

Graphite mineralization in the Oshirabetsu Gabbroic Complex (Hokkaido, Japan)

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INTRODUCTION

The mantle is the largest reservoir of carbon on earth (Coltice et al., 2004). Mantle-derived carbonate and carbon-bearing rocks are direct indicators of the Earth's solid carbon cycle. The mantle provides CO₂ to the surface through degassing and magmatism whereas carbon from sediments (as carbonaceous matter) and altered oceanic crust (mostly as calcite veinlets) can be recycled into the mantle through subduction. The competition between degassing and incorporation of carbon into the mantle by subduction is the basis of the geodynamic carbon cycle. This idealized cycle can be disrupted as a consequence of the incorporation of crustal carbon to magmas rising from the mantle to upper crustal levels. Thus, carbon can be assimilated by mantle-derived magmas and, in some instances, re-deposited as solid carbon, i.e. graphite.

The aim of this paper is to present preliminary data of a graphite-sulfide occurrence in mantle-derived rocks from Oshirabetsu (Hokkaido, Japan). The association of graphite with sulfides is investigated in order to establish the mutual relationships between the origin of sulfur and carbon and also between the deposition of sulfides and that of graphite.

GEOLOGICAL SETTING

The graphite-sulfide mineralization studied in this paper is located within the Oshirabetsu Gabbroic Complex (OGC), a basic-intermediate intrusive complex in the Hidaka Metamorphic Belt (HMB). The HMB is a tilted island-arc assembly of crustal layers developed during Paleogene to Neogene times.

The HMB comprises the Nakanogawa Group (considered as an accretionary complex made from coherent, turbidite and mélangé facies; Nanayama, 1992) to the west, and the Hidaka metamorphic rocks to the east (Fig. 1). Metamorphic conditions reached amphibolite and granulite facies, and within these metamorphic rocks there is a large amount of associated gabbroic and granitic intrusions.

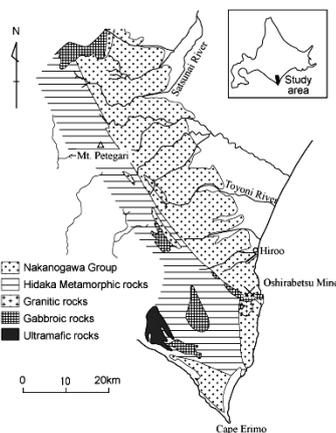


fig 1. Simplified geological map of the Hidaka Metamorphic Belt

The OGC is mainly composed of olivine gabbro, troctolite, coarse-grained gabbro, norite and diorite (Fig. 2). The chemical composition of these rocks (except the cumulus olivine gabbro) shows calc-alkaline affinity.

Graphite, pentlandite and nickel-bearing pyrrhotite mineralization was found in the OGC. The Oshirabetsu mine operated until 1958 as nickel and graphite deposit. The deposit was studied at the two main outcrops remaining after mine works: Taisho and Nisho adits (Fig. 2).

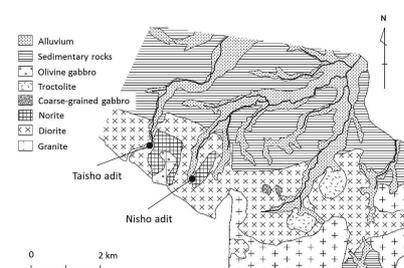


fig 2. Geological map of the study area and location of sampling points

The best exposures are found at Taisho adit, where a more or less tabular ore body occurs. It is oriented N150°, coincident with one of the main directions of the fault system in the area. Thus, the mineralized body appears to be structurally controlled and show sharp contacts with the wall rocks. The thickness of the graphite ore body is some 30 cm (Fig. 3). Graphite mainly occurs as nodules (from 1-2 millimetres to 2-3 centimetres in diameter) and irregular patches embedded in a greenish white host-rock (Fig. 4). Locally, graphite nodules and patches form massive concentrations with very scarce host-rock. The host rock may be stained by the oxidation of sulphides associated with graphite.



fig 3. Detail of the graphite ore body at Taisho adit



fig 4. Hand sample of nodular graphite in diorite

PETROGRAPHY AND MINERAL CHEMISTRY OF THE HOST-ROCK

The host-rock to graphite can be classified as a diorite to quartz-diorite. Primary minerals include plagioclase, amphibole, pyroxene, quartz, and minor amounts of biotite, K-feldspar, and ilmenite. Secondary minerals include muscovite and chlorite.

Plagioclase occurs as euhedral to subeuhedral grains, 100 to 400 μm long, often showing compositional zoning. Rims are more sodic (An_{30} in average) than the inner part of the crystals (An_{45} in average).

Amphibole grains, from anhedral to subeuhedral, show greenish colours. EMPA analyses reveal that the inner part of the crystals is usually richer in Mg and Fe relative to Ca, whereas the outer part of the crystals are richer in Ca.

Pyroxene is scarce and it is commonly replaced by amphibole. Euhedral to subeuhedral basal sections can be readily distinguished. Its composition is intermediate between those of the diopside-hedenbergite series.

Quartz is scarce occurring as interstitial crystals and as graphic intergrowths with plagioclase. Biotite is found as platy crystals, usually partially transformed into chlorite and/or muscovite.

GRAPHITE CHARACTERIZATION

Graphite occurs as rounded nodules containing abundant inclusions. These inclusions may form rings inside the nodules or be unevenly distributed. Frequently graphite nucleates on these inclusions. Graphite is commonly associated with sulphides, mainly pyrite and chalcopyrite. Locally, the nucleation of graphite on these sulphides can be recognized. During the optical microscopy and EMPA studies, other minerals on which graphite nucleates inside the nodules were observed,

including titanite, ilmenite, apatite, zoisite and chlorite.

The most abundant morphology of graphite crystals is platy, although spherulite-like forms can be also recognized. Flaky graphite (some 100 μm long in average) is often bent resulting in ring-like forms (Fig. 5).

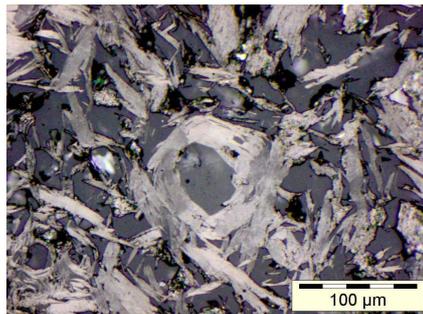


fig 5. Reflected light micrograph of graphite crystals

Locally, graphite nodules are surrounded by hydrous minerals (e. g., chlorite) that can be also included within the nodules.

The structural characterization of graphite has been carried out by XRD and Raman spectroscopy. The results indicate that graphite is highly crystalline, both along the stacking direction and the basal plane. The DTA and TG curves of the graphite are in good agreement with this high crystallinity. The maximum of the exothermic peak due to graphite combustion is close to 830 $^{\circ}\text{C}$.

The $\delta^{13}\text{C}$ values of graphite from Oshirabetsu samples are very uniform and show low $^{13}\text{C}/^{12}\text{C}$ ratios ($\delta^{13}\text{C}$ values from -21.6 to -22.3‰). Samples from different points (some millimetres away one from each other) within the same graphite nodule yield virtually the same $\delta^{13}\text{C}$ values.

DISCUSSION

Graphite occurrences in ultrabasic and basic, mantle-derived rocks are rather unusual and scarce information exists about the mantle or crustal origin of carbon in these rocks in which graphite is commonly associated with sulphides (e.g., Luque et al., 1992; Crespo et al., 2006; Tomkins et al., 2012).

The light $\delta^{13}\text{C}$ values of graphite from Oshirabetsu point to the organic derivation of carbon, as previously stated by Tsuchiya et al. (1991). This is in good agreement with the sulfur

isotopic systematics in the norites of the OGB which indicates that at least half of the sulfur was of sedimentary origin (Takahashi and Sasaki, 1983).

Thus, the assimilation of carbonaceous metasediments seems to have played a significant role in the segregation of an immiscible carbon-rich sulfide magma in the OGC from which graphite and sulfides crystallized. Recently, Tomkins et al. (2012) have suggested that oxidized mafic magmas in which sulfur is dissolved as sulfate can reach sulfur saturation by reduction of their oxidation state. The incorporation of reductant components, as for example graphite, into the magma can decrease its oxygen fugacity and consequently its capacity for dissolving sulfur, thus promoting the segregation of the sulfur content initially dissolved into the magma.

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REFERENCES

- Coltice, N., Simon, L., and Lecuyer, C. (2004): Carbon isotope cycle and mantle structure. *Geophys. Res. Lett.*, **31**, L05603.
- Crespo, E., Luque, F.J., Rodas, M., Wada, H., and Gervilla, F. (2006): Graphite-sulfide deposits in Ronda and Beni Bousera peridotites (Spain and Morocco) and the origin of carbon in mantle-derived rocks. *Gondwana Res.*, **9**, 279-290.
- Luque, F.J., Rodas, M., and Galán, E. (1992): Graphite vein mineralization in the ultramafic rocks of southern Spain: Mineralogy and genetic relationships. *Min. Deposita*, **27**, 226-233.
- Nanayama, F. (1992): Stratigraphy and facies of the Paleocene Nakanogawa Group in the southern part of central Hokkaido, Japan. *J. Geol. Soc. Japan*, **98**, 1041-1059.
- Takahashi, T., and Sasaki, A. (1983): Isotopic composition of sulfur in the Oshirabetsu gabbroic complex and the associated nickeliferous pyrrhotite ore - Magmatic sulfide mineralization and the external source of sulfur. *Mining Geol.*, **33**, 399-409.
- Tomkins, A.G., Rebryna, K.C., Weinberg, R.F., and Schaefer, B.F. (2012): Magmatic sulfide formation by reduction of oxidized arc basalt. *J. Petrol.*, **53**, 1537-1567.
- Tsuchiya, N., Suzuki, S., and Chida, T. (1991): Origin of graphite in the Oshirabetsu gabbroic body, Hokkaido, Japan. *Jour. Min. Petrol. Econ. Geol.*, **86**, 264-272.