Carbon isotope fractionation between calcite and graphite during high temperature metamorphism

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The carbon isotope exchange thermometer between calcite and graphite have been recently widely applied to amphibolite and granulite facies marbles (e.g. Kitchen and Valley, 1995). It has been proved that the temperature dependant fractionation is reliable up to temperatures of the order of 800°C. The fractionation between calcite and graphite nears unity at higher tempertures and hence is difficult to calibrate the thermometer at temperatures higher than 800°C. Here we try to emperically test the high tempertaure fractionation between calcite and graphite using marble samples from the high temperature granulite facies terrains of southern India and East Antarctica.

Marbles from the Trivandrum and the Madurai Block, from the southern granulite terrain were examined in this study. The Trivandrum Block comprises of granulite facies supracrustal rocks, while in the Madurai block massive charnockitic rocks predominate. Marbles bands occur in these two terrains as conformable units intercalated with quartzites. Texturally these are very coarse (up to several centimeters) and highly crystalline graphite crystals can be seen embedded within calcite. Calcite constitutes more than 80 modal % in most of the samples. The silicate mineral phases include phlogopite, forsterite, clinopyroxene and spinel; with occasional clinohumite, pargasite, and other calc-silicate mineral phases. Marbles from Lutzow-Holm complex, which is a granulite to amphibolite facies terrain with a regional peak granulite facies metamorphism at temperatures in the range 760-830°C and pressures of 7 ± 1 kbar were also examined.

Peak metamorphic temperatures were determined from fractionation of C-isotopes between calcite-graphite pairs using the recent calibration of Kitchen and Valley (1995). For example the marbles from the Trivanrum Block in Southern India gave fractionation range from 2.46‰ to 3.76‰, corresponding to a temperature range of 700 to 800°C. Out of the ten calcite-graphite pairs, 6 gave similar results. These results are significant that the carbon isotope thermometer can be used to determine accurate peak metamorphic temperatures in granulite facies rocks. The marbles form the Madurai block and the Lutzow-Holm Bay gave temperatures between 800 and 900°C.

Textural characteristics of graphite

Textural characteristics of graphite is often used as a sensitive indicator for isotopic equilibrium between calcite and graphite. Studies have shown that highly crystalline graphite in marbles normally preserve isotopic signatures of peak metamorphic equilibration, while isotopic disequilibrium has been reported in lower grade marbles which comprises of less crystalline graphite (Wada *et al.*, 1994). The textures and surface features of graphite from marbles were observed in detail. Two major types were identified; 1. Those which have crystalline hexagonal to semi-hexagonal shape with smooth high reflecting surface and 2. Those with irregular shapes and having dull surfaces. The textural features can be clearly identified under a reflecting microscope and more precisely in SEM. Arita and Wada (1991) has documented and discussed in detail about the origin of dull surfaced graphite, which they ascribed to the overgrowth of graphite on earlier coarse flakes. The present finding of dull surfaced graphite in crystalline granulite facies marbles corresponds well with their observations and is considerd to be similar overgrowth features.

Graphite with different surface features and textures were separated and analysed for their carbon isotopes, and the results indicate that there is a consistent depletion of d13C for graphite with rough surface. The rough surface is limited to a single surface layer only (as can be observed with the delamination of a layer shows high reflecting surface). In order to check this we measured the isotope ratio of graphite as a function of the grain size of dull surfaced graphite. Our results together with those of Arita and Wada (1991) show that graphite with rough surfaces indicates an overgrowth

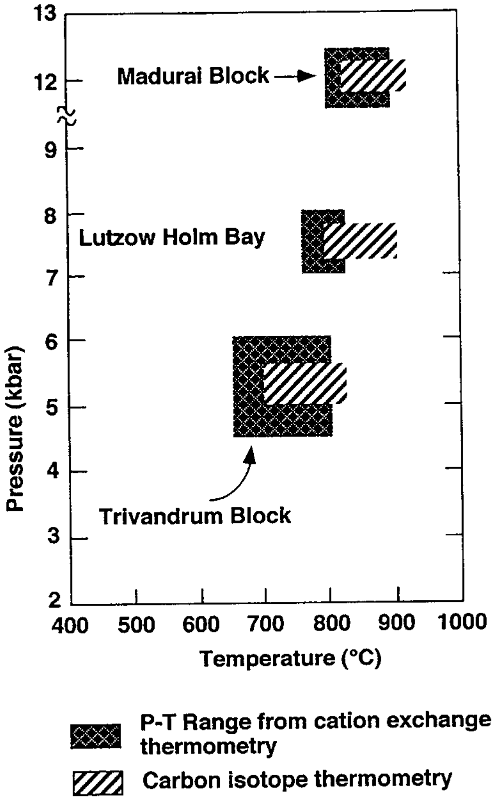

FIG. 1. A comparison of cation exchange thermometry and carbon isotope thermometry in the three terrains of the present study. Cation exchange thermometry for Madurai Block is after Raith *et al.* (1997) and for Lutzow Holm Bay is after Motoyoshi *et al.* (1989).

during the later stages of metamorphism and results in depletion of d13C. With out proper identification of the textural features the $\delta^{13}C$ values of graphite may give erraneous peak metamorphic temperatures.

Empirical test for carbon isotope thermometry

Cation exchange thermometers for orthopyroxene-bearing assemblages, near to the marble horizon from Trivandrum Block, southern India, gave temperature estimates of about 800 ± 50°C (Fig. 1). The results of carbon isotope thermometry using calcite-graphite fractionation (762 $\pm$ 65°C) is concordant with the cation exchange thermometery. In the Madurai Block, the carbon isotope thermometry points to high temperature metamorphic conditions. This is consistent with the recent findings of saphirine bearing assemblages from this terrain and the ultra high temperature metamorphism in Madurai Block (Raith *et al.*, 1997). The phase equilibria constraints suggest to a peak metamorphic temperatures of about 900 to 1000°C, which is comparable to the carbon isotope thermometry results of the present study (872°C$\pm$48). In the Skallen area of East Antarctica, Motoyoshi *et al.* (1989) estimated the peak metamorphic conditions during the regional granulite facies metamorphism in the Lützow Holm Bay to be between 760–830°C based on garnet-orthopyroxene thermometry. Here also the carbon isotope thermometry gave consistent results (848 ± 55°C).

In summary the carbon isotope exchange thermometry in granulite grade marbles yield reliable peak metamorphic temperatures. Precise measurement of isotopes and careful observation of textural features are critical in using the carbon isotope thermometry at high temperature metamorphic rocks.

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