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Infiltration-driven metamorphism, New England, USA: Regional CO_2 fluxes and implications for Devonian climate and extinctions

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ABSTRACT

We undertake thermodynamic pseudosection modeling of metacarbonate rocks in the Wepawaug Schist, Connecticut, USA, and examine the implications for CO_2 outgassing from collisional orogenic belts. Two broad types of pseudosections are calculated: (1) a fully closed-system model with no fluid infiltration and (2) a fluid-buffered model including an H_2O–CO_2 fluid of a fixed composition. This fluid-buffered model is used to approximate a system open to infiltration by a water-bearing fluid. In all cases the fully closed-system model fails to reproduce the observed major mineral zones, mineral compositions, reaction temperatures, and fluid compositions. The fluid-infiltrated models, on the other hand, successfully reproduce these observations when the X_{CO_2} of the fluid is in the range ~0.05 to ~0.15. Fluid-infiltrated models predict significant progressive CO_2 loss, peaking at ~50% decarbonation at amphibolite facies. The closed-system models dramatically underestimate the degree of decarbonation, predicting only ~15% CO_2 loss at peak conditions, and, remarkably, <1% CO_2 loss below ~600 °C. We propagate the results of fluid-infiltrated pseudosections to determine an areal CO_2 flux for the Wepawaug Schist. This yields $\sim 10^{12}$ mol CO_2 km^{-2} Myr^{-1}, consistent with multiple independent estimates of the metamorphic CO_2 flux, and comparable in magnitude to fluxes from mid-ocean ridges and volcanic arcs. Extrapolating to the area of the Acadian orogenic belt, we suggest that metamorphic CO_2 degassing is a plausible driver of global warming, sea level rise, and, perhaps, extinction in the mid- to late-Devonian.

1. Introduction

Since the turn of the twentieth century, the scientific community has recognized the global carbon cycle's effect on Earth's climate (Arrhenius and Sandström, 1903; Chamberlain, 1899). Geochemical box models (e.g. Berner, 1989) are commonly used to understand the mass balance associated with carbon cycling. While these models continue to improve, our progress in understanding the history of the global carbon cycle is ultimately limited by our knowledge of carbon fluxes in the past. In particular, the addition of CO_2 to the atmosphere via metamorphic processes remains poorly constrained. With estimates for the metamorphic carbon flux varying by well over an order of magnitude (e.g. Dasgupta and Hirschmann, 2010; Hayes and Waldbauer, 2006; Keleman and Manning, 2015; Kump et al., 2000), it is clear that more observational constraints are needed.

Decarbonation can be significantly enhanced by the infiltration of a water-bearing fluid during prograde metamorphism (e.g. Ferry, 1976, 1992, 1994, 2016; Ferry et al., 2013; Kerrick, 1977). Infiltration of H_2O lowers the activity of CO_2 in the fluid which drives reaction progress and increases CO_2 production as the system attempts to return to equilibrium (e.g. Kerrick, 1977). These CO_2-producing reactions are strongly dependent on fluid composition and cannot be modeled without knowledge of the amount and nature of fluid infiltration. Most significantly, a closed-system model may underestimate the degree of decarbonation and the mass of metamorphic CO_2 which is released. This effect is most pronounced at moderate temperatures (e.g. greenschist, amphibolite facies), when the infiltrating fluid has a relatively low concentration of CO_2, or when the time-integrated fluid flux is high.

Despite these complications, the fully closed-system approach to modeling metamorphism is common. With the relatively recent advent of pseudosection modeling (Connolly and Petrini, 2002; De Capitani and Petrakakis, 2010; Powell et al., 1998) it has become computationally efficient to calculate pressure–temperature phase diagrams for a fixed bulk composition. This tool is often utilized to estimate the pressure–temperature conditions reached by a rock with the assumption that the bulk composition observed today represents the rock's composition during the metamorphic stage of interest.

In particular, the classic closed-system decarbonation calculations of Kerrick and Connolly (2001a, 2001b) were instrumental in

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forming a basis for models hypothesizing that subducted lithologies undergo minimal CO_2 loss during prograde reaction. Similar modeling has been applied in collisional settings (e.g. Groppo et al., 2013, 2017). Gorman et al. (2006) demonstrate that limited fluid infiltration during subduction will drive decarbonation reactions, but suggest that the majority of carbon still remains as a solid in the subducting slab. Importantly, these results are sensitive to the degree of fluid infiltration; a more heavily infiltrated slab would be expected to release more CO_2 via metamorphism (Gorman et al., 2006).

Many global models do not explicitly account for continental decarbonation (e.g. Jagoutz et al., 2016), and some papers suggest it is negligible except at very high temperatures (e.g. Dasgupta, 2013). High temperature reaction is certainly a viable means to release CO_2, but fluid infiltration can depress the temperatures of decarbonation reactions and allow for significant carbon loss even at moderate metamorphic grades. Thus, constraining the nature and magnitude of fluid infiltration is essential to further consideration of metamorphic devolatilization and its impact on global-scale carbon cycling.

We therefore aim to constrain the extent to which open-system processes (e.g. fluid infiltration) were at play in a Barrovian metamorphic setting. By testing the viability of both open- and closed-system models, we can constrain the degree and nature of fluid infiltration during metamorphism and its effect on decarbonation. Ideally we would acquire this constraint using an efficient and computationally simple approach.

With these considerations in mind, we present the results of systematic thermodynamic modeling of regionally metamorphosed carbonate rocks from the Wepawaug Schist, Connecticut. This serves as a proof-of-concept for the use of closed-system thermodynamic modeling to constrain the history of metamorphic fluid infiltration. We calculate two broad types of pseudosections using bulk compositions measured in low-grade precursor rocks: (1) a fully closed-system model with no fluid infiltration and (2) fluid-buffered models including an H_2O–CO_2 fluid of a fixed composition. Consequently, we utilize closed-system modeling to consider the open-system process of fluid infiltration and its effect on metamorphic decarbonation.

Finally, we extrapolate these results to estimate a CO_2 flux for the metamorphism of the Wepawaug Schist and the Acadian orogenic belt as a whole. We compare this result to independent metamorphic flux estimates from the literature, and consider the timing of CO_2 release and its relationship to Devonian climate, sea level, and extinction events.

2. Geological setting

The Wepawaug Schist in southern Connecticut consists primarily of metapelitic rocks with intercalated metapsammitic beds and impure metacarbonate rocks which underwent Barrovian-style metamorphism during the Acadian orogeny from ~410 to ~380 Ma (Lancaster et al., 2008; Lanzirotti and Hanson, 1996). It is lithologically similar to the Waits River Formation in eastern Vermont which was the subject of multiple classic studies on metamorphic decarbonation in New England (e.g. Ferry, 1992; Léger and Ferry, 1993). The metaclastic rocks account for ~90% of the unit volume; metacarbonate beds are on the order of 1 cm up to 10 m thick with most falling in the range of ~10 to ~100 cm. Metamorphic grade increases from east to west with metapelitic rocks ranging from chlorite-zone conditions up to the staurolite–kyanite zone. The pressure was ~7 to 9 kbars and peak temperatures range from ~420 °C to ~625 °C (Ague, 1994, 2002; Hewitt, 1973).

Metacarbonate rocks can be broadly separated into four metamorphic zones. From lowest to highest grade they are the ankerite, biotite, amphibole, and diopside zones (Ague, 1994, 2002; Fritts, 1963, 1965a, 1965b; Hewitt, 1973; Palin, 1992), similar to elsewhere in New England (e.g. Ferry, 1992) (Fig. 1). Importantly, thermobarometry in the metapelitic beds allows us to constrain the spatial variation in P–T conditions (e.g. Ague, 1994, 2002; Hewitt, 1973) and then apply these robust constraints to the intercalated metacarbonate rocks. Additionally, the mole fraction of CO_2 in the metamorphic fluid (X_{CO_2}) has been previously constrained to lie between 0.01 and 0.15 for most samples – Ague (2002) estimates X_{CO_2} using the program TWQ (Berman, 1991) together with measured mineral compositions and field-based P–T estimates. Tracy et al. (1983) find consistent results using mineral equilibria from the three independent decarbonation reactions they observed. Thus, this unit offers an ideal opportunity to test the viability of open- versus closed-system modeling for the decarbonation of metamorphic rocks in a well-understood regional metamorphic setting at a large scale and over a range of metamorphic grades.

3. Sample description

Eight samples from the lowest grade ankerite zone were considered in this study (sample names in Appendix A; see Ague, 2002, 2003 for detailed sample descriptions). They have not undergone large amounts of metamorphic CO_2 loss but are otherwise similar in composition to the higher-grade rocks of the biotite, amphibole, and diopside zones (Ague, 2003). We therefore use their modern bulk compositions to represent the precursors of the higher-grade rocks. By forward modeling the metamorphism of these low-grade rocks up to higher temperatures we expect to reproduce the observed mineral zones and volatile changes.

Herein we focus our analysis on three representative samples – 184a, 189a, and Wep-29a. They contain calcite + ankerite + muscovite + quartz + rutile + plagioclase; samples 184a and 189a contain albite whereas sample Wep-29a has a higher Na/K ratio and instead contains abundant oligoclase. It is likely that at lower-grade Wep-29a contained paragonite, but it was consumed to produce plagioclase (Ague, 2003). Samples also contain minor graphite/organic carbon that likely contributed a small amount of methane to the metamorphic fluid. However, the mole fraction of methane in the fluid (X_{CH_4}) should be small ($<$~0.02) at the relevant P–T conditions (e.g. Ague, 2002; Chu and Ague, 2013), and we therefore ignore this component. In addition, there is minor pyrite (and at higher grades pyrrhotite) in some samples. However, at $<$1 wt% the bulk sulfur content of the samples is small and will have little effect on phase assemblages (Evans et al., 2010).

In addition, we consider sample W5, a higher-grade rock from the amphibole zone. W5 is of interest because its phase equilibria record an anomalously high X_{CO_2} for the region (Ague, 2002). Thus, W5 may record some different conditions or processes. It contains calcite + quartz + plagioclase + biotite + clinozoisite + amphibole + garnet + titanite. Despite reaching temperatures in excess of 600 °C, there is no evidence that W5 ever contained diopside (Hewitt, 1973; Ague, 2002).

The molar composition of each sample used for pseudosection modeling is given in Appendix A (Table A1), together with calculation details.

4. Methods

We perform two types of pseudosection modeling in the system NCKFMASHTC using Theriak-Domino (De Capitani and Petrakakis, 2010) and the thermodynamic data of Holland and Powell (1998) together with compatible activity models (Appendix A). The first type of pseudosection assumes the rocks were reacting in a fully closed-system that is well represented by the modern measured