METAMORPHIC FLUIDS

Kevin Schweinar
RWTH Aachen University
Fieldtrip to Naxos, Greece. Summer term 2014

Abstract – Early investigations on fluid inclusion data and isotopic signatures of different lithologies reveal CO₂-rich pervasive fluids with CO₂ deriving from a deep source and decarbonation of carbonates. Later studies disproved these results based on further isotopic data. The authors suppose that the fluids with significantly lower X CO₂ as previously assumed to origin from dehydration reaction and metamorphic recrystallization.

INTRODUCTION

Naxos is the largest of the Cycladic islands in the Aegean Sea, Greece. It forms part of the Attic-Cycladic Massif which is situated between the crystalline areas of Attica and the Menderes Massif in Turkey and consists of a crystalline belt of marbles, schists and intrusive rocks. It has undergone at least two Alpine regional tectono-metamorphic events involving the pre-Alpine basement as well as the Mesozoic marbles and schists (Andriessen, et al., 1979; Buick & Holland, 1989; Urai, et al., 1990). The geology of Naxos may be divided into four units: (a) The migmatite complex surrounded by (b) the metamorphic complex (alternating calcitic/dolomitic marbles, mica schists, metavolcanics and metabauxites) which has undergone intense deformation and metamorphism of Alpine age, (c) a post-M2 granodiorite in the western part of the island (intruded into the metamorphic complex) and (d) a sequence of non-metamorphic, allochtonous rocks in tectonic contact with (b) and (c) (Buick & Holland, 1989; Urai, et al., 1990). This paper will deal with the metamorphic fluid present during the M2 event, its flow behaviour, composition and origin.

METAMORPHIC EVENTS

M1 was a compressional event induced through the subduction of the continental margin of Apulia below the active margin of Eurasia (Jolivet, et al., 2003). The subduction zone was approximately N-dipping and with an “upper plate moving south” sense of transport (Urai, et al., 1990). This metamorphic event had blueschist facies character (HP/LT) and has only been preserved in the south-east corner of Naxos where mineral assemblages such as glaucophane-epidote-chlorite-albite are still present (Buick & Holland, 1989). In other locations most of the M1-characteristics have been overprinted by the M2 event. The M1 event has been dated at 45 ± 5 Ma by Andriessen et al. (1979), based on K-Ar measurement in micas.

M2 may be divided into two phases. Phase M2a was a regional greenschist facies metamorphic event (25±5 Ma; Andriessen et al. (1979)), followed by M2b which was more locally restricted and had HT-LP (amphibolite-facies) characteristics (16 Ma), producing thermal domes. Both phases were the result of extensional tectonics forming a back-arc basin behind the subduction zone. M2 produced a metamorphic zonation (Barrovian metamorphism) surrounding a migmatite dome which was the result of the anatexis of mica schists and gneisses (Jansen & Schuiling, 1976; Urai, et al., 1990). Jansen & Schuiling (1976) estimated peak M2 conditions to range from 400°C SE on Naxos up to 700°C in the deepest part of the migmatite core, with pressures between 5 and 7 kbar.

Two further post-M2 can be distinguished. M3 was caused by the intrusion of the granodiorite in the western part of the island around 11.1±0.7 Ma ago. The relatively fluid magma intruded into metamorphic complex, causing a contact-metamorphism and metasomatism of the surrounding rocks. M4 is seen as retrograde metamorphism reflecting Late Alpine overthrust movements about 10 Ma ago (Andriessen, et al., 1979).

Figure 1 - Simplified geological map of the island Naxos (Buick & Holland, 1973).
METAMORPHIC FLUIDS
Already Schuiling & Jansen (1976) presumed a pervasive fluid phase to have been present during the metamorphic event only by petrographic investigations on mineral assemblages. Although they realised that the composition of the fluid phase was locally buffered and varied from place to place, they proposed that water and CO$_2$ played a major role (Jansen & Schuiling, 1976). Later studies also used fluid inclusion and stable isotope data (particularly $\delta^{13}$C and $\delta^{18}$O values) to distinguish fluid composition and its origin (cf. Rye et al., 1976; Kreulen, 1980; Baker et al., 1989).

FLUID FLOW EVENTS
Two major fluid flow events during M$_2$-phase can be distinguished based on observations of calc-silicate assemblages within the marble horizons (see fig. 2).

PROGRADE INFILTRATION
Upwards advection and diffusion of fluids from stratigraphically lower units through the low-permeable marbles led to randomly orientated mineral clusters at the basal contact to the pelitic schists (Baker, et al., 1989).

RETROGRADE INFILTRATION
The second fluid flow event formed the calc-silicate veins within the marbles. The infiltrated fluids were channelled along pull-apart fractures and more permeable zones within the marbles. They form, in contrast to the first generation, a well-developed lineation and thus, they have grown during peak to post-peak M$_2$ extensional phase of deformation (Baker, et al., 1989).

FLUID COMPOSITION AND ORIGIN
As mentioned above, fluid inclusions were used to determine the composition of the metamorphic fluids and additional stable isotope data give hints on the origin of these fluids.

Fluid inclusions containing CO$_2$ ± H$_2$O (mostly 60-90 mol-% CO$_2$) are predominant in schists and quartz segregations from almost all metamorphosed lithologies. Besides in quartz, inclusions in minerals such as kyanite, andalusite, corundum, garnet, feldspar, dolomite, calcite, beryl, tourmaline, scapolite and tremolite have been reported. In addition to these CO$_2$-rich inclusions, also aqueous inclusions with no CO$_2$-content have been identified, restricted to lenses of vesuvianite, grossularite and diopside in high-grade marbles, as well as to schists and quartz segregation below the corundum isograd. The latter might derive from dehydration reactions of adjacent pelitic rocks. Interestingly, no direct relationship between the metamorphic grade, lithology and the fluid composition has been found, also the change in time, which is indicated by successive generations of CO$_2$-rich inclusions, is very limited. Even the least

![Figure 2](image-url)

Figure 2- Schematic illustration of the calc-silicate assemblage locally developed at the contact of siliceous dolomite and underlying (higher-grade) pelites. Two different generations of minerals are distinguishable, as described in the text. Abbreviations used in this figure are as follows: diopside (di), tremolite (tr), calcite (cc) and dolomite (dol); f.g. and m.g. refer to fine grained (<0.1mm) and medium grained (0.1mm – 2mm) minerals (Baker et al., 1989).
metamorphosed schists contain CO₂-rich inclusions which are not likely to be related with their mineral assemblages. This gives rise to the idea that the fluids must have originated from somewhere else, such as from mineral reactions in siliceous dolomite or even from a deeper source (Kreulen, 1980).

The isotopic composition of fluids in terms of δ¹³C values can be seen in fig. 3. These values are considered to represent the common metamorphic fluids. Many of the δ¹³C values fall into a range between -1 and -5‰. Lower values are considered to be locally controlled by the interaction of graphite (δ¹³C = -22 to -27‰ - recent marine organic material) and the fluids (isotope exchange) (Kreulen, 1980).

Possible sources of the CO₂ represent:

a. CO₂ derives from decarbonation reactions within siliceous dolomites and other carbonate rocks. CO₂ liberated under the given metamorphic condition can be expected to have a δ¹³C value between +2 and +5‰. Lower values are considered to have a δ¹³C value between +2 and +5‰.

b. CO₂ produced by oxidation of organic matter in the rocks. Since the isotopic composition of graphite is very low, the resulting CO₂ will also have a low δ¹³C value.

c. CO₂ derives from a deep-seated source such as the upper mantle (degassing) or it might also be homogenised crustal CO₂. The isotopic composition of carbon dioxide from such sources is usually assumed to be low (-2 to -7‰).

Small amounts of calcite in some schists have δ¹³C values of -2 to -7‰ which is close to the equilibrium with the fluid and therefore, they might also be a source of CO₂. But since there are hints for a high fluid/rock-ratio (see below), it is more likely that the calcite lost its initial isotopic signature through isotope exchange with external fluids (Kreulen, 1980).

The difference between the slightly lower δ¹³C values for a deep-seated source of CO₂ and the values obtained from inclusions is explained by the mixture of 1/3 CO₂ from decarbonation reactions in marbles and 2/3 CO₂ from a deeper source. If all CO₂ had derived from decarbonation reactions, its δ¹³C value would have had to be lowered, which is again explained by the interaction with graphite. However, mass-balance calculations have shown that an unrealistic large amount of graphite would have been needed to do that in that extend (Kreulen, 1980).

Decarbonation reactions of siliceous marbles can be observed in isolated quartz lenses which show reaction rims of tremolite + calcite, following this reaction:

\[ 5 \text{ dol} + 8 \text{ qtz} + \text{H}_2\text{O} = 1 \text{ trem} + 3 \text{ cc} + 7 \text{ CO}_2 \]

Fluid inclusions samples from such lenses yield δ¹³C values ranging from -7 to +5‰. About 50% have positive values and are considered to derive from in-situ reactions. The negative values indicate that the fluids were not in equilibrium with the marbles. Furthermore, the values are in the same range as the ones obtained from the adjacent schists. This is an indication for possible leakage of the marbles which may have led to infiltration of externally produced fluids (cf. Baker et al, 1989). However, inclusions in schists within a few meters distance from the marble band show usual δ¹³C signature of -1 to -5‰ again which show that the amount of CO₂ produced by decarbonation were only small compared to those circulating through the schists. There is also further evidence that may prove a high fluid/rock ratio during metamorphism. Firstly, the mentioned independence of the fluid composition of lithology and metamorphic grade indicate that more fluid migrated trough the rocks than was produced in-situ by dehydration and decarbonation of the rocks. Furthermore, the overall isotopic composition falls into a narrow range of δ¹³C values between -1 and -5‰. As mentioned before, the δ¹³C values of calcite minerals in schists are too low for common marine carbonate sediments which indicate extensive isotope exchange with the metamorphic fluid (Kreulen, 1980).

However, Baker et al. (1989) stated in their newer investigations that the fluids in the prograde phase of

![Figure 3 – δ¹³C of fluid inclusion in quartz segregations in schists, arranged according to metamorphic grade. No trend is distinguishable. Average δ¹³C range from -1 to -5‰. Lower values are explained in the text (Kreulen, 1980).](image-url)
the metamorphism derived from dehydration of (partly graphite-bearing) pelites and $X_{CO2}$ was with a value of 0.3 considerably lower as reported by Kreulen (1980) ($X_{CO2} = 0.5-0.8$). Their conclusions were based on isotopic composition ($\delta^{18}O$ and $\delta^{13}C$) of minerals which are part of the meter-scale alterations in the basal marble band (fig. 2). The development of the calc-silicate veins described above, are explained by the infiltration-driven decarbonation reactions. They assume that the retrograde fluids derive from the movements of melts at peak $M_2$ and post-peak metamorphic recrystallization of the migmatite complex ($X_{CO2}$ initially <0.05). They found no evidence for such high amounts of CO$_2$ as reported by Kreulen (1980) nor that CO$_2$-rich fluids were pervasive during $M_2$. They showed that even a small amount of graphite in pelites, at temperatures below the equilibrium temperature of calcite-graphite (at 650°C), can explain the isotopic signature observed and this makes the presence of mantle carbon needless (Baker, et al., 1989).

REFERENCES


