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Gold–graphite association in granulite terrains — Implications for ore genesis

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ABSTRACT

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The gold occurrences of Sri Lanka are closely associated with the graphite deposits and are genetically related. The quartz–graphite margins of the vein graphite are shown to be metal accumulating. The movement of CO_2-rich fluids, formation of graphite and the concentration of Au are closely related.

Whereas the CO_2-rich fluids may well be the "carbon-carriers" in the formation of graphite, the original source of CO_2 is still debated. Hydrothermal solutions, when in contact with the graphite tend to activate the carbon, thereby producing sites for the enrichment of gold. The genetic link between the graphite veins and gold deposition has useful implications in the investigation of ore genesis in high-grade metamorphic terrains and the exploration for gold.

1. Introduction

The origin of graphite in granulitic terrains presents many intriguing problems. Studies on granulites and associated charnockites have revealed that CO_2 plays a major role in their petrogenesis (Janardhan et al., 1979; Wendtlandt, 1981; Peterson and Newton, 1989). The abundance of CO_2 in rocks of granulitic terrains has important implications in that the CO_2 forms a ready source of carbon for graphite formation. Even though current debate is centered on the question of whether the CO_2-rich fluids are ultimately derived from reservoirs fixed near the Earth's surface (carbonate sediments, organic carbon and seawater-derived hydrothermal carbonates), originate from the mantle, or represent recycled mixtures of both, an important issue arising from this debate is the role played by CO_2 and organic carbon in the geochemistry of gold. Recent observations by Groves et al. (1988), on carbon isotope measurements in Archean gold deposits, indicate that seawater alone could not have been the sole source of carbon for the CO_2 in the metamorphic fluids, some carbon at least being derived from a source with a negative $\delta^{13}C$-value such as the mantle. Nisbet and Kyser (1988) commented on the work on Archean high-grade terrains which had shown that rocks originally formed on the surface within the biosphere often constitute part of the deep continental crust. They suggest that this may be a source of carbon with low $\delta^{13}C$-values in the gold mines, especially as bacteria may have lived in the hydrothermal systems that eventually degassed during metamorphism to give rise to auriferous fluids.

It seems imperative that the paths of CO_2 movement need to be mapped better in order to understand more about the history of degassing. This study shows that carbon dioxide, graphite formation in granulitic terrains and gold transport in a fluid medium appear to be interrelated.

2. Occurrences of graphite in the granulitic terrain of Sri Lanka

Sri Lanka presents a unique example of a situation where this particular interrelationship is clearly seen. The graphite of Sri Lanka occurs as:

(1) a common accessory mineral in a large number of rock types such as metasediments, garnet–biotite gneisses and charnockites;

(2) a constituent of quartz and quartz-feldspathic veins and segregations in the migmatitic and granitic gneisses and in pegmatites;

(3) veins, pockets and lenses of pure graphite (95–99% C) occupying fissures and cracks in the crystalline rocks.

What is most significant in the distribution of graphite of Sri Lanka is that it is entirely confined to the central Precambrian granulitic belt comprising the Highland and Southwest Groups. The gold occurrences are also confined to this terrain and a very close association of the graphite deposits with gold, particularly in the Southwest Group, is seen (Fig. 1). Neither graphite nor gold are found in the amphibolite-facies rocks that flank the Highland Group.

The origin of the graphite deposits of Sri Lanka has been the subject of much debate. The association of vein graphite deposits with calcareous rocks led Hapuarachchi (1977) to conclude that CO_2 derived from decarbonation reactions was the source of carbon for graphite. Dobner et al. (1978) and Dissanayake (1981) were of the view that vein graphite was of biogenic origin and it is the originally dispersed carbonaceous matter which was transported to the veins as a suspension in a fluid phase. More recently Katz (1987) concluded that graphite is a consequence of granulite-facies metamorphism in the presence of CO_2-rich fluid. Central to all these suggestions are, however, the source of carbon, the transport mechanism such as a fluid, and mechanism of deposition. Whereas the CO_2 may well be the "carbon-carrier" in the formation of graphite, the original source of the CO_2 is a point of much discussion.

3. Gold–graphite association

Whenever large volumes of fluids move in the crust there is ore potential (Fyfe, 1986, 1987). With the potentially very deep extent of major faults, a mantle source for CO_2 is not untenable (Stewart et al., 1986). Random qualitative analyses using the electron microprobe has shown that the occurrence of gold is highest in the quartz veins at the contact margins of the vein-type graphite deposits of Sri Lanka (Fig. 2). In most cases iron sulphides are also abundant at these contacts. Similar Au-rich graphitic, quartz veins have been observed in the Archean rocks of the Abitibi belt, Canada (Springer, 1985), where the graphite zones are commonly Au-rich.

The origin of the gold–graphite relationship in Sri Lanka can be postulated along the following lines. The present Highland Group in which gold and graphite are confined, was a sedimentary basin of Precambrian age. Schidlowski (1988) commented that an increased $^{12}C/^{13}C$ ratio, an indicator of the principal carbon-fixing reaction of photosynthesis, is found in sedimentary organic matter dating back to almost 4 Ga ago. This was a sign of the existence of prolific microbial life not long after the Earth's formation. Partial biological control of the terrestrial carbon cycle has been established very early and was in full operation when the oldest sediments were formed. On the other hand, in some earlier work by Schidlowski et al. (1979), on the Isua sediments of West Greenland, the markedly positive $\delta^{13}C_{org}$-values of their "graphitic" constituents (mean $\delta^{13}C_{org} = +15.3 \pm 6.2‰$ vs. PDB) was interpreted as being the result of metamorphism, indicating the significance of the role of meta-

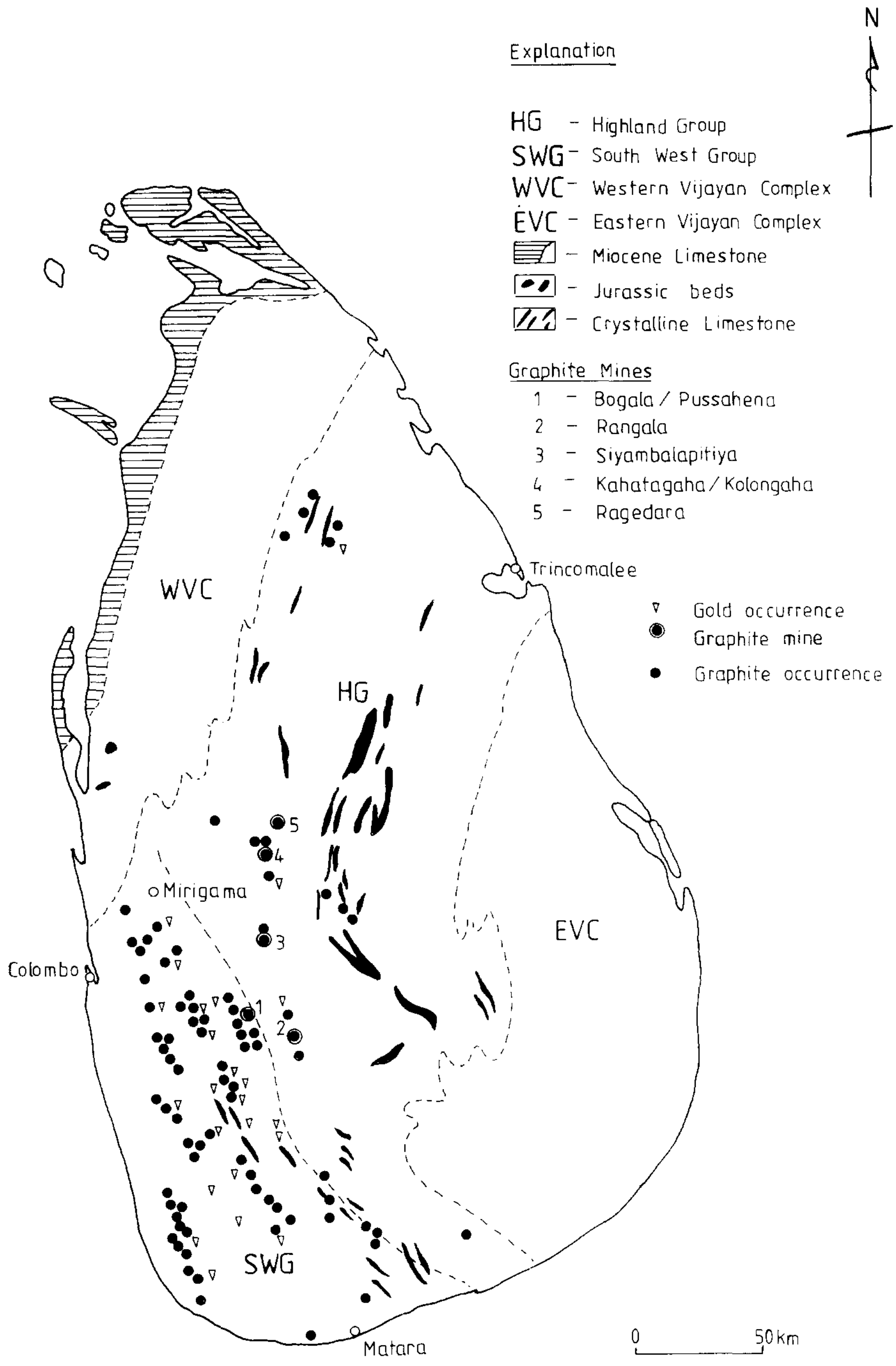

Fig. 1. Map showing the close association of gold occurrences with graphite deposits in Sri Lanka.

morphism in carbon isotope fractionation.

Therefore, the use of $\delta^{13}C$-values in the interpretation of the biogenic origin of graphite or carbonaceous matter should be viewed with extreme caution in view of the factors that affect isotopic fractionation. Katz (1987) and Silva (1987) who have put forward hypotheses on the origin of the graphite deposits

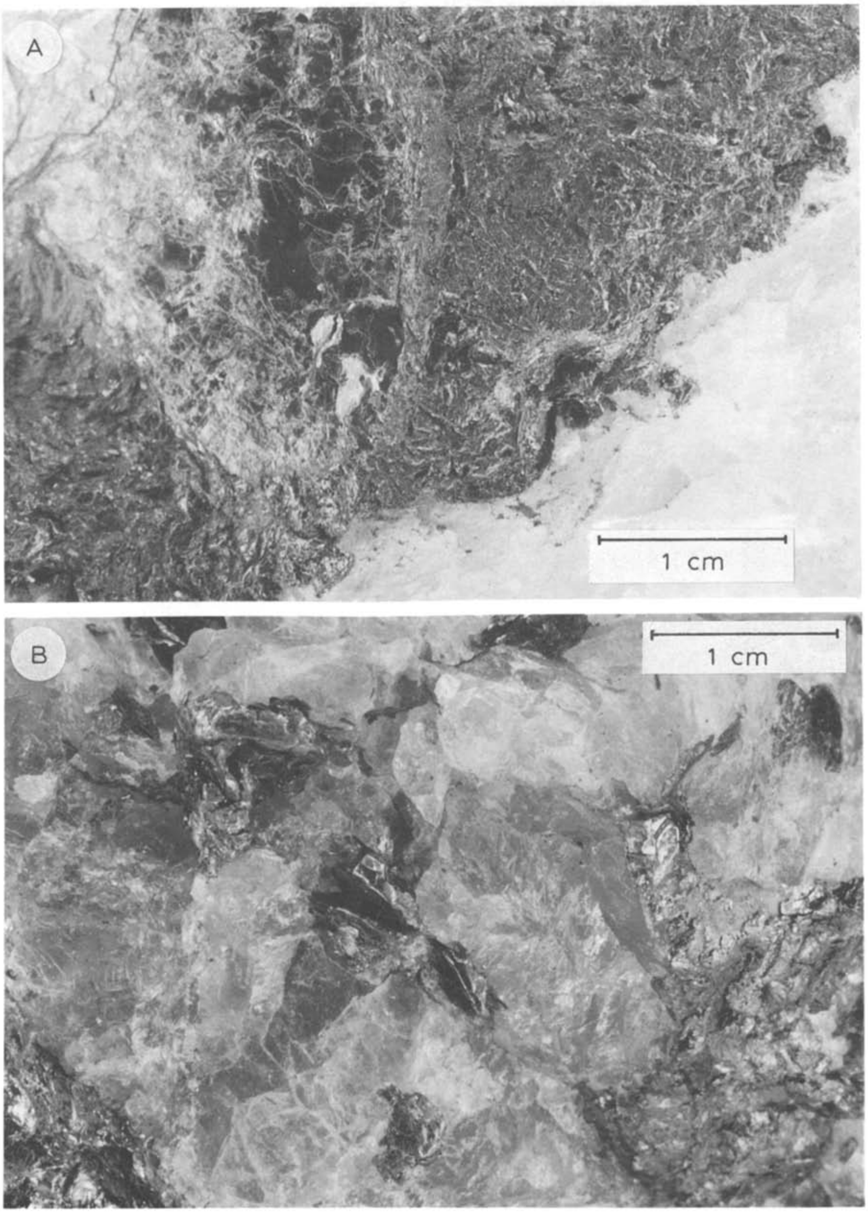

Fig. 2. A. Quartz vein cross-cutting vein-type graphite
B. Contact of quartz vein with massive graphite. Gold accumulation takes place at these margins.

of Sri Lanka may well have been led into such erroneous conclusions. It is worthy of note that Javoy et al. (1986) argued that oceanic basalts also contain carbon with very low δ^{13}C-values (down to +25‰) and that δ^{13}C-values of CO_2 outgassed in magma erupted above subduction zones varied substantially with depth of origin and distance from the trench.

Given such a scenario as described by Schidlowski et al. (1979), one could expect an enrichment of organic matter and carbonates in the earlier Precambrian Highland Basin of Sri Lanka. The Highland Group consists of metasediments, quartzites, marble sillimanite–garnet gneisses and schists originating from a sequence of sandstones, limestones and argillaceous shales. Charnockites are found intimately associated with these metasediments. The garnet–sillimanite rocks nearly always contain tiny flakes of graphite, probably derived from organic plant remains in the original sediments (Cooray, 1984). Graphitiferous schists which occur as very narrow bands rich in graphite and sulphate–sulphide minerals were noted by Cooray (1961) in the Rangala area in the Central Highlands. The presence of these two minerals in such high proportions was explained by Cooray (1984) as having been formed from sediments which were originally accumulation of mud, sand and decayed vegetable matter in stagnant water. Subsequently, the sedimentary sequence underwent folding and deformation accompanied by metamorphism to form the present Highland Group of rocks (Dissanayake and Munasinghe, 1984).

The CO_2-rich fluids originating during the folding and thrusting could be either due to metamorphic degassing (Groves et al., 1988) or pervasive magmatic phenomena (Burrows et al., 1986). Some (e.g., Nisbet and Kyser, 1988) may argue that organic matter carried down subduction zones to the mantle act as a source of CO_2 for later massive outgassing while others (e.g., O'Nions and Oxburgh, 1988) have used He isotope studies to estimate the amounts of CO_2 entering the crust from the mantle and conclude that the present-day CO_2 fluxes are too low to cause regional hydration of the lower crust at least in some tectonic areas.

The eventual mapping of the paths of movement of CO_2 may resolve some of the issues pertaining to the history of degassing of CO_2. However, further knowledge on the source of carbon for the CO_2 so outgassed and its volume will be of paramount importance in resolving the origin of graphite and the gold associated with such graphite-bearing veins.

4. Migration of gold-bearing fluids

The nature of the Archean lode–gold mineralization has been the subject of several recent investigations (Bohlke and Kristler, 1986; Brown and Lamb, 1986; Cameron, 1988). Much emphasis has been on the chemical nature of the Au-bearing ore fluids, the role of CO_2 in granulite formation (Harris, 1989) and the relation of gold ore deposition to the petrogenesis of granulites (Cameron, 1988). These ore fluids have been shown to be CO_2-rich and of low to moderate salinity. Elements that migrate at high temperature mainly as chloride complexes such as base metals do not concentrate in the veins while Au with elements such as As and Sb that form soluble sulphur complexes are strongly enriched (Cameron and Hattori, 1987). Major faults, deep-seated fractures and lineaments act as conduits for the transport of these ore fluids as shown by numerous field studies.

One of the most significant features of the vein graphite deposits of Sri Lanka is that they are structurally controlled and are confined to the north–south anticlinal or domal structures and lie along the fold axes (Silva, 1974; Katz, 1987). As observed by Silva (1987) the deep-seated fractures that are sites of graphite mineralization may well have formed during the formation of the anticlinal structures. The fact that gold has been concentrated at the epigenetic graphite vein margins suggests that the Au-bearing ore solutions may also have migrated along the same deep-seated fractures that carried the CO_2-rich fluids which gave rise to the graphite veins.

The relationship between the Au-bearing fluids and the graphite-bearing granulites is illustrated in Fig. 3. Granulites show a wide variation in oxidation state from graphite-bearing to varieties containing hematite (Newton, 1986), oxidation conditions being critical to CO_2 streaming. For a C–O–H fluid at 700°C and 7 kbar, CO_2-rich vapour can exist only at f_{O_2} greater than that of the fayalite–

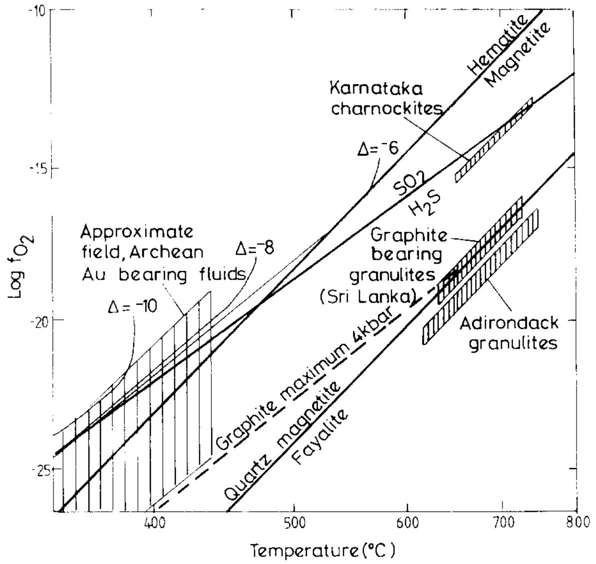

Fig. 3. Temperature vs. f_{O_2} plot (modified after Cameron, 1988). Data for the Sri Lankan granulites obtained from Hansen et al. (1987).

magnetite–quartz (FMQ) buffer (Cameron, 1988). At lesser f_{O_2}, graphite is stable and a vapour phase ceases to exist because its pressure is less than rock pressure. The graphite-bearing Adirondack granulites, New York, U.S.A. (Lamb and Valley, 1984) and the graphite-bearing Sri Lankan granulites (Hansen et al., 1987) belong to this condition (Fig. 3). The gold occurrences of Sri Lanka are hosted by the graphite-bearing supracrustal rocks, the graphite helping to fix the Au by reducing the f_{O_2} of ore fluids. Due to the high partition function of Au in the sulphide phase of the magma, it is invariably associated with the sulphides and it is worthy of note that sulphides are particularly abundant in the epigenetic vein graphite deposits of Sri Lanka.

At high temperatures, gases of the system H_2O–CO_2–S are produced. Species such as CO and COS become significant due to their behaviour as excellent complexers and transport agents of a wide range of metals including Au (Fyfe, 1986, 1987).

The work of Muetterties (1982) as quoted by Fyfe (1986) shows that "cluster molecules" in reduced C–O systems could indeed be significant. Recent work by Dissanayake et al. (1988) on the trace elements in the vein graphite of Sri Lanka supports the view that the graphite-precipitating fluids are indeed metal-rich. It is now known that almost all primary Au concentration processes involve the interactions of fluids with primary rocks and that the dominant component of such fluids is water. Fluid-inclusion data from gangue minerals and stable isotope data confirm that such fluids could transport Au and provide solutions from which gold can be precipitated (Fyfe and Kerrich, 1984). The mechanism of Au extraction is that a large fluid volume must flow through an even larger rock volume on a microscale and the output focussed on a small volume.

5. Mechanism of gold adsorption by graphite

The problem of interest is the mode of Au transport in relation to the carbon-rich fluids that apparently carried and precipitated graphite. It seems likely that graphite only plays a role in the trapping of gold at the final stages of cooling. However, the species that act as "carbon-carriers" in the formation of graphite may also be responsible for the complexation of Au in the fluid medium. The species Cl^-, Br^-, NH_3, HS^-, S^{2-}, CO and COS are complexing species known to be thermodynamically stable at high temperatures. The latter two species are of particular interest in the formation of graphite. A large number of metals including Pt, Rh, Re, Ir and Os form complexes with the species CO, of the type MCOCl and $MCONR_3$ (Fyfe and Kerrich, 1984).

The coexistence of hydrothermal vein quartz and pure graphite-bearing gold-rich veins dispersed among the granulitic rocks of the granulite terrain of Sri Lanka indicates a common conduit system for the transport of fluids carrying both gold-forming complexes and the "carbon-carriers" — the precursors of graphite. A likely mechanism is that the graphite in a hot fluid acts as activated carbon which then adsorbs gold on its surface. Wilson and Rucklidge (1987) described the mineralogical and geological aspects of the Owl Creek and Hoyle Pond gold mines, located in Archean metasediments and metavolcanics in the Abitibi greenstone belt in northern Ontario, Canada. They observed that in carbon-filled fractures in vein quartz, the quartz–carbon interface is a typical setting for native gold.

Arsenic, best known as an "indicator element" for gold, commonly accompanied the gold-related carbonaceous lithologies. In the presence of graphitic materials, the metal-transporting complexes are destabilized on account of structural and chemical factors. Springer (1985) suggested that the reactivity of carbon can be enhanced by hot hydrothermal fluids flowing up shear-zone conduits. On final cooling, gold will appear at the graphite–quartz contacts in the vein systems.

McDougall and Hancock (1981) observed that activated carbon is an excellent scavenger for small concentrations of dissolved Au ($\leqslant 0.2$ mg l^{-1}) and that it has applications in removal of gold cyanide from gold plant effluents and dam return water. Activated carbon is a generic term for a family of substances which cannot be characterized by a definite structural formula or by chemical analysis, the various products being differentiated by their adsorptive properties.

The activated carbon is believed to be composed of tiny graphite-like platelets. The overall structure is considered to be very disordered with broken-up hexagonal carbon rings that are randomly oriented (Mattson and Mark, 1971). A porous structure with a large surface area (600–1500 $m^2 g^{-1}$) provides sites for metal accumulation. Activated carbon can function as a reductant and in the presence of oxygen as an oxidation catalyst. It can quite easily reduce gold complexes such as $AuCl_4$, $AuBr_2$ and AuI_2 into metallic gold. The Au atoms are retained on the external surface of the carbon by Van der Waals forces (McDougall and Hancock, 1981).

The gold–graphite association at vein margins in shear zones and fracture systems in granulitic terrains holds promise for gold exploration. The marked electrical conductivity of graphite makes it highly amenable to geophysical exploration. Frost et al. (1989) made observations on grain-boundary graphite in rocks with implications for high electrical conductivity in the lower curst.

6. Conclusions

The gold occurrences of Sri Lanka are closely associated with the vein graphite deposits and are genetically related. While CO_2 forms a ready source of carbon for graphite formation, the CO_2-rich fluids are also important as a transporting medium for gold. Even though several recent studies have clearly shown the enrichment of gold in carbon-rich rocks, crystalline carbon occurring as graphite such as the vein graphite of Sri Lanka, has not been studied in any detail for their geochemistry of gold.

This study shows that CO_2-rich fluid migration, graphite formation in high-grade metamorphic rocks and gold accumulation appear to be interrelated. During the passage of hot hydrothermal solutions, activated graphite provides sites for metal accumulation.

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