Graphite Deposits: Origin and Economic Significance

George J. Simandl[1, 2], Suzanne Paradis[3], Michaela Neetz[1], and Carlee Akam[1]

[1]British Columbia Geological Survey, Victoria, BC

[2]University of Victoria, School of Earth and Ocean Sciences, Victoria, BC

[3]Geological Survey of Canada, Pacific Division, Sidney, BC

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Executive Summary

Microcrystalline graphite deposits form by maturation of organic material in sedimentary rocks (coal seams) followed by regional or contact metamorphism attaining sub-greenschist to greenschist facies. It is used mainly in greases and forging lubricants and has no known use in high-technology applications.

Economically minable graphite veins are typically hosted by sedimentary successions that have been subjected to granulite facies metamorphism and intruded by minor igneous bodies. Mining of graphite veins similar to those that are mined in Sri Lanka involves underground methods and is labor intensive. Graphite morphology, open-space filling textures, and thermodynamic models indicate that these veins originate by precipitation from C-H-O fluids.

Most exploration projects target crystalline flake deposits. Low concentrations of crystalline flake graphite in marbles and paragneisses probably result from maturation of organic material in precursor sediments, followed by graphitization at pressure and temperature conditions approaching or reaching granulite grade. Graphite-rich zones in disseminated crystalline flake deposits (e.g., Asbury Graphite mine in Quebec, AA deposit in British Columbia) are typically at or near marble-paragneiss contacts and in the crests of folds. These zones are characterized by porphyroblastic textures in marbles, skarn mineralogy at or near the contacts, and decreasing concentrations of scapolite in the paragneiss with increasing distance from the contacts. Sub-granulite facies minerals (e.g., prehnite and clinozoisite) observed in some veins and high-grade portions of disseminated flake graphite deposits suggest post-metamorphic peak (retrograde) temperatures of formation. In these settings, graphite enrichment is likely the result of: a) mixing of fluids produced by decarbonation reactions in marbles and dehydration reactions in paragneiss, or fluids derived from pegmatites and other minor intrusions; or b) cooling of C-H-O fluids.

Forecasted increase in use of natural graphite in high-technology applications turns graphite into a 'hot' commodity; however, fundamental technical and economic parameters of individual deposits have to be taken into consideration when prioritizing exploration and development targets. Enriched zones of crystalline flake graphite deposits are of particular interest to industrialized countries because they are mined by open pit methods (not labour intensive) and provide critical material for high-technology applications. British Columbia has excellent geological potential to host economic deposits.

Introduction

Graphite is an opaque, gray-black, and soft (1-2 on Mohs hardness scale) mineral with a metallic luster. It is characterized by a greasy feel, low density (2.09-2.23 g/cm3), high resistance to thermal shock, and high electrical conductivity (Anthony et al., 2003). Inertness, compressibility, elasticity, and lubricity are other important physical properties (Wissler, 2006). The 2014 world natural graphite production was estimated at 1.17 million tonnes (Fig. 1; Olson, 2015), with most of it originating in China, India, Brazil, Canada, Turkey, and North Korea. Globally, most natural graphite is used in electrodes, refractories, lubricants, foundries, batteries, graphite shapes, recarburising, steelmaking, and friction products such as brake linings (Fig. 2; Shaw, 2013).

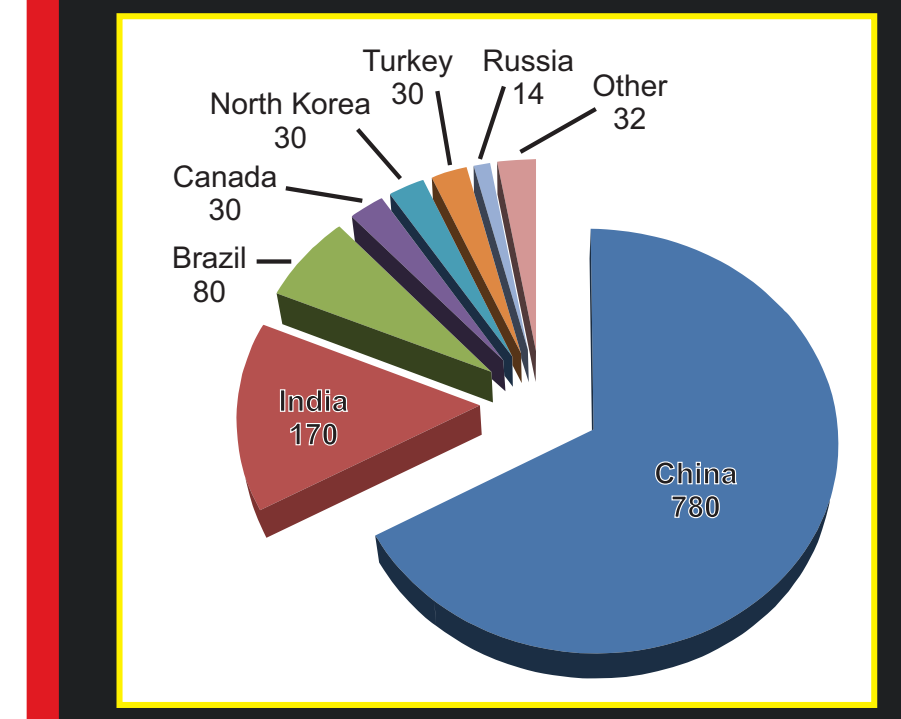


Fig. 1. Global graphite production, in thousands of tonnes, totalling 1.17 million tonnes, for 2014. Based on data from Olson (2015).

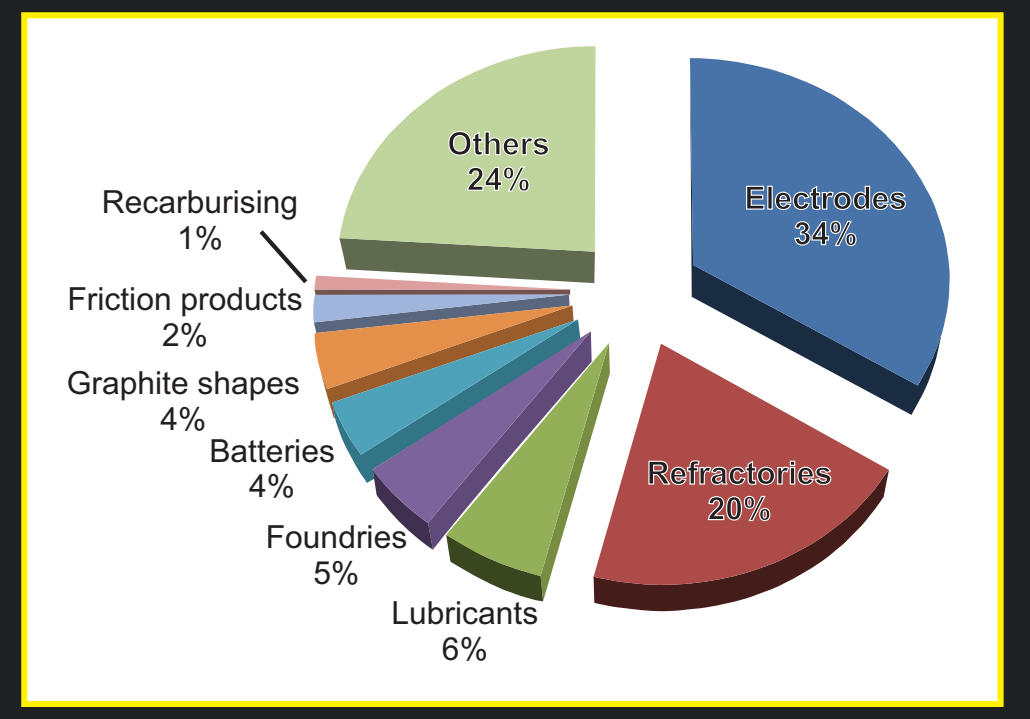


Fig. 2. Main uses of graphite for 2012. Based on data from Shaw (2013).

Natural graphite products currently on the market are grouped into three main categories: 1) microcrystalline (commercially referred to as 'amorphous graphite'; Fig. 3); 2) vein graphite ('lump' and 'chip' graphite; Fig. 4); and 3) crystalline flake graphite (Fig. 5). Prices of selected products are shown in Table 1.

Fig. 3. Microcrystalline graphite.

Fig. 4. Vein graphite, Clot mine, Quebec.

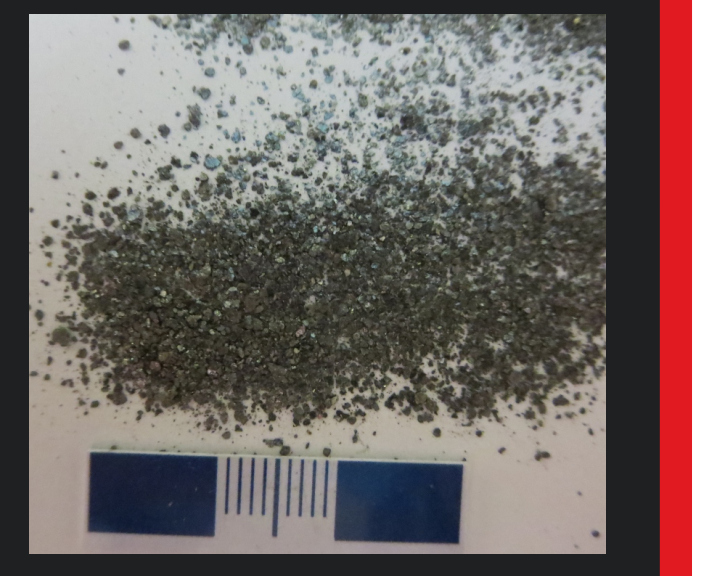


Fig. 5. Crystalline flake graphite, Asbury mine, Quebec.

Table 1. Prices of selected graphite products in US$/tonne. The purity of concentrate and, for some applications, size of crystalline flake are two key parameters. Abbreviations: FOB, free on board; CIF, Cost of Insurance and freight included; FCL, Full Container Load; ex-works, direct from the factory, excluding delivery costs, distribution costs, commission. Sources of data are: [a] Sawlan (2015), [b] Industrial Minerals (2015), and [c] Moores (2015).

Vein (lump and chip)[a]	US$/tonne
99.1% C, +1 mesh (>25.4mm), FOB Sri Lanka	2800
93% C, +60 mesh, FOB Sri Lanka	1550
Amorphous Graphite[b]	
80-85% C, -200 mesh, China, FCL, CIF European port	430-480
Ore, 70-75% C, ex-works Austria	500-550
Flake Graphite[b]	
85-87% C, +100 mesh -80mesh, FCL, CIF European port	700-800
90% C, +100 mesh -80 mesh, FCL, CIF European port	850-950
94-97%C, -100 mesh, FCL, CIF European port	900-950
90% C, +80 mesh, CIF, European port	950-1050
94-97% C, +100 mesh -80 mesh, FCL, CIF European port	1050-1150
94-97% C, +80 mesh, FCL, CIF European port	1200-1300
Spherical graphite[c]	7000-10000
Synthetic Graphite[b]	
97-98%, CIF Asia	950-1450
98-99% CIF Asia	1000-1500
99.95% C, Switzerland	7000-20000

Refractory and high-technology applications make natural and synthetic graphite a critical material in industrialized countries. High-technology uses of graphite represent a portion of the market with fastest forecasted growth.

Examples of high-technology applications are: lithium-ion batteries for electric motor vehicles; large-scale electric energy storage devices; and graphite derivatives such as graphene, spherical graphite, expanded graphite, and graphite foil. Spherical graphite is a product originally developed for use in lithium-ion batteries. It can be either synthetic or derived from crystalline flake graphite concentrate by processing that involves milling, physical rounding, purification, and surface treatment. It takes approximately 100 kg of crystalline flake graphite concentrate (95% C) to produce 30 kg of spherical graphite assaying 99.9% C (Shaw, 2013). This is enough to produce a battery for one electric vehicle. Batteries will account for ~5% of the global market by 2016 (Shaw, 2013). Expanded graphite (Figs. 6-8) is produced by insertion of non-graphite atoms between graphite sheets followed by expansion triggered by rapid temperature increase.

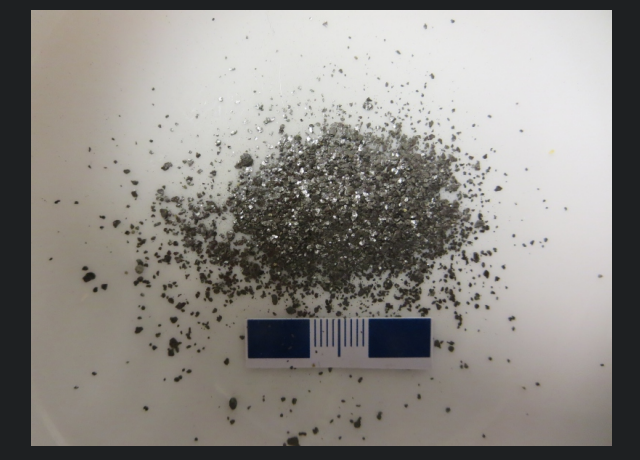


Fig. 6. Chemically-treated (intercalated with acid) crystalline flake graphite concentrate from Asbury mine, Quebec.

Fig. 7. Expanded graphite. Same sample as figure 6 after exfoliation (15 seconds at max. power in microwave oven), notice the large increase in volume, vermicular texture, and loss of metallic lustre.

Fig. 8. Expanded graphite after being compressed by hand, between two sheets of paper. The same principle is used to produce graphite foil.

Geology of Graphite Deposits

Graphite deposits of economic interest are grouped into three categories determined by their products. Deposit profiles by Simandl and Keenan (1998 a,b,c) provide an introduction to the main deposit types for exploration geologists and prospectors.

Microcrystalline graphite deposits

Main host rocks: Chlorite and muscovite schists (Fig. 9), phyllites, quartzites, metagraywackes, limestones, sandstones and conglomerates which may be cut by diabasic or granitic intrusions with associated and andalusite-bearing hornfels.
Metamorphic grade: Sub-greenschist to greenschist contact, or regional.
Deposit geometry: Stratiform or lens-shaped; beds may be up to a few metres thick, deformed and/or repeated by folding and faulting; pinching and swelling of beds is common.
Ore characteristics: 30-95% graphite, in many cases >80%, mainly consists of small graphite particles intergrown with impurities.
Mining/processing: Mainly by surface mining; ore is hand sorted and milled.
Main use: Forging lubricants and for applications where high ash content and low crystallinity is acceptable or preferred.

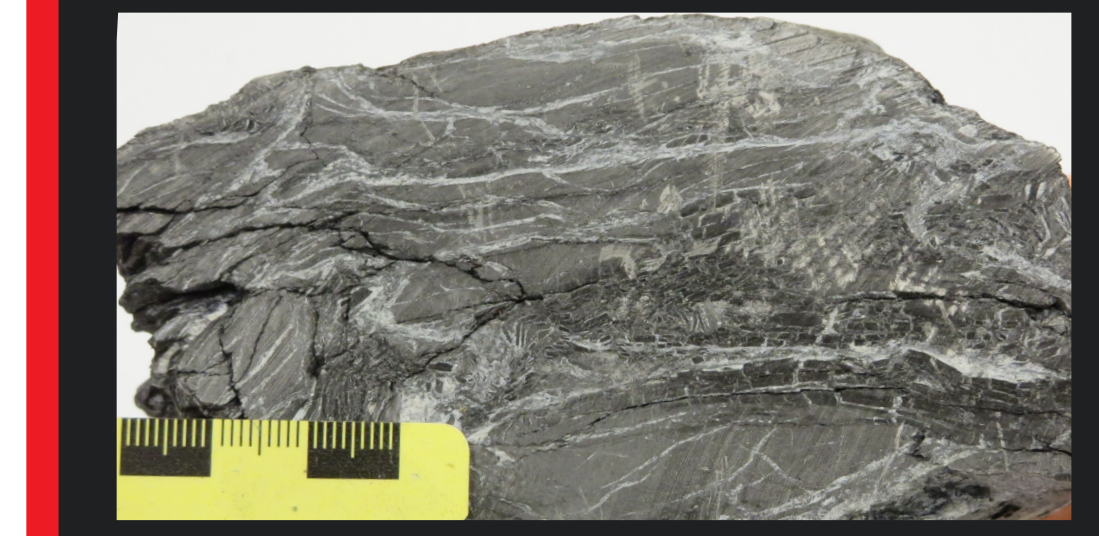


Fig. 9. Microcrystalline graphite in chlorite-sericite schist, Kaiserberg, Austria.

Fig. 10. Vein graphite cutting clinopyroxenite, Clot Mine, Quebec.

Vein graphite deposits

Main host rocks: Marble, paragneiss, iron formation, quartzite, pegmatite, syenite, and in rare cases mafic (Fig. 10) and serpentinized ultramafic rocks. A typical example is Walker mine, Quebec (Figs. 11, 12).
Metamorphic grade: Upper amphibolite and granulite facies; in skarn-type assemblages (Fig. 13) adjacent to igneous intrusions, in igneous intrusions, and in zones with a retrograde overprint.
Deposit geometry: Veins and other graphite-filled open spaces form pods and lenses, irregular bodies, stockworks, breccias, and saddle reefs. Thickness of veins varies from a few mm to over one m, most are < 0.3m thick.
Ore characteristics: Typically >90% graphitic-carbon. Rosettes, coarse flakes, fibers or needles oblique or perpendicular to wall rock. In some cases, schistosity subparallel to the vein walls.
Mining/processing: Mainly by underground mining; ore is hand sorted and milled. Currently mined only in Sri Lanka routinely to depths in excess of 600 m.
Main use: Graphite-rich lumps and chips, typically 0.5-0.8 cm in diameter, were traditionally used in refractories. Pre-2009 disruptions in the supply forced the refractory industry to switch from vein to crystalline flake graphite, once this transition was made vein deposits lost their economic prominence.

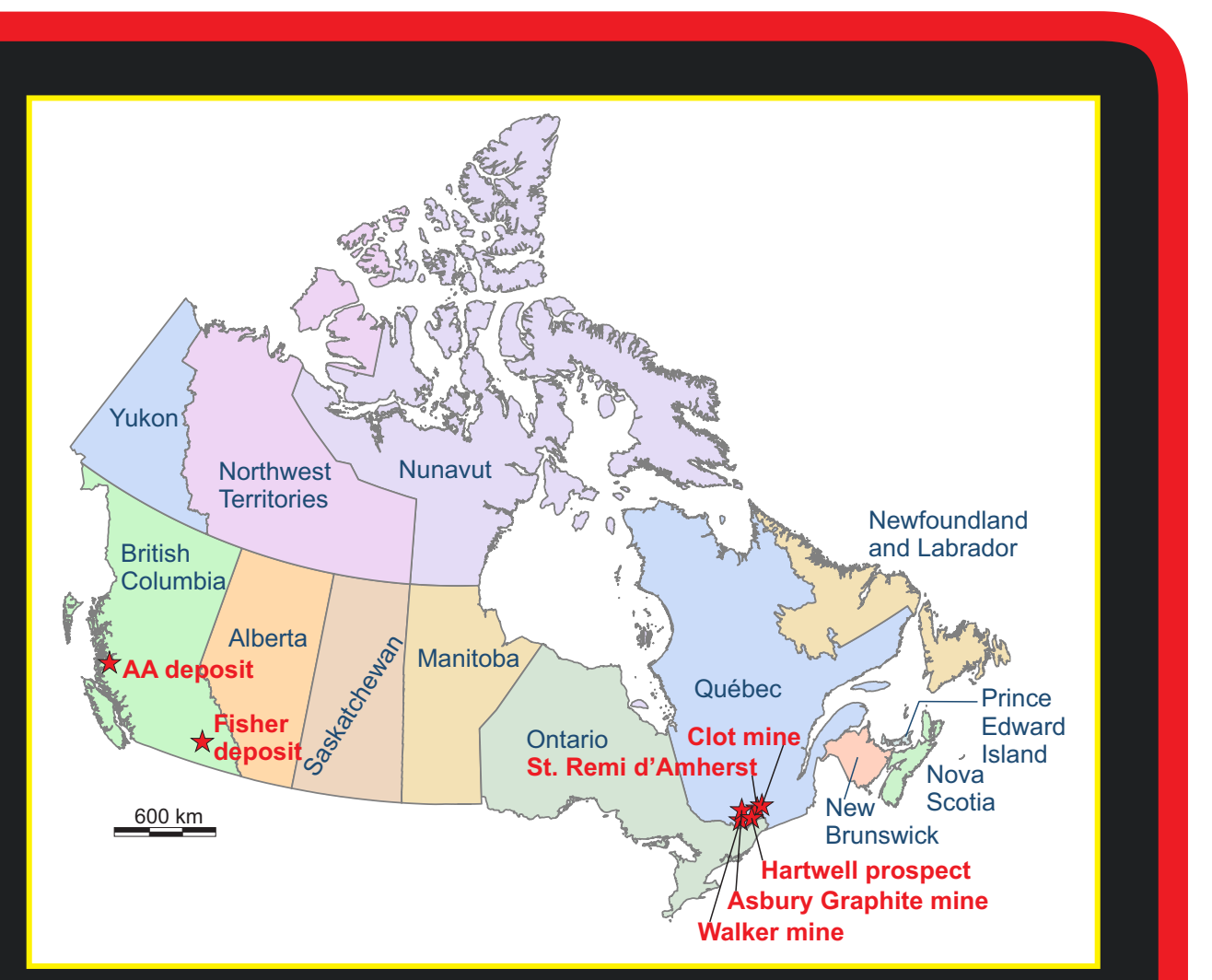


Fig. 11. Location of selected Canadian graphite deposits.

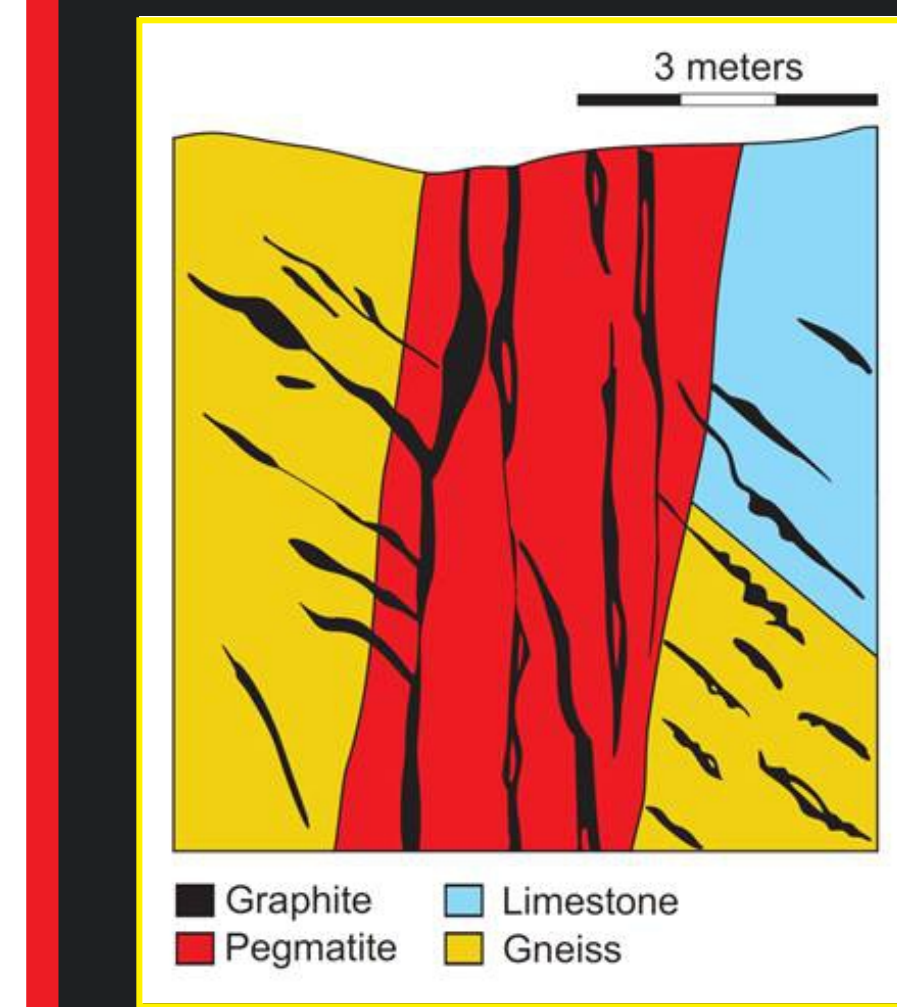


Fig. 12. Cross section showing graphite veins at the Walker Mine, Quebec. Modified from Cirkel (1907).

Fig. 13. Graphite in skarn, St. Rémi d'Amherst, Quebec.

Fig. 14. Crystalline flake graphite in porphyroblastic marble, Orwell prospect, Quebec.

Fig. 15. Sharp graphite-quartzite contact, Asbury mine, Quebec.

Fig. 16. Crystalline flake graphite in weathered paragneiss, Hartwell prospect, Quebec.

Fig. 17. Crystalline flake graphite in gneiss, Fisher showing, BC.

Crystalline flake graphite deposits

Main host rocks: Marble (Fig. 14), quartzite (Fig. 15), paragneiss (Figs. 16, 17), iron formation, pegmatite, syenite and, in extremely rare cases, serpentinized ultramafic rocks.
Metamorphic grade: Upper amphibolite to granulite facies.
Deposit geometry: Thick sequences of paragneisses and marbles. The highest grades are along or near paragneiss-marble contacts and in the crests of folds.
Ore characteristics: Grades from <2-15% graphite; flakes vary in size from <1-5 mm.
Paragneisses are evenly mineralized and typically grade <3% graphitic-carbon. Enriched zones occur along or near paragneiss-marble contacts (e.g., Hartwell prospect, Quebec; Figs. 11, 16, 18), in the crests of folds (e.g., AA deposit, British Columbia; Fig. 11; Marchildon et al., 1993), and contain retrograde minerals such as epidote and chlorite.
Marbles (granoblastic) generally contain <0.5-3% graphite. Silicates account for <5% per volume. Enriched zones (porphyroblastic marble) contain from <0.5-25% graphite and contain 2-10 mm clinopyroxene crystals around which graphite flakes are concentrated. Corrosion or overgrowth on the graphite flakes indicate disequilibrium. Quartz, pyrite, garnet, titanite, magnetite, chlorite, and trace chalcopyrite, clinozoisite, and prehnite, account for <3% of the rock. An example is the Asbury graphite mine, Québec (Figs. 11, 15, 19).
Mining/processing: Mostly by open pit. Typically, the ore is crushed, milled, processed using flotation; depending on impurities and intended use the ore may be further processed.
Main use: Crystalline flake graphite concentrate consists of flakes typically larger than 200 mesh (~74 microns). It is used in refractories, powder metallurgy, graphite foil, expanded graphite, spherical graphite, fuel cell bi-polar plates, coatings, thermal materials, friction moderators, lubricants, pencils, gaskets, and other advanced polymer systems, including rubber compounds.

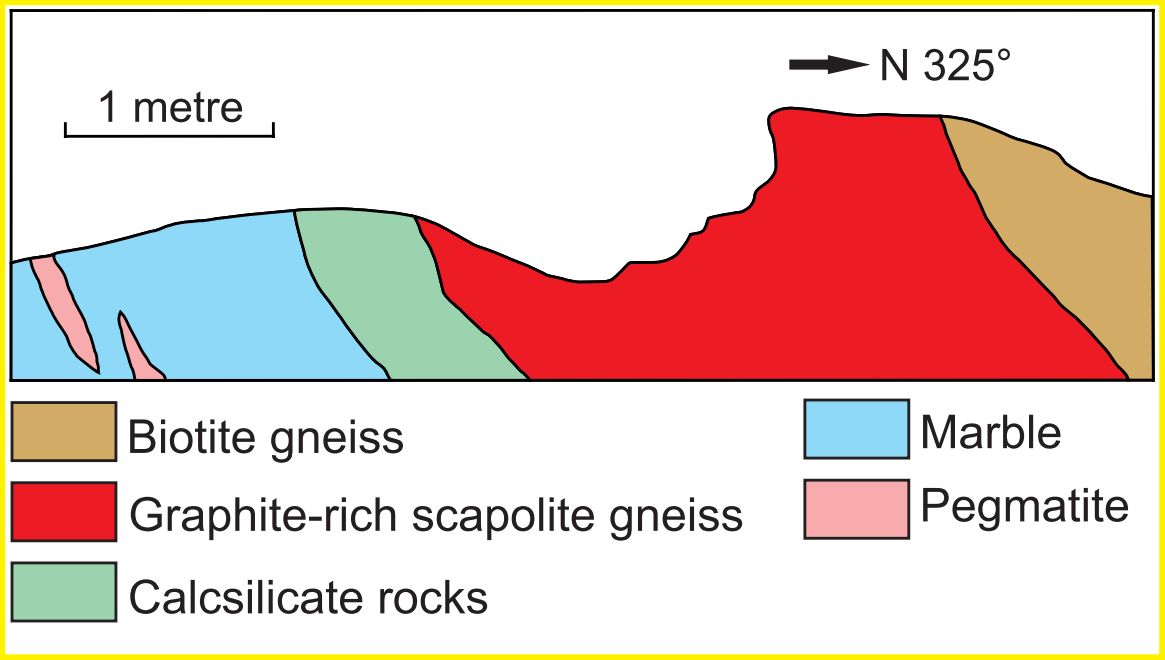


Fig. 18. Geological cross section of the Hartwell graphite prospect, Quebec (graphite grades of 3-15%). The contact between the graphite-rich unit and the biotite-gneiss is gradational and graphite content decreases with increasing distance from the calcsilicate rocks. No vertical exaggeration. After Simandl et al. (1995, 2015).

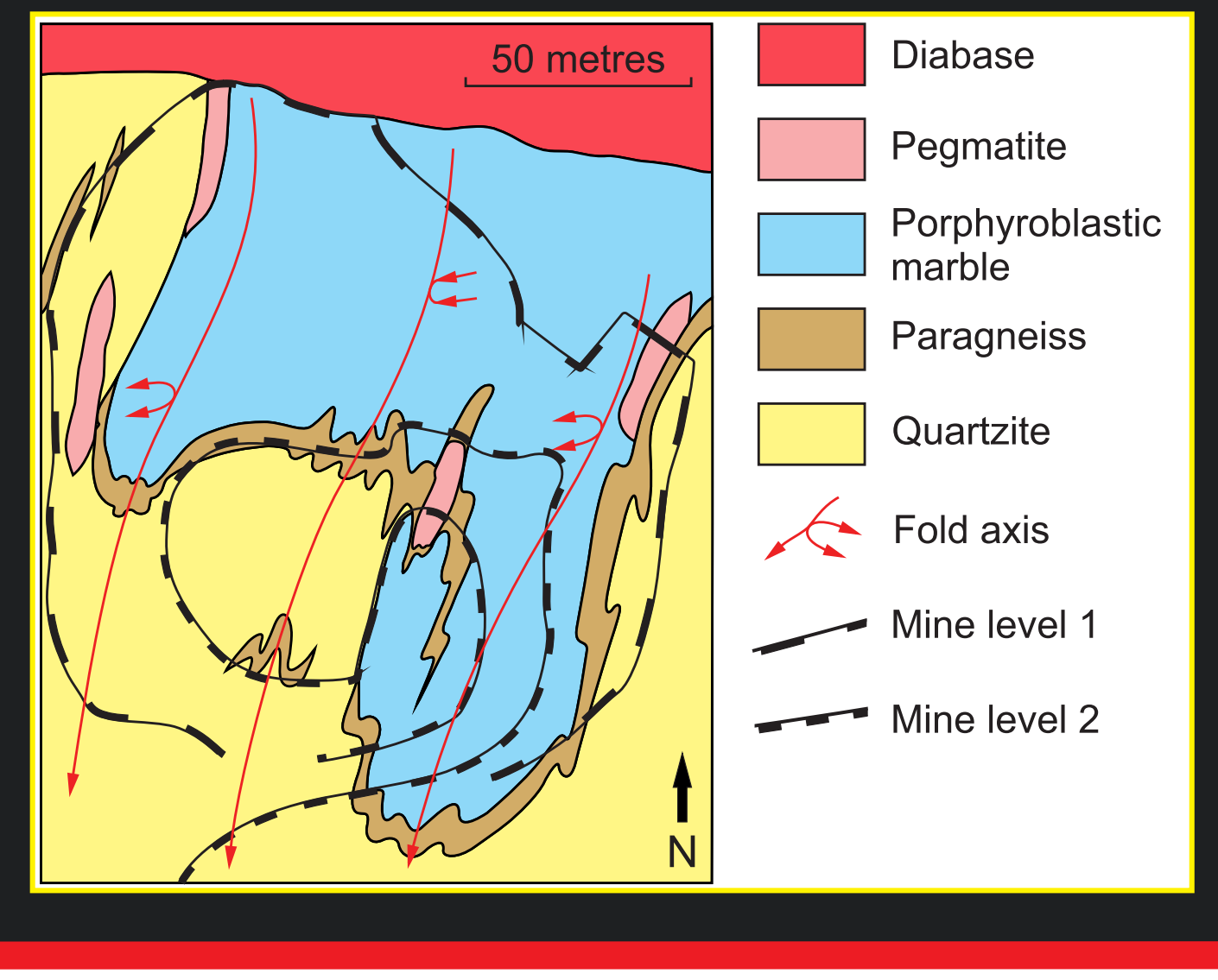
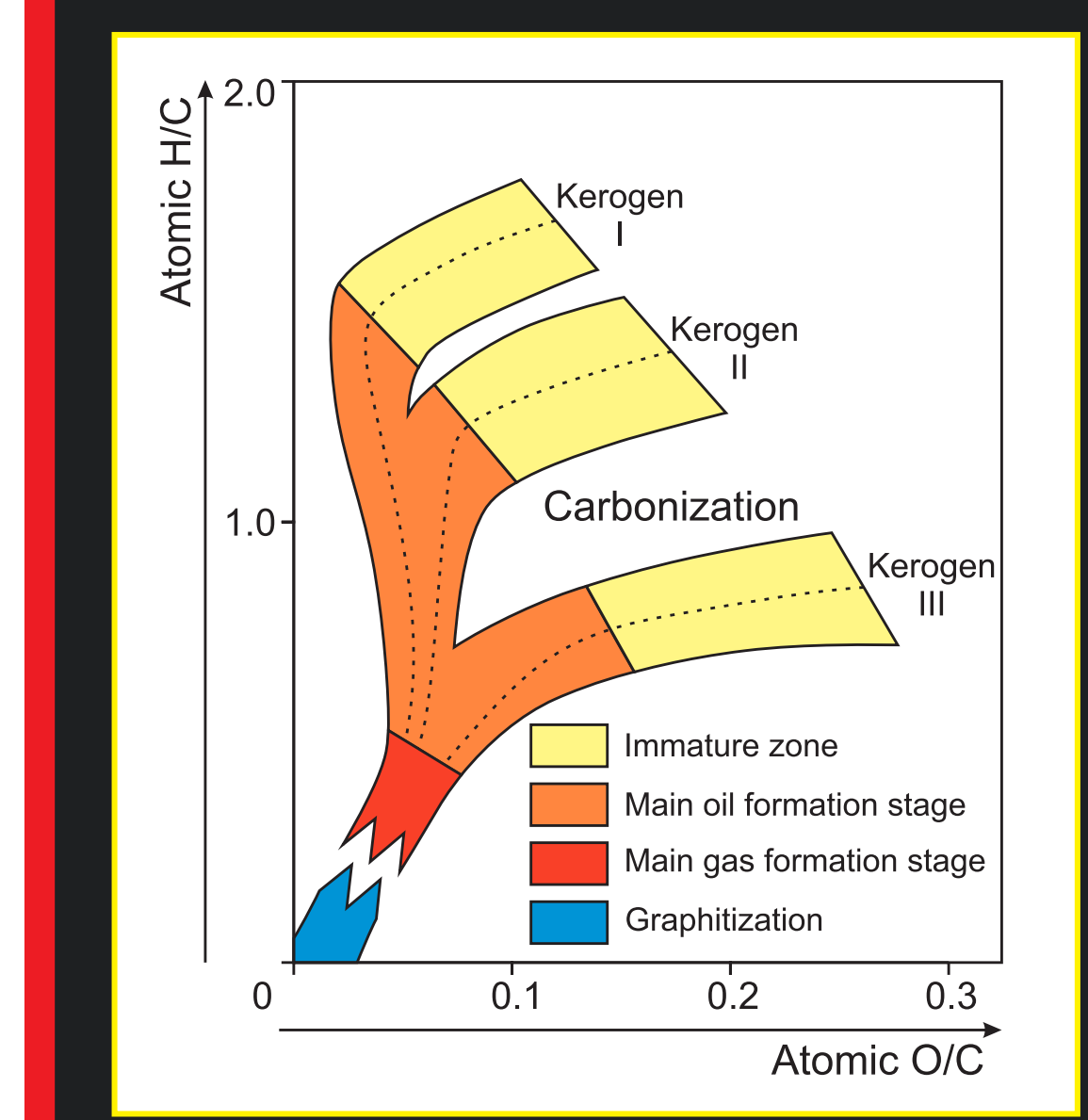


Fig. 19. Geological map of Asbury Graphite mine, Quebec. At this site, near-surface reserves were estimated to be 485, 180 tonnes at 10.75% graphite (Séguin, 1974) and the mine was in production from 1980 to 1988 on seasonal basis. Drilling in 1984, combined with a structural study, suggests additional resources at depth (Simandl, 1992). Locally, graphite is observed as inclusions inside clinopyroxenes. After Simandl et al. (1995, 2015).

Origin of Graphite Deposits

Graphite deposits of economic interest are formed by: 1) the maturation and metamorphism of organic material, and 2) precipitation from C-O-H fluid (metamorphic or metasomatic) triggered by changes in temperature and pressure conditions, fluid buffering, or by mixing of C-O-H fluids of different compositions.

Maturation and metamorphism of organic material



The transformation of immature organic material to graphite begins with carbonization and is followed by graphitization (Fig. 20). This hypothesis explains the origin of microcrystalline and low-grade crystalline flake graphite deposits. During carbonization, kerogens go from immature to oil and gas forming stages. The carbon-enriched residue stays in place, while hydrocarbons are expelled. Further burial accompanied or followed by regional or contact metamorphism results in a well-ordered graphite crystal structure.

Fig. 20. Kerogen maturation in terms of H/C and O/C atomic ratios. Kerogens I, II, and III are derived largely from lacustrine algae (H/C > 1.25), marine micro-organisms (1.1<H/C<1.5), and terrestrial plants (coal deposits; H/C<1), respectively. Modified from Buseck and Beyssac (2014); based on data of Grew (1974), and Vandenbroucke and Largeau (2007).

Precipitation of graphite from C-O-H fluids

Origin of graphite veins and enriched zones within low-grade crystalline flake graphite deposits (e.g., Hartwell prospect and Asbury Graphite deposit) can be explained using ternary C-O-H diagrams (Figs. 21-23).

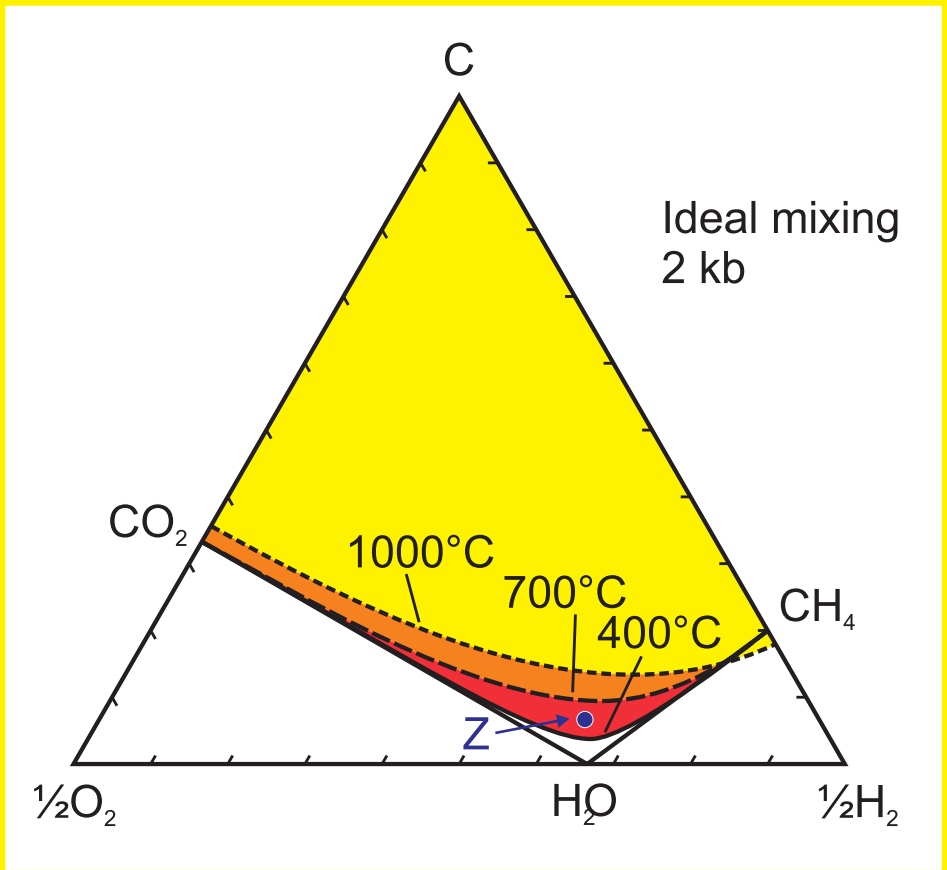


Fig. 21. Ternary C-O-H diagram showing increasing size of graphite stability field with decreasing temperatures from 1000° to 400°C for constant pressure of 2 kb. Modified from Ferry and Baumgartner (1987). Graphite can't precipitate from cooling of a C-O-H fluid of the composition Z at 1000° or 700°C, but will start to precipitate before the fluid cools below 400°C.

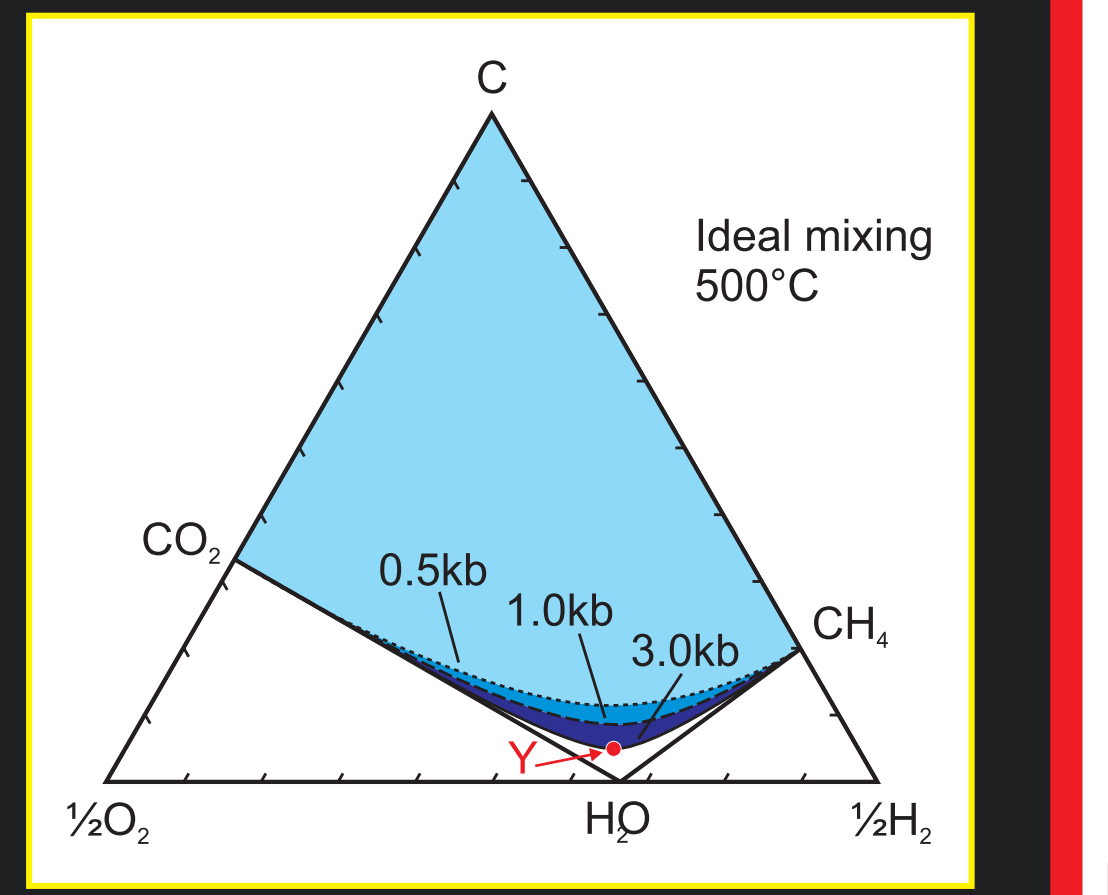
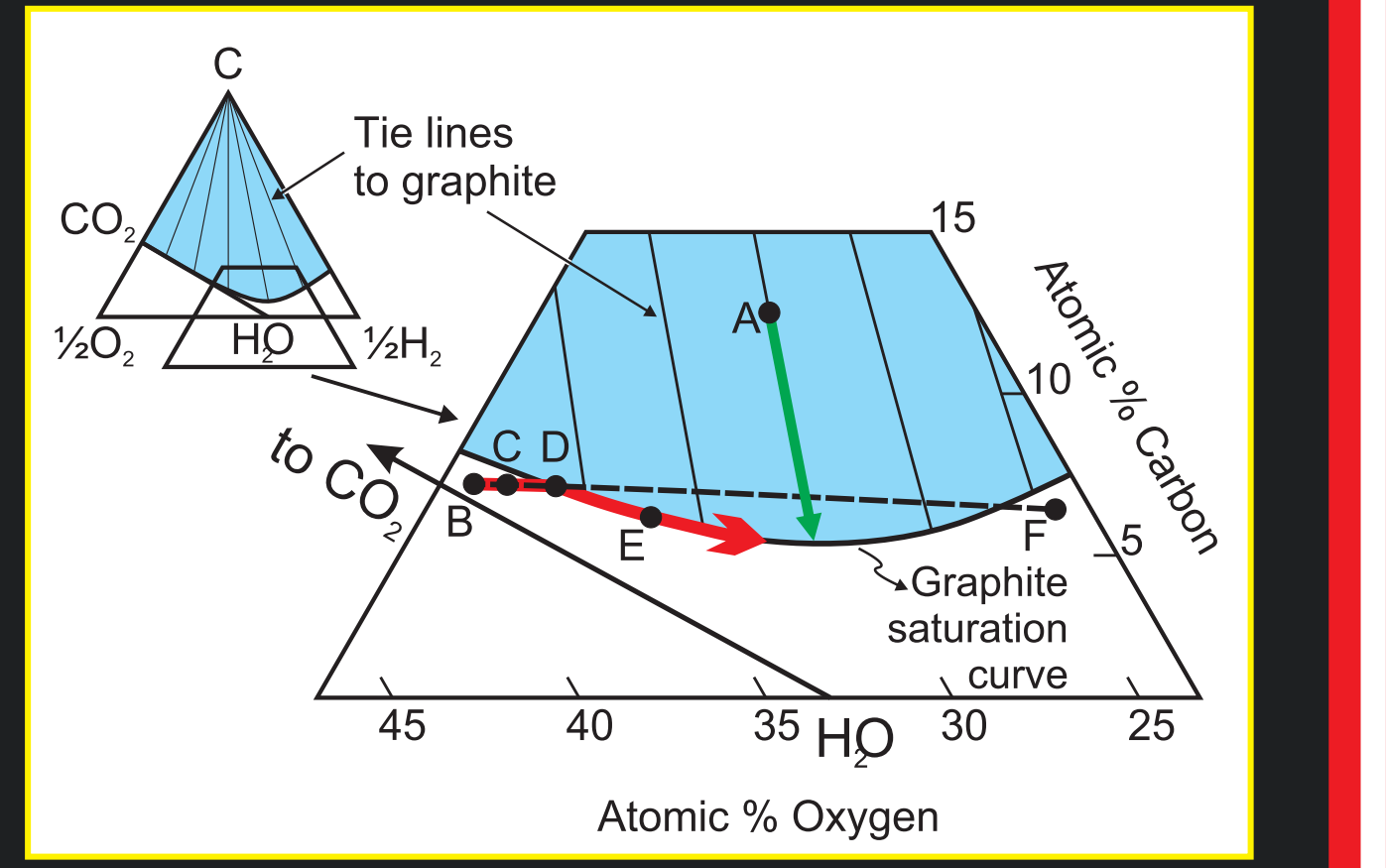


Fig. 22. Ternary C-O-H diagram showing increasing size of graphite stability field with increasing pressure from 0.5 to 3.0 kb for constant temperature of 500°C. Modified from Ferry and Baumgartner (1987). Graphite will not precipitate from a fluid of composition Y at pressures of 0.5 and 1.0 kb, but will precipitate at pressures of 3 kb or greater.

Fig. 23. Ternary C-O-H diagram at 600°C and 3.5 kb. Modified from Rumble et al. (1982).

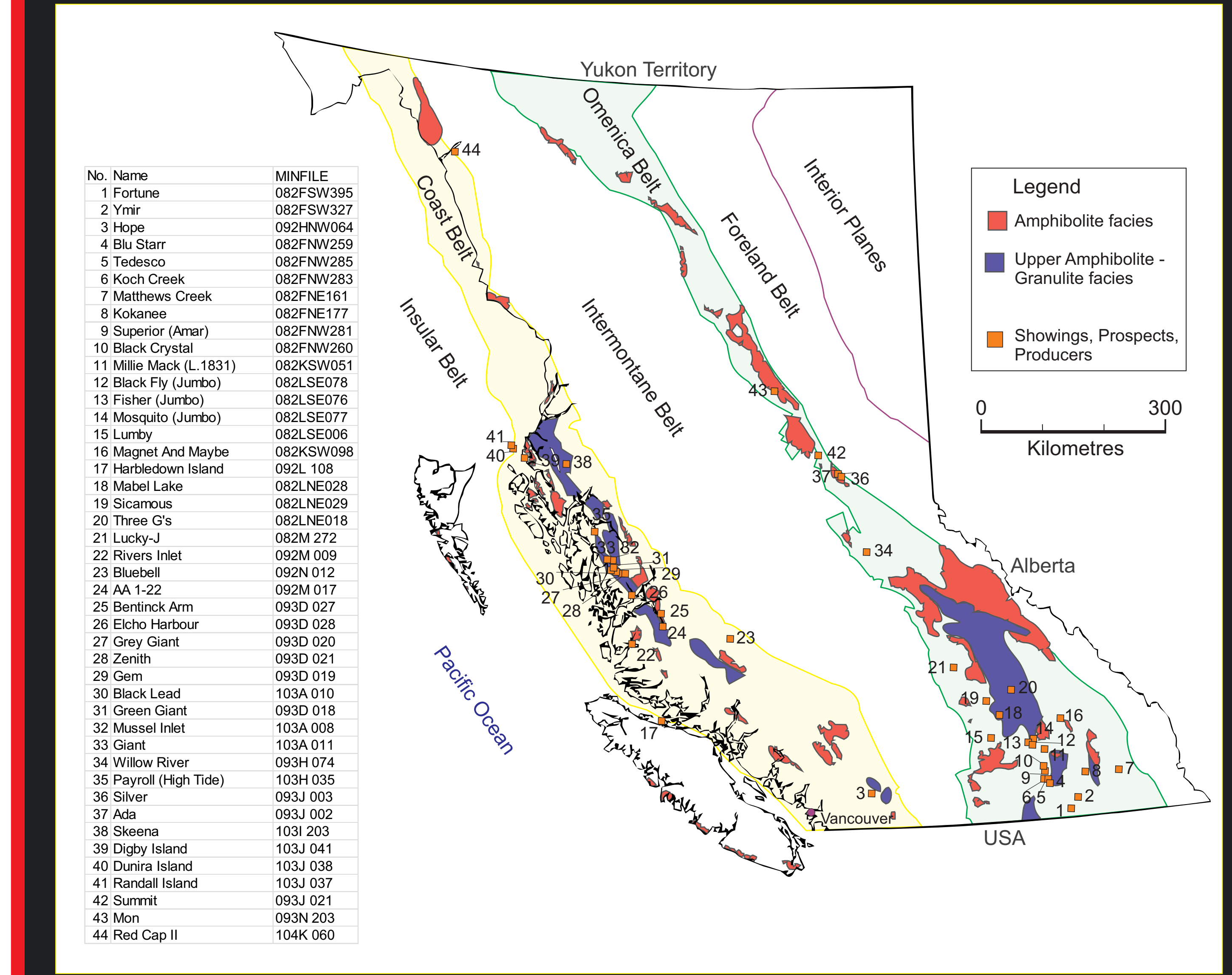


A fluid of composition A plots within the graphite stability field. As graphite precipitates, the composition of the fluid evolves along the corresponding tie-line, as shown by the green arrow, towards the graphite saturation curve.

Fluids of compositions B and F lie outside the graphite stability field. It would be impossible to precipitate graphite from either of these fluids alone. However, if we mix these two fluids, the composition of the resulting mixture will lie somewhere along the mixing line B-F.

If a small quantity of fluid F is added to fluid B, then the composition of the resulting fluid will shift slightly to the right (point C). As more fluid F is added to the system, the composition of the resulting fluid will keep shifting to the right until point D is reached and the first crystal of graphite precipitates. As more fluid of composition F enters the system, the composition of the fluid follows the graphite saturation curve, passing through point E, and graphite keeps precipitating.

Graphite Occurrences in British Columbia



No.	Name	MINFILE
1	Fortune	082FSW395
2	Ymir	082FSW327
3	Hope	092HNW064
4	Blu Starr	082FNW259
5	Tedesco	082FNW285
6	Koch Creek	082FNW283
7	Matthews Creek	082FNE161
8	Kokanee	082FNE177
9	Superior (Amar)	082FNW281
10	Black Crystal	082FNW260
11	Millie Mack (L.1831)	082KSW051
12	Black Fly (Jumbo)	082LSE078
13	Fisher (Jumbo)	082LSE076
14	Mosquito (Jumbo)	082LSE077
15	Lumby	082LSE006
16	Magnet And Maybe	082KSW098
17	Harbledown Island	092L 108
18	Mabel Lake	082LNE028
19	Sicamous	082LNE029
20	Three G's	082LNE018
21	Lucky-J	082M 272
22	Rivers Inlet	092M 009
23	Bluebell	092N 012
24	AA 1-22	092M 017
25	Bentinck Arm	093D 027
26	Elcho Harbour	093D 028
27	Grey Giant	093D 020
28	Zenith	093D 021
29	Gem	093D 019
30	Black Lead	103A 010
31	Green Giant	093D 018
32	Mussel Inlet	103A 008
33	Giant	103A 011
34	Willow River	093H 074
35	Payroll (High Tide)	103H 035
36	Silver	093J 003
37	Ada	093J 002
38	Skeena	103I 203
39	Digby Island	103J 041
40	Dunira Island	103J 038
41	Randall Island	103J 037
42	Summit	093J 021
43	Mon	093N 203
44	Red Cap II	104K 060

Fig. 24. Distribution of known graphite occurrences in British Columbia. Detailed descriptions of individual graphite occurrences can be obtained from MINFILE at: http://minfile.gov.bc.ca/searchresults.aspx?23=867&27=Any&t=1 . The area most favourable for crystalline flake graphite exploration are coloured in red (amphibolite facies with kyanite and garnet present) or blue (amphibolite-granulite facies). Metamorphic map modified from Monger and Hutchinson (1970).

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