# Mineral magnetic properties of granodiorite, metagabbro and microgabbro of Petermann Island, West Antarctica

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## Abstract

The research focuses on studying the magnetic properties and mineralogy of iron-bearing minerals of granodiorite, metagabbro, and microgabbro of Petermann Island, West Antarctica. The predominant iron-bearing minerals of the rocks are ilmenite, magnetite, and iron sulphides. Magnetite in metagabbro and microgabbro is pointed out to be present as two morphological types with different grain size and morphology. The rocks owe their magnetic properties to the presence of different amounts of magnetite with the Curie temperatures of 570–575°C for granodiorite, 555–560°C for metagabbro and 560–565°C for microgabbro. Magnetite in the rocks is stable under heating to 650°C. A slight decrease in magnetisation at 350-400°C is attributed to the conversion of maghemite or maghemite-like phase into hematite. Variation of the magnetite content within each sample has a strong expression in the saturation magnetisation. The latter increases in sequence: granodiorite (0.8–1.3 Am<sup>2</sup>/kg), microgabbro (1.8–3 Am<sup>2</sup>/kg) and metagabbro  $(3.1-3.5 \text{ Am}^2/\text{kg})$ . The saturation magnetisation of rocks increases with the increasing content of iron. However, the inverse relation is observed for metagabbro and microgabbro due to the replacement of titanite for magnetite in the latter. The magnetic fraction of microgabbro reveals the wasp-waisted hysteresis loop suggesting bimodal size distribution. According to X-Ray Diffraction, the characteristic peaks (d-spacing) of pure magnetite are identified for magnetic fraction of granodiorite and metagabbro, while magnetite of microgabbro form stable intergrowth with titanite and chlorite.

Key words: Graham Land, rock magnetic properties, magnetite, thermomagnetic analysis

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## Introduction

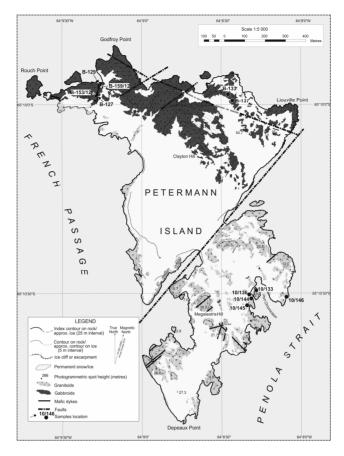
Mineral magnetic properties of the rocks provide outstanding information on geological structure and tectonics of the Earth's crust. The magnetic properties of rocks are usually attributed to one or more minerals revealing the magnetic ordering such as ferrimagnetism, antiferromagnetism, and ferromagnetism (Cornell et Schwertmann 2003). The most abundant minerals, which determine rock magnetic properties are magnetite, hematite, maghemite, goethite, titanomagnetite, and ilmenite (Dekkers et Linssen 1989, Frank et Nowaczyk 2008, Frederichs et al. 2003, Lattard et al. 2006, Strangway et al. 1968). In general, they are hardly identified by traditional mineralogical techniques, such as optical microscopy (these minerals are opaque) and electron microprobe (in a case of very small or skeletal grains with the fine lamellae).

In the field of geology, quantitative identification of magnetic minerals as well as investigation of their properties is critical for deciphering the process of magmatic crystallization, ore body emplacement, secondary alteration as well as structural analysis of almost all rock types. On the other hand, the mineral magnetic properties can serve as sensitive indicators of geochemical conditions the rock formed and developed in.

Graham Land is the part of the Antarctic Peninsula that lies north of a line joining Cape Jeremy and Cape Agassiz. Systematic geological investigations of the Andean Intrusive Suite of Graham Land, Antarctic Peninsula, were performed by the British Graham Land Expedition (BGLE) during 1934–1937 and later by Falkland Islands Dependencies Survey (FIDS). The latter was renamed British Antarctic Survey (BAS) in 1962. Since 1996 the Ukrainian Antarctic Center has commenced geological and geophysical investigations of the Argentine Islands and the adjacent area.

Petermann Island is a small, low and

rounded island, lying off the northwest coast of Kiev Peninsula in Graham Land, a short distance south of Booth Island and the Lemaire Channel. The geology of the Island is represented by plutonic and hypabyssal igneous rocks (Fig. 1): gabbros, granodiorites, microgabbros and porphyrites (a porphyritic rock of diorite composition) are common. At the north-west corner of the island (Rouch Point) there are exposures of the Andean Intrusive Suite hornblende-gabbros and granodiorites, which intrude them. Both granodiorites and gabbros are cut by at least two generations of mafic dykes: the older porphyritic diabase and the younger diabase (Mytrokhyn et al. 2017). Rb-Sr whole-rock dating of a late granodiorite intrusion at Rouch Point, gave 93±8 Ma with the initial ratio  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.7045 (Pankhurst 1982). Isotopic dating of zircon grains of granodiorites by U-Pb gave 95.9±1.0 and 96.1±0.7 Ma (Bakhmutov et al. 2013). The southern part of Petermann I., near Port Circumcision, is composed entirely of granitoids of the Andean Intrusive Suite (Curtis 1966) with a granodiorite being the most typical rock among them. These granitoids host a significant amount of volcanic and gabbroic xenoliths. Furthermore, the granitoids are intruded by mafic dykes, similar to those occurring at the northern part of the island: porphyritic and diabase dykes are common here (Mytrokhyn et al. 2017). Guenthner et al. (2010) performed thermochronometric dating of the granodiorite from the southern part of the Petermann I. Thus, apatite (U-Th)/He (apatite He) with a closure temperature of ~50-70°C gave 11.1±0.9 Ma; apatite fission track (apatite FT) with a closure temperature of ~100-120°C gave 30.6±9.6 Ma; zircon (U-Th)/He (zircon He) with a closure temperature of  $\sim 170$ – 200°C gave 42.8±0.9 Ma; zircon fission track (zircon FT) with a closure temperature of ~220–260°C gave 35.6±4.2 Ma.



**Fig. 1.** Geological map of Petermann Island, Graham Coast. The map is developed using a topographic surface map of BAS/4/05; frame numbers 244-247 (acquired January 2005) and the existent geological sketch map of Petermann Island after Mytrokhyn et al. (2017).

Brief petrographic descriptions of hornblende gabbros of the north-western part and the tonalites and granodiorites of the southern part of the Petermann I could be found in Curtis (1966). The author concluded that there are two types of gabbroids: the first type with ophitic augite (6 mm) and high content of magnetic minerals, and the second type with the remnants of augite around big crystals of amphibole (1–5 mm) and less content of magnetic minerals.

More recently, Artemenko et al. (2011) identified the mineralization of pyrite, chalcopyrite and magnetite in the granitic intrusion and attributed it to post-tectonic hydrothermal quartz veins and epigenetic processes in the tectonic faults. Artemenko et al. (2013) identified the presence of compositional layering in the late intrusive phase of Petermann I. gabbroids: it is claimed to consist of light (up to 20 mm) and dark (up to 30 mm) layers composed of different amounts of pyroxene and magnetic minerals. The author concluded that these rocks host up to 20% of iron minerals and iron mineral "dust". Iron magnetic minerals occur near pyroxene crystals, which are altered to green hornblende on its edges. However, mineralogy and mineral magnetic properties of the rocks of Petermann I. remain virtually unstudied. Since geological position and geodynamic conditions of the formation and secondary alteration of these rocks is a controversial piece of data, new mineralogical and magnetic findings may partially fill the gap in the existing data.

The aim of this work is to identify the magnetic minerals of plutonic and hypabys-

sal rocks of Petermann I., West Antarctica, and to describe the mineral magnetic properties of these rocks by thermomagnetic, X-Ray Diffraction, optical microscopy, magnetometry methods, and electron microprobe analysis. The proceedings of this research may lead to a more comprehensive understanding of the geology and genesis of the intrusive igneous rocks found on Graham Land.

## **Material and Methods**

The research is performed based on the samples collected during Ukrainian Antarctic expeditions (1998-2008). In total, 11 samples from Petermann I are used in our research (Fig. 1): 5 samples of granodiorite (10/133, 10/136, 10/144, 10/145, 10/146) from the southern part of the island; 2 samples of metagabbro from gabbroids (B-133, B-137) of the northeastern part of the island; 2 samples of porphyritic diabase dyke (B-127, B-129) which cuts the gabbroids at the northwestern part; 2 samples of microgabbro from diabase dyke (B-153/12, B-159/12) which cuts the porphyritic diabase dyke and gabbroids at the northwestern part. All samples are studied into the mineralogy by optical microscopy and are classified into three petrographic groups according to the recommendations of the IUGS Subcommission on the Systematics of Igneous Rocks (Le Maitre et al. 2002). They are: granodiorite, amphibole metagabbro and microgabbro. All the samples are studied through thermomagnetic analysis, electron microprobe analysis, and magnetometry. Mineral and magnetic properties of the samples among each petrographic group are pointed out to be identical. Thus, one representative sample (10/144, B-133, B-159/12) from each petrographic group is selected for undergoing X-Ray Diffraction and magnetic properties (the dependence of magnetisation on temperature and the dependence of magnetisation on an applied field). Samples are crushed to the size  $<5 \mu m$  at the Laboratory of Mineralogical and Geochemical studies of the Institute of Geology, Taras Shevchenko National University of Kyiv, Ukraine.

Petrographic examination of samples was carried out both in transmitted and reflected light using NIKON ECLIPSE LV100 POL. The samples were polished, graphite-coated and analyzed with a microprobe X-ray spectral microanalysis on a raster electron microscope REMMA-202M with an energy-dispersive X-ray spectrometer. The composition of Fe-Ti oxides is analyzed using an acceleration voltage of 20.0 kV, a beam current of 1.40 nA, and 9–10 µm beam diameter.

X-Ray Diffraction analysis is performed with a diffractometer DRON-3M in filtered emission CuK $\alpha$  ( $\lambda$ =0.154184 nm) with recording geometry by Bragg-Brentano. The mineral phases were identified using d-spacing from PCPDFWIN (PDF-2) of USA database.

Magnetisation measurements as a function of an applied field were carried out with a magnetometer with Hall sensors at a room temperature. An external magnetic field of magnetometer varied in a range of  $0\pm0.45$  T. Thermomagnetic analysis was performed with a custom-built facility that consists of a digital balance with a built-in permanent magnet. The applied steady field is 300 mT. The heating and cooling runs of the samples are carried out in a quartz reactor with the rate of 65°/minute. Thermomagnetic data includes the derivative thermomagnetic curves (DTMC) in addition to the integral thermomagnetic curves (TMC). Curie temperatures are identified as a minimum of a peak on DTMC.

Magnetic fractions are extracted from the rocks by electromagnetic separator with an altered magnetic field. A preliminary magnetisation of magnetic fraction is also performed in a field of 300 mT with the use of a permanent magnet (NdFeB).

Chemical composition of rocks is determined by means of X-ray Fluorescence analysis (XRF) at Thermo ARL Optim'X spectrometer equipped with a Rh-anode Xray tube of 50 W power, goniometer with three crystals (AX06, PET, LiF 200), and two detectors (FPC, SC). Preparation for XRF analysis included milling of the samples to the powder and pressing into pellet with a boric acid.

#### **Results and Discussion**

#### 1. Mineralogy

## 1.1. Granodiorite

Isometric magnetite crystals occur primarily in association with biotite, chlorite and titanite, more rarely with epidote. Often, magnetite appears as inclusions in biotite and chlorite. Magnetite is chemically pure and the size of grains fluctuates from

#### 1.2. Metagabbro

Magnetite in metagabbro has two morphological types. The first type occurs as relatively large, 0.4-0.6 mm in size, subhedral grains, which are in association with ilmenite and form intergrowths with it. The latter indicate that magnetite crystallized later then ilmenite. Often, this type of magnetite hosts microscopic tabular lamellae of ilmenite, which are oriented parallel to one of the crystallographic faces. The second morphotype is represented by much smaller, 0.01-0.05 mm in size, subhedral and euhedral microcrystals that are heterogeneously scattered throughout the rock-forming minerals. This type of magnetite is relatively pure, while the first one contains insignificant impurities of TiO<sub>2</sub>

0.1 to 0.3 mm. Ilmenite forms euhedral to subhedral crystals from 0.1 to 0.4 mm. Titanite associates with biotite, epidote and forms thin rims around magnetite grains. Pyrite occurs as accessory opaque alteration mineral.

(0.21-0.67 wt%) and V<sub>2</sub>O<sub>3</sub> (0.64-0.89 wt%). However, elevated TiO<sub>2</sub> contents can be explained by partial involvement of ilmenite in the magnetite analysis either due to analysis of a lamella just below the mineral surface or very small ilmenite splinters. Ilmenite is less common than magnetite. It forms euhedral to subhedral tabular crystals from 0.5 to 0.7 mm. The majority of grains contains microscopic exsolution lamellae of hematite, 0.02-0.04 mm, which are oriented parallel to the crystal face (0001). Ilmenite contains impurities of MnO (2.21-2.93 wt%) and MgO (0.46–1.25 wt%). Pyrite, chalcopyrite and sphalerite were identified in metagabbro. Morphological features and mineral

associations indicate the secondary origin of sulphides. Titanite anhedral crystals of about 0.05–0.1 mm in size, tend to occupy

#### 1.3. Microgabbro

Magnetite is the predominant Fe-Ti oxide mineral of microgabbro. It is pointed out that two morphological types of magnetite are present. The first type forms anhedral to subhedral crystals of cubic, octahedral and combined habits with crystal sizes from 0.06 to 0.09 mm. It forms intergrowths with ilmenite and contains lamellae of ilmenite, which are oriented parallel to one of the crystallographic faces. The chemistry of magnetite is characterized by elevated TiO<sub>2</sub> (0.14–0.78 wt%) and V<sub>2</sub>O<sub>3</sub>

#### 2. Thermomagnetic analysis

Thermomagnetic analysis performed in air up to 650°C (Fig. 2) shows that samples owe their magnetic properties to the presence of different amounts of magnetite. Curie temperatures, determined as a peak on DTMC, lie within the range of 570-575°C for magnetic phase of granodiorite, 555-560°C for metagabbro, and 560-565°C for microgabbro. The obtained Curie temperatures are close to the Curie temperature of pure stoichiometric magnetite (580°C) (Kudryavceva 1988). A slight shift of Curie temperature of the investigated rocks to lower values could be explained by substoichiometry or/and isomorphous substitution of iron by other cations (Isambert et al. 2003, Lattard et al. 2006, Ponomar et al. 2017).

On heating, a slight decrease in magnetisation is observed at temperatures of 350–400°C. This change in magnetisation does not rehearse on cooling curve, which indicates the irreversibility of this transformation. According to Kudryavceva (1988) a decrease in magnetisation at 350°C can be attributed to the transformation of maghemite or maghemite-like phase into hemthe boundaries between Fe-Ti oxide minerals and amphiboles.

content (0.28–0.87 wt%). The second type of magnetite contains no impurities and is represented by smaller (~0.02 mm) subhedral grains which heterogeneously saturate hornblende crystals. Ilmenite flattened skeletal crystals are usually less than 0.09– 0.1 mm in size. Pyrite crystals are up to 0.2 mm and occur as xenomorphic and anhedral inclusions in titanite. Trace amounts of galenite are identified in pyrite. Secondary titanite develops after magnetite grains.

atite. In addition, this drop in magnetisation is not typical for pure stoichiometric magnetite. Therefore, we assume a partial oxidation of magnetite to maghemite or maghemite-magnetite solid solution.

Generally, maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) can be considered as a non-stoichiometric defect magnetite with incomplete spinel cation site occupancy (De Boer et Dekkers 2001). Moreover, magnetite is known to form a solid solution with maghemite. Phase transformation of metastable maghemite into hematite commonly occurs at about 350°C (Chen 2013, Cornell et Schwertmann 2003), which is close to the temperature observed in our studies.

Thermal stability of the magnetic phases of rocks is estimated from the thermomagnetic curves under heating to 650°C in air. The losses of magnetisation after heating are less than 5% for all samples. Consequently, magnetite in plutonic and hypabyssal rocks of Petermann I. is relatively stable to heat. A slight decrease in magnetisation can be linked with the conversion of maghemite or maghemite-like phase into hematite.

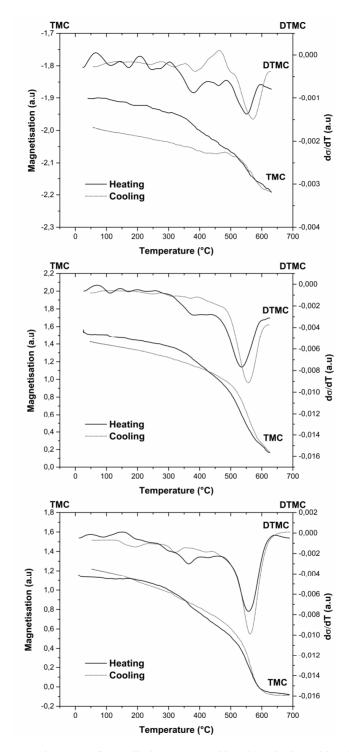


Fig. 2. Thermomagnetic curves of granodiorite (a), metagabbro (b) and microgabbro (c).

#### 3. Magnetisation measurements

The saturation magnetisation was initially measured for the samples prior to magnetic separation and subsequently for the magnetic fractions extracted by electromagnetic separation in an alternating magnetic field.

Fig. 3 shows the distribution of saturation magnetisation values and iron (Fe<sub>2</sub>O<sub>3</sub>) content in the rocks of Petermann I. The content of iron varies through different groups of rocks and increases in sequence: granodiorite – metagabbro – dykes. By contrast, the saturation magnetisation of rocks increases in a different sequence: granodiorite – dykes – metagabbro. The saturation magnetisation of granodiorite lies in the range of 0.8–1.3 Am<sup>2</sup>/kg. The higher values are typical for dykes (1.8–3 Am<sup>2</sup>/kg) and metagabbro  $(3.1-3.5 \text{ Am}^2/\text{kg})$ . This indicates that all samples contain a small amount of magnetite.

The saturation magnetisation of the investigated samples increases with the increasing content of iron. However, there is an inverse relation for metagabbro and dykes. Despite higher content of iron in dykes than in metagabbro, dykes tend to have lower values of magnetisation. Generally, the saturation magnetisation of dykes is quite variable and weakly correlated with the content of iron. This is due to the replacement of titanite for magnetite (*see* Section 4), which was probably caused by secondary alteration. Therefore, the higher the degree of magnetite substitution, the lower the magnetisation of rock.

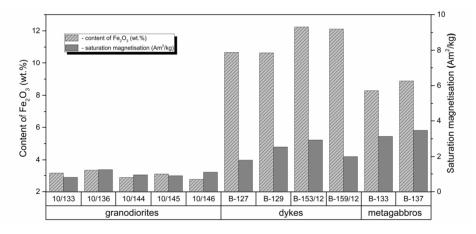


Fig. 3. Diagram of iron content and saturation magnetisation of plutonic and hypabyssal rocks of Petermann Island.

One representative sample from each petrographic group was divided into highly magnetic and weakly magnetic fractions by means of magnetic separation. The percentage of magnetic fraction, by mass, is 0.6% for granodiorite, 0.8% for metagabbro, and 1.1% for microgabbro. Magnetisation measurement as a function of an applied field is performed for the magnetic

fractions of rocks with the results displayed in Fig. 4. The saturation magnetisation of magnetic fractions is 74  $\text{Am}^2/\text{kg}$  for granodiorite, 79  $\text{Am}^2/\text{kg}$  for metagabbro, and 23  $\text{Am}^2/\text{kg}$  for microgabbro.

The saturation magnetisation value of the magnetic fraction of granodiorite and metagabbro is close to the saturation magnetisation of pure magnetite, which equals 92 Am<sup>2</sup>/kg at a room temperature (Kudryavceva 1988). According to X-Ray Diffraction (*see* Section 4), the magnetic fractions of granodiorite and metagabbro contain virtually magnetite.

The saturation magnetisation of microgabbro magnetic fraction is about three times lower than the corresponding values for granodiorite and metagabbro. The observed decrease in magnetisation is due to the presence of mineral impurities, such as titanite and chlorite, as determined by X-Ray Diffraction (*see* Section 4). According to mineralogical investigations, secondary processes have led to the replacement of titanite for magnetite and, consequently, to the formation of fine mineral intergrowths.

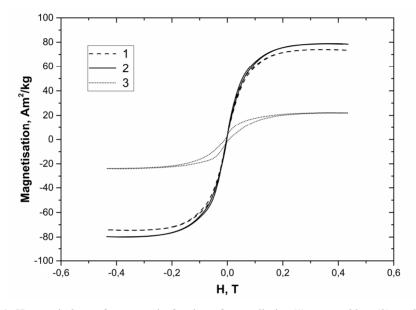


Fig. 4. Hysteresis loops for magnetic fraction of granodiorite (1), metagabbro (2), and micro-gabbro (3).

Magnetite of granodiorite and metagabbro reveals very low remanence and coercivity (Fig. 4), which is typical for pure magnetite grains. Magnetite from microgabbro has a remarkable higher coercivity, remanence and a wasp-waist shape of the magnetisation curve. These characteristics indicate a bimodal distribution of particle sizes, which is consistent with mineralogical observations.

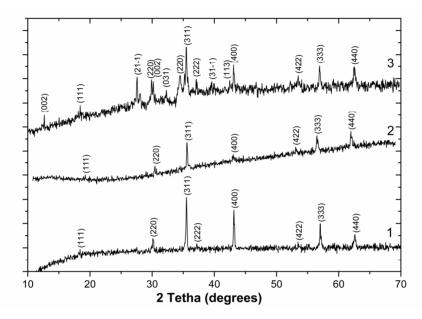
According to mineralogical studies (Section 1), both metagabbro and microgabbro contain two types of magnetite with different grain sizes. Nevertheless, the waspwaisted magnetisation curve is observed only for microgabbro. It is assumed that if the size of the magnetite grains of both types is quite large, this may not affect the magnetisation curve. On the other hand, if the size of grains is very small, it may change the shape of magnetisation curve. As the crystallization of dykes proceeds with rapid cooling, this results in a smaller grain sizes in dykes than in metagabbro.

We assume that the wasp-waist hysteresis behaviour observed in microgabbro is due to the bimodal size distribution of magnetite grains. In metagabbro, the difference in size may not be high enough to cause the wasp-waisted hysteresis loop.

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## 4. X-Ray Diffraction

Mineral composition of the magnetic fractions of rocks was investigated using X-Ray Diffraction. The main magnetic phase of all rocks is magnetite (Fig. 5), which corresponds to the magnetometry data. Table 1 reports the characteristic peaks (d-spacing) for magnetite from plutonic and hypabyssal rocks of Petermann I. and a comparison with the standard d-spacing for magnetite from the Power Diffraction File (PDF 85–1533). There is a slight difference between the structures of magnetite from plutonic and hypabyssal rocks of Petermann I.



**Fig. 5.** XRD patterns of magnetic fraction of granodiorite (1), metagabbro (2), and microgabbro (3). Numbers correspond to Miller's indexes.

The magnetic fraction of microgabbro consists of chlorite and titanite in addition to magnetite. Titanite with characteristic peaks (d-spacing) of  $d_{2\Pi}$ =3.222 Å,  $d_{002}$ = 2.978 Å,  $d_{031}$ =2.597 Å,  $d_{3\Pi}$ =2.266 Å corresponds to the calcium titanium aluminum silicon oxide hydroxide with the chemical formula Ca<sub>0.996</sub>(Ti<sub>0.714</sub>Al<sub>0.282</sub>Fe<sub>0.004</sub>)Si<sub>0.992</sub> (O<sub>0.674</sub>(OH)<sub>0.326</sub>)O<sub>4</sub> (according to PDF 80–2297). A characteristic peak with d-spacing  $d_{002}$ =7.012 Å indicates the presence of chlorite.

Note that the diffraction pattern of magnetite is close to some other minerals with a spinel structure, such as maghemite,

jacobsite, or magnesioferrite. For instance, maghemite and magnetite have lattice parameters of 8.3515 Å and 8.397 Å, respectively, implying a slight shift of the maghemite's peaks to higher 20 values in comparison with the peaks of magnetite (Kim et al. 2012, Salazar-Camacho et al. 2013). However, the lattice parameters obtained in this paper (Table 1) lie between that of magnetite and maghemite complicating the structure identification. Therefore, it is difficult to decide whether the magnetic fractions of rocks consist of magnetite or maghemite. Nevertheless, thermomagnetic and magnetic properties (*e.g.* thermal stability, Curie temperature, saturation magnetisation) of magnetite strictly differs from the other minerals with the spinel structure. Therefore, the characteristic peaks of the spinel structure obtained in our work are identified as magnetite. Consequently, the magnetic fraction of plutonic rocks – granodiorite and metagabbro – consists of relatively pure magnetite, while the magnetite of microgabbro forms intergrowth with titanite and chlorite.

	Characteristic peaks (d-spacing), Å			
hkl	Magnetite from granodiorite	Magnetite from metagabbro	Magnetite from microgabbro	Standard for magnetite (85-1533)
111	4.817	4.746	4.817	4.8480
220	2.969	2.95	2.95	2.9687
311	2.528	2.521	2.52	2.5317
222	2.419	n/d	2.419	2.4240
400	2.097	2.092	2.092	2.0992
422	1.712	1.713	1.708	1.7140
333	1.614	1.614	1.611	1.6160
440	1.482	1.482	1.481	1.4843
Lattice parameter, Å	8.388	8.369	8.364	8.397

**Table 1.** Characteristic peaks (d-spacing) (Å) of magnetite from plutonic and hypabyssal rocks of Petermann Island and standard d-spacing of magnetite (PDF 85–1533).

## Conclusions

The paper presents the results of mineralogical and magnetic properties studies of iron-bearing minerals of granodiorite, metagabbro, and microgabbro of Petermann Island, West Antarctica. Iron oxides, such as magnetite and ilmenite, and iron sulphides are identified for all rocks. The rocks owe their magnetic properties to the presence of different amounts of magnetite.

Metagabbro and microgabbro, in contrast to granodiorite, are characterized by the presence of ilmenite exsolution lamellae in magnetite and similar chemistry of magnetite. The latter suggests that gabbroids and dykes are co-genetic and derived from the magma of similar composition. The high-Ti magnetite, in comparison with pure magnetite, causes a slight shift of Curie temperatures to lower values.

The remanence and coercivity are very low for magnetite in granodiorite and metagabbro. On the other hand, magnetite from hypabyssal microgabbro has a wasp-waisted hysteresis loop and a higher coercivity and remanence compared to the plutonic rocks, which is determined by bimodal distribution of the size of magnetite and substitution of magnetite for titanite. This effect is attributed to low-grade metamorphic processes under the near-surface conditions.

The proceedings of the research can be helpful in further geological investigations of the igneous rocks in the area of Petermann I and can serve as a basis for magnetic anomaly mapping.

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