Rare hydrated magnesium carbonate minerals of the kimberlite pipe Obnazhennaya, The Yakutian Kimberlite Province

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Abstract. The first discovery of hydrated magnesium carbonates, dypingite and nesquehonite, in the kimberlite pipe Obnazhennaya of the Kuoyka field, the Yakutian kimberlite province is described. The pipe is composed of kimberlite breccia with abundant diverse xenoliths of practically intact mantle rocks. Olivine in phenocrysts and mantle rock is generally intact. The main body of the rock is carbonate-serpentine. Nesquehonite and dypingite are rare minerals and have first been observed in relation to kimberlites. The minerals were found in the bedrock outcrop of the Obnazhennaya pipe as white crusts up to 5 mm thick scattered over an area of a few tens of square meters. To identify and study the crusts we used the following methods: powder X-ray diffraction, electron microscopy, and Raman scattering spectroscopy. A comprehensive study suggests that the main minerals of these epigenetic formations are hydrated carbonates: nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and dypingite $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. Also, Raman scattering spectroscopy revealed a small proportion of hydromagnesite $\text{Mg}_3(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Hydrated magnesium carbonate minerals we found make a significant contribution to the collection of kimberlites. They are epigenetic in nature, with their origin being related to weathering of silicates, in particular serpentine. Mechanisms of carbonate formation appear to be close to that suggested by Wilson et. al., 2009, with $\text{CO}_2$ being trapped from the atmosphere to form nesquehonite. In the case of the Obnazhennaya pipe, mineral solutions form when rainwater filters through the talus at the top of the outcrop. They are enriched in Mg from minerals and trap $\text{CO}_2$ from the atmosphere. After filtering, solutions reach the vertical wall of kimberlite breccia where modern precipitation of nesquehonite upon evaporation occurs. Further, dypingite and hydromagnesite form via decomposition of nesquehonite. A lip extending over the rock wall significantly contributes to the development and stability of nesquehonite and dypingite aggregates. Crusts of nesquehonite and dypingite are not found on rock outcrops without lips at the top. Thus, despite the fact that intrusion of the kimberlite pipe occurred during the Jurassic (Zaitsev, Smelov, 2010), formation of nesquehonite and dypingite in association with kimberlite rocks continues in the modern time due to favorable environmental factors, first of all, a unique natural outcrop of kimberlite.

1. Introduction
Carbonates are major minerals of kimberlite pipes. Calcite and dolomite are found in diamonds, xenoliths of mantle rock [1-3, etc.]. Calcite, dolomite, siderite, ankerite, aragonite, pyroaurite, shortite, strontianite, magnesite, hydromagnesite, hantite, etc. that formed at the igneous and post-igneous stages...
of crystallization have been identified in kimberlite proper [4]. At the same time, hypergenic processes of carbonate crystallization are possible well after the development of kimberlite bodies. So, hydrated carbonate coalingite $\text{Mg}_6\text{Fe}_2(\text{CO}_3)(\text{OH})_2\cdot2\text{H}_2\text{O}$ [5] was found in the kimberlite pipe Manchary, the Khompu-May field (Central Yakutia), its origin is related to the transformation of rocks by underground water along tectonic faults. Here, we describe the first discovery of hydrated magnesium carbonates, nesquehonite and dypingite, found on kimberlite outcrops in the Obnazhennaya pipe, the Kuoyka field, the Yakutian kimberlite province (figure 1).

![Figure 1. Kimberlite fields of the North-Eastern Siberian platform: 1 – Malo-Botuobinsk, 2 – Alakit, 3 – Daldyn, 4 – Verkhne-Muna, 5 – Chomurdakh, 6 – Zapadno-Ukukit, 7 – Vostochno-Ukukit, 8 – Ogoner-Yuryakh, 9 – Kuranakh, 10 – Luchakan, 11 – Dyukken, 12 – Ary-Mastakh, 13 – Starorechensk, 14 – Orto-Yargin, 15 – Merchimden, 16 – Molodinsk, 17 – Toluop, 18 – Kuoyka, 19 – Nakyn, – Obnazhennaya pipe](image)

The formation of these minerals results from unique characteristics of the kimberlite pipe that outcrops on the Kuoyka River. The outcrop is 18 m high and about 30 m long (figure 2, a). The top 7 m is a kimberlite slack talus. Rock outcrops with scattered white dense crusts of carbonates are located lower. The area of these sections is as great as a few tens of square meters. Only a small area of 1 m$^2$ under the extended lip shows a crust up to 5 mm thick which is not dense but granular. It is a new fine-grained acicular aggregate that was sampled to identify minerals (figure 2, b). The crust is easily removed from the outcrop along with dark kimberlite fragments containing mica, serpentine, olivine, and calcite. It is an aggregate of grains and crystals of hydrated magnesium carbonates, nesquehonite
and dypingite. Since the minerals are quite rare and this is the first time they were found in association with kimberlite, we decided to study them to clarify their genesis.

![Figure 2. Outcrop of the Obnazhennaya pipe (a) and white crust of hydrated magnesium carbonates nesquehonite and dypingite on kimberlite breccia (b)]](image)

Nesquehonite, a hydrated magnesium carbonate MgCO$_3$$\cdot$3H$_2$O, forming under subsurface conditions was first discovered in the coal mine at Nesquehoning, Pennsylvania, USA [6]. It was also identified on the surface of serpentinites [7]. In Russia, the mineral was first discovered at the Baley gold deposit where, as Pisarskiy described, it forms crusts 2-5 mm thick on rock walls around the heads of horizontal boreholes drilled into mineral groundwater circulating along the tectonic zones [8]. Nesquehonite was diagnosed among minerals of volcanic exhalation in the Kamchatka peninsula [9], new minerals in Chelyabinsk coal dumps [10], and as white crusts in the Titov magnesia-skarn deposit of borate ores [11].

Dypingite, a hydrated magnesium carbonate Mg$_5$(CO$_3$)$_4$(OH)$_2$$\cdot$5H$_2$O, also usually forms under subsurface conditions. It has the same associate minerals as nesquehonite. It occurs on the surface of serpentinites [7]. In Russia, the mineral was found together with nesquehonite in the Kamchatka peninsula and in the Chelyabinsk coal field [9, 10].

Thus, nesquehonite and dypingite are low-temperature epigenetic minerals. Dypingite forms when nesquehonite further transforms into hydromagnesite Mg$_5$(CO$_3$)$_4$(OH)$_2$$\cdot$4H$_2$O, which later transforms into the more stable magnesite MgCO$_3$. These phase transitions in the system Mg-CO$_2$-H$_2$O are dealt with in detail in [12].

2. Methods
Initially, minerals were identified with the X-ray powder diffractometer D2 PHASER (on powder samples with reference to the PDF 2 database). Considering that the crusts under investigation are generally aggregates of at least two minerals, nesquehonite and dypingite, the samples were additionally studied with Raman scattering spectroscopy using the measuring system INTEGRA SPECTRA with the exciting wavelength of solid state neodymium laser 5352 nm, <1 μm output beam power ~3,5 mW. Chemical composition and morphology of grains, crystals, and aggregates were characterized using a scanning electron microscope Jeol JSM-6480LV equipped with a system of energy dispersive
microanalysis INCA Energy 350 Oxford Instruments (20 kV, 1nA, beam diameter 1 μm) and Jeol JSM-7800F.

3. Results

Morphology and chemical composition. To characterize morphology and mineral composition, small segments of carbonate crusts were fixed on adhesive tape or epoxy and sprayed with carbon. Some segments were polished. It was found that nesquehonite EDS spectra (transparent grains) showed no other components but MgO. Dypingite constantly contains about 1 % of SO2 impurities. A great number of voids and cracks in aggregates did not permit us to receive quantitative MgO data for the minerals.

Nesquehonite is found in the samples under investigation mostly as chaotically oriented and closely packed aggregates of prismatic crystals (figure 3, a, b). All nesquehonite grains show cracks parallel to their lineation. The grain size is less than 50 μm, sometimes reaching 100 μm. More rarely parallel prismatic nesquehonite grains form aggregates as translucent reniform crusts. In this case, crusts can be as thick as 0.4 mm (figure 3, c).

Figure 3. SEM image of nesquehonite crystals: prismatic crystals (a, b), fragment of nesquehonite grain aggregate as reniform crusts (c), N - nesquehonite

In the studied samples, dypingite occurs more rarely than nesquehonite. Textural relationships suggest that dypingite develops on nesquehonite (figure 4, a). In this case, dypingite has no formed crystals. However, white aggregates show segments where it forms micro-acicular or rose-like aggregates from scaly crystals up to 30 μm (figure 4, b, c). The crystalloids are less than 1 μm thick and 10 μm long.

Figure 4. SEM image of the polished surface of carbonate crust fragment (a) and dypingite as aggregate of scaly crystals (b, c), Dy-t – dypingite, N – nesquehonite
**X-Ray** Specimens of carbonate crusts with fragments of bulk-rock kimberlite were analyzed in bulk with powder X-ray diffraction. It was found that fragments of kimberlite bulk in contact with the crust are present in the specimen. It explains the presence of common kimberlite minerals in the specimen: serpentine, mica, calcite, olivine with predominant nesquehonite and minor dypingite. Watery-transparent grains and white fine-grained aggregates were picked and analyzed. Practically pure nesquehonite was observed in the specimen of transparent grains (figure 5). Hydromagnesite, lansfordite as well as other magnesium carbonates common in assemblage with nesquehonite were not identified in the specimens using this method.

![Image](image-url)

**Figure 5.** X-ray powder diffraction patterns of white aggregate (a) and transparent crystals (b): Dy – dypingite, N – nesquehonite, x – impurity line

**Raman Spectroscopy.** Samples containing prismatic crystals and white fine-grained replacement aggregates were characterized with Raman spectroscopy. Raman spectra were obtained at three different spots of the samples. The spectrum of transparent prismatic crystals is characterized by bands 705, 1117-1124, 1469 cm\(^{-1}\) corresponding to nesquehonite (figure 6, Spectrum 1). In the Raman spectrum at the boundary with nesquehonite, hydromagnesite was present (725, 1124 cm\(^{-1}\)) (figure 6, Spectrum 2). In the spectrum of fine-grained aggregates, zones of dypingite (950-1099 cm\(^{-1}\)) and hydromagnesite (figure 6, Spectrum 3) are present at interfaces. Hydromagnesite is determined by weak stretch bands at the interface between nesquehonite and dypingite and by more intensive ones in the aggregates with dypingite.
Figure 6. Raman spectra at different spots in the sample: 1 – spectrum of transparent prismatic nesquehonite crystals, 2 – spectrum at the boundary with nesquehonite, 3 – spectrum of fine-grained aggregates, HM – hydromagnesite, Dy-t – dypingite, N – nesquehonite

4. Conclusions
Hydrated carbonates nesquehonite and dypingite found on the outcrops of kimberlite breccia of the Obnazhennaya pipe form through silicate weathering similarly to magnesium carbonate minerals of the chrysotile mine tailings - nesquehonite, dypingite, hydromagnesite, and lansfordite MgCO$_3$·5H$_2$O - at Clinton Creek, Yukon Territory [7]. The mechanism of formation of the studied hydrated carbonate minerals through trapping and storing CO$_2$ appears to be similar to that suggested in [7]. In the case of the Obnazhennaya pipe, solutions result from rainwater filtering through the talus at the top of the outcrop. They are enriched in Mg containing minerals and trap CO$_2$ from the atmosphere. Filtered solutions arrive on the vertical surface of kimberlite breccia where modern precipitation of nesquehonite upon evaporation occurs. Later, when it decomposes, releasing water, dypingite and hydromagnesite form. A lip extending over the rock wall plays an important role in creating favorable conditions for nesquehonite and dypingite aggregates to form and stay stable. The outcrops without lips at their top do not show crusts of nesquehonite and dypingite. Thus, although the kimberlite pipe intruded during the Jurassic [13], the formation of nesquehonite and dypingite in association with kimberlite rocks continues in the modern time due to favorable environmental factors, first of all, a unique natural outcrop of kimberlite.

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