

CALCITE-GRAPHITE AND CALCITE-DOLOMITE THERMOMETRY OF HIGH PRESSURE MARBLES AND CALC-SILICATES: SYROS, CYCLADES, GREECE

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INTRODUCTION

Marbles and calc-silicates of the island of Syros have been divided into three distinct units: the Pirgos Marble, the Kastri Marble, and the Upper Marble Unit, based on their mineralogical characteristics observed on an outcrop scale (Schumacher and Helffrich, 2003). All of these units contain evidence of both the high pressure-low temperature metamorphic event ~ 55 Ma (or perhaps 80 Ma) and the later greenschist metamorphic overprint thought to have occurred ~ 25 Ma (see Bröcker and Enders, 1999).

The purpose of this study is to use stable isotope analyses of calcite + graphite and major element analyses of calcite + dolomite to estimate peak metamorphic temperatures for those rocks. Carbon and oxygen isotope analyses of calcite will also be used to determine the possible presence and role of fluids during the metamorphism of these marbles. Geothermometry and oxygen and carbon systematics are then compared with petrographic and microstructural data to determine relationships between variations in peak metamorphic conditions and final mineral assemblages.

Collectively, the results of this study will help determine geographic patterns of metamorphism. For example, the Oligo-Miocene greenschist overprint may not have had a homogenous effect on Syros marbles. Variations in temperature conditions, and in particular fluid motion, may be a cause of the variety seen in the calc-silicates and marbles

across the island. Additionally, knowledge of fluid interactions within marbles may help delineate open system behavior during metamorphism throughout Syros, and perhaps constrain fluid composition both within marbles and their neighboring silicate rocks.

By characterizing the crystallization patterns of marbles on Syros island, a better understanding of carbonate metamorphism in blueschist regimes both in the Cyclades and in subduction zone settings globally is possible.

METHODS

Calcite-Graphite Thermometry

Graphite in marbles is commonly derived from sedimentary organic matter deposited in carbonate (Valley and Cole, 2001). As graphite crystallizes within a marble, it exchanges carbon isotopes with the surrounding calcite. Because isotope exchange involves little volume change, the reaction is effectively independent of pressure, but rather is determined by the original carbonate-organics ratio, possible devolatilization reactions and presence of fluids, and ultimately peak temperature of formation (Clayton, 1981).

Exchange of carbon isotopes between calcite and graphite begins at about 300°C , usually attaining equilibrium at temperatures above 600°C . As the two materials equilibrate, the $\Delta^{13}\text{C}$ of graphite typically rises with increasing metamorphic grade, while the $\delta^{13}\text{C}$ of calcite becomes lower. Assuming no or little fluid

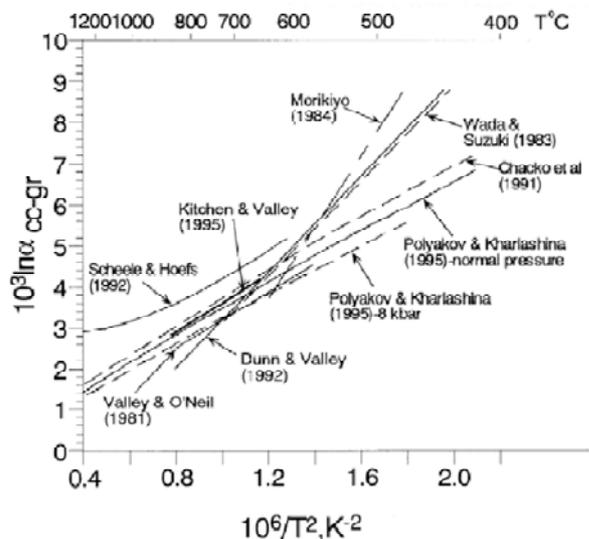


Figure 1: Multiple Cc-Gr versus temperature relationships, based on individual theoretical and empirical analyses. Modified from Satish-Kumar et al. (2002).

involvement, the whole rock $\delta^{13}\text{C}$ remains constant (Valley et al., 1986). Preservation of peak metamorphic temperatures is possible due to slow exchange, rate-limited by graphite, which helps prevent reequilibration during cooling (Valley and Cole, 2001).

Multiple relationships between the ratio of calcite and graphite isotopes and the temperature at which they have been equilibrated have been determined both empirically and theoretically (Figure 1). The equation devised by Dunn and Valley (1992) is considered to agree the most with other geothermometers, and is the one being used in this analysis. Their equation is:

$$\Delta^{13}\text{C}(\text{Cc-Gr}) = 5.81 \cdot 10^6 \text{T}^{-2} - 2.61 (\text{T,K})$$

Samples for this research were analyzed using mass spectrometry at the University of Iowa for calcite and at the University of Arizona for graphite. Material that was analyzed came from crushed samples of calcite, and graphite flakes separated from the same cubic inch of material.

Calcite-Dolomite Thermometry

Peak metamorphic temperatures can also be estimated using the distribution of Mg between calcite and dolomite (Rathmell et al., 1999). Magnesium partitioning between calcite and dolomite is a function of temperature along the calcite-dolomite

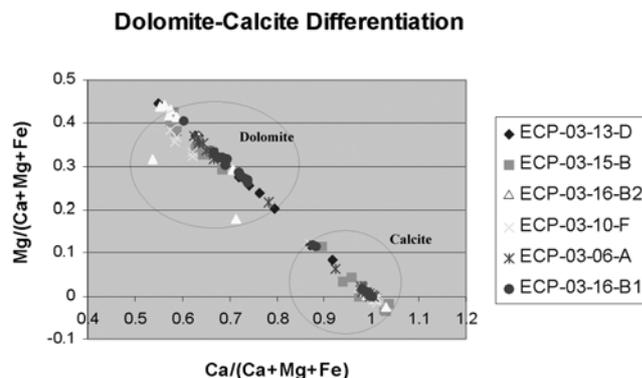


Figure 2: Mg and Ca proportions of dolomite-bearing samples. Only samples whose Ca fraction was greater than 0.85 were used in the calcite-dolomite thermometry.

miscibility gap (Letargo et al., 1995). This thermometer, unlike calcite + graphite, is generally independent of fluid composition, but can reequilibrate quickly during retrograde conditions, so it offers only a minimum in temperature estimates (Essene, 1983).

The chemical compositions of calcite and dolomite were measured using energy dispersive x-ray spectrometry at Colorado College. Because dolomite exsolves from calcite during retrograding, and is often associated with reequilibration, multiple analyses were collected for each sample. Samples determined to be dolomite (Figure 2) were not used in temperature estimation. Temperatures were estimated using the empirical equation of Anovitz and Essene (1987), which corrects for the presence of iron as a chemical component.

Fluid-Rock Interaction

By taking a series of samples of carbonate along transect from calcite to calc-silicate minerals, it may be possible to determine whether fluid movement associated with decarbonation reactions was present in Syros marbles, and if so, whether it was controlled by the presence of silicate minerals. Siliceous carbonates are commonly more favorable zones of fluid flow than pure carbonates, because they offer pathways through which fluid can travel (Valley et al., 1986). Changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ moving away from the silicic layer in a marble may determine how much decarbonation has occurred.

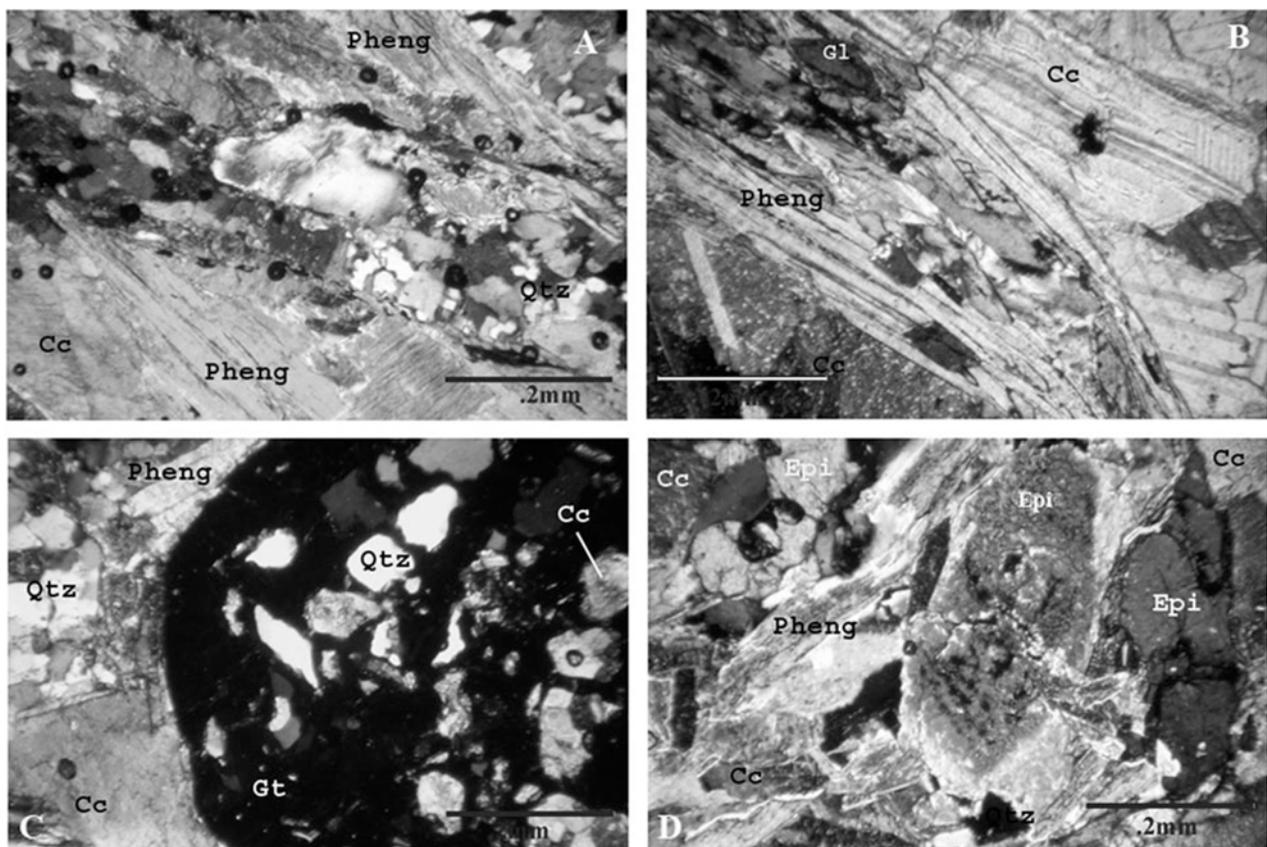


Figure 3: Mineral assemblages of different marble units on Syros: A = Pirgos, B, C = Kastri, D = Upper Marble.

RESULTS

Petrography

Although every unit contains some calc-silicate minerals, the Pirgos Marble has the smallest proportion of non-carbonates (Figure 3A). Being primarily composed of calcite, with some massive dolomite layers, it also shows equilibrium textures with quartz and white mica. In contrast to the Pirgos, both the Kastri and the Upper Marbles have complex calc-silicate assemblages (figure 3B-D). Mineral assemblages of the Kastri Marble vary geographically. For example, a sample from the southeastern corner of the island, near Vari, shows euhedral garnet overgrowing calcite, quartz and white micas. This was the only location where garnets were observed in marbles. Kastri Marble from the northern part of the island is also more glaucophane- and epidote- rich and dolomite-poor than more southern outcrops of the unit. Silicic sections of the Upper Marble Unit are rich in quartz, white mica, epidote and some glaucophane. It is noticeably different from Kastri Marble in its lack of dolomitic or graphitic marbles.

All marble units show evidence of dynamic metamorphism, primarily through oriented

micas and occasionally epidote, but also from elongate calcite and quartz crystals. In some samples, particularly in the Kastri Marble, evidence of static mineral overgrowth is also present.

Geothermometry

Initial estimates of peak metamorphic temperatures have been determined by calcite-dolomite thermometry. Six samples were evaluated, using mineral grains that had proportions of calcite endmember higher than 85 mole percent, implying calcite rather than dolomite or another carbonate endmember

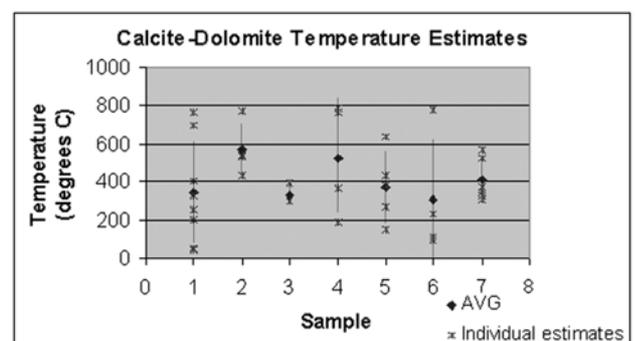


Figure 4: Temperature values of marble samples from Syros, determined using the calcite-dolomite thermometer outlined by Anovitz and Essene, 1987. Multiple calcite analyses were taken from each sample. Wide variety in estimated temperatures is likely due to reequilibration of calcite during retrograding.

(Figure 2). Of the six samples, one is from the Upper Marble Unit (6-U), two are from the Kastroi Marble (1-K, 2-K), and three are from the Pirgos Marble (3-P, 4-P, 5-P). Some of these samples yield a wide variety of temperature estimates, likely due to either reequilibration, or increased fluid movement due to an increase in silica content. On average, temperature estimates range between 300 and 500°C (Figure 4), with no consistent correlation to marble unit. Temperatures from the Upper Marble (6-U) are particularly variable, and may be an unreliable estimate of temperature due to excessive reequilibration. When the stable isotope data are available, analysis of graphite + calcite thermometry will be useful in narrowing the peak temperature margins shown. In addition, interpretations of fluid activity from the isotope data may also help explain current calcite-dolomite data.

DISCUSSION

The observed variety in the mineral assemblages of Syros marbles may be due to greenschist retrograding during the Oligo-Miocene, to variations in the bulk chemical composition of the original limestone and possibly to metamorphic fluid composition. For example, the garnets forming in marbles near the Vari unit imply higher temperature conditions, and appear to be overgrowths of previous minerals, and so may have grown during the Oligo-Miocene metamorphic event. A better understanding of geographic patterns related to metamorphic temperatures and fluids through isotopic analysis will be useful in analyzing sources of the mineral variety seen on Syros.

Initial temperature estimates using calcite + dolomite geothermometry imply peak metamorphic temperatures not higher than 550°C. These temperature estimates are quite variable, and may be less reliable due to reequilibration, likely associated with greenschist retrograding. It is hoped that stable isotope data will illuminate the possible metamorphic processes, specifically constraining temperatures at peak metamorphism, and help determine the role of fluids during metamorphism on Syros.

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