Variable liquid decarbonation methods for $\delta^{13}C_{org}$ analyses in sedimentary rocks

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1. Motivations

- Carbon isotope analyses ($\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$) are important for carbon isotope stratigraphy, carbon cycle modeling, and understanding of Earth history [e.g. 1]
- Sample preparation (e.g. **carbonate removal**, or "**decarbonation**" may bias measurements in $\delta^{13}C_{org}$ [6,7]
- No standard methodology for preparing samples; goal is to remove carbonate C (with distinct $\delta^{13}C$ signature) while preserving organic carbon (OC)

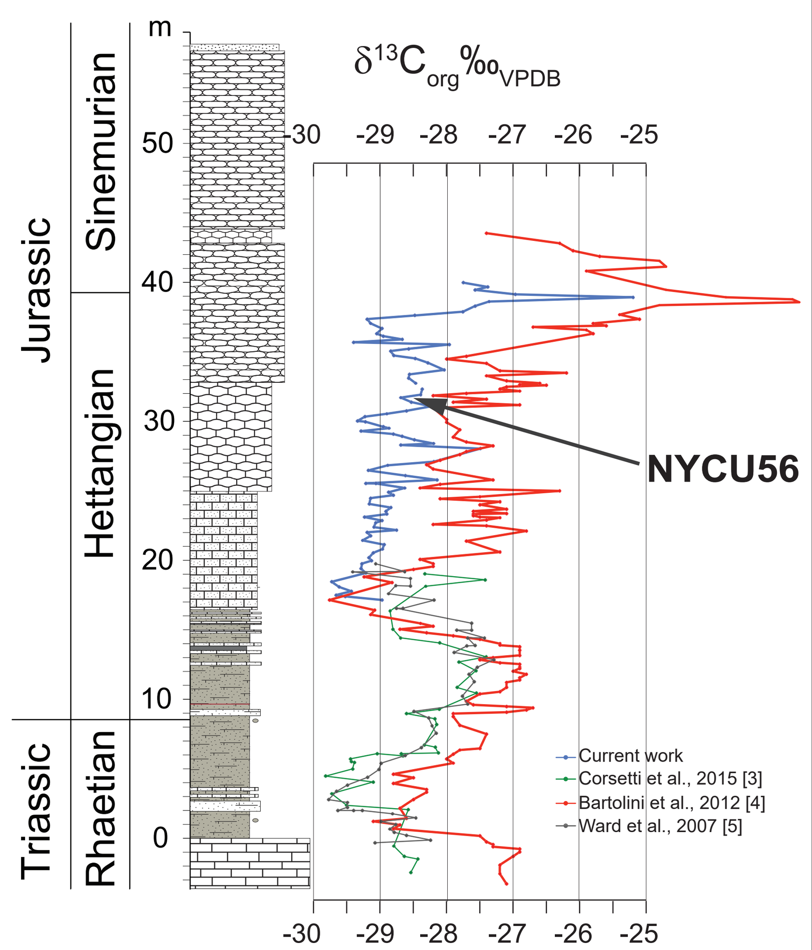
Ex: Discrepant C isotope records: due to different decarb methods?

Figure 1.

- $\delta^{13}C_{org}$ curves from same section (New York Canyon, Nevada Triassic-Jurassic boundary section) from multiple studies [3-5]
- **Red [4]** and **blue (this study)** curves are offset by 1-2‰ and show different timing
- Differences in $\delta^{13}C_{org}$ results can change interpretations of carbon cycle perturbations

This study aims to understand why the same analyses do not produce the same results

We hypothesized that discrepancy between curves is due to recalcitrant dolomite left over in samples after treatment



Here, we test variable liquid decarbonation methods: temperature, time, and sample grain size

2. This study

- Test variable decarbonation temperatures (20°C, 70°C), times (10min, 1hr, 2hr, 4hr, 8hr), and grain sizes (<75µm, 75-250µm, 425-991µm) on samples [e.g. 6,7]
- Samples from two localities that span the Triassic-Jurassic boundary, and a dolomitic rock for reference
- Petrographic observations to identify samples containing dolomite (e.g. Fig 2)
- Measured $\delta^{13}C_{org}$ values of samples to understand effect of decarbonation temperature, time, and grain size

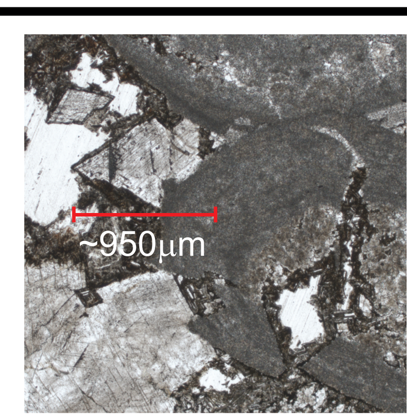


Figure 2. Beck Springs Dolomite; contains ~950µm dolomite rhombs, observed petrographically

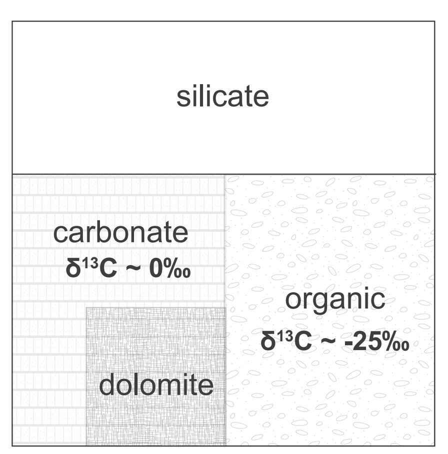


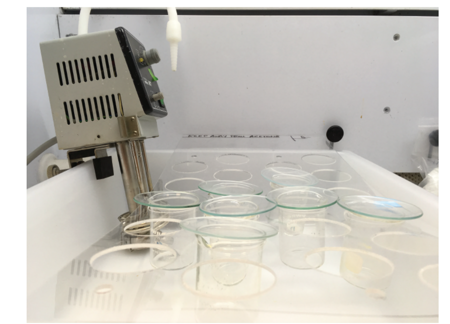
Figure 3: Schematic makeup of a sedimentary rock
Dolomite is more difficult to dissolve, so if left in measurements of $\delta^{13}C_{org}$, the sample's isotopic value will be heavy [6,7]

3. Methods

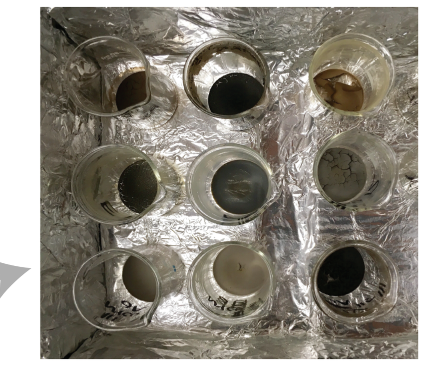
1. Samples cut to eliminate weathered surfaces and powdered with Rocklabs disk crusher or SPEX mixer/ball mill

2. Medium and large grain samples separated with Duall standard sieves

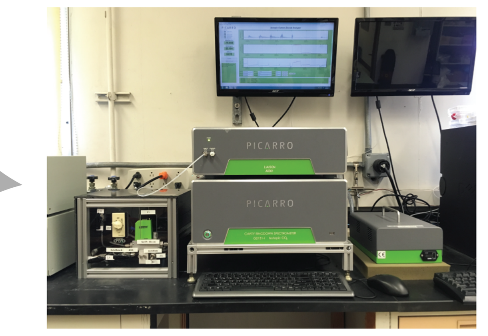
3. Samples weighed out (~1-1.5g) in beakers; acidified in 1M HCl and heated in water bath, varying time and temperature in the water bath *Medium & Large grains treated at 70°C for 60min



4. Samples rinsed 3X in DIW, placed in drying oven at 50°C, then scraped and re-crushed into a fine powder



5. Samples then combusted in elemental analyzer coupled to a Picarro Cavity Ring Down Spectrometer to measure $\delta^{13}C_{org}$ and %OC

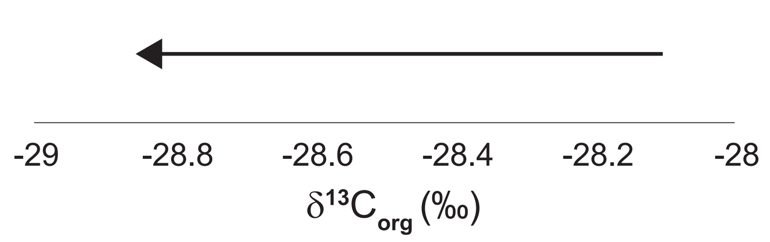


4. Results and discussion: Deviation from mean $\delta^{13}C_{org}$ values for all samples tested represented as $\Delta\ \delta^{13}C_{org}$

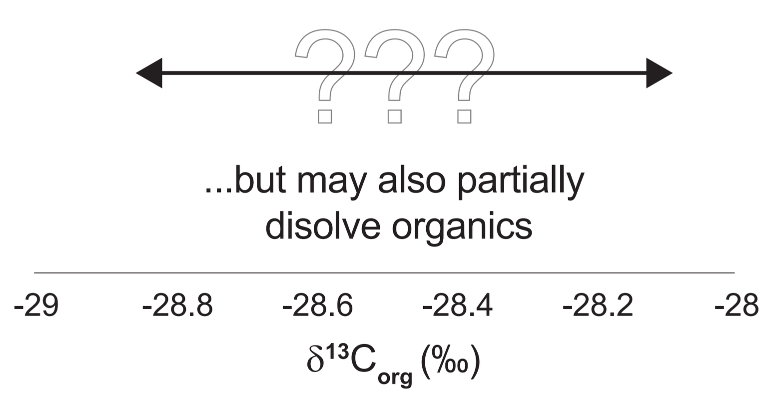
Figure 4: Hypothetical trends

What might we expect the data to look like with each changing variable?

5a. Increased temperature should aid dolomite dissolution



5b. Increased time should allow acid to fully react ...but may also partially disolve organics



5c. Larger grains = decreased total surface area = incomplete decarb?

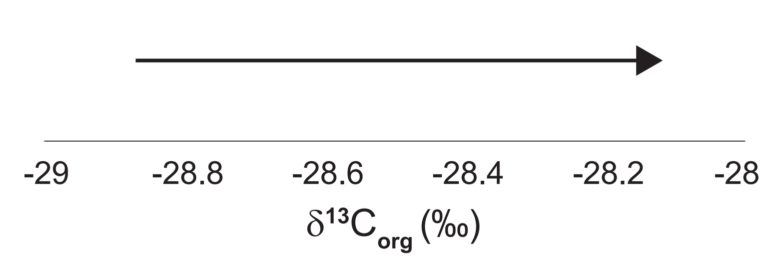
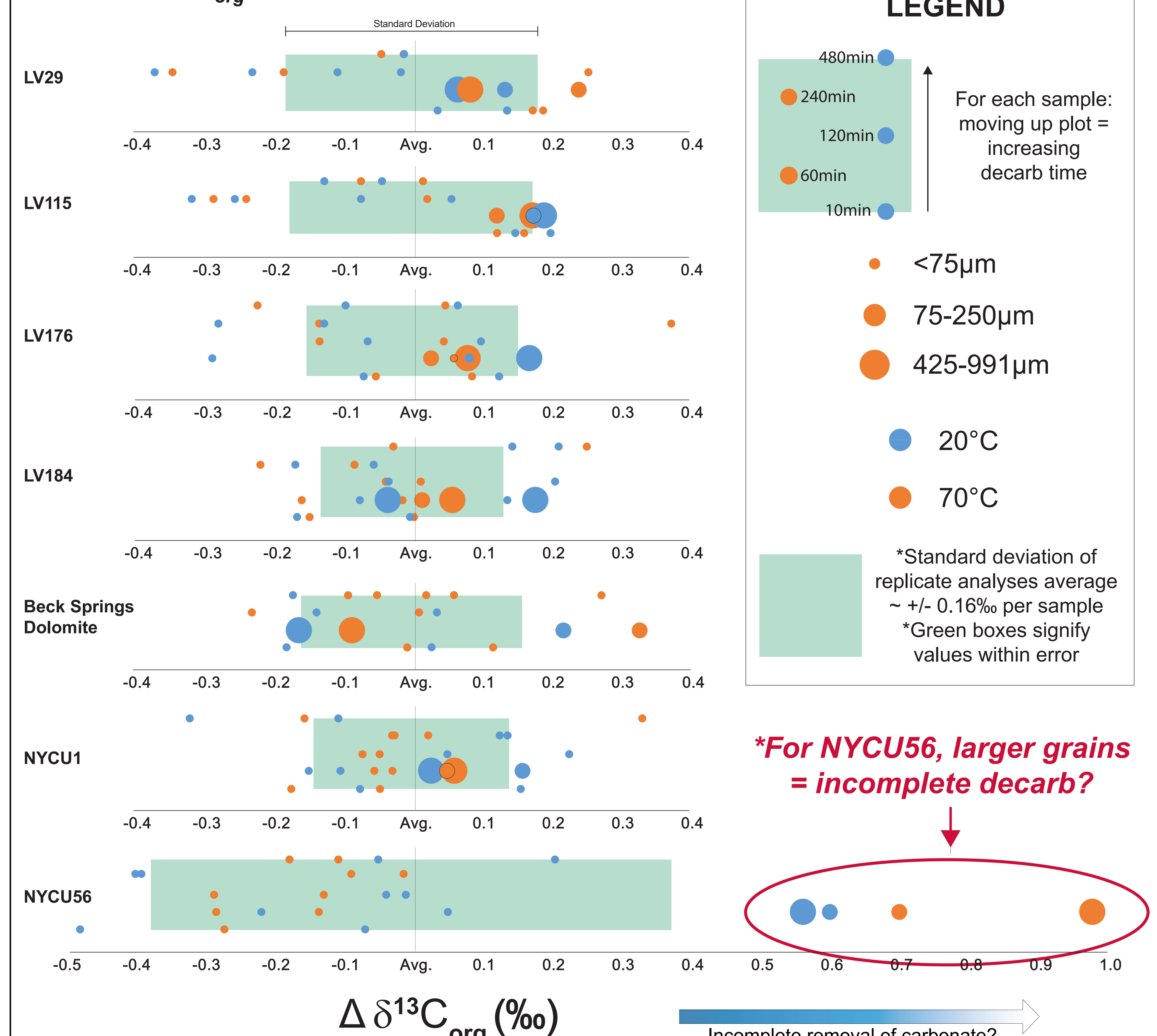


Figure 5: $\delta^{13}C_{org}$ deviation from sample average



$\Delta\delta^{13}C_{org}$:
- ± variation from a sample's average $\delta^{13}C_{org}$ value
- More negative ‰ values = "lighter" value, favoring ^{12}C
- More postive ‰ values = "heavier" value, favoring ^{13}C

5. Take home ideas

1) Temperature and time

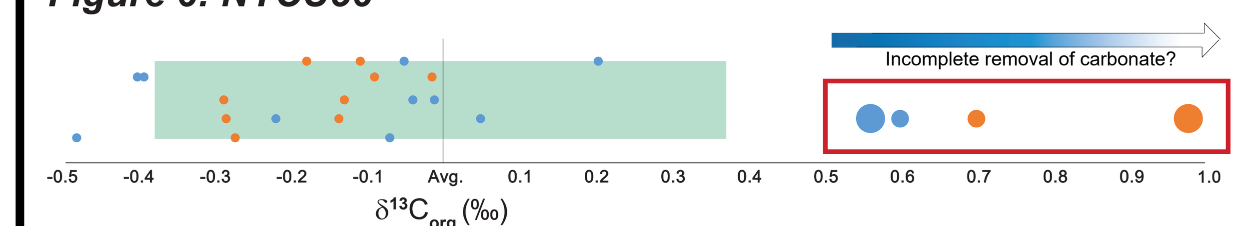
- For most samples, variations in decarb temperature and time ***do not*** yield systematic trends in $\delta^{13}C_{org}$ values outside of reproducibility between analyses (typically between ~0.1 - 0.2 ‰)

Surprising result: **This contrasts with canonical view that high temperature is needed to remove dolomite [7]**

2) Grain size

- Larger grain sizes produce heavier $\delta^{13}C_{org}$ values for NYCU56, suggesting larger grain size may be important for some samples

Figure 6: NYCU56



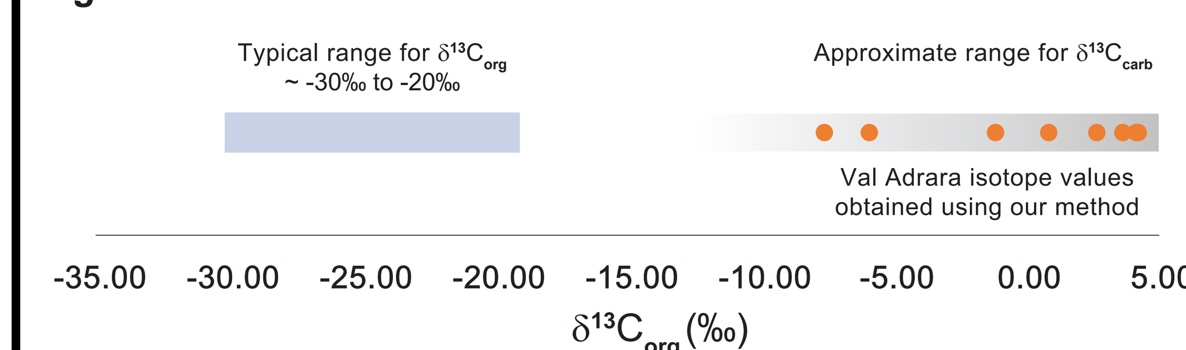
Surprising result: **This is not recognized in existing literature [6,7]**

- Grain size effects might explain discrepencies observed in New York Canyon $\delta^{13}C_{org}$ records (Figure 1)
- NYCU56 is from a part of the New York Canyon section with observed discrepancy

Addendum: Lessons from decarbonation of Val Adrara limestone

- "Standard" high-T liquid phase decarbonation (70°C, 60 min, <75µm grains) of carbonate rocks from Val Adrara Triassic-Jurassic boundary section (Italy) failed to remove inorganic carbon

Figure 7: Val Adrara



- Previous workers [9] successfully treated Val Adrara samples with 20% HCl (~6M) and a centrifuge method
- Different stratigraphic sections may require different decarbonation methods

Acknowldgements

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References

[1] Kump and Arthur, 1999, Chem. Geol., 161:181-198; [2] Kump and Garrels, 1986, Am. J. Sci., 286:337-360; [3] Corsetti et al., 2015, The Sed. Record, 13:4-10 [4] Bartolini et al., 2012, Geochem., Geophys., Geosys., 13:Q01007; [5] Ward et al., 2007, Palaeog., Palaeoc., Palaeoec., 244:290-296; [6] Brodie et al., 2011, Chem. Geol., 282:67-83; [7] Galy et al., 2007, Geost. and Geoan. Research, 31:199-207; [8] Subhas et al., 2015, Geoch. et Cosmo. Acta, 170:51-68; [9] Bachan et al., 2012, Geochem., Geophys., Geosys., 13:Q09008