Carbon isotope “stratigraphy” in a single graphite crystal: Implications for the crystal growth mechanism of fluid-deposited graphite

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ABSTRACT

A 2 cm long and 0.8 cm thick, single graphite crystal embedded in quartz, feldspar, and orthopyroxene of a granulite-facies metamorphic rock from southern India exhibits unique homogeneity in δ13C values along layers parallel to the (0001) surface and smooth unidirectional variation of about 1‰ along the c-crystallographic axis. The fluid-precipitated graphite shows isotope homogeneity indicative of crystal growth along the (0001) plane. The C-isotope data along with the textural features suggest that the formation of graphite initiates in a layer perpendicular to the c-axis, possibly by a spiral growth mechanism. The initial layer is followed layer after layer, until the final stages of graphite growth. A second stage of graphite growth unrestricted by surrounding minerals is inferred from the un-deformed idiomorphic hexagonal form of the overgrown crystals. The C-isotope values in the overgrown rim of the crystal are lowered by about 2‰, suggesting a multistage precipitation. Morphologic and stable isotope studies thus confirm uniform crystal growth of graphite recording an isotope evolution pattern relating to fractionation from a fluid in an infinite reservoir during the main crystal formation. Spiral growth parallel to the (0001) face can explain the perfect uniformity of stable isotope composition in a single layer, whereas the variation across the (0001) surface gives insights into the time-integrated fluid evolution attending the crystal growth.

INTRODUCTION

Graphite occurs as an accessory mineral in a variety of terrestrial and extraterrestrial lithologies, and forms over a wide range of pressure-temperature conditions. However, its stability is also partly controlled by the redox conditions. Graphite has a wide economic potential, principally due to its unique physical and chemical properties. Terrestrial economic concentrations as stratiform deposits or as epigenetic vein concentrations occur in many Precambrian high-grade metamorphic terrains including the erstwhile Gondwana crustal fragments of Madagascar, Sri Lanka, and India (e.g., Radhika et al. 1995; Dissanayake and Chandrajith 1999). Graphite, in most high-grade rocks, was derived by “graphitization” involving the conversion of biogenic matter trapped within sediments (Wada et al. 1995). Therefore, the C-isotope signature of graphite [δ13C per mil (‰) relative to PDB] in high-grade rocks is characterized generally by low values (<25‰, Eichmann and Schidlowski 1975; Vry et al. 1988). However, other possibilities exist for the formation of graphite, a common alternative to the biogenic mechanism being epigenetic precipitation from COH fluids (Rumble and Hoering 1986; Farquhar and Chacko 1991; Santosh and Wada 1993a; Luque et al. 1998; Pasteris 1999). This process leads to the formation of massive vein deposits such as those found in Sri Lanka. Although there is general consensus on the origin of graphite, there is still ambiguity on the crystal growth mechanism during metamorphism and related fluid processes.

Fractionation of C isotopes between co-existing mineral and fluid phases during metamorphism has been a topic of interest because of large difference in distinct isotope reservoirs in terrestrial regimes. Although carbonates/graphite/diamond forms important crustal C reservoirs, the role of C-bearing fluids cannot be underestimated. Carbon isotope fractionation between calcite and graphite has been constrained from theoretical, experimental, and empirical methods (Valley 2001; Satish-Kumar et al. 2002). However, only theoretical estimates of C-isotope fractionation between graphite and CO2 are reliable at present because of difficulties arising from experimental conditions (Polyakov and Kharlashina 1995). Graphite precipitation from CO2 fluids can be used as a potential case for estimating the fractionation, provided temperatures are well constrained. Before attempting such studies, however, it is necessary to consider the effects of closed-system crystal growth and related fractionation during graphite formation.

With the advent of high-resolution electron microscopy, several new findings on crystal forms and growth patterns on the nanoscale have been reported (e.g., Double and Hellawell 1974; Jaszczak 1997). The formation of idiomorphic, hexagonal flakes of graphite has been attributed to a spiral growth mechanism (Horn 1952; Austerman et al. 1967; Jaszczak 1991; Kvasnitsa and Yastsenko 1997; Rakovan and Jaszczak 2002). This theory postulates that once nucleated, graphite grows in a plane parallel to the (0001) surface to form hexagonal crystals. Subsequent growth occurs by addition of layers perpendicular to the (0001) surface. If this interpretation is correct, then single