# Supplementary Materials: Incorporating far infrared data into carbonate mineral analyses

Stephen Campbell[1] and Kristin M. Poduska[1,*]

Supplementary Materials

Attenuated total reflectance (ATR) measurement repeatability

Repeated measurements of a single powdered sample highlights that attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopic measurements have some variability in peak positions and shapes. Large particle sizes can cause broad and asymmetric peak shapes. This effect can be reduced by grinding powder samples thoroughly prior to measurement. Even after repeated grindings, spectra that involved repressing the same powder against the ATR crystal multiple times resulted in a peak position shift of as much as ± 4 cm^{-1}. As an example, Figure S1 shows representative spectra near the B1 band for a calcite reference sample. Thus, while it is necessary to have a well ground sample, it is also important to record spectra when the powder is repressed against the ATR crystal in different ways. Failure to do so could lead to mis-attributing subtle spectral changes to crystallinity-related differences that are, in fact, related to heterogeneous particle distributions that are in contact with the ATR crystal.
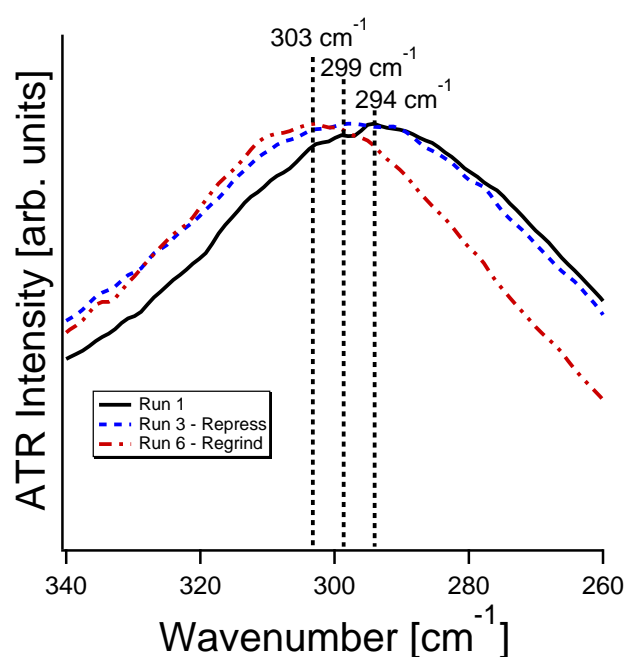
Figure S1. The inherent variability associated with repeated measurements of a calcite reference powder. Further grinding results in more narrow peaks. Peak maxima can shift ± 4 cm^{-1}.

Powder X-ray diffraction (PXRD) data

JADE software (MDI)[1] facilitated our assessments of crystalline grain size, microstrain fluctuation values and lattice strain, all of which were based on background subtracted, z-corrected, whole pattern fits for calcite identified diffraction peaks. Microstrain fluctuations and crystalline domain size information can be determined in the JADE software using the Williamson-Hall relation:[2,3]

$$\text{FWHM} \cos \theta = \frac{K\lambda}{r} + 4\sigma \sin \theta \,, \tag{1}$$

where FWHM is the full-width at half maximum for a given diffraction peak, θ is the Bragg diffraction angle of the same peak, r is the crystalline domain size, σ is the microstrain fluctuation, λ is the incident X-ray wavelength and K is a dimensionless shape factor. Typically a value of 0.9 is used for particles approximated to be roughly spherical. We considered both crystallite size fixed (large) and free (determined from data).

As described by Equation (1), the crystalline domain size, r is related inversely to the y-intercept and the microstrain fluctuation values are directly proportional to the slope of Williamson-Hall plot. These fits can only be as good as the quality of the PXRD peak fits; in other words, poor peak fit data can result in large changes to the slope and intercept used to extract the domain size and microstrain fluctuations. In our analyses, we took significant care in selecting which peaks were accurately fit by JADE's whole pattern fit routine. By removing any poorly fit peaks, we improved the confidence in resultant slope and intercept. Figure S2 shows a representative example for a calcite reference (C1).

Letting the slope and intercept run free, the slope tends to refine to near zero (corresponding to microstrain fluctuation values near zero) with large non-zero intercepts (corresponding to crystalline domain sizes that are unreasonably small, on the order of a few nanometers). Alternatively, fixing the intercept at zero (for large crystalline domain sizes, on the order of hundreds of nm) leads to a range of different microstrain fluctuation values and a poor linear fit. The uncertainty values for both the crystalline domain size and microstrain are rather large.

Even when using only the diffraction peaks for which we have higher confidence about their fits, interpretation of our Williamson-Hall data is dicey. All PXRD peak widths appear to artificially large, which forces the Williamson-Hall fit to have a large intercept, which translates to an interpretation of unphysically small (nm-range) crystalline domain sizes. We believe the origin of these broad PXRD peaks is not likely specimen-related; instead, we suspect that peaks widths were dominated by instrumental broadening effects. Thus, we do not draw any conclusions about crystalline domain size or microstrain fluctuation values from our PXRD data.
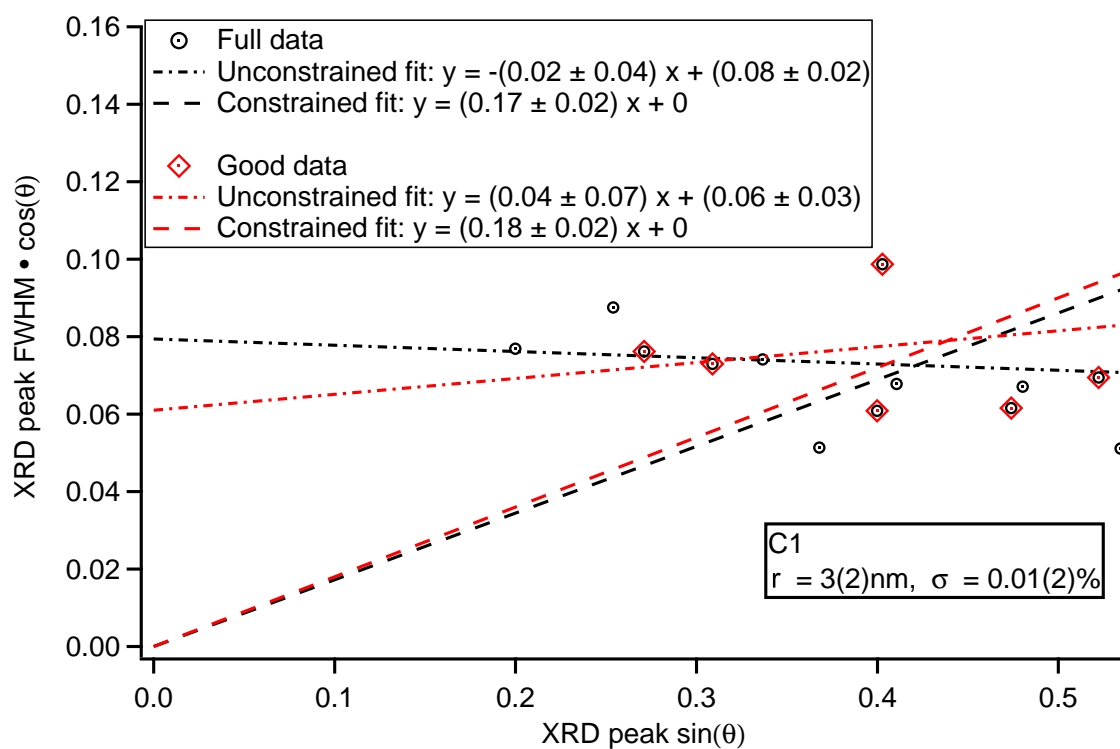
Figure S2. Williamson-Hall plot of calcite sample C1. The entire data set (black) and a subset of peaks (red) were fit with either unconstrained intercepts (dot-dashed) or with the intercept forced to zero (dashed).

References

1. MDI. JADE (Computer software, Version 2010) **2010**.
2. Williamson, G.; Hall, W. X-ray line broadening from filed aluminium and wolfram. *Acta Metall.* **1953**, *1*, 22–31.
3. Xu, B.; Toffolo, M.B.; Regev, L.; Boaretto, E.; Poduska, K.M. Structural differences in archaeologically relevant calcite. *Anal. Methods* **2015**, *7*, 9304–9309.