The new discovery of native iron in traps of the Siberia

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Abstract. A massive manifestation of native iron nodules weighing up to four hundred kilograms was established in a trap intrusive near Aikhal settlement. In addition to large segregations, the native iron occurs as drops in the rock-forming minerals of dolerites rimming the iron nodules. In terms of petrochemical composition, dolerites of the sill belong to typical tholeites of the traps of the Siberian platform, and correspond to low-Ti basites (\(\text{TiO}_2 \sim 1\%\)) with increased magnesium content (\(\text{Mg}^{II} = 56-63\)) that have passed through the deep (pre-chamber) stage of melt crystallization. The dominant mineral in the nodules is native iron, with subordinate cohenite (\(\text{Fe}_3\text{C}\)), troilite (\(\text{FeS}\)) and magnetite (\(\text{Fe}_3\text{O}_4\)). X-ray phase analysis revealed that the native iron has the \(\alpha\)-\(\text{Fe}\) structure with the unit cell parameter \(a=0.2860\) nm. The Brinell hardness is in the range of 110-117 HB units (or 1080-1150 MPa). With regard to the low Ni content (< 1%), the native iron corresponds to the mineral species ferrite. It is assumed that the main condition for the presence of native iron in megascopic quantities in traps is the fractionation of a basaltic melt in the deep-seated intermediate chamber. In this situation, the interaction of the basaltic melt with a high-temperature intratelluric fluid, characterized by highly reducing properties, led to the dispersion of the initially homogeneous basaltic liquid into liquates of silicate and metal composition. It is the finely dispersed state of the fluid-magmatic system that favored the appearance of the native phase, above all of iron.

1. Introduction

The main native phase of terrestrial and space origin is iron. It occurs in all rock types as minute drop-like separations. Large segregations of iron are very rare, they were first found in the rocks of andesite-basaltic composition on Disco Is., Greenland [1, 2]. Another large occurrence was reported from Germany, near the town of Kassel [3]. In Russia, large native iron occurrences were discovered in four trap intrusions in the northern part of the Siberian platform: Dzheltula, Khunktukan, Khininda, and Maimecha [4, 5]. The new native iron occurrence was found within the Aikhal sill in the eastern Siberian platform [6]. Accumulations of native iron range from millimeter-size spherules to nodules about 20-40 cm across, and rarely form large blocks. Native iron segregations occur both in bedrocks and placers, sometimes covering large areas. The weight of iron nodules varies from hundreds of grams to a few hundreds of kilograms. Iron nodules measuring 60, 150 and 250 kg in weight were reported from the Khunktukan intrusion. In one of the solid rock exposures, an iron block was discovered with its protruding part weighing 10 tons. The weight of the iron block from the newly discovered occurrence in the Aikhal sill is about 400 kg. New discovery of the manifestation of native iron a trap intrusive Aikhal will expand the information on this unique natural phenomenon and will make it possible to clarify the look at its genesis.
2. Analytical methods

Ferrit, cohenite and troilite were analyzed by with an X-ray Camebax-Micro microanalyzer at accelerating voltage of 20 kV and beat current of 50 nA. The chemical composition of minerals from the dolerites was determined using a JSM-6480LV scanning electron microscope with INCA energy-dispersion (EDS) and wavelength-dispersion (WDS) spectrometers. Carbon-coated polished thick sections were used for analyses. Operation conditions were: 20 kV accelerating voltage and 1nA beam current. Major element concentrations were obtained by the classical wet chemical analysis at the Department of Physic-Chemical Analytical Methods, DPMGI, SB RAS. Trace elements in the dolerites and the native iron were analyzed by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) using an Elan 6100 DRC instrument in standard mode (JMGRE RAS). Structural-textural relations between the rock-forming minerals and native phases were studied in polished thick and thin sections. The X-ray diffraction analysis of iron samples in the form of chips and polished thick sections was conducted with a Bruker D2 PHAZER diffractometer with CuKα radiation (30 kV, 10 mA). The PDF2 database was used. The Brinnel hardness measurements of native iron were made with a Heckert hardness tester (Institute of Physico-Chemical Problems of the North) in accordance with GOST 9012-89 (State Russian Standard) at a load of 1840 HB and a wait time of 10 s.

3. Native iron from basites and its composition

The new native iron occurrence was found within the Aikhal sill in the eastern Siberian platform (Yakutia). The sill belongs to Permo-Triassic traps of the Tunguska syncline, and overlaps the Zarya kimberlite pipe. The thickness of the intrusion exposed in a quarry is about 60 m. The sill is composed of fine- to medium-grained ophitic and taxitic-ophitic dolerites. The Aikhal sill rocks are higher (10 to 16%) in olivine content with respect to typical dolerites of the Tunguska syncline. Dolerites of the sill invariably contain the first generation minerals of pre-chamber crystallization. These are bytownite, Mg-rich augite and, likely, idiomorphic crystals and small rounded grains of olivine. The dolerites also contain a minimum amount of mesostasis (no more than 2%). The data available on the chemical composition of the Aikhal sill (Table 1) indicate that it was formed from a tholeiitic-basaltic melt. Chemical composition of the sill is characterized by higher Mg and lower Fe\text{tot} contents relative to the average composition of the most widespread type of traps in the eastern Siberian platform. The dolerites rimming the iron nodules (sample Ai-0) contain drops of native iron with very high Fe and Mg and low SiO\text{2} values (Table 1).

|    | SiO\text{2} | TiO\text{2} | Al\text{2}O\text{3} | FeO | MnO | MgO | CaO | Na\text{2}O | K\text{2}O | P\text{2}O\text{5} | H\text{2}O+ | Σ   |
|----|-------------|-------------|---------------------|-----|-----|-----|-----|-----------|---------|------------|-----------|------|
| \text{A*} | 48.38       | 1.02        | 15.39               | 10.70 | 0.19 | 9.25 | 10.74 | 1.94      | 0.41    | 0.1        | 0.86      | 99.8 |
| \text{B*} | 48.57       | 1.48        | 14.62               | 12.29 | 0.19 | 7.04 | 10.77 | 2.23      | 0.64    | 0.19       | 0.8       | 99.8 |
| \text{C*} | 41.26       | 0.93        | 12.85               | 22.08 | 0.22 | 11.25| 7.32  | 1.16      | 0.22    | 0.08       | 0.54      | 99.4 |

\text{A*} - average for the sill without Ai-0 (dolerite from the rim); \text{B*} - average for the traps in the east of the Tunguska syncline (435 an.) - data of the authors; \text{C*} - Ai-0 - the dolerites rimming the iron nodules.

In the upper part of the quarry, several native iron nodules have been found among the trap blocks. The presence of intergrowths of the native phase with the rock-forming minerals of basites and a compact crust of fine-grained dolerites around the iron nodules indicate a natural origin of iron segregations. Native iron is rarely present in macroscopic quantities in basic rocks. This new kind of iron will increase our knowledge of this unique natural phenomenon and provide constraints on its genesis.

The samples studied are represented by segregations of flattened, ellipsoidal form (Figure 1 of sample Ai-1a), 21x13x3 cm in size and 3.95 kg in weight, as well as by nodule sections. There is a rim (up to 2 cm thick) of fine-grained dolerites at the nodule margins. The internal structure of the nodules
is heterogeneous. The massive central part consists of 95% of iron. The fraction of the silicate component increases to 25-30% outward, and the structure of iron nodules becomes spongy due to cohesion of iron drops and segregations into a single metallic framework with the residual silicate matter inside (Figure 1 of sample Ai-1b). Relics of the silicate phase preserve occasionally the structural pattern of the dolerites, but at the boundary with iron, a rim of high-Fe minerals develops. In the matrix of native iron, there are observed evenly distributed small inclusions of dark-grey glassy matter consisting of Si and Fe.

![Figure 1. Sample Ai-1: a - general view; b - a nodule in section](image)

Native iron from the Aikhal sill corresponds to α-Fe structure with a unit-cell parameter a=0.2860 nm. The Brinnel hardness measured with a Heckert hardness tester is within 110-117 HB (or 1080-1150 MPa). In terms of chemical composition, the null-valent iron of the Aikhal sill is ferrite with insignificant Ni amount (less than 1%) (Table 2). Its C content 2.14 wt.%, which permits assigning it to a high-C variety.

| Table 2. The chemical composition of ferrite, cohenite, troilite, wt% |
|-------------------------|----------------|----------------|----------------|
|                         | Ferrite |             | Cohenet |             | Troilite |             |
|                         | Ai-1    | Ai-2    | Ai-1    | Ai-2    | Ai-1    | Ai-2    |
| Fe                      | 98.69   | 98.72   | 92.54   | 92.44   | 61.65   | 62.64   |
| Ni                      | 0.06    | 0.06    | 0.05    | 0.05    | -       | -       |
| Co                      | 0.08    | 0.09    | 0.07    | 0.07    | -       | -       |
| Cu                      | 0.20    | 0.16    | 0.16    | 0.14    | -       | -       |
| Sn                      | 0.03    | 0.03    | -       | 0.014   | -       | -       |
| Ge                      | 0.33    | 0.32    | 0.10    | 0.33    | -       | -       |
| S                       |         |         |         |         |         |         |
| Total                   | 99.39   | 99.38   |         |         | 99.14   | 99.64   |

Iron occurs in association with cohenite, troilite, and magnetite. Cohenite is second in abundance in the iron nodules. As known from metallurgy data, a limiting C value to dissolve in iron is 2.14%, the excess C is exsolved as cohenite. Being a product of decomposition of a Fe-C melt, cohenite forms flame-like or intricately curved worm-shaped segregations in iron (Figure 2). Small (2.5x3.0 mm) areas of perlite occur occasionally. Perlite (a mixture of ferrite and cohenite) is a product of eutectic decomposition of a Fe-C melt on its slow cooling to below 723° C (data of metallurgy). In this case, the content of cohenite in iron may amount to 40 vol. %).
Troilite (FeS) in paragenesis with ferrite is found in two morphological forms (Figure 3 a, b). Most frequently it occurs as a rim around the periphery of iron at its boundary with the silicate rock. The second form includes drop-like segregations often with a discontinuous cohenite margin. In terms of chemical composition, troilite is close to pyrrhotite, but unlike the latter, it is etched (or comes to the boil) in acids. Sulfide in a ferrite nodule from the Aikhal sill boils up in HCl, and X-ray analysis confirmed that it belongs to a low-S variety – troilite. Troilite is virtually free of other element impurities.

Iron is able to concentrate on many elements that can form solutions in liquid and solid metal. Nickel and cobalt in liquid metal are dissolved in a wide range (Table 3). Copper is poorly soluble in iron, and therefore it forms an independent phase – nickel copper. It is present in the nodules as an auxiliary mineral, forming spherules in the Fe-phase or it occurs in association with troilite or cohenite. The concentration of Ag in the host basites and in the Fe-phase is within the same range of 0.1-1.5ppm. This suggests the lack of high Ag accumulations in the metallic phase of the basic rocks. Silver is quite insoluble in iron, and most likely forms small emulsion segregations, as does copper.

Geochemical analysis of native iron showed the presence of gold and platinum-group elements in concentrations hundreds and even thousands of times higher than in the enclosing silicate rocks. Along with the noble metals, the metallic liquid intensely concentrates Ge, W, Mo, As and Sn with distinct siderophile properties. There is a direct correlation between these elements and the amount of nickel.
High concentrations of radioactive elements such as Th (up to 32 ppm) and U (up to 9 ppm) are established in the native iron, with their amounts in the rock not exceeding 1-2 ppm.

Table 3. Trace elements in native iron, ppm

| Ni  | Co  | Cu  | Au  | Pt  | Pd  | Rh  | Ru  | W   | Mo  | As  | Sn  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 489 | 240 | 1449| 0.14| 0.083| 0.047| 0.006| 0.100| 7.94| 4.24| 13.8| 11  |
| Basit| 160 | 45  | 100 | 0.004| 0.009| 0.019| 0.0002| 0.0002| 1.0 | 1.4 | 2.0 | 1.5 |

4. Conclusions

So, what is the origin of the unique native metallic mineralization? When A. Nordenskiold found the iron boulders on the south-west coast of Disco Island, he first described them as meteorites. However, later, the scientists came to the conclusion about their telluric origin. The fact that metal spherules are found as inclusions in the rock-forming minerals of basites definitely means that the metal drops appeared in the silicate melt at the early magmatic stage. It is assumed that the main condition for the presence of native iron in megascopic quantities in traps is the fractionation of a basaltic melt in the deep-seated intermediate chamber. Two hypotheses have been put forward to explain the origin of the macroscopic native mineralization. Both are based on the view that first, iron accumulations can only form under the influence of fluid and second, native iron is a product of reduction of a silicate melt. But they differ in the notions of the source of the reducing fluid, and the space and time of occurrence of the native phase. Some researchers believe that the reduction of metals in magma occurred under the effect of reducing gases produced in the dissociation of carbonaceous sedimentary rocks [4]. However, intrusions with native mineralization are known from Disko Is., in places where subjacent carbonaceous rocks are lacking. Investigation of numerous basitic objects in contact with carbonaceous and bituminous matter showed absence of any evidence in favor of iron reduction to null-valent state in the liquid.

Other investigators and authors of this paper with colleagues [5] explain the origin of native iron in basites of ancient platforms as a result of the interaction of a basaltic melt with a reducing transmagmatic fluid in a deep-seated intermediate chamber. In this situation, the initially homogeneous basaltic liquid decomposes into liqueats of silicate and metal composition. The fluid had largely a hydrogen-methane composition. The fluid played also a substantial part as a supplier of many metals, among them noble ones, which accumulated in native iron segregations. Studies of the gaseous phase of native iron (Djaltul intrusion) show that it consists of a mixture of gases with dominating hydrogen (>75%) and subordinate amounts of CH₄, Na₂+CO and CO₂.

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