Kinetics of Green River Oil Shale

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What is Oil Shale?

- Organic carbon known as *Kerogen* bound to an inorganic mineral matrix
- It can be precursor to oil given enough heat and time
- It is considered a non-conventional oil resource

Oil Shale

Siskin Model

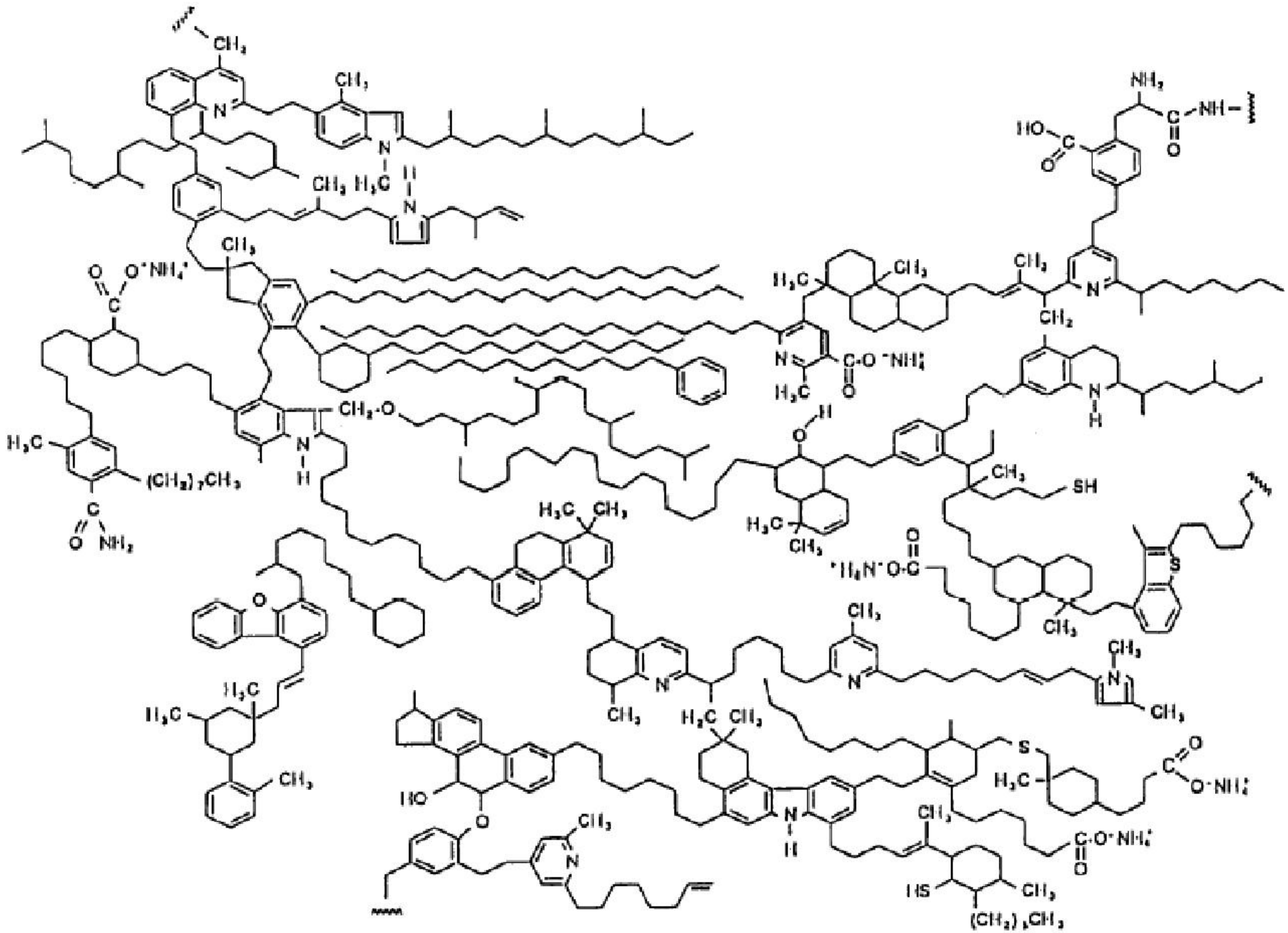
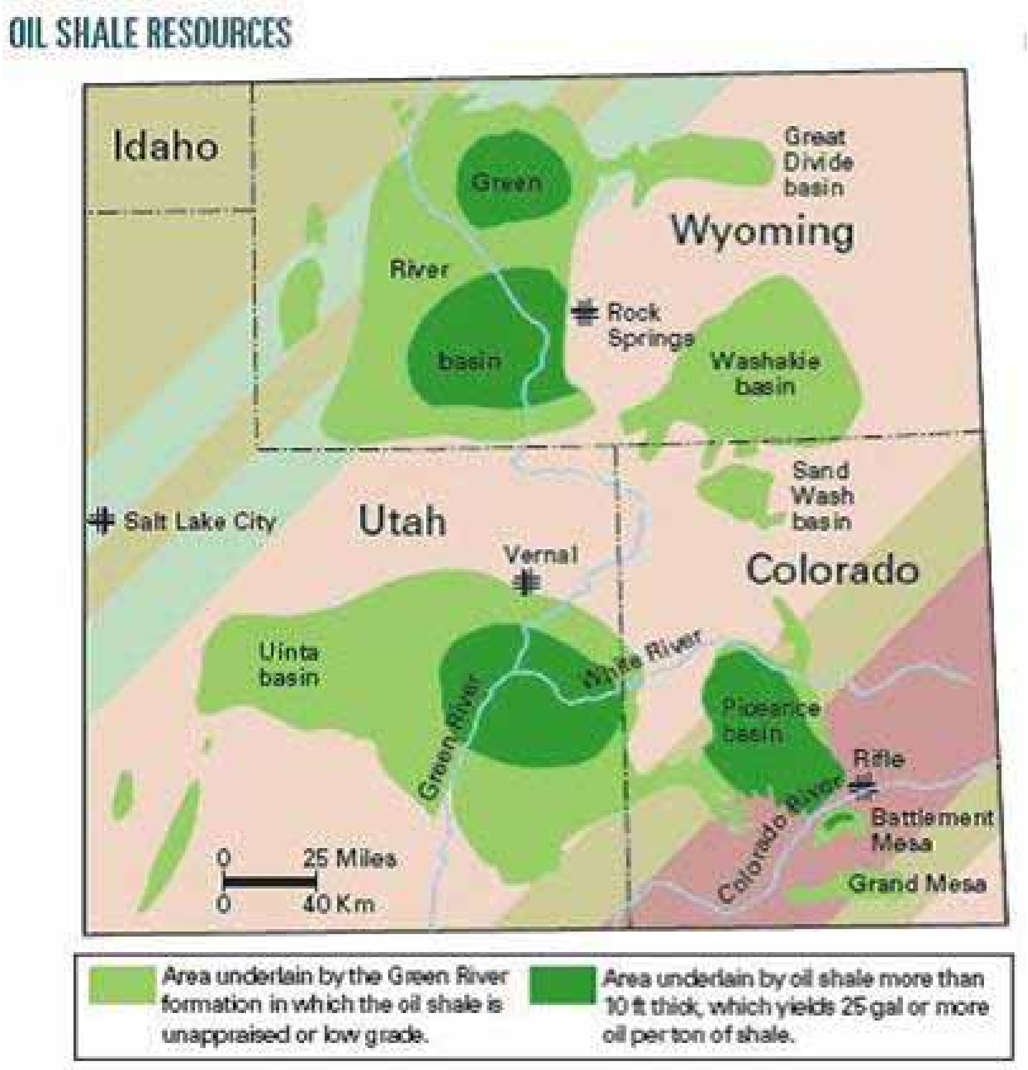


Figure 1. Siskin's model of organic material in Green River Oil Sale.[6]

Where is it located?



How much is there?

- Conservative estimates are 2.9 trillion barrels world wide which is twice the proven reserves of conventional oil
- In the United States there are estimates of 2 trillion barrels of which some fraction is recoverable
- The Energy Information Administration reports that the United States uses approximately 7.6 billion barrels per year

Past Work

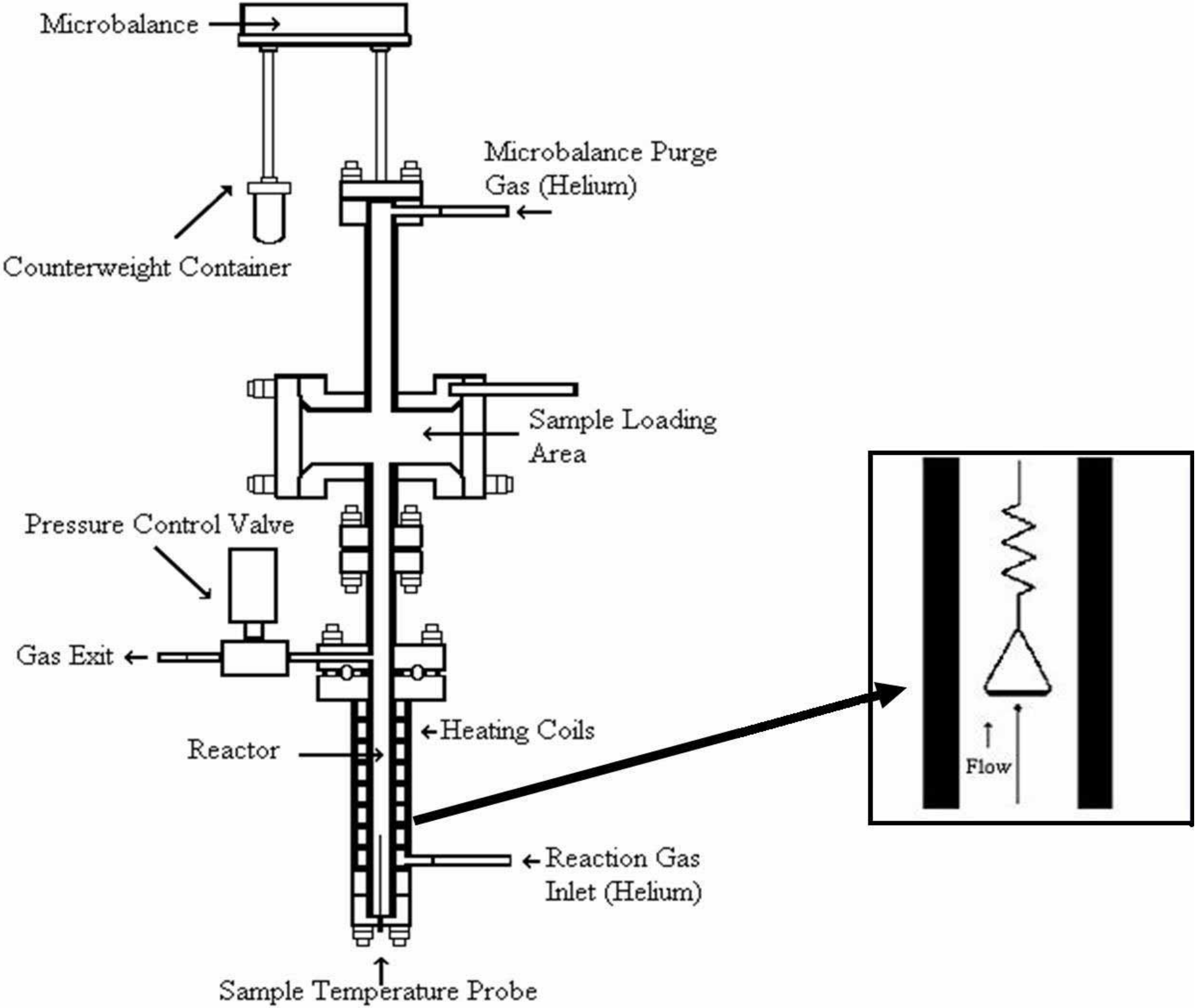
- A few decades ago there was moderate interest in characterizing and exploiting the oil shale resource
- The methodology of recovering the resource was to mine it and retort it on the surface which was environmentally harmful
- Consequently almost all characterization of the resource was done at atmospheric retorting conditions

Current Work

- Some of the recent approaches (as reported publicly) are to recover the resource in an *in-situ* process
- The conditions for *in-situ* differ somewhat than the previous atmospheric methods
- Pressure is one notable difference

Our Work

- We use non-isothermal TGA methods to determine kinetic parameters at various pressures and heating rates
- We can then determine the effect of pressure and heating rate on the kinetic parameters
- We also perform the same TGA work on oil shale and extracted kerogen to determine the effect of the mineral matrix

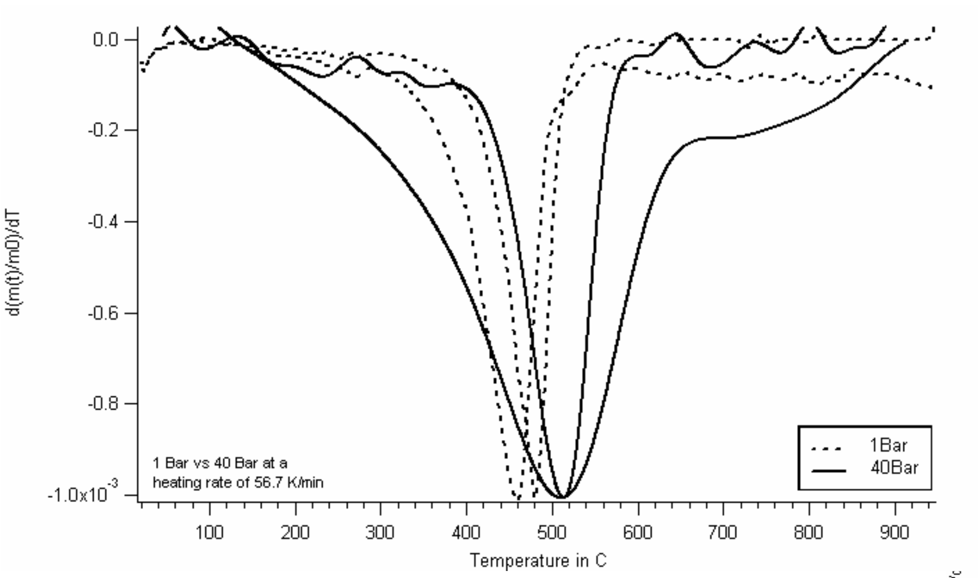

Microbalance
Microbalance Purge
Gas (Helium)
Counterweight Container
Sample Loading
Area
Pressure Control Valve
Gas Exit
Heating Coils
Reactor
Flow
Reaction Gas
Inlet (Helium)
Sample Temperature Probe

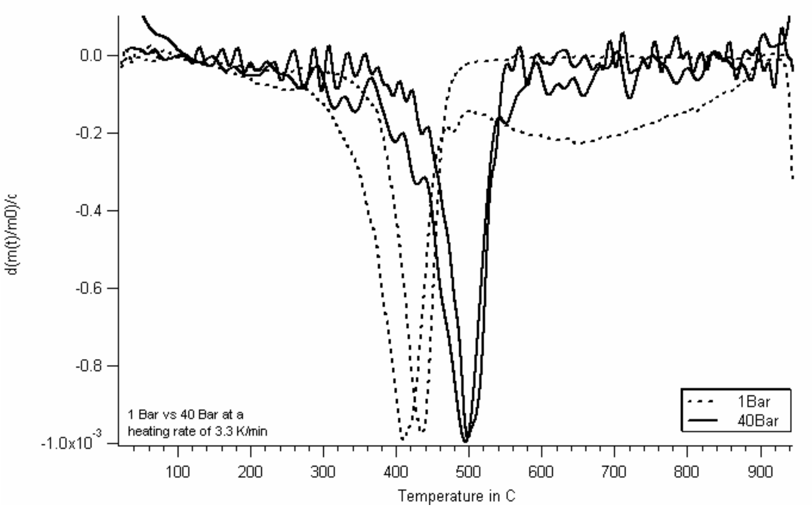
Experimental Matrix

Pressure (bar)	Heating rate (°C/min): 4	Heating rate (°C/min): 60
1	Low Heating Rate Low Pressure	High Heating Rate Low Pressure
40	Low Heating Rate High Pressure	High Heating Rate High Pressure

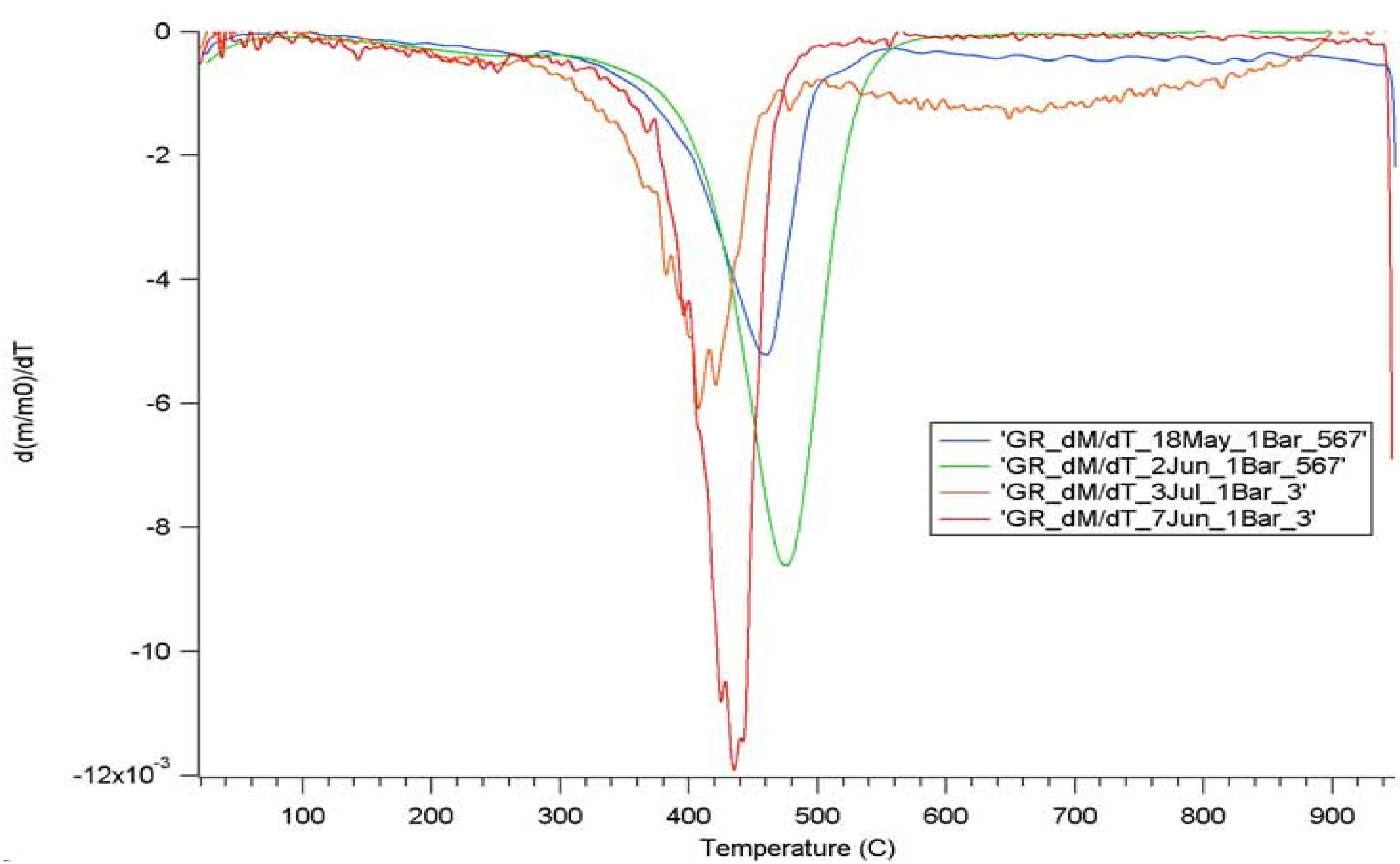
Carrier gas: He (1.4 slpm), ≈30 mg sample

Overview of Results

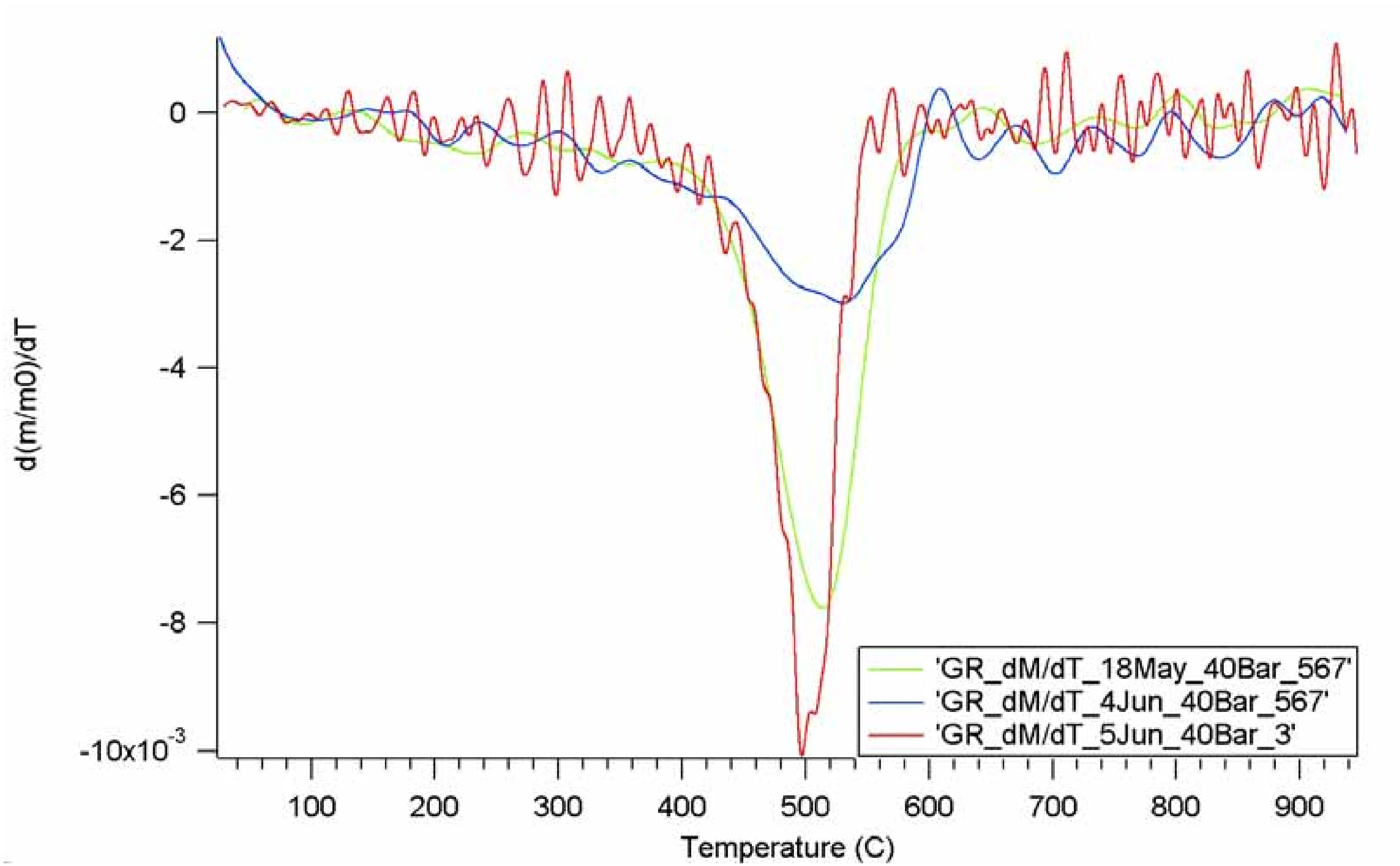




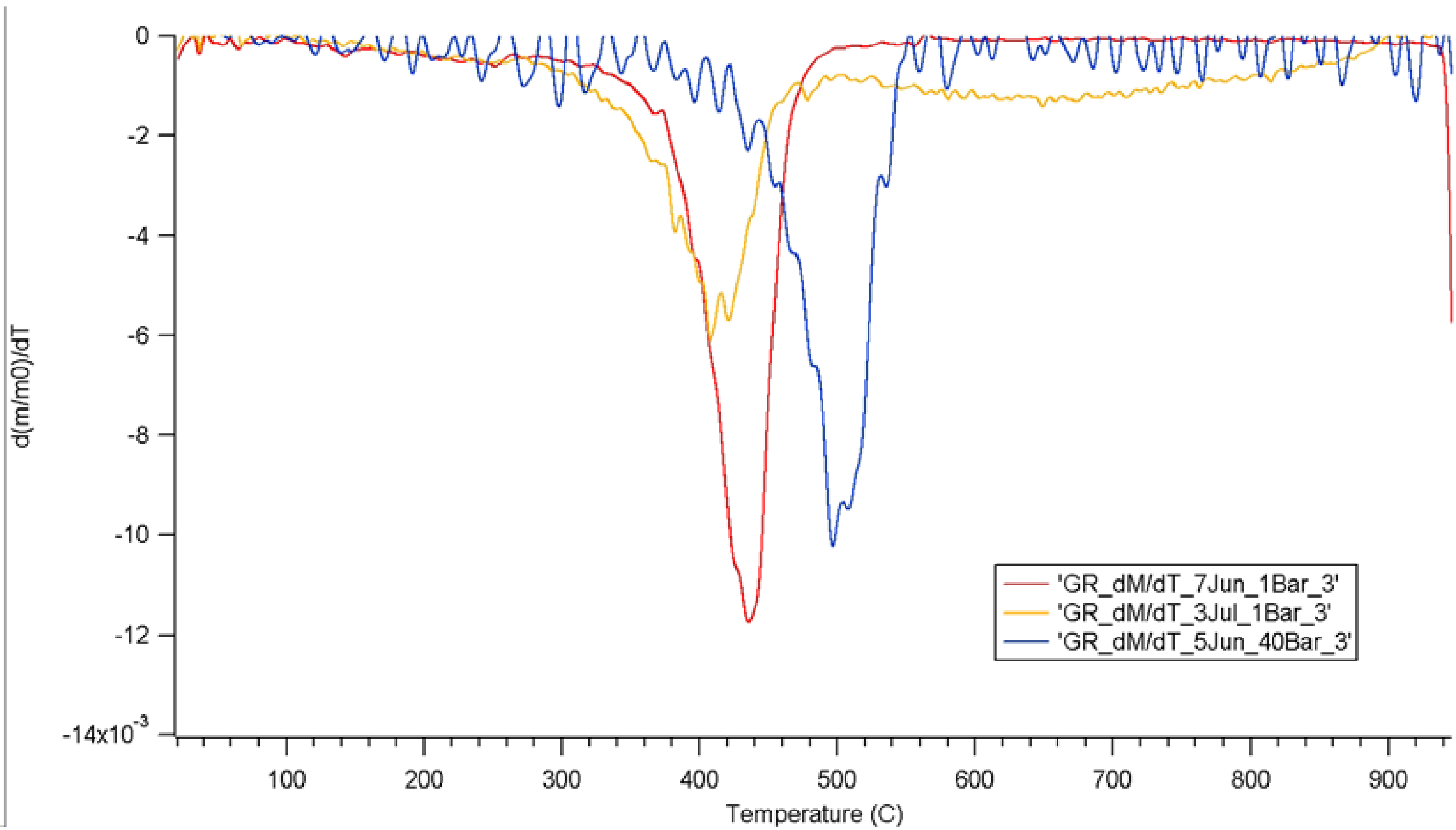
GR 1 Bar 3.3 C / min vs 56.7 C / min



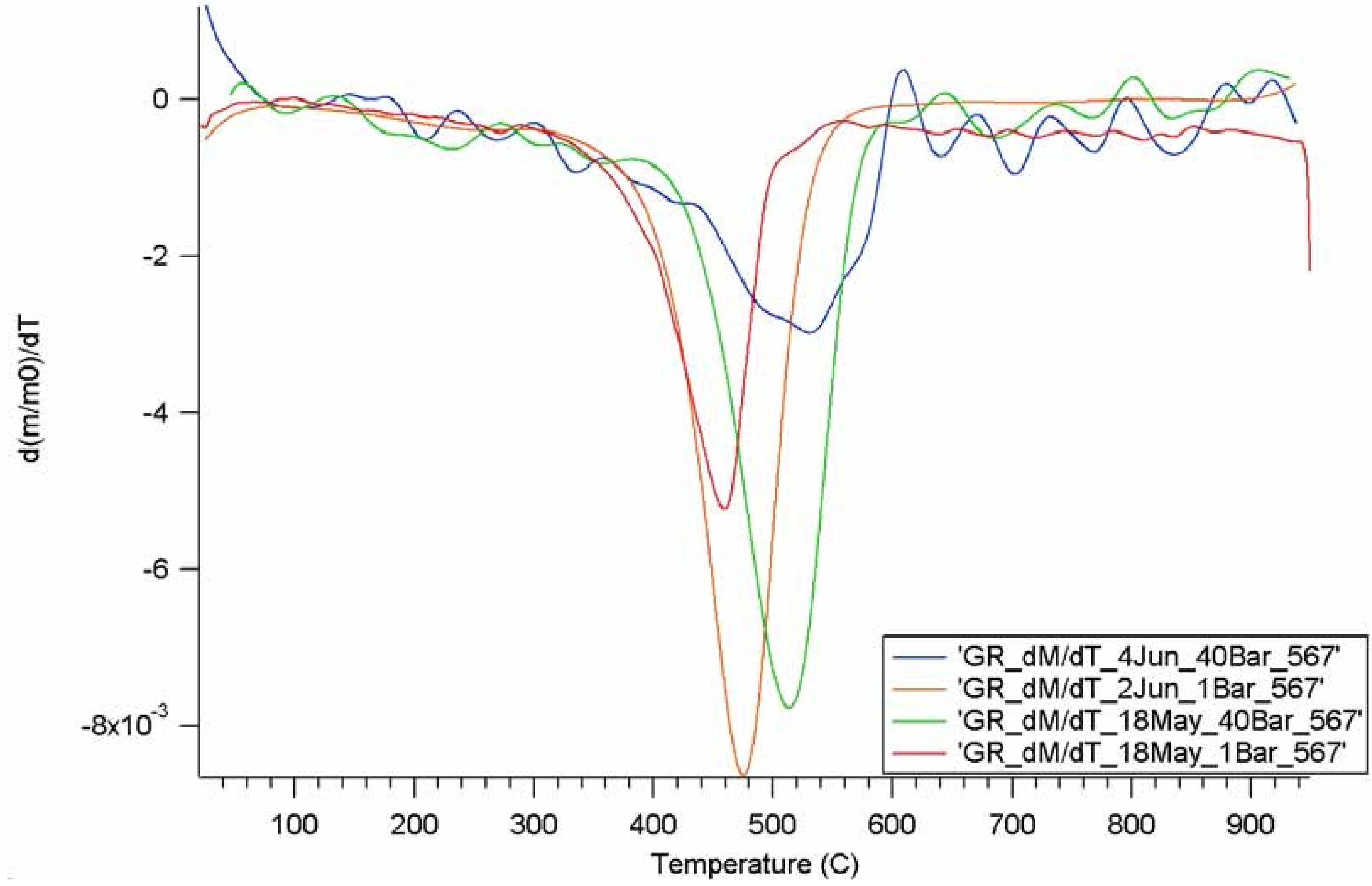
GR 40 Bar 3.3 C / min vs 56.7 C / min



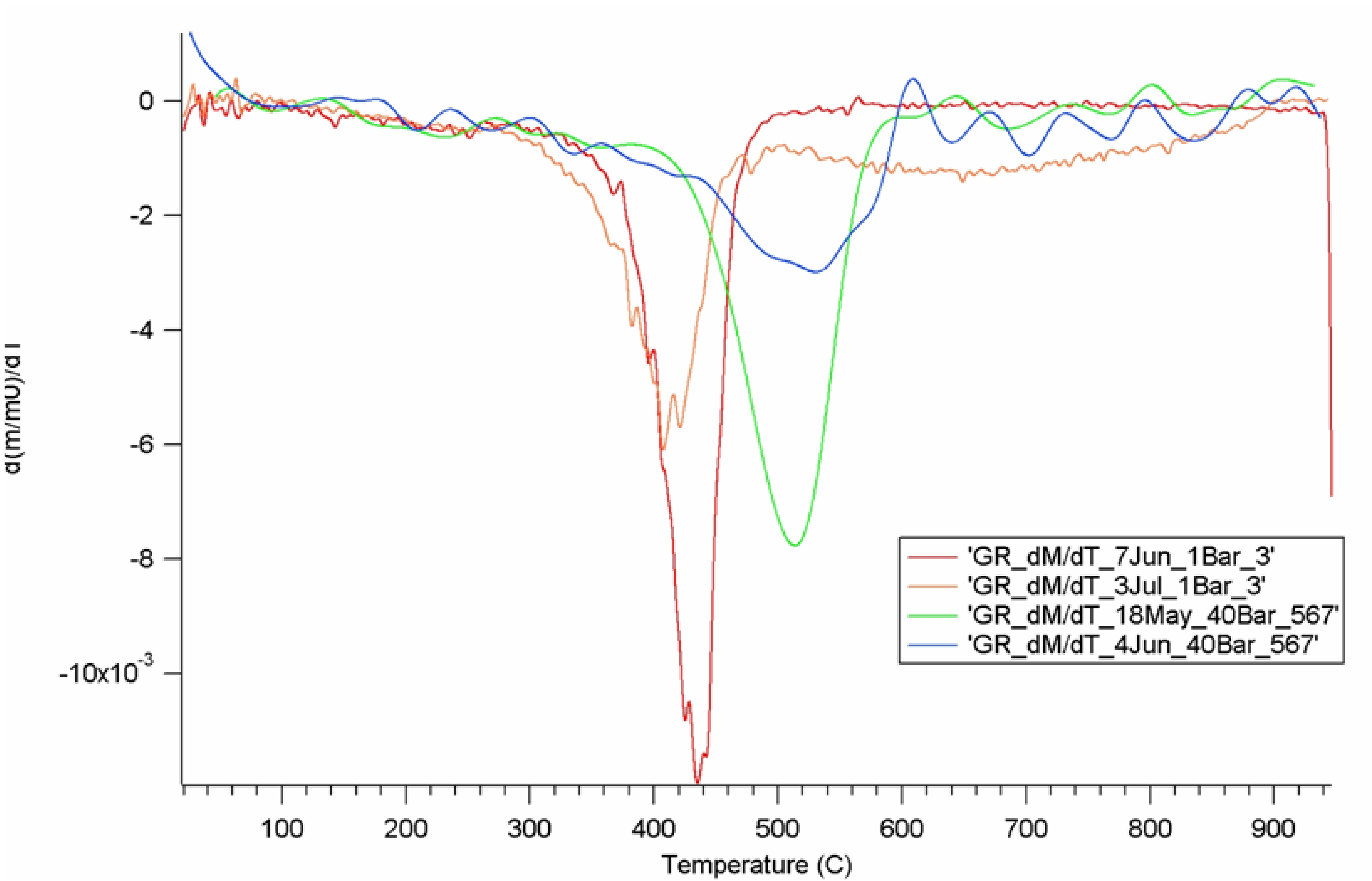
GR 1 Bar vs 40 Bar 3.3 C / min



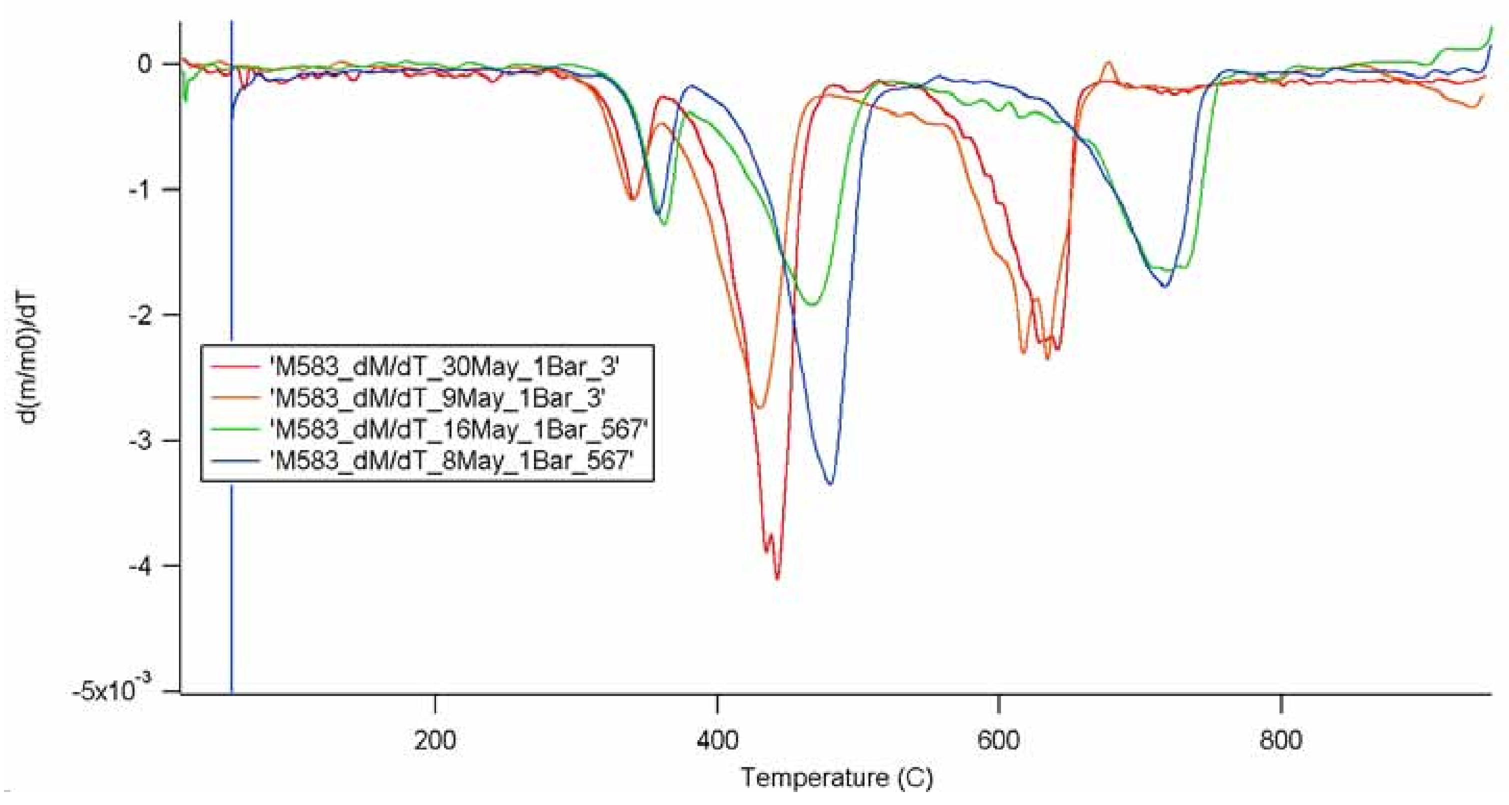
GR 1 Bar vs 40 Bar 56.7 C / min



GR 1 Bar 3.3 C / min vs 40 Bar 56.7 C / min



M583 1 Bar 3.3 C / min vs 56.7 C / min

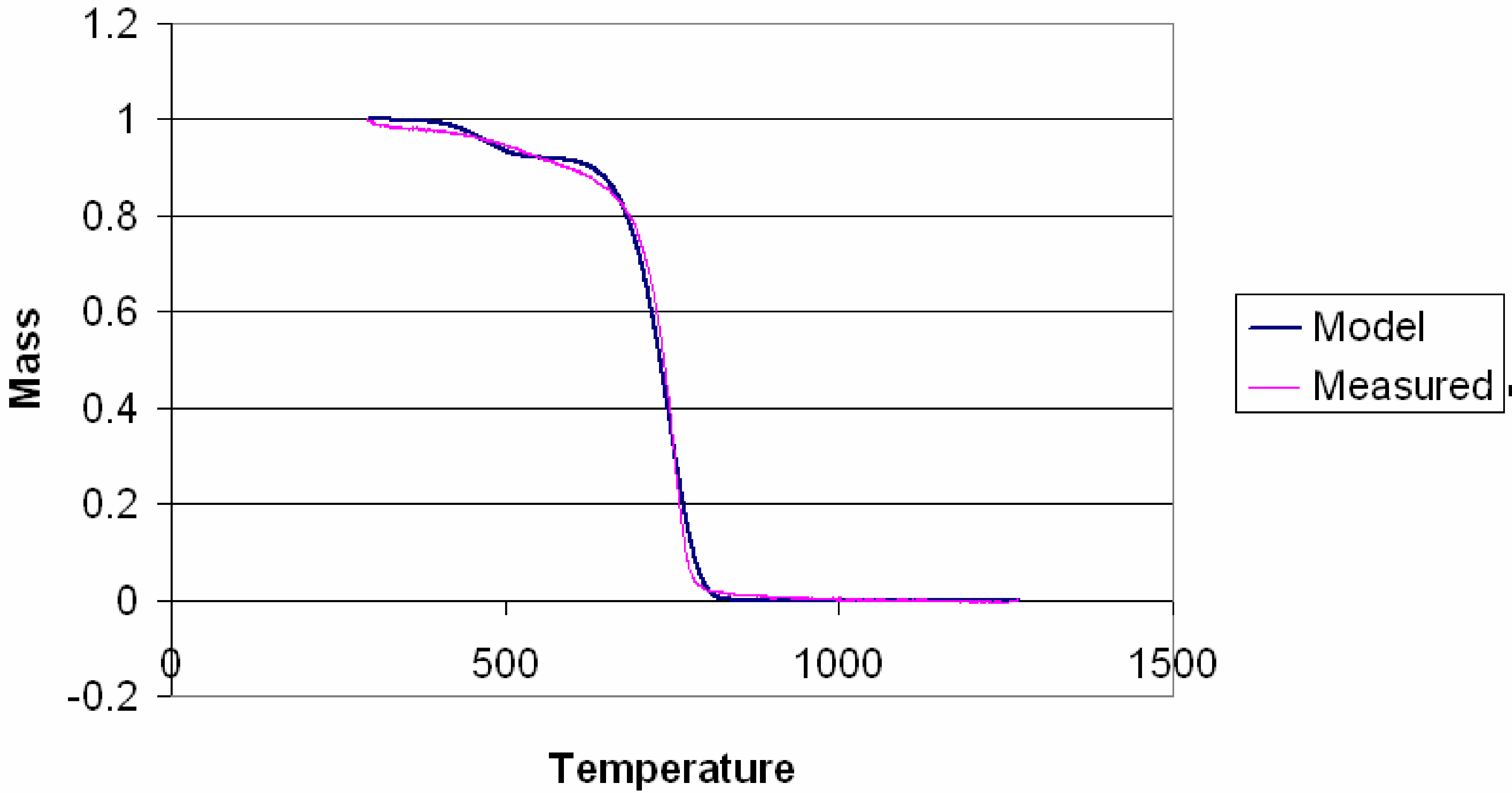


Activation Energy

- Assumed parallel global first order reactions
- Uses Arrhenius equation with the activation energy and pre-exponential factor as adjustable parameters

$$\frac{dm_i}{dt} = k \cdot m_i^n$$

Activation Energy Result



Our Results for Kerogen

	1 bar 3.3 K/min	1 bar 56.7 K/min	40 bar 56.7 K/min
m_1	0.74	0.84	0.74
A_1 (1/s)	3.91×10^8	7.27×10^9	3.70×10^{10}
E_1 (kJ/mol)	168	157	174
m_2	0.26	0.16	0.26
A_2 (1/s)	0.07	1.11	574
E_2 (kJ/mol)	35.3	24.0	45.3

Questions?