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Relationship between structure, morphology, and carbon isotopic composition of graphite in marbles: Implications for calcite-graphite carbon isotope thermometry

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Abstract

Carbon isotope exchange between calcite and graphite is a useful and reliable geothermometer for medium- to high-grade marbles. However, in rare instances, such as at Naxos, Greece, apparent disequilibrium carbon isotope fractionation between calcite and graphite has been previously reported. In this study, new results are presented on the morphological features, X-ray diffraction studies, Raman spectroscopic studies, and carbon isotope studies of graphite. Three morphologically distinct graphite types are identified. The first type is fine grained with distinct polygonal crystal aggregates having smooth pinacoid faces. The second type consists of large botryoidal aggregates with typical crystal overgrowth features, and the third type is "normal" large platy crystals associated with phlogopite. Graphite morphological features using an FE-SEM suggests that the botryoidal aggregates are composed of complexly intergrown and stacked graphite layers, comprised of cone-helix structures. Different types of graphite display distinct Lc(002) and DG values as well as a sharp first-order Raman peak at ~1580 cm^{-1} with disordered bands. The presence of Raman disordered bands in fine-grained well-crystallized graphite is attributed to edge effects. Carbon isotope analysis of graphite reveals that marble with fine-grained well-crystallized graphite show a consistent isotope fractionation with the calcite, which perfectly match temperature estimates based on the mineral isograds. In contrast, coarse botryoidal graphite gives heterogeneous carbon isotope values (about a few per mill) and show anomalous carbon isotope fractionation between the calcite and graphite. The graphite associated with phlogopite also shows variations in the carbon isotope values. Combining morphologic, crystallographic, and carbon isotopic data we conclude that the variations in carbon isotopic composition were caused by the overgrowth of graphite on the preexisting grain and that morphological observations and structural characterizations of graphite crystals is a key for predicting isotopic equilibration during metamorphism.

Keywords: Graphite, calcite, marble, crystal morphology, Raman spectra, carbon isotopes, oxygen isotopes, Naxos