Jervois Marbles Decarbonation Spreadsheet & Graph— Notes

Introduction

This spreadsheet uses published calcite (Cc) $\delta^{13}C$ data to illustrate how modeling of batch and Rayleigh decarbonation can be used to detect anomalous isotope depletions that may be caused by infiltration-driven metamorphism. The effects of closed system decarbonation in Jervois marbles are modeled by the method of Valley (1986) using end-member "batch" and Rayleigh devolatilization models. During "closed system" devolatilization reactions, like the reaction:

$$\text{calcite + quartz => wollastonite} + CO_2$$

$\delta^{13}C(Cc)$ is predicted to decrease as $^{13}C/^{12}C$ preferentially fractionates higher ratios into CO_2 (Valley, 1986). Batch devolatilization models a single event in which CO_2 and calcite exchange carbon, according to a temperature-dependent fractionation, and then CO_2 is removed from the rock. Batch devolatilization predicts less depletion and higher $\delta^{13}C$ values and defines the minimum value of $\delta^{13}C$ depletions due to decarbonation. Rayleigh devolatilization models $\delta^{13}C$ depletions as a continuous process whereby infinitely small aliquots of CO_2 equilibrate with the calcite and leave the rock. Detailed discussion of these models is given in Valley (1986).

The $\delta^{13}C$ (calcite) and wt. % calcite values used in the spreadsheet were measured on regionally metamorphosed [P = 2–3 kbar, T = 600°C] marbles in the Jervois region of central Australia (Cartwright et al., 1997). Since calcite is the primary carbon-bearing phase in the rocks studied, wt. % calcite in each sample may be used to approximate reaction progress.

The Spreadsheet

The below figure shows the spreadsheet graph—plotted as wt. % calcite vs. $\delta^{13}C$ with model curves. The pattern of $\delta^{13}C(Cc)$ vs. wt. % calcite recorded in samples from two parts of the Jervois area (Breakneck Hill and Bustard Ridge) rather different, likely reflecting differences in both initial rock $\delta^{13}C$ and fluid flow history. The graph in the spreadsheet is ideal for illustrating how these models are set up and how parameters like temperature and initial $\delta^{13}C(Cc)$ will affect batch and Rayleigh decarbonation models. I have not considered different workers' equilibrium fractionation factors—the Chacko et al. (1991) calibration is used—though this certainly is a point that could be mentioned. Highlighted cells indicated values for parameters that are "hotlinked" directly into the models so students can see immediately how the batch and Rayleigh model curves adjust to changing model conditions.

Try adjusting temperature first. Even though the temperatures at Jervois are fairly well constrained, varying it shows the sensitivity of the models to this factor. When you're done, return the temperature to its original value.

Now try varying initial $\delta^{13}C(Cc)$. It's apparent that this parameter is fairly important. Recall that if values fall outside the limits of the two models, their $\delta^{13}C$ values likely have been shifted by open system exchange with an infiltrating fluid. It's clear that the two suites cannot be modeled by a single initial $\delta^{13}C$ value. This likely reflects the variability in protolith $\delta^{13}C$. I found that the best configuration is to run the batch model through the values of unaltered marbles (see below figure), but to run the Rayleigh model through the Bustard Ridge data cluster at 70-80 wt. % calcite.

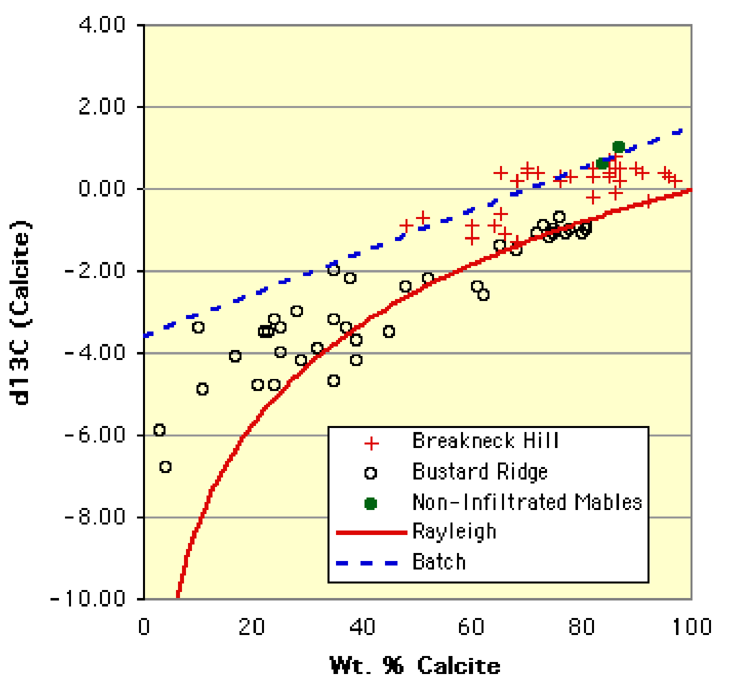
As expected for cases where there is infiltration-driven metamorphic reaction, a number of values fall below the Rayleigh model limit. Note that the Bustard Ridge marbles are also considerably metasomatised, so in this case, they have been infiltrated, and decreasing wt. % reflects reaction progress accompanying introduction of mass from igneous fluid sources.

There are a few take-away points of this exercise: (1) variable infiltration of fluids and both open and closed system behavior may be operative, as is observed worldwide; (2) knowing the initial $\delta^{13}C(Cc)$ of a system is helpful, but litholigic heterogeneity often requires that the batch and Rayleigh models are set to different values of initial $\delta^{13}C$ to account for this heterogeneity; (3) a data set can be fit by any model, but the rocks don’t lie. Read the Cartwright et al. (1997) paper.

Jade Star Lackey
UW—Madison

Evaluating measured d13C depletions by Batch and Rayleigh decarbonation Models

Temp (° C)	CO_2-Cc Δ13C	BATCH		RAYLEIGH	
600	3.62	Initial d13C (Cc)		Initial d13C (Cc)	
		1.5		0.0	
	10^6/T^2	Wt. % Cc	d13C	Wt. % Cc	d13C
	1.31	100	1.5	100	0.00
		0	-3.62	95	-0.19
				90	-0.38
				85	-0.59
				80	-0.81
				75	-1.04
				70	-1.29
				65	-1.56
				60	-1.85
				55	-2.16
				50	-2.51
				45	-2.89
				40	-3.31
				35	-3.79
				30	-4.35
				25	-5.01
				20	-5.81
				15	-6.84
				10	-8.30
				5	-10.79
				4	-11.59
				3	-12.61
				2	-14.06
				1	-16.53
				0.05	-27.14



References:

Cartwright, I., Buick, I., Maas, R., 1997, Fluid flow in marbles at Jervois, central Australia: oxygen isotope disequilibrium and zoning produced by decoupling of mineralogical and isotopic resetting: Contributions to Mineralogy and Petrology, v. 128, p. 335–351.

Chacko, T. Mayeda, T. K., Clayton, R. N., Goldsmith, J. R., 1991, Oxygen and carbon isotope fractionation between CO_2 and calcite: Geochimica et Cosmochimica Acta, v. 55, p. 2867–2882.

Valley, J. W., 1986, Stable isotope geochemistry of metamorphic rocks, *in* Valley, J. W., Taylor, H. P., and O'Neil, J. R., eds., M.S.A. Reviews in Mineralogy Series, v. 16 p. 445-489.