Vietnam Academy of Science and Technology

 Vietnam Journal of Earth Sciences

 http://www.vjs.ac.vn/index.php/jse

Vietnam Journal of Earth Sciences, 39(4), 324-336, DOI: 10.15625/0866-7187/39/4/10728

Mineralogical characteristics of graphite ore from Bao Ha deposit, Lao Cai Province and proposing a wise use

Hoang Thi Minh Thao*1, Tran Thi Hien2, Dao Duy Anh2, Pham Thi Nga1

¹VNU University of Science, Vietnam National University, Hanoi, 334 Nguyen Trai Road, Thanh Xuan District, Hanoi, Vietnam

²National Institute of Mining, Metallurgy Science and Technology, 79, An Trach street, Dong Da District, Hanoi, Vietnam

Received 30 June 2017. Accepted 07 August 2017

ABSTRACT

Graphite, especially, high quality graphite can be used in many industrial applications including metallurgy, batteries, fuel cells, and refractories. In 2011, Vietnam Ministry of Natural Resources and Environment issued a mineral exploration license to explore Bao Ha graphite deposit, Bao Yen district, Lao Cai Province. The studied samples were taken from 3 drill holes of the Bao Ha largest ore body. Different methods including light microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and carbon and sulfur analyzer were performed to identify its lithological and mineralogical characteristics as well as graphite quality, then propose a wise use of the resource. The Bao Ha graphite is characterized as disseminated flake graphite in massive form, which developed in the sillimanite schist and quartz-biotite schist of the Ngoi Chi formation. Graphite flakes occur as distorted clusters of flaky plates/flakes within $50\div500 \mu m$, which is the medium size in comparison with the general grain size of graphite flake. Graphite particle makes up $33\div43\%$ by volume and graphitic content (Cg) makes up $10.0\div11.7 \text{ wt.}\%$. Impurities include mainly quartz, biotite, and feldspar (combining of K-feldspar and anorthite, the primary ore) or kaolinite (the weathered ore). This graphite ore should be refined to reach an ore concentration of at least 90% Cg for domestic industries of metallurgy, batteries, thermal materials, and refractories as well as for exports.

Keywords: Bao Ha graphite deposit, flake graphite, graphitic content, mineral composition.

©2017 Vietnam Academy of Science and Technology

1. Introduction

Graphite (black lead or plumbago) is used in many industrial applications due to its high electrical and thermal conductivity, lubricity, and chemical inertness. High-quality graphite can be used in metallurgy, molding, brake linings, batteries, and fuel cells. Graphite, composed exclusively of Carbon element, is a common mineral, but their idiomorphic crystals are rare. Graphite is soft (hardness 0.5-1 of the Mohs scale), layered, planar structure. The mineral occurs in platy or acicular (occasionally) morphology (Pierson, 1993).

Natural graphite deposits of economic interest are grouped into three main categories: (i) microcrystalline graphite (commercially, referred to amorphous graphite); (ii) vein graphite (lump and chip); and (iii) crystalline

^{*}Corresponding author, Email: hoangminhthao@vnu.edu.vn

flake graphite (plumbago) (Asbury Carbons, 2015; Pierson, 1993; U.S Geological Survey, 2007). Microcrystalline graphite is the most abundant form but occurs at the lowest in grades. This type of graphite is used for lower value graphite products, such as pencils, brake pads, and rubber additives. Large microcrystalline graphite deposits are found in China, Mexico, and United States (Plumbago Co., 2013; Pierson, 1993; U.S Geological Survey, 2007). Vein graphite is the epigenetic origin, formed by direct deposition of solid, graphitic carbon from subterranean, high-temperature fluids. This type is the most valuable and of the highest quality, but also the rarest source. Up to date, Sri Lanka is the only country that produces vein graphite.

Flake graphite is less common but more favorable than microcrystalline graphite because of its higher quality. Flake graphite is used in many applications including, but not limited to, powder metallurgy, fuel cell bipolar plates, coatings, thermal materials, friction moderators, electrically conductive materials, refractories (bricks which line furnaces in the steel industry), general lubricant applications, pencils, gaskets, rubber compounds, and other advanced polymer systems. China, Brazil, and Canada are the largest producers of flake graphite (Asbury Carbons, 2015; Pierson, 1993; Plumbago Co., 2013; U.S Geological Survey, 2007). Flake graphite deposit fall in the category of syngenetic origin, formed through the metamorphic evolution of carbonaceous matter dispersed in the sediments (Mitchell, 1993; Rodas et al., 2000). Simandl and his team (Simandl et al. 1995, 2015) also concluded that disseminated graphite flakes are in a variety of rocks including marble, paragneiss (a meta sedimentary gneiss), iron formation, quartzite, pegmatite, syenite, and, in extremely rare cases, serpentinized ultramafic rocks.

The importance of graphite has been emphasized by the EU. In 2010, the European Commission created a list of 41 different Critical Raw Materials (CRMs) for the European economy, in which graphite was named in the first 14 materials ranked at a high level in both economic importance and supply risk (European Commission, 2010). According to Persistence Market Research (2015), the global graphite market was valued at US\$13.6 billion in 2013 and is estimated to reach US\$17.5 billion by 2020, growing at a compound annual growth rate of 3.70% from 2014 to 2020. Worldwide consumption of graphite steadily increased since 2012 and into 2016. This increase resulted from the improvement of global economic conditions and its impact on industries that use graphite (U.S. Geological Survey, 2017). Graphite industry is dominated by large manufacturers located mainly in China, India, Brazil, and some other countries. China, the world's leading producer of natural graphite, now focuses on serving their own domestic needs as well as pushes to manufacturer higher value goods. Since 2010, the price of high-quality flake grades of natural graphite has increased by 140% as a result of Chinese policy and struggling production elsewhere (Industrial Minerals, 2012). Graphite produced in India and Brazil is also mainly consumed within the domestic markets, with demand pouring in from refractories, foundries, lubricants, pencils, and other relevant applications. Facing to this situation, countries including Vietnam, which own some graphite resource, need to have policies for finding raw materials, developing processing technologies, and using it sustainably.

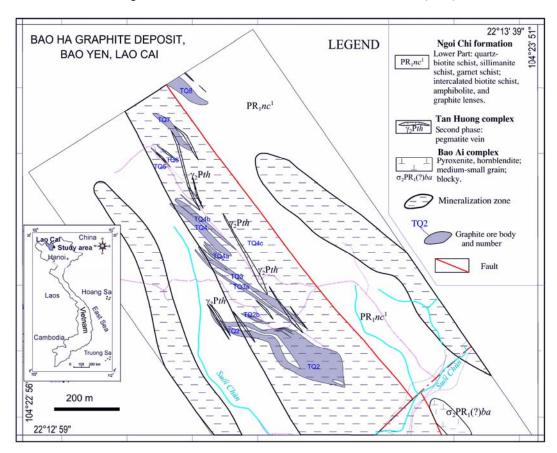
The small reserves and inferred resources of graphite in Vietnam, calculated for the 10 assessed and explored deposits and mines, concentrated mainly in the northwest region, are 16.56 and 5.833 million tons, respectively (Tran Van Tri and Vu Khuc, 2001). The Vietnamese graphite resources were formed with 2 origins: (1) sedimentary-metamorphic origin distributed in the Red River metamorphic zone and Quang Nam, Quang Ngai Provinces; the typical one is Nam Thi mine (Lao Cai Province) including 3 areas, namely Nam Thi, Nam Cay and Lang Oi; (2) metasomatic origin - distributed in Tuyen Quang, Thai Nguyen, Thanh Hoa and Quang Nam Provinces. Vietnamese graphite products have reached just medium grade, from 80÷85% graphitic carbon (Cg) and the small amount of ~92% Cg (Tran Thi Hien et al., 2008). In order to find high-grade graphite for domestic industries of metallurgy, batteries, thermal materials, and refractories, we have imported graphite.

Bao Ha graphite deposit is situated within the Red River metamorphic zone, which consists of also the well-known Nam Thi graphite mine. The Ministry of Natural Resources and Environment (Vietnam) issued a mineral exploration license No. 1095/GP-BTNMT dated on 07/6/2011 for Song Da Lao Cai Mining Joint Stock Company to explore the Bao Ha graphite deposit. The Bao Ha graphite must be used wisely and sustainably. Therefore, an understanding of lithological and mineral characteristics is necessary and useful for developing a suitable and specific mineral processing flowsheet for the Bao Ha graphite. Further, detail investigation on graphite crystals can help to evaluate the quality of the Bao Ha graphite product and propose a wise use this resource.

2. Geology of Bao Ha graphite deposit

The Bao Ha graphite deposit is located in Bao Ha commune, Bao Yen district, Lao Cai Province. The deposit belongs to the middle part of the Red River tectonic structure, which characterized by paleo-metamorphic formations lying between the Red River and the Chay River faults and extending from the Vietnam-Chinese border to the Bac Bo Plain. The deposit includes 11 graphite ore bodies, whereas 6 bodies present higher grade than the others (Bien Xuan Thanh, 2014; Luu Huu Hung, 2001) (Figure 1). The ore bodies extended in the northwest-southeast and plunged into monocline dipping to the northeast with dip angle varying from 30-60°. Some bodies have been deformed and pulverized, so that their structure is discontinued and complicated. Almost of the ore bodies has been exposed to the surface and partly weathered.

All of the 11 ore bodies are located in the lower part of Ngoi Chi formation $(PR_1 nc_1)$ (Pham Van Long et al., 2004; Garnier et al., 2008; Tran Xuyen, 1988) (Figure 1). The formation was observed comprising of sillimanite schist (± biotite, garnet), quartz-biotite schist (± sillimanite, garnet), garnet schist (± biotite), biotite gneiss lens, and small amphibolite vein. The two first ones hold graphite mineralization. Geological characteristics of the deposit also include pyroxenite and hornblendite of the second phase of the Bao Ai complex ($\sigma_2 PR_1 ba$?) (Hoang Thai Son et al., 2000) as well as pegmatite veins of the second phase of the Tan Huong complex ($\gamma_2 P th$) (Hoang Thai Son, 1997). Besides, the Bao Ha area was formed by also high-grade metamorphism rocks of Nui Con Voi formation (PR1 cv) (Nguyen Vinh & Phan Truong Thi, 1973) and undivided Quaternary sediment. The Nui Con Voi Complex part 2 occurs with paragneiss rich in plagioclase, biotite, sillimanite, and almandine containing many amphibolite lenses. The formation was observed with some ore bodies which contain low-grade graphite.



Hoang Minh Thao, et al./Vietnam Journal of Earth Sciences 39 (2017)

Figure 1. Geological map of Bao Ha graphite Deposit (adopted from Bien Xuan Thanh, 2014)

3. Material and Methods

3.1. Material

Twenty tons of ores were collected from 3 drill holes 110, 111, and 112 of the ore body TQ.2, the largest ore body of the Bao Ha graphite deposit. The ores were divided into primary ores and weathered ores. The representative samples were named: G-LK 110, G-LK 111, G-LK 112 for primary ores of the drill holes 110, 111, 112, respectively; and G-PH 110, G-PH 111, G-PH 112 for weathered ores of the drill holes 110, 111, 112, respectively. The grinded mixtures of primary ore (BH-GC01), weathered ore (BH-PHC02), and the whole ore (BH-C0) were also studied. Graphite

ore concentrations (BH-QTC1 for -35+100 mesh and BH-QTC2 for -100 mesh), which were treated with one froth flotation cycle at National Institute of Mining - Metallurgy Science and Technology, Vietnam (VIMLUKI), were subjected to investigate in details the single particles of graphite.

3.2. Methods

3.2.1. Light microscopy

The hand samples of graphite-bearing rocks were made into thin sections, measuring roughly 30 microns in thickness. The slides were studied under a Leica DM750P light microscope with an integrated camera and a 10× objective lens (at VNU University of Science)

to obtain mineralogical and petrographic details of ore-bearing formation.

3.2.2. X-ray diffraction (XRD)

The mineralogical composition of randomly oriented powdered samples with <40 μ m size fraction of the Bao Ha ore was investigated using a Siemens D5005 X-ray diffractometer (Cu tube, K $\alpha_{1,2}$ radiation, 40 kV, 30 mA) at VNU University of Science. The XRD data were processed using BGMN Rietveld software (Bergmann et al., 1998; Kleeberg et al., 2005; Ufer et al., 2008).

3.2.3. Scanning electron microscopy (SEM)

Mineral analyses were carried out at the Department of Mineralogy and Petrology, Institute of Earth Sciences, University of Graz using a JEOL JSM-6310 scanning electron microscope (SEM) equipped with a Link ISIS (Oxford) energy dispersive X-ray (EDX) spectrometer. Analytical conditions were an acceleration voltage of 15 kV and a probe current of 6 nA. Detection limit is 0.10 wt.%. The grinded or powder ore samples were mixed with Canada balsam to prepare thin plate for the technique.

3.2.4. Carbon and sulfur analyzer

Carbon and sulfur contents of the Bao Ha raw ores were analyzed by a Horiba EMIA-320V2 carbon & sulfur analyzer at National Institute of Mining - Metallurgy Science and Technology, Vietnam.

4. Lithological and mineral characteristics of Bao Ha graphite deposit

In regard to the host rocks and deposit types, the classification scheme most widely accepted for graphite deposits was introduced by Cameron (1960). It classifies known graphite deposits into five categories reflecting the different types of graphite: (i) Disseminated flake graphite in silica-rich metasediments; (ii) Disseminated flake graphite in marbles; (iii) Metamorphosed coal seams; (iv) Contact metasomatic or hydrothermal deposits in metamorphosed calcareous sediments or marble; and (v) Vein deposits. Based on the geological characteristics of the Bao Ha deposit and surrounding area, it is expected that the study deposit falls into the first type. The Bao Ha graphite was observed as flakes disseminated in schist of the lower part of the Ngoi Chi formation $(PR_1 nc_1)$ as mentioned above. Thin section study (Figure 2-5) also verifies this identification. Under light microscopy, graphite flake can be recognized based on its opaque property. The typical mineral assemblage of the foliated host rock observed is feldspar, quartz, and biotite. Feldspar particles often showed <0.2 mm (Figures. 2, 5), seldom showed ~ 0.5 mm (Figure 3). Some feldspar particles showing clear polysynthetic twinning were identified as plagioclase. Striation and fracture surfaces were usually observed for feldspar. This mineral has been altered into kaolinite, epidote, and zoisite. Quartz presents an amount as high as the amount of feldspar but with smaller particle size. Biotite is also very popular in the samples, presents <0.6 mm (Figure 2-5), sometimes very fine particle. This sheet silicate occurred interlayered with graphite (Figure 5) which may be difficult to remove during froth flotation.

This type of graphite deposit and host rock was described for the well-known Bissett Creek deposit in western Ontario, Canada (Northern Graphite Corporation, 2015). The Bissett Creek graphite flakes are disseminated in silica-rich meta-sediments associated with older rocks, notably those of Precambrian age, which have undergone a high degree of regional metamorphism, forming gneisses, schists, and quartzites. The host rocks of Bissett Creek graphite vary from quartz-mica schists, to quartz-feldspar-biotite gneisses with and without garnet, to semi-pelitic schists.

Hoang Minh Thao, et al./Vietnam Journal of Earth Sciences 39 (2017)

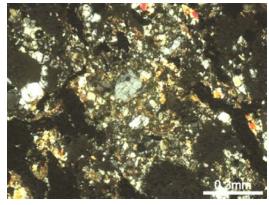
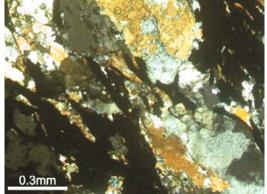


Figure 2. Fine particles of biotite (yellow) and quartz integrated with coarser particle of feldspar; black particles are graphite (sample G-LK 110, Nicol +)



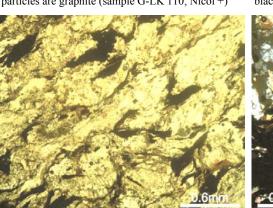


Figure 4. Block of fine grain of quartz, biotite, feldspar contains graphite flake (sample G-LK 111, Nicol -)

Semi-quantity evaluation of the mineral composition of the Bao Ha graphite ore was carried out by XRD study using randomly oriented powder samples, which were represented by the whole collected samples of drill holes 110, 111, and 112 of the ore body TQ.2. The results (Table 1, Figure 6) show that graphite ranges up to 43% by volume. Quartz and biotite make up from 26÷29% and 4÷10% by volume. Total proportions of feldspar comprising both plagioclase and K-feldspar of primary ores are as high as the proportions of **Figure 3.** Assemblage of quartz (dark grey), biotite (yellow), feldspar (light grey) altered to kaolinite and epidote; black particles are graphite (sample G-LK 111, Nicol +)

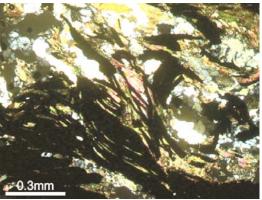


Figure 5. Dissemination of graphite flake(black) in the rock comprising of quartz, biotite, and feldspar (sample G-LK 112, Nicol +)

quartz. However, almost feldspar was altered into kaolinite in the weathered ores. A trace amount of kaolinite and other minerals in the primary samples could not be detected by XRD measurement.

Besides main minerals, some minor and trace minerals including garnet (Grt), pyroxene (Px), sphene or titanite (Ttn), limonite (Lm), pyrite and/or pyrrhotite (Py), chalcopyrite (Cpy), and ilmenite (Ilm) were identified by SEM-EDX study (Figures 7, 8). By this technique, feldspar species were chemically examined as K-feldspar and anorthite (Cafeldspar).

Vietnam Journal of Earth Sciences, 39(4), 324-336

Mineral	G-LK 110	G-LK 111	G-LK 112	G-PH 110	G-PH 111	G-PH 112
Graphite	35	33	37	38	42	43
Quartz	27	29	29	29	28	26
Biotite	10	8	7	6	7	4
Feldspar	28	29	27	0	0	3
Plgioclase+K-Feldspar)	(14+14)	(19+10)	(13+14)	(0+0)	(0+0)	(0+3)
Caolinite	0	0	0	22	23	24
Others	0	1	0	5	0	0
Fotal	100	100	100	100	100	100
10.14 Å Biotite 7.20 Å Kaolinite 4.26 Å Quartz	3.34 A Quartz + 3.35 A Graphite 3.18 À Plagioclase			1.81 Å Quartz	1.5/ A Graphite 1.54 Å Quartz	
						G.PH 11
		1				G.PH 11
			A			G.PH 11
		k	·····			G-LK 11
		-				G-LK 11
	ment Villen				· · · · · · · · · · · · · · · · · · ·	G-LK 11
4 12 20	28	36 °2Θ CuKα	44	52	60	68

 Table 1. Mineral composition of Bao Ha graphite ore, as determined by XRD study, %

Figure 6. XRD patterns of Bao Ha graphite ore samples, °2O CuKa position

In the Bissett Creek graphite deposit, the minor rock-forming minerals and ubiquitous trace minerals reported are quite similar to the Bao Ha graphite deposit: amphibole, clinopyroxene, chlorite, carbonate, garnet, sphene, apatite, zircon, pyrite and pyrrhotite (Northern Graphite Corporation, 2015). Pestpaksha graphite deposit in Russia holds the similar mineral composition: quartz, feldspar, biotite, garnet, pyroxene, amphibole, chlorite, kaolinite, kyanite, pyrrhotite, rutile, and anatase (Volkova et al., 2011). All of the associated minerals need to be removed during ore refining processes. Therefore, mineral processing technology for the Bao Ha graphite can learn from the two mentioned deposits.

In conclusion, Bao Ha graphite deposit is characterized by disseminated flake graphite in mostly quartz-biotite schist of the Ngoi Chi formation. Main minerals of the host rocks include quartz, biotite, and feldspar (K-feldspar and anorthite), which was altered into kaolinite (and traces of epidote and zoisite) in the weathered samples. Minor and trace minerals can be listed with garnet, pyroxene, sphene or titanite, limonite, pyrite and/or pyrrhotite, chalcopyrite, and ilmenite.

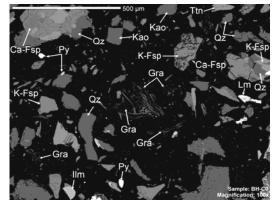


Figure 7. SEM image showing flake graphite (Gra), quartz (Qz), K-feldspar (K-Fsp), anorthite (Ca-Fsp), kaolinite (Kao), sphene (titanite: Ttn), limonite (Lm), ilmenite (Ilm) and pyrite or pyrrhotite (Py)

5. Quality of Bao Ha graphite and proposing a wise use

Type of graphite particle, impurities, and graphitic content are key criteria to evaluate quality of the Bao Ha graphite.

Observing the Bao Ha graphite ore samples with the naked eye and light microscopy identified graphite crystals consisting of distorted clusters of flaky plates/flakes on a matrix. Other type of graphite like large thick hexagonal crystals or rounded ball-like aggregates or radiating spheres could not be found. The Bao Ha graphite which occurs as crystalline flake disseminated within 50÷500 µm (Figure 2-5). Asbury Carbons (2015) reviewed general size for flake graphite as 50÷800 µm whereas Bissett Creek (Northern Graphite Corporation, 2015) was reported that its graphite generally forms flakes averaging 300÷1500 µm long and 30÷70 µm wide. Therefore, the Bao Ha graphite flake falls into the medium level.

Based on lithological and mineralogical results, impurities of the Bao Ha graphite are common minerals of the host rock, particularly quartz, biotite, feldspar, and kaolinite. Mica, a sheet silicate, can be interlayered with graphite. Kaolinite, also a sheet silicate and very fine particle, may coat the graphite. The-

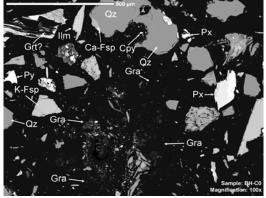


Figure 8. SEM image showing flake graphite (Gra), quartz (Qz), K-feldspar (K-Fsp), anorthite (Ca-Fsp), pyroxene (Px), garnet (Grt), chalcopyrite (Cpy), pyrite or pyrrhotite (Py), and ilmenite (Ilm)

se minerals will complicate graphite processing. With the exception of mica and kaolinite, theoretically, most of the impurities are easily separated because graphite is the easiest to float using froth flotation (Michell, 1993; Northern Graphite Corporation, 2015; Lu and Forsberg, 2001, 2002). However, the growth of these minerals will decide purity of products of graphite processing.

A SEM-EDX mapping analysis (Figure 9) of ungrounded primary ore shows obviously that graphite flake associated intimately with other minerals represented by Si, Al, Fe, Ca, K, and Ti elements, even at small scale (\sim 10 µm). The presences of both K-feldspar and anorthite (Ca-feldspar) were proved with these mapping images, too.

To evaluate the quality of the Bao Ha graphite ore, graphitic content (Cg) was analyzed (Table 2). The weathered ore samples present higher Cg than that of the primary samples. Cg varies within a narrow range of $10.2\div11.7$. The values are suitable with the proportions of graphite by volume yielded from XRD analyses combining with Rietveld refinement (Table 1). The Cg of the Bao Ha ore is a little bit lower than that of the 2 greater (among total 8) ore bodies of the Nam Thi graphite mine with 12.45 % (Tran Van Tri & Vu Khuc, 2001). However, the yielded Cg

Vietnam Journal of Earth Sciences, 39(4), 324-336

values are much higher than those of the Bissett Creek deposit with only 1.65-1.74% (at a 1.02% cut off grade) (Northern Graphite Corporation, 2015).

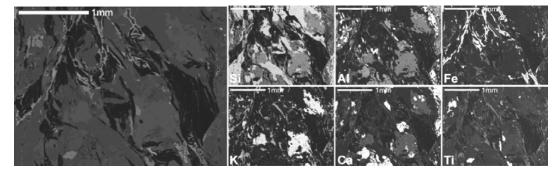


Figure 9. SEM-EDX mapping shows graphite flakes associated intimately with other minerals represented by Si, Al, Fe, K, Ca, and Ti elements

In order to investigate upgrade possibility of Cg and separation performance between graphite and impurities, the Bao Ha ore concentrations treated with one froth flotation cycle were carried out by SEM-EDX. Both coarser particles (-35+100 mesh) and finer particles (-100 mesh) show that graphite seems to be intimately associated with other minerals (Figure 10). One froth flotation cycle could not remove mostly neither free impurity nor integrated impurity. Some more froth flotation cycles and even chemical purification are essential to produce high purity graphite. Lu and Forssberg (2001, 2002) mentioned that, in general, by the process of scrubbing and two-step flotation, a fine graphite concentrate containing 87-88% Cg can be upgraded to about 95% Cg, but further upgrading by flotation is difficult. With such observed intimate association of the Bao Ha graphite and impurities, it seems to be impossible to catch a product with more than 95% Cg without chemical refining.

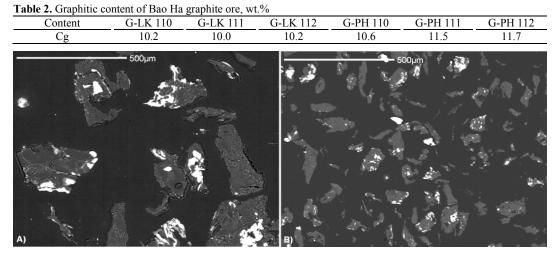


Figure 10. Graphite ore concentration treated with one flotation cycle shows small particles of other minerals associated with graphite. A) -35+100 mesh sample (BH-QTC1), B) -100 mesh sample (BH-QTC2)

The sulfur content in the whole collected raw ore (sample BH-C0) reaches 2.0%, which is unacceptable in many applications such as lubricants and dry cell batteries. Lu and Forssberg (2002) suggested an alkali roasting process, which consists of roasting with caustic soda, water washing, and sulfuric acid leaching, as an effective method for graphite purification which can reduce sulfur content to be low 0.05% in the end product.

Combining all of the criteria, the Bao Ha ore (TQ.2) can be roughly graded as mediumquality flake graphite: medium flake size (positive), the intimate growing of minerals (negative), high Cg (positive), and high sulfur content (negative).

Because flake graphite is more valuable and more favorable than microcrystalline (amorphous) graphite, the Bao Ha graphite ore should be refined to get high-grade graphite for domestic industries or value-added product exports. As mentioned in the introduction chapter, Vietnam has to import highgrade graphite for metallurgy, batteries, thermal materials, and refractories, but Chinese graphite production and exports are likely to decline in the future. Therefore, stable and secure sources of high-quality graphite supply in Vietnam are needed.

For the domestic industries, following TCVN 4688:1989 (Vietnam Standards and Quality Institute, 1989), the best graphite type, marked as Gr-S, with Cg of 95% or more can be used for electrodes and high-end pencil; the second best graphite type, marked as Gr - P, with Cg of 82% or more can be used for batteries. However, high-quality batteries, electrodes, and bricks (for refractories) need refined graphite with much higher Cg (about $95\div99\%$).

In regard to the exports, Circular No. 12/2016/TT-BCT dated 5 July 2016 of the Ministry of Industry and Trade (amending a number of articles of the Circular No. 41/2012/TT-BCT dated 21 December 2012)

on the export of minerals included that refined graphite with Cg of 90% or more is allowed to export until the end of 2020 (Ministry of Industry and Trade, 2006). All types of commercial flake graphite traded in the global market have to have more than 85% Cg (U.S. Geological Survey, 2012; Industrial Minerals, 2011, 2012). Therefore, the Bao Ha refined graphite has to reach at least 90% Cg if an investor wishes to export.

In conclusion, with medium flake size and high Cg, the Bao Ha graphite ore should be refined with a suitable mineral processing flowsheet to reach an ore concentration of at least 90% Cg for domestic industries and exports. Because of the intimate growing of minerals and high sulfur content, processing, and refining technology study as well as cost-benefit study should be performed to understand the possibility of upgrading refined graphite of Bao Ha ore to 95% Cg or more.

6. Conclusions

Graphite of the Bao Ha deposit developed in the silica-rich schist of the Ngoi Chi formation $(PR_1 nc_1)$. Two elements observed comprising sillimanite schist (± biotite, garnet) and quartz-biotite schist (± sillimanite, garnet) present graphite mineralization. Studying the samples taken from the drill holes 110, 111, and 112 of the TQ.2, the largest ore body, shows that the graphite of the TQ.2 seems to be associated with quartzbiotite schist (Figures 2-5). Impurities in the Bao Ha graphite are minerals of the host rock, particularly quartz (26÷29% by volume), bio-(4÷10% by volume), and feldspar tite (27÷29% by volume for the primary ore) (Table 1). The feldspar species were substituted by mostly kaolinite in the weathered samples. Minor and trace minerals identified by SEM-EDX measurements include garnet, pyroxene, sphene (titanite), limonite, pyrite and/or pyrrhotite, chalcopyrite, and ilmenite (Figures 7, 8). SEM-EDX analyses and mapping also prove that feldspar includes K-feldspar and anorthite (Figures 7-9).

Bao Ha graphite ore occurs in massive form. The graphite is characterized as disseminated flake graphite, which occurs as distorted clusters of flaky plates/flakes within 50÷500 µm (Figures 2-5). Graphite flakes associated intimately with the impurities even at very small scale (~10 µm) (Figures 9-11). Based on XRD measurement combining with BGMN Rietveld refinement, graphite crystal makes up 33÷43% by volume, in which the proportions in the weathered samples are higher than those in the primary samples (Table 1). Carbon analysis shows Cg for the Ha graphite ore varying from Bao 10.0÷11.7 wt.%. In comparison with general grain size and graphitic concentration of the flake graphite deposit, it can be roughly concluded that Bao Ha graphite present medium grade. This graphite ore should be refined to reach an ore concentration of at least 90% Cg for domestic industries of metallurgy, batteries, thermal materials, and refractories as well as for exports (if necessary). Upgrading refined graphite of Bao Ha ore to 95% Cg or more is very difficult because of the intimate growing of minerals and high sulfur content. The Bao Ha ore concentrations treated with one froth flotation cycle still show many small particles of impurities in both coarser particles (-35+100 mesh) and finer particles (-100 mesh) (Figure 10), so that some more froth flotation cycles and even chemical purification are essential to produce high purity graphite.

Acknowledgements

This research was supported by the Ministry of Science and Technology, Vietnam under grant number 44/15-DTDL.CN-CNN. We are very grateful to Prof. Christoph A. Hauzenberger, Dr. Le Thi Thu Huong (Graz Geocenter - Petrology & Geochemistry, Karl-Franzens-University Graz, Austria), Dr. Nguyen Thi Minh Thuyet and Dr. Nguyen Van Huong (VNU University of Science) for some analyses and supports. We also thank two anonymous reviewers and the Editor for their evaluation.

References

- Asbury Carbons, 2015. Natural graphite Introduction to natural graphite. http://asbury.com/technicalpresentations-papers/materials-in-depth/naturalgraphite/(Accessed on April 26, 2015).
- Bergmann J., Friedel P., Kleeberg R., 1998. BGMN a new fundamental parameters based Rietveld program for laboratory X-ray sources, its use in quantitative analysis and structure investigations. CPD Newsletter 20, 5-8.
- Bien Xuan Thanh (Editor), 2014. Exploration of graphite deposit in Bao Ha area, Bao Ha community, Bao Yen district, Lao Cai province. Report. Song Da Lao Cai Mining Joint Stock Company.
- Cameron E., 1960. Graphite: Industrial Minerals and Rocks. Seeley W. Mudd Series, AIME (Chapter 20).
- European Commission, 2010. Report lists 14 critical mineral raw materials. http://europa.eu/rapid/pressrelease_MEMO-10-263_en.htm?locale=en. (Accessed on April 26, 2015).
- Garnier V., Giuliani G., Ohnenstetter D., Fallick A.E., Dubessy J., Banks D., Vinh H.Q., Lhomme T., Maluski H., Pêcher A., Bakhsh K.A., Long P.V., Trinh, P.T., Schwarz D., 2008. Marble-hosted ruby deposits from Central and Southeast Asia: Towards a new genetic model. Ore Geology Reviews, 34, 169-191.
- Hoang Thai Son (Editor), 1997. Geological and Mineral Resources Map of Vietnam at 1:50,000 scale, sheets Doan Hung - Yen Binh. General Department of Geology and Minerals of Vietnam.
- Hoang Thai Son, Pham Ngoc Thach, Nguyen The Trung, Chu Hong Phong, Nguyen Ngoc Dung, Pham Xuan Doanh, 2000. Disscussion about metamorphism facies of Song Hong Series. Proceedings. General Department of Geology and Minerals of Vietnam.
- Industrial Minerals, 2011. Supply Situation Report: Graphite demand soars above precrisis levels.

http://www.indmin.com/Print.aspx?ArticleId=27975 90 (Accessed on April 04, 2011).

Industrial Minerals, 2012. The Natural Graphite Report 2012-Data, analysis and forecast for the next five years.

http://www.indmin.com/downloads/reports/graphite 2012.pdf.

- Kleeberg R., Ufer K., Bergmann, 2005. The Quantification of Disordered Clay Minerals by the Rietveld Method - Some Practical Aspects. Presentation at the 42nd Annual Meeting of the Clay Minerals Society, June 11-15, 2005, Burlington/Vermont.
- Lu X. and Forssberg E., 2001. Flotation selectivity and upgrading of Woxna fine graphite concentrate. Mineral Engineering, 14(11), 1541-1543.
- Lu X. and Forssberg E., 2002. Preparation of high-purity and low-sulphur graphite from Woxna fine graphite concentrate by alkali roasting. Minerals Engineering. 15(10), 755-757.
- Luu Huu Hung (Editor), 2001. Evaluation on graphite of Bao Ha area, Bao Yen, Lao Cai. Report. General Department of Geology and Minerals of Vietnam.
- Ministry of Industry and Trade, 2016. Circular amending and supplementing a number of articles of the Minister of Industry and Trade's circular no. 41/2012/TT-BCT of December 21, 2012, providing the export of minerals (July 05, 2016). https://thuvienphapluat.vn/van-ban/Xuat-nhapkhau/Thong-tu-12-2016-TT-BCT-sua-doi-41-2012-TT-BCT-xuat-khau-khoang-san-316914.aspx
- Mitchell C.J., 1993. Industrial Minerals Laboratory Manual - Flake Graphite. Technical Report. British Geological Survey.
- Nguyen Vinh, Phan Truong Thi, 1973. Distribution of contact and dynamic metamorphic rocks in Yen Bai
 Nghia Lo area. Journal of Sciences and Techniques of Mining and Geology (ISSN: 1859-1469), 22, 1-13. Hanoi University of Mining and Geology.
- Northern Graphite Corporation, 2015. Bissett Creek Project. http://northerngraphite.com/bissett-creekproject/ Accessed on April 30, 2015.
- Persistence Market Research, 2015. Global market study on graphite: Battery segment to witness highest growth by 2020.

- http://www.persistencemarketresearch.com/marketresearch/graphite-market.asp.
- Pham Van Long, Hoang Quang Vinh, Garnier V., Giuliani G., Ohnenstetter D., Lhomme T., Schwarz D., Fallick A., Dubessy J., Phan Trong Trinh, 2004. Gem corundum deposits in Vietnam. Journal of Gemmology, 29(3), 129-147.
- Pierson H.O., 1993. Handbook of carbon, graphite, diamond and fullerenes - Properties, Processing and Applications. Noyes Publications.
- Plumbago Co., 2013. What is graphite. http://www.plumbagographite.com/graphitestory/what-is-graphite. (Accessed on April 26, 2015).
- Rodas M., Luque F.J., Barrenechea J.F., Fernández-Caliani J.C., Miras A., Fernández Rodríguez C., 2000. Graphite occurrences in the Low-Pressure/High-Temperature metamorphic belt of the Sierra de Aracena (Southern Iberian Massif). Mineralogical Magazine, 64, 801-814.
- Simandl G.J., Paradis S., Valiquette G., Jacob H.L., 1995. Crystalline graphite deposits, classification and economic potential. Proceedings of 28th Forum on the Geology of Industrial Minerals, Marinsburg, West Virginia, May 3-8, 1992, 168-174.
- Simandl G.J., Paradis S., Akam C., 2015. Graphite deposit types, their origin, and economic significance. In: Simandl G.J. and Neetz M., (Eds.), Symposium on Strategic and Critical Materials Proceedings, November 13-14, 2015, Victoria, British Columbia, British Columbia Ministry of Energy and Mines, British Columbia Geological Survey Paper 2015-3, 163-171.
- Tran Thi Hien, Vu Tan Co, Chu Van Hoan, Vu Van Ha, Bui Van Ngu, Nguyen Duc Minh, Nguyen Bao Linh, Tran Duc Dung, 2008. Study about mineral processing technology for graphite ore from Nam Thi mine - Lao Cai province. Report. National Institute of Mining - Metallurgy Science and Technology, Vietnam.
- Tran Van Tri, Vu Khuc (Editors), 2001. Geology and Earth Resources of Vietnam. General Department of Geology and Minerals of Vietnam. Publishing House for Science and Technology, 645p.

- Tran Xuyen (Editor), 1988. Geological and Mineral Resources Map of Vietnam at 1:200,000 scale, sheets Bac Quang - Ma Quan. Map explanation. General Department of Geology and Minerals of Vietnam.
- U.S Geological Survey, 2007. 2007 Minerals Yearbook -Graphite. U.S Geological Survey, 10.
- U.S Geological Survey, 2012. Mineral commodity summaries 2012. U.S Geological Survey, 68-69.
- U.S Geological Survey, 2017. Mineral commodity summaries 2017. U.S Geological Survey, 74-75.
- Ufer K., Stanjek H., Roth G., Dohrmann R., Kleeberg R., Kaufhold S., 2008. Quantitative phase analysis

of bentonites by the Rietveld method. Clay Mineral 56(2), 272-282.

http://dx.doi.org/10.1346/CCMN.2008.0560210.

- Volkova S.A., Il'icheva O.M., Kuznetsov O.B., 2011. X-ray study of the graphite-bearing rocks from the Pestpaksha ore occurrence and structural features of graphite. Lithology and Mineral Resources, 46(4), 363-368.
- Vietnam Standards and Quality Institute, 1989. TCVN 4688:1989 Graphite concentrate - Marks and technical requirements.