IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

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To cite this article: A A Kompanchenko and Yu N Neradovsky 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **302** 012045

Vanadium in the Arctic zone of Russia on the Kola region example: prevalence, sources, industrial potential

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Abstract. This article gives a brief overview of the prevalence, sources and industrial potential of vanadium in the Arctic zone of Russia on the Kola region example. Within the Kola region many solid minerals is mining: apatite-nepheline ores of the Khibiny, rare earth elements ore of Lovozero, baddeleyite-apatite-magnetite ores of the Kovdor, ferruginous quartzites of Olenegorsk, copper-nickel deposits of Pechenga etc. In the region potential deposits of platinum group elements, chromium, titanium, lithium and beryllium are explored. Recent studies conducted by the workers of the KSC RAS, in combination with geological and exploration data of predecessors, indicate that within the Kola region there are large sources of vanadium. Numerous occurrences of vanadium mineralization, as well as deposits of vanadium, are mainly localized within the entire Paleoproterozoic Pechenga-Imandra-Varzuga (PIV) rift belt, which stretches for more than 500 km across the entire Kola Peninsula - from the throat of the White sea in the North-East to the Norwegian Caledonian in the North-West. The time of the belt development is considered to be at the period 2.5-1.7 Ga. Elevated concentrations of vanadium is installed in metasomatites at the contact of volcanics and dolomite in Prikhibin'e, in sedimentary rocks of the North Pechenga area and throughout the black-shale strata of the entire PIV zone. Mineralization, composed by extremely rare vanadium minerals, established in massive sulfide ores of the PIV belt, however, has only scientific interest. Potential sources of industrial extraction of vanadium are complex Fe-Ti-V ores, which are components of mafic/ultramafic layered intrusions. The study of Fe-Ti-V ores of the region continues.

1. Introduction

The Arctic zone of Russia is known primarily for the largest natural gas deposits. On the Kola region territory, which is the north-western sector of the Russian Arctic, deposits of solid minerals are discovered and developed: apatite-nepheline ores of Khibiny, ores of rare earth elements (Ta, Nb, etc.) of Lovozero, baddeleyite-apatite-magnetite ores of Kovdor, ferrous quartzites of Olenegorsk, copper-nickel deposits of Pechenga, etc. Potential deposits of platinum group elements, chromium, titanium, lithium and beryllium are explored in the region [1-3]. However, our studies in recent years, in conjunction with geological and prospecting data of predecessors, indicate that the Kola region can also be a source of such a valuable element as vanadium.

Vanadium is an extremely important element that is used in a wide variety of industries. Together with scandium, titanium, chromium, manganese, iron, cobalt and nickel vanadium belongs to the so-called transition elements isolated in a separate family of iron. Chemically, trivalent vanadium is closest to trivalent chromium and iron [4]. Minerals of endogenous origin contain, as a rule, V^{3+}, and minerals of exogenous - V^{4+} and V^{5+} [4, 5]. On prevalence in the earth's crust, vanadium belongs to the IV decade by V. I. Vernadsky, i.e. to the group of such elements, which are contained in earth's crust in amounts from 10^{-2} to 10^{-1} % and have a total weight of 10^3 to 10^6 t. Vanadium clark in the earth's crust was determined by Clark and Washington as 0.016%, and by A. E. Fersman as 0.018-0.020%. The average content of vanadium in lithosphere, according to A. P. Vinogradov, is 0.015 wt. % and 0.006 at. %. Clark's weight of this element by V. M. Goldschmidt, with Rankam and Sukhama supplements, is also 0.015% [6] or 138 pm [7].

High chemical activity of vanadium, its variable valence and ability to complexation lead to the fact that vanadium is the main or one of the main components of about 150 minerals. Most of them contain groups $(V^{5+}O_4)_3$ - and are classified as natural vanadates. In addition, part of the minerals of vanadium refers to the oxides (about 25), sulphides (about 7), silicates (about 35), sulfate (about 9), arsenate (about 10) and phosphate (about 10). Among the vanadium minerals only a few have commercial value, chief among them is corvusite $V_2O_4*V_2O5*nH_2O$, vanadinite $Pb_5Cl(VO_4)_5$, carnotite $K_2(UO_2)_2(VO4)*2H_2O$, tyuyamunite $Ca(UO_2)_2(VO_4)_2*8H_2O$, deklarite $Pb(Zn,Cu)(VO_4)(OH)$, roscoelite $KV_2(AlSi_3O_{10})(OH,F)_2$, patronite VS_4, mottramite $Pb(Cu,Zn)(VO_4)(OH)$, and vanadium-bearing titanomagnetite $(Fe,Ti)Fe_2O_4$ (up to 1.5 % V_2O_3). About 25 vanadium minerals, mainly oxides (karelianite V_2O_3, paramontroseite VO_4, scherbinaite V_2O_5, coulsonite FeV_2O_4, montroseite $(V,Fe)O(OH)$, nolanite $(V,Fe,Fe,Ti)_{10}O_{14}(OH)_2$, etc.) were found under endogenous conditions. However, all of them have limited distribution and are not subject to independent extraction [4].

The content of vanadium in the rock will depend on its mineral composition: the more dark-colored minerals in the rock that easily accumulate vanadium (pyroxenes, spinels, etc.), the more vanadium content. Granites, leucocratic granites particularly, are poor in vanadium. Nepheline syenites and, primarily, their melanocratic varieties, rich in aegirine and magnetite, which is enriched by vanadium, while leucocratic and nepheline-rich urtite, like granites, are characterized by low contents of vanadium. The main rocks - gabbro and hornblendite, as well as pyroxenites of the dialagite type, are the main carriers of vanadium, which is contained in their dark-colored, especially iron-titanium ore minerals. Consequently, the content of vanadium increases from ultrabasic to basic rocks and then gradually decreases to medium and especially acidic igneous rocks [4].

Vanadium is very characteristic for black shale, where its concentration, according to the literature, reaches as much as percent. In this respect, sulfide-carbonaceous shales of the north-west of the Kola Peninsula are moderately enriched in vanadium, surpassing its average concentration of black shales of North America, but yielding the same species of the Outokumpu district, and especially vanadium-bearing shales of Central Asia. Own minerals of vanadium, particularly characteristic for black shales - sulphides of vanadium, we have not yet determined. It is in the scattered state, being closely related to organic matter in Pechenga sulphide-carbon schist, to a lesser extent to graphite in rocks of amphibolite and granulite facies [8, 9].

2. Vanadium mineralization occurrences

The most complete description of vanadium mineralization occurrences in the Kola region are given in [10]. These occurrences are usually confined to the volcanogenic-sedimentary complexes of the South Pechenga (SP) and Prikhibin'e, was formed in the time interval 1.9-1.7 Ga and have undergone by metamorphism not lower then amphibolite facies. Vanadium mineralization that is located in metamorphosed massive sulfide ores and SP, and Prikhibin'e, are presented by rare vanadium minerals: karelianite, coulsonite, nolanite, kyzylkumite, roscoelite, goldmanite, etc. [10, 11]. A significant admixture of vanadium is fixed in rutile, ilmenite, crichtonite group minerals, etc. Feature of vanadium mineralization in massive sulfide ores is its close connection with chromium and scandium, which also occurre themselves in the various mineral forms. However, despite the richness of the mineral forms of vanadium, massive sulfide ores are not interested for vanadium industrial extraction, because the content of V_2O_5 often does not exceed 0.025%, and significantly sulfide composition of ores makes its extraction almost impossible. Vanadium mineralization in the massive sulfide ores of the Kola region is currently has only a great mineralogical value.

In the Dolomite Quarry deposit in Prikhibin'e, in alkiline metasomatites localized on the contact of volcanics and dolomites vanadium and vanadium-bearing minerals are established which represented by pyroxenes of natalyite-aegirine series and magnesioribeckite. The V_2O_5 content in metasomatites is 0,41% which is significant [12]. The industrial potential of this vanadium occurrences has yet to be assessed.

According to A. M. Akhmedov [13], increased concentrations of vanadium are occurred in the North Pechenga zone, in the formations of the third and fourth sedimentary strata. The study of the vanadium migration process showed that 80-95 % of vanadium is sorbed by iron hydroxides, and the remaining small part - by manganese hydroxides and clays. That is why the main carriers of vanadium in the rocks of the third sedimentary strata are ore minerals - hematite and magnetite. The content of vanadium in the hematite of the third strata is in the range of 0.14-0.20% and in the magnetite - 0,08-0,12%. High-iron terrigenous deposits of the third sedimentary strata are characterized by the highest concentrations of vanadium. Ferrous pelite zone of weathering, developed on albitophyre at the base of the third sedimentary strata is enriched by vanadium.

The high content of vanadium accounts for black high-carbon-sulfide shales of the fourth sedimentary strata. With the increase of organic carbon in the shale the content of vanadium increases to. Thus, carbon-sulfide shales of the lower part of the fourth strata at organic carbon values of 0.24-0.28% contain 0.030-0.056% of vanadium. High-carbon shales of the upper part of the fourth strata are distinguished by high vanadium values (0,2-0,36%) [13]. Minerals of vanadium in these formations are not established.

3. Vanadium deposits

Vanadium is a concomitant element in complex Fe-Ti-V ores associated with intrusions of mafic/ultramafic rocks. On the territory of the Murmansk region there are 13 deposits of iron-titanium ores, where vanadium is a passing component [14]. Primarily, these ores are confined to the intrusive rocks and its age is about 2.5 Ga [15]. Vanadium is mainly concentrated in oxide minerals - titanomagnetite and ilmenite, and partially dispersed in rock-forming minerals. Ores are difficult to enrichment, but the effective extraction of vanadium and other elements is solved on the Kolvitsa deposits Fe-Ti-V ores example [16, 17], which refers to the Paleoproterozoic intrusive clinopyroxenite-verlite formation, the content of V_2O_5 is 0.2% [18, 19].

A large Deposit of titanium-magnetite ores with a high vanadium content (up to 1% V_2O_5) is known within the PIV rift, dedicated to the Imandra lopolite, which is now being actively studied to determine its prospects and for technological tests.

4. Source of vanadium

Paleoproterozoic formations localized in the PIV riftogenic belt are characterized by almost universal high content of vanadium. According to geochronological data, it can be assumed that the initial source of vanadium is deep mantle, and as the intrusion cooled down and crystallized, vanadium in a trivalent form was distributed among the minerals. The formation of complex Fe-Ti-V ores in the composition of the layered intrusions were dated by the period of 2.5-2.4 Ga, at the boundary of Neoarchean and Paleoproterozoic [15]. The re-activation of the rift zones development began in 2.1-1.95 Ga ago. The PIV rift was completely or partially transformed into a relatively narrow oceanic structure as the Red sea type, and about 1.9 Ga ago the ocean was closed [20]. At this time, apparently, there was an intensive destruction of already formed rocks, including Fe-Ti-V ores and part of the material got dissolved in the ocean. It is known that the organic material easily absorbs vanadium from sea water [9] and increased content of vanadium in carbonaceous shales is confirmed that. There was also an additional introduction of vanadium, together with scandium and other elements, by hydrothermal solutions, through cracks and fractures that permeate the entire PIV belt [10]. Imposed metamorphism led to the redistribution of many elements, including vanadium, and the formation of occurrences of vanadium mineralization throughout the belt. However, the primary sources of vanadium had a deep character [10].

5. Conclusion

In the Kola region there are numerous occurrences of vanadium in different geological settings. However, only complex Fe-Ti-V ores confined to layered intrusions have industrial potential. These deposits have industrially significant concentrations of vanadium, and, importantly, the ores are amenable to enrichment and processing. Since the demand for vanadium is growing every year, it is likely that the industrial development of Kola Fe-Ti-V ores will begin soon.

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