

# THERMAL DECOMPOSITION OF VARIOUS CARBONATES: KINETIC RESULTS AND GEOLOGICAL TEMPERATURES OF CONVERSION

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## Introduction

The standing paradigm by organic geochemists seems to be that thermal decomposition of carbonates does not occur until geological temperatures of 300°C+ are reached (e.g., Cathles and Schoell, 2006). However, measured kinetic parameters for various carbonates suggest a range of temperatures for the onset of thermal decomposition of carbonates ranging from 100°C to 280°C. The likely cause of this misconception is that carbonates require such high temperatures to decompose under laboratory conditions, i.e., upwards of 800°C for calcite. The problem with this assumption is that decomposition rates are governed by kinetic parameters, probability factors (A) and activation energies (Ea).

## Experimental

Kinetic data were measured by open-system, non-isothermal pyrolysis with the effluent coupled to an infra-red detector on the pyrolysis instrument.

## Results

Decomposition profiles from multiple heating rates and the Kinetics2000 program were used to calculate kinetic parameters for 3 different carbonate rock matrices (Table 1).

These kinetic data were used to calculate carbonate transformation ratios and vitrinite reflectance at an arbitrary, average geological heating rate of 3.3°C/Ma (Figure 1). Interestingly these data are supported by a number of studies by inorganic geochemists who have conducted kinetic experiments using TGA or other techniques (e.g., Gotor et al., 2000 (siderite); Rao, 1996 (calcium carbonate)). Siderite decomposition was the reason Rock-Eval S3 analysis was held to 390°C or less – to avoid inorganic decomposition inflating the S3 organic CO<sub>2</sub> value.

## Discussion

From these data it is obvious that siderite decomposes at temperatures contemporaneous with early oil generation, calcium carbonates with early gas generation, and calcites at the dry gas deadline. Dolomites and dirty carbonates are much more complex showing a range of decomposition profiles and, in many matrices, bimodal decomposition profiles due to the relative percentages of metal complexes within dolomites, e.g., iron-rich vs. magnesium-rich dolomites.

While CO<sub>2</sub> gas may be part of a given gas pool, it is reactive so it may not necessarily result in increased yields of carbon dioxide in a reservoir. However, it may impact the early fracturing of the rock fabric prior to extensive hydrocarbon generation.

Siderite		Dolomite-1		Calcite	
A=	3.03E+05 /sec	1.00E+08 /sec	1.00E+10 /sec		
Ea (cal/mole)	Reaction (%)	Ea (cal/mole)	Reaction (%)	Ea (cal/mole)	Reaction (%)
35175	0.44	42300	0.22	59170	0.44
35538	5.40	42750	0.88	59780	5.40
35900	24.20	43200	2.70	60390	24.20
36263	39.89	43650	6.48	61000	39.89
36626	24.20	44100	12.10	61610	24.20
36988	5.40	44550	17.60	62220	5.40
37351	0.44	45000	19.95	62830	0.44
		45450	17.60		
		45900	12.10		
		46350	6.48		
		46800	2.70		
		47250	0.88		
		47700	0.22		

Table 1. Kinetic parameters determined on three rock samples composed of different carbonate minerals. Siderite and calcite carbonate minerals were very consistent in their decomposition profiles; however, dolomites proved to be highly variable depending on the carbonate-complex.

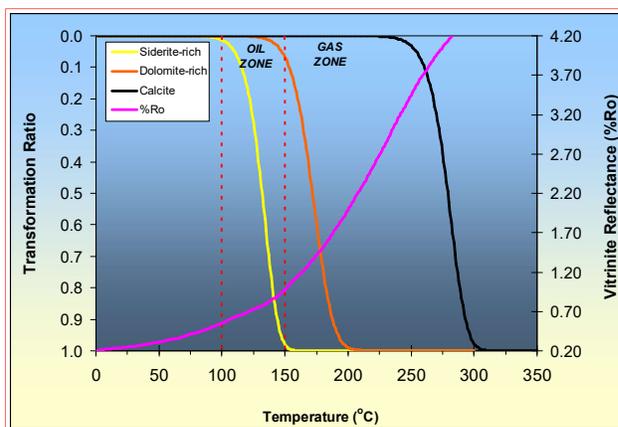


Figure 1. Decomposition profiles of various dirty carbonates contained in a variety of rock matrices. These data are derived from open-system pyrolysis experiments using infra-red detectors and calculated Gaussian kinetic parameters. The kinetic data are modeled at an arbitrary heating rate of 3.3°C/Ma. Error functions are relatively high for the dolomite and it was necessary to use a Gaussian model to fit the multiple peaks. The dolomite kinetics have by far the highest error function, whereas the error function in the siderite and calcite was very low yielding excellent fits.

Of course a potential side reaction of CO<sub>2</sub> release could lead to increased acidity of formation waters, thereby increasing further CO<sub>2</sub> release and perhaps additional micro-fracturing and porosity.

Unconventional shale gas reservoirs have variable percentages of CO<sub>2</sub> (<1%) to upwards of 15% of the total gas, but it is not known whether this gas is from diagenetic reactions releasing CO<sub>2</sub> from kerogen or if some of the gas is derived from labile carbonate decomposition either from thermal or decarbonation processes.

Generation of carbon dioxide also impacts saturation of available adsorption sites in organic matter. As carbon dioxide has stronger adsorption affinity than methane, but lower than other gaseous hydrocarbons such as ethane, propane, and butanes, it can displace methane or restrict methane from being adsorbed by solid organic matter surfaces. This enhances the release of methane for migration (also possibly fractionation) and production, e.g., from coals or shales. Thus understanding the carbonate composition is an important parameter to evaluate unconventional shale gas and coalbed methane production and stimulation.