4—65° 2θ intervals of angles, with a 0.1 degr. / min sampling interval. For mineral diagnostics, a catalog of reference samples of the PDF-2 database (International Diffraction Data Center, ICDD) 2003, and the PCPDFWIN software were used (Program Powder Diffraction Files from ICDD). Positions of X-ray pattern diffraction maximum were compared with specified reference mineral values of the above database.

The chemical composition of minerals was examined using a JXA-733 X-ray microanalyzer (Jeol, Japan) using wave and energy-dispersion spectrometers in a laboratory of IGMOF of the NAS of Ukraine; the analyst — L. I. Kanunikova. Operation mode: accelerating voltage 20 kV, operating current 20 nA, probe 1—5 μm.

Contents of rare and trace elements in the rocks were determined using the ICP-MS method in the Institute of Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences (IMTM RAS), Chernogolovka, Russia. The validity of analyses was checked by means of determination of international and Russian reference samples GSP-2, VM, SGD-1A, ST-1. Concentration measuring errors were from 3 to 5 wt. % for most elements.

The quantitative spectrum analysis was carried out in IGMOF of the NAS of Ukraine.

Petrographic studies of rock sections were carried out using MIN-8 polarized-light microscope, transmittingly and reflectingly.

RESULTS

Wolfram, copper, zinc and lead were discovered in the deformed lamprophyric dike in Andean complex granodiorites (exposure on a little island in the Roca Islands (S65°10.734′; W064°29.455″)). This dike is semiorbicular and had been, probably, introduced into granodioritic intrusion before its crystallization (Fig. 2). The dike thickness is up to 0.5 m. The dike inclination angle is appr. 70° (sample 10/93).

This is the charcoal-grey porphyritic coarse rock. The porphyritic structure is caused by biotite porphyries up to 5 × 5 mm, available in the medium-grained amphibole-quartz structure. Mineral composition: clinopyroxene — 5—7%; amphibole — 40%; feldspar — 20—25%; biotite — 30%; ore minerals — 2—3%; apatite up too 1%; zircon – single grains. Amphibole is represented by hornblende and cummingtonite. Clinopyroxene includes unaltered well-preserved crystals as well as amphibole-replaced crystals. Feldspar is replaced with secondary products. Apatite is present as hornblende and quartz inclusions.

Fig. 2. Deformed lamprophyric dike in granodiorites (Roca Islands)

According to their chemical composition (SiO_2 — 48.32%; TiO_2 — 2.08%; Al_2O_3 — 7.59%; Fe_2O_3 — 3.33%; FeO — 12.93%; MnO — 0.42%; MgO — 11.28%; CaO — 5.82%; Na_2O — 0.42%; K_2O — 4.29%; S_{tot} — absent; P_2O_5 — 0.45%; H_2O^- — 0.62%; LOI — 2.21%; total — 99.76%), the lamprophyres correspond to the basic rock. On a TAS diagram, they fall into the alkali rock field. They have elevated concentrations of Y (41.6 ppm) and Yb (11.5 ppm); this reflects absent garnet in a magmatic source. The lamprophyres are enriched with REEs. They are poorly differentiated — $(La/Yb)_N$ = 3.64) (Fig. 3). A deep negative europium anomaly — Eu/Eu* = 0.36 is remarkable, which is probably caused by plagioclase fractionation in a crust magmatic source. This dike rock has been probably formed based on residual magma in the granodioritic intrusion. Zircon of these lamprophyres is identical to zircon of granodiorites.

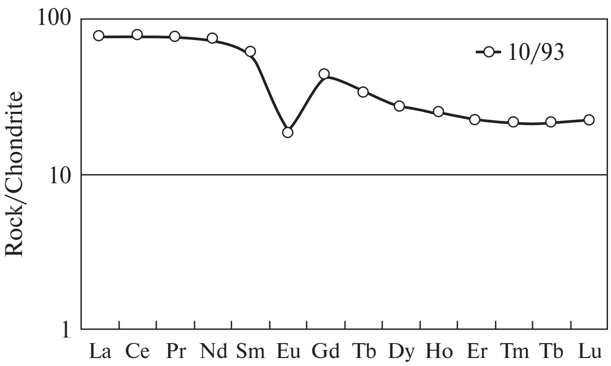

Fig. 3. REE distribution diagram for lamprophyres (sample 10/93)

According to results of ICP-MS rock analysis, elevated concentrations of wolfram (28.7 g/t), copper (445 g/t), zinc (207 g/t) and lead (123 g/t) have been discovered in lamprophyres, which significantly exceeds clarkes of these elements for this rock (Table 1).

Cobalt and gold in metasomatites on Cruls Islands

In the eastern part of an island in the Cruls Islands (S65°11.845′; W64°32.068′), in granodiorites, an up to 10 m wide steeply falling tectonic zone with three bands of metasomatites, one of which reaches a power of up to 0.5 m, was studied.

Metasomatites include pyrite-plagioclase rocks, epidosites and pyrite-epidote rocks, which have been

Table 1. **Contents of elements in lamprophyres and metasomatites determined using the ICP-MS method and quantitative spectral analysis*, g/t**

Elements, g/t	10/93	10/251*	Clark (Vinogradov, 1962)	Elements, g/t	10/93	10/251*	Clark (Vinogradov, 1962)
Li	32.1	—	30	La	22.3	—	49
Be	0.69	—	3.8	Ce	58.4	—	70
Sc	56.2	—	10	Pr	8.1	—	9
Rb	131	—	150	Nd	38.8	—	37
Sr	28	—	340	Sm	9.9	—	8
Ba	571	—	650	Eu	1.0	—	1.3
V	377	300	90	Gd	8.7	—	—
Cr	137	8	83	Tb	1.25	—	—
Co	58.8	800	18	Dy	7.0	—	5
Ni	52.5	100	58	Ho	1.3	—	1.7
Cu	445	200	47	Er	3.8	—	3.3
Zn	207	80	83	Tm	0.52	—	—
Ga	13.7	10	19	Yb	3.8	—	3.3
As	2.3	—	1.7	Lu	0.52	—	0.8
Y	41.6	50	29	Mo	2.7	—	1.1
Nb	11.5	3	20	Sn	14.3	6	2.5
Ta	0.72	—	2.5	Sb	0.89	—	0.5
Zr	25.4	—	170	Cs	3.2	—	3.7
Hf	1.3	—	1.0	W	28.7	—	1.3
U	2.0	—	2.5	Pb	123	6	16
Th	9.9	—	13	Au	ПО	0.1—0.3	0.0043
Bi	0.36	—	0.009	Ag	0.10	<1	0.07

Note. * — results of quantitative spectral analysis.

formed due to hydrothermal and metasomatic changes of granodioritic tectonic breccia (Fig. 4, 5). The tectonic breccia consists of granodioritic debris, which is concrete-bound with the high-magnetic "black rock". The term "black rock" is a conventional one and is used for the determination of this rock during descriptions of sections, polished sections and samples of breccias and vein (dike) rocks. Macroscopically, the brecciated structure is observed in the "black rock", which is caused by available 5—10 mm rectangular or wedge-shaped debris.

Short petrographic description of rocks available in the tectonic zone

Granodiarite, which is quartz-bearing in metasomatite-contact areas, sample 10/249. Composition: hornblende ~25—30%; biotite ~ 25—30%; quartz ~20—25%; pyroxenes ~10—15%; ore mineral ~2%; apatite ~2%. The rock structure is hypidiomorphic, medium- to coarse-grained (1.5—5 mm). Hornblende forms up to 0.5—2.0 mm isometric and short-columnar crystals. Biotite is represented by 1.5—5.0 mm tabular crystals. Quartz forms sharply irregular 0.5—2.0 mm grains. In some places, it corrodes hornblende crystals. Monoclonal and rhombic pyroxenes are available as relict grains (1.0—2.0 mm) in hornblende. Ore mineral is represented by 0.08—0.6 mm oval grains. Apatite forms 0.12—0.2 mm grains or isomorphous crystals.

Hydrothermal-metasomatic rock in the granodioritic tectonic breccia. *Pyrite-plagioclase rock, sample 10/250.* Composition: plagioclase ~65—70%; quartz ~5—8%; epidote ~5—8%; actinolite ~5%; pyrite ~25%; sericite is developed over plagioclase in some places. It forms sharply irregular 1.0—2.0 mm grains. Quartz is available in feldspar mass as <1 mm irregular or hypidiomorphic grains epidote usually forms isolated aggregates, but sometimes is developed over plagioclase. Actinolite forms columnar crystals, which are accumulated in clusters (pockets). Pyrite is available as several isolated clusters of 0.8—4.0 grains.

Epidosite (sample 10/251 a). Composition: epidote ~70%, pyrite ~30%, actinolite ~single grains.

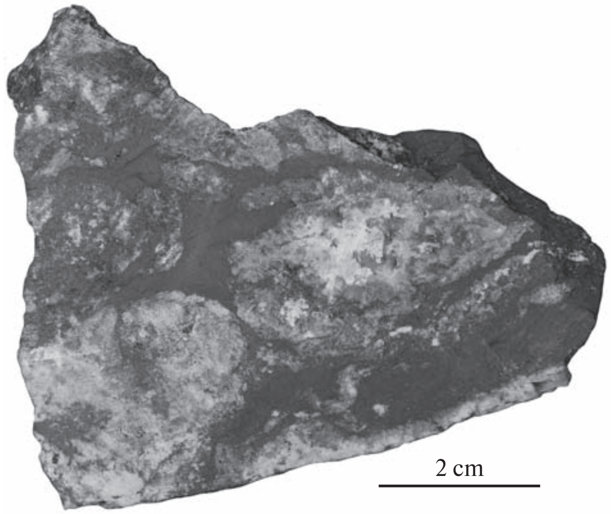

Fig. 4. Granodioritic tectonic breccia concrete-bound with epidote-plagioclase rock and "black rock" (sample 10/252)

Fig. 5. Hydrothermal-metasomatic rock in the cleaved granodioritic tectonic breccia (sample 10/250a)

Pyritic rock (sample 10/251 b). Composition: pyrite ~85%; magnetitic aggregates ~15%; quartz ~ <1%; actinolite ~1%; epidote ~ single grains.

Feldspar-pyritic rock (sample 10/251 c). Composition: pyrite ~70% (up to 10 mm aggregates); feldspars (plagioclase and potassic feldspar) ~25—30%; actinolite ~1%; epidote ~2—3% (up to 0.8—1.0 mm aggregates); magnetitic aggregates (as pyrite inclusions, up to 0.08—0.8 mm) ~3—5%; quartz ~1% (feldspar inclusions).

Pyrite-epidotic rock (sample 10/251 d). Composition: epidote ~50%; pyrite ~30—35%; quartz ~20%; actinolite – under 1 %.

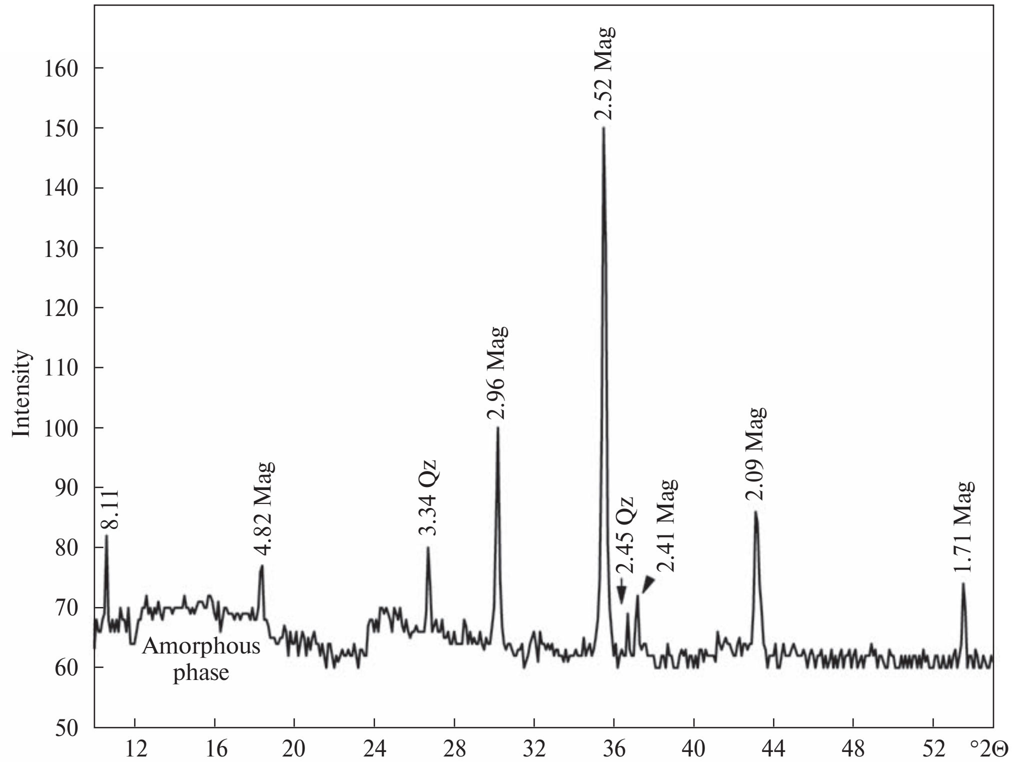

Fig. 6. X-ray diffraction pattern of magnetite obtained from granodioritic tectonic breccia concrete-bound by epidote-plagioclase and "black rock" (sample 10/252)

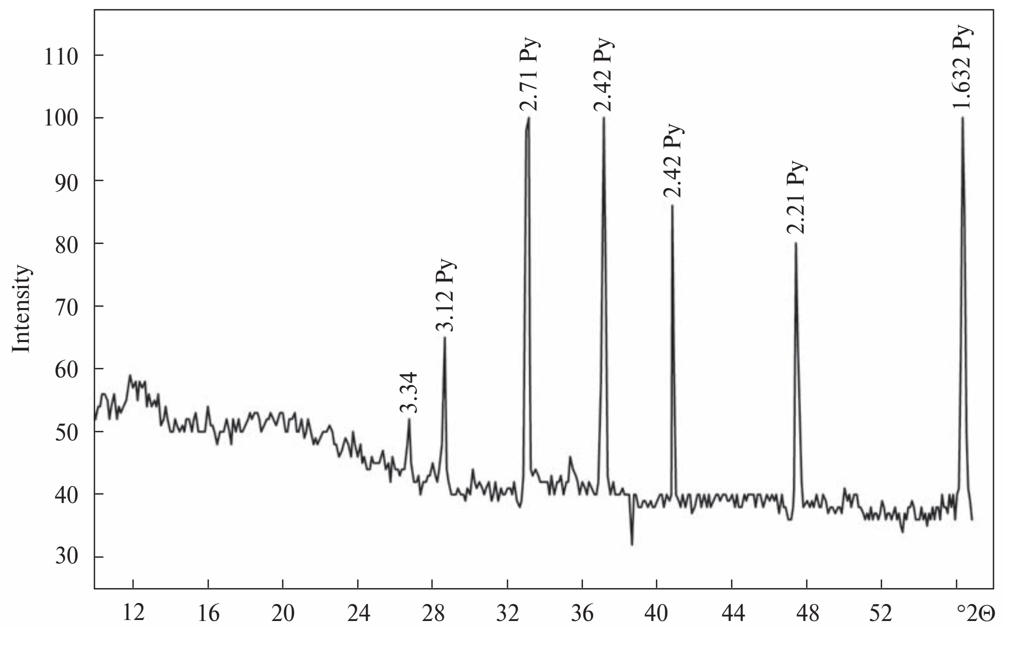

Fig. 7. X-ray diffraction pattern of sulphide obtained from granodioritic tectonic breccia concrete-bound by epidote-plagioclase and "black rock" (sample 10/252)

In the investigated sections, pyrite is the latest mineral. It includes crystals of feldspar, epidote and small debris of magnetitic aggregates.

Epidote-plagioclase rock (sample 10/252). Composition: feldspar (oligoclase) ~30—35%, quartz ~5%; epidote ~10—15%; actinolite ~5—10%, magnetitic aggregates ~40%.

This rock is magnetic. The polished section includes feldspar, magnetitic aggregates and single pyritic grains. Under an ore microscope, 0.007—0.02 grained and ribbon-shaped magnetite is observed, which forms subparallel same-directional chains (“slices”), causing microplicature.

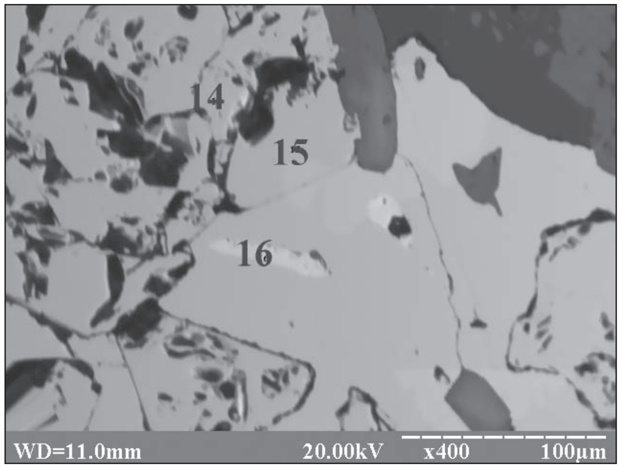

Fig. 8. Image of polished section of hydrothermal-metasomatic rock, along the cleaved granodioritic tectonic breccia under an electronic microscope (sample 10/250a)

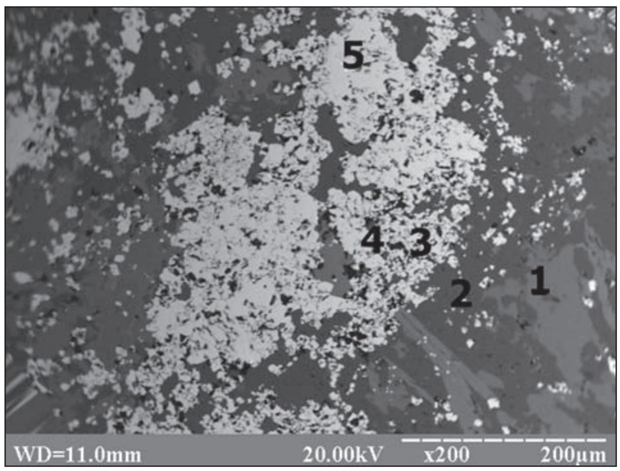

Fig. 9. Image of polished section of granodioritic breccia, which is concrete-bound by epidote-plagioclase and “black” rock, under an electronic microscope (sample 10/252)

Results of the X-ray phase analysis obtained for the black rock from granodioritic tectonic breccia concrete-bound by epidote-plagioclase and black rock (sample 10/252)

The qualitative phase analysis has shown that the black-colored rock consists predominantly of magnetite (Mag) (Fig. 6). Some quantities of quartz and amorphous phase (amorphous silica) are available. A calculation of magnetitic unit cell has shown that parameter $a = 0.8391$ nm is slightly lowered compared to a reference sample (a = 0.8399 nm, card no. 89-0950 acc. to PCPDFWIN catalog, PDF-2, 2003). Most probably, iron in magnetite has been partially replaced with cobalt, which has a smaller ionic radius ($r_{Fe} = 0.062$ nm, and $r_{Co} = 0.059$ nm). In the sample 10/252, sulphide is represented by pyrite (Fig. 7).

Electron microscope investigation results of metasomatitic minerals for granodioritic tectonic breccia. In hydrothermal-metasomatic rock, along the cleaved granodioritic tectonic breccia (sample 10/250a) such ore minerals as magnetite, pyrite, copper pyrite and pyrrhotite are investigated. Pyrrhotite and magnetite produce pyritic inclusions. Pyrite includes Co (0.42%) impurity, and magnetite includes MnO (up to 0.35%) impurity (Table 2, Fig. 8). As of rock forming minerals, composition of epidote and amphibole has been investigated.

In the granodioritic tectonic breccia, which is concrete-bound by epidote-plagioclase and “black” rock (sample 10/252), magnetite composition has been investigated (Fig. 9). Magnetite includes impurities of MnO (up to 0.25%) and CoO (up to 0.23%) (Table 3). As of rock forming minerals, composition of albite and amphibole has been investigated.

Results of total geochemical investigations of rock metasomatites

Using the quantitative spectrum analysis (laboratory of IGMOF of the NAS of Ukraine), elevated contents

Table 2. **Mineral composition of hydrothermal-metasomatic rock, along the cleaved granodioritic tectonic breccia (sample 10/250a)**

Oxides, %	an. 8	an. 14	an. 13	an. 15	an. 16	an. 1	an. 5
	Magnetite	Magnetite	Chalco-pyrite	Pyrite	Pyrrhotite	Epidote	Amphibole
Na_2O	0.00	0.00	0.46	0.97	—	0.11	0.00
MgO	0.00	0.00	0.35	0.84	—	0.83	13.40
Al_2O_3	0.17	0.57	0.66	0.73	0.68	21.87	6.78
SiO_2	1.41	0.95	0.37	0.52	0.30	36.55	51.15
SO_3	2.87	0.40	36.84	53.51	40.28	0.29	1.29
CaO	0.19	0.00	0.00	0.01	—	20.48	11.72
Cr_2O_3	0.12	0.00	0.00	0.01	—	0.19	0.02
MnO	0.35	0.30	0.11	0.11	—	0.27	0.55
FeO	94.12	86.25	35.00	43.46	55.84	13.43	16.39
CoO	—	0.00	—	0.42	0.00	—	—
NiO	0.00	0.10	0.03	0.00	0.00	0.26	0.19
Cu_2O	0.77	0.18	29.80	0.00	—	0.08	0.19
Summ	100.00	88.75	103.63	100.59	99.24	94.35	101.69

Note. Points of microprobe analyses 14, 15, 16 are shown in Fig. 8.

Table. 3. **Mineral composition of granodioritic breccia, which is concrete-bound by epidote-plagioclase and "black" rock (sample 10/252)**

Oxides, %	an. 1	an. 2	an. 3	an. 4	an. 5
	Chlorite	Albite	Magnetite	Albite	Magnetite
Na_2O	0.08	9.62	0.00	9.31	—
MgO	16.08	1.32	0.00	1.11	—
Al_2O_3	19.27	21.60	0.54	21.17	—
SiO_2	26.52	66.77	0.92	67.61	1.27
V_2O_5	0.00	0.00	0.00	0.00	0.08
Cr_2O_3	0.00	0.00	0.00	0.00	0.01
MnO	0.67	0.04	0.24	0.00	0.25
FeO	25.37	0.54	84.79	0.71	85.24
CoO	0.00	0.10	0.23	0.15	0.00
Summ	87.99	100.00	86.72	100.06	86.85

Note. Points of microprobe analyses are shown in Fig. 9.

of cobalt (800 g/t) and copper (200 g/t), as well as small content of gold (0.1—0.3 g/t), which significantly exceed clarkes of elements for this rock type (Table 1) have been discovered in the metasomatic rock along the cleaved granodioritic tectonic breccia.

CONCLUSION

After geological and geochemical surveys, for the first time mineralization of wolfram (28.7 g/t), copper (445 g/t), zinc (207 g/t) and lead (123 g/t) in a lamprophyric dike in an Andean complex granodiorite intrusion on Roca Islands has been discovered. In hydrothermal-metasomatic rock along the cleaved granodioritic tectonic breccia, in the crush zone of the north-eastern (NE 50°) strike on Cruls Islands, an occurrence of cobalt (800 g/t), copper (200 g/t) and gold (up to 0.3 g/t) has been discovered. In these metasomatites, magnetite, pyrite, copper pyrite and pyrrhotite are available. Cobalt is present as magnetitic and pyritic impurities. The obtained data allow clarifying of perspectives of exploration activities in West Antarctica.

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Прояви мінералізації вольфраму, міді, кобальту і золота в районі Аргентинських островів (Західна Антарктида)

Реферат. **Мета.** Метою наших досліджень був пошук проявів рудної мінералізації на островах Рока та Крулс у районі Аргентинських островів Західної Антарктиди. **Методи**. Зразки гірських порід з проявами рудної мінералізації були відібрані під час проведення польових робіт 2010 та 2012 рр. Силікатні аналізи порід виконувались методом "мокрої хімії" в Інституті геохімії, мінералогії та рудоутворення ім. М.П. Семененка Національної академії наук України (ІГМР НАН України). Рентгеноструктурний аналіз порід проводився на дифрактометрі ДРОН-2 з випромінюванням міді ($Cu_{K\alpha}$ = 1,54178 Å). Зразки були обстежені у інтервалі кутів 4—65° 2θ з 0,1 град/хв інтервал вибірки. Для діагностики мінералів використовувався каталог еталонних зразків бази даних PDF-2 (Міжнародний центр дифракційних даних, ICDD) 2003. Хімічний склад мінералів досліджувався на рентгенівському мікроаналізаторі JXA-733 (Jeol, Японія) з використанням хвильового і енерго-дисперсійного спектрометрів. Вміст рідкісних і розсіяних елементів у породах визначався методом індукційно-зв'язаної плазми з мас-спектрометричним закінченням аналізу (ICP-MS) та кількісним спектральним методом. Правильність аналізів контролювали шляхом вимірювання міжнародних і російських стандартних зразків GSP-2, BM, СГД-1А, СТ-1. Помилки визначення концентрацій становили від 3 до 5 мас. % для більшості елементів. Кількісний спектральний аналіз виконувався в лабораторії ІГМР НАН України. Петрографічні дослідження прозорих шліфів порід виконувались за допомогою оптичного поляризаційного мікроскопа МІН-8. **Результати.** Вольфрам, мідь, цинк і свинець були виявлені в дайці лампрофірів у гранодіоритах андійського комплексу на невеликому острові в архіпелазі Рока. Ця дайка, потужністю до 0,5 м, яка вкорінювалась у ще не закристалізовану інтрузію гранодіоритів, має форму півкола. Кут падіння дайки близько 70°. У ній була виявлена мінералізація вольфраму (28,7 г/т), міді (445 г/т), цинку (207 г/т) та свинцю (123 г/т). У східній частині одного з островів архіпелагу Крулс серед гранодіоритів була вивчена крутопадаюча (аз. пад. ПнЗ 345°, кут 82°) тектонічна зона шириною до 10 м, до якої приурочені три смуги метасоматитів, одна з яких досягає потужності до 0,5 м. Серед метасоматитів виділяються епідозити, пірит-плагіоклазові і пірит-епідотові породи, які утворилися в результаті гідротермально-метасоматичної переробки тектонічної брекчії по гранодіоритам. У них виявлено кобальт (800 г/т), мідь (200 г/т) та невелику кількість золота (до 0,3 г/т). У цих метасоматитах спостерігаються магнетит, пірит, халькопірит і пірротин. Кобальт присутній як домішка у магнетиті та піриті. **Висновки.** За час геологічних досліджень у 2010 та 2012 рр. були вперше виявлені прояви мінералізації вольфраму, міді, свинцю, кобальту та золота. Рудна мінералізація такого генезису була раніше невідома в цьому районі. Отримані дані дозволяють уточнити перспективи на пошуки корисних копалин у Західній Антарктиді.

Ключові слова: Аргентинські острови, дайка, брекчія гранодіоритів, метасоматити, точка мінералізації, вольфрам, мідь, кобальт, золото.