CEST fitting algorithm

The method

- Fitting multi-B_1 Z-spectra via numerical solution of Bloch-McConnell equations for two pools.
- Bayesian paradigm, sampling via Hamiltonian Monte Carlo.

$$Z_i = \tilde{Z}_i + \epsilon_i, \qquad \epsilon_i \sim \mathrm{Normal}(0, \sigma),$$

where $\{\tilde{Z}\}$ are simulated values from BM equations at measured offsets.

Why go Bayesian?

- Bayes's Theorem naturally defines *inversion* of probability, and thus can be used to treat inversion problems (e.g., fitting) probabilistically.

- Bayesian analysis produces *credible intervals*, instead of confidence intervals, which are more meaningful in case of empirical parameter estimation.

- Trivially enables inspection of relationship between parameters, by inspecting their joint posterior.

Why Hamiltonian Monte Carlo?

- The traditional Random Walk Metropolis sampling algorithm fails in high dimensions, where only a singular number of directions in sample space feature both high probability densities **and** sufficient volume for integration.

- Hamiltonian Monte Carlo utilizes the shape of the posterior to effectively explore sample space, and to generate informational, less correlated samples from the posterior.

- Modern software implementing HMC informs on divergent Markov transitions, so that incomplete sampling may be avoided.

Example: LP30 @323K

$$Z_i \sim \text{Normal}(\tilde{Z}_i, \sigma)$$

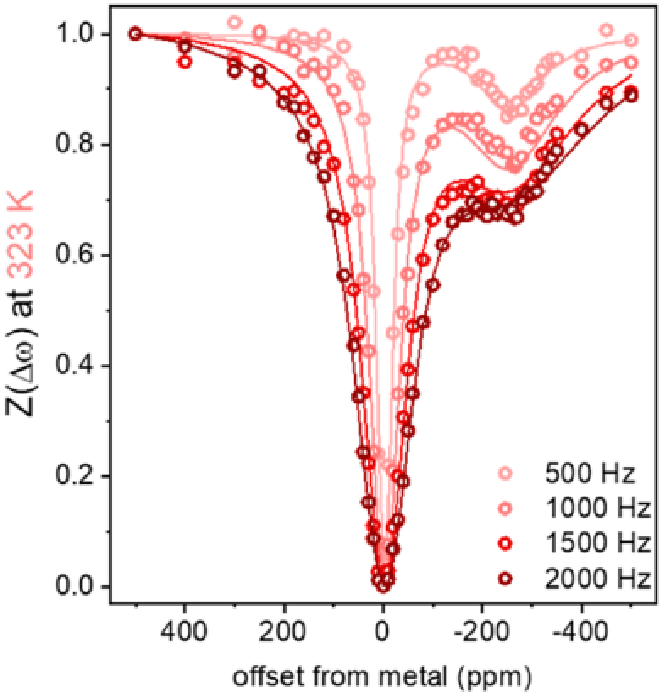
$$\frac{1}{T_{1B}} \sim \text{Half-Normal}(0, 5)$$

$$\frac{1}{T_{2B}} \sim \text{Normal}(27000, 3000)$$

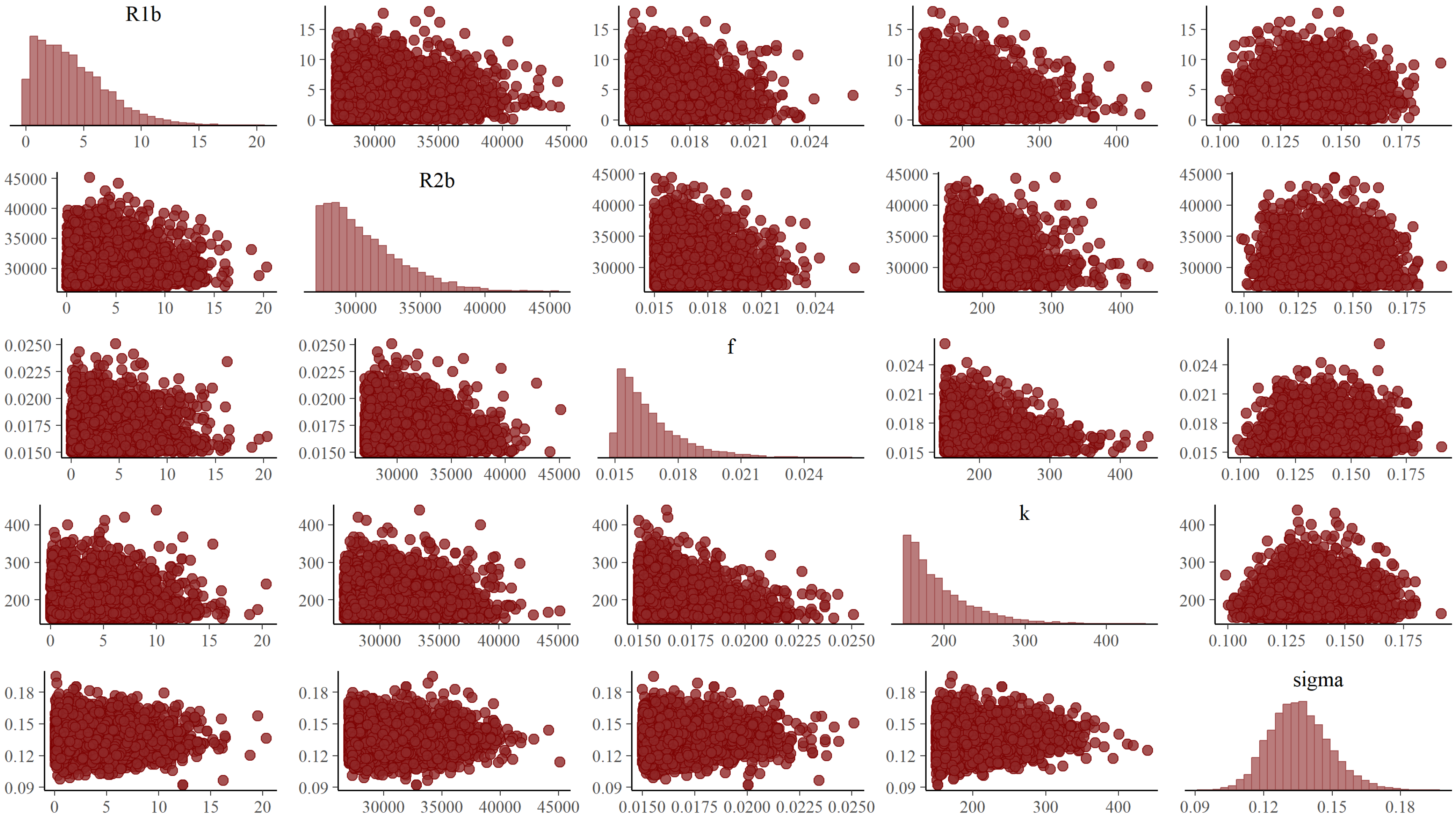
$$k_{\text{BA}} \sim \text{Normal}(150, 100)$$

$$f_B \sim \text{Normal}(0.015, 0.005)$$

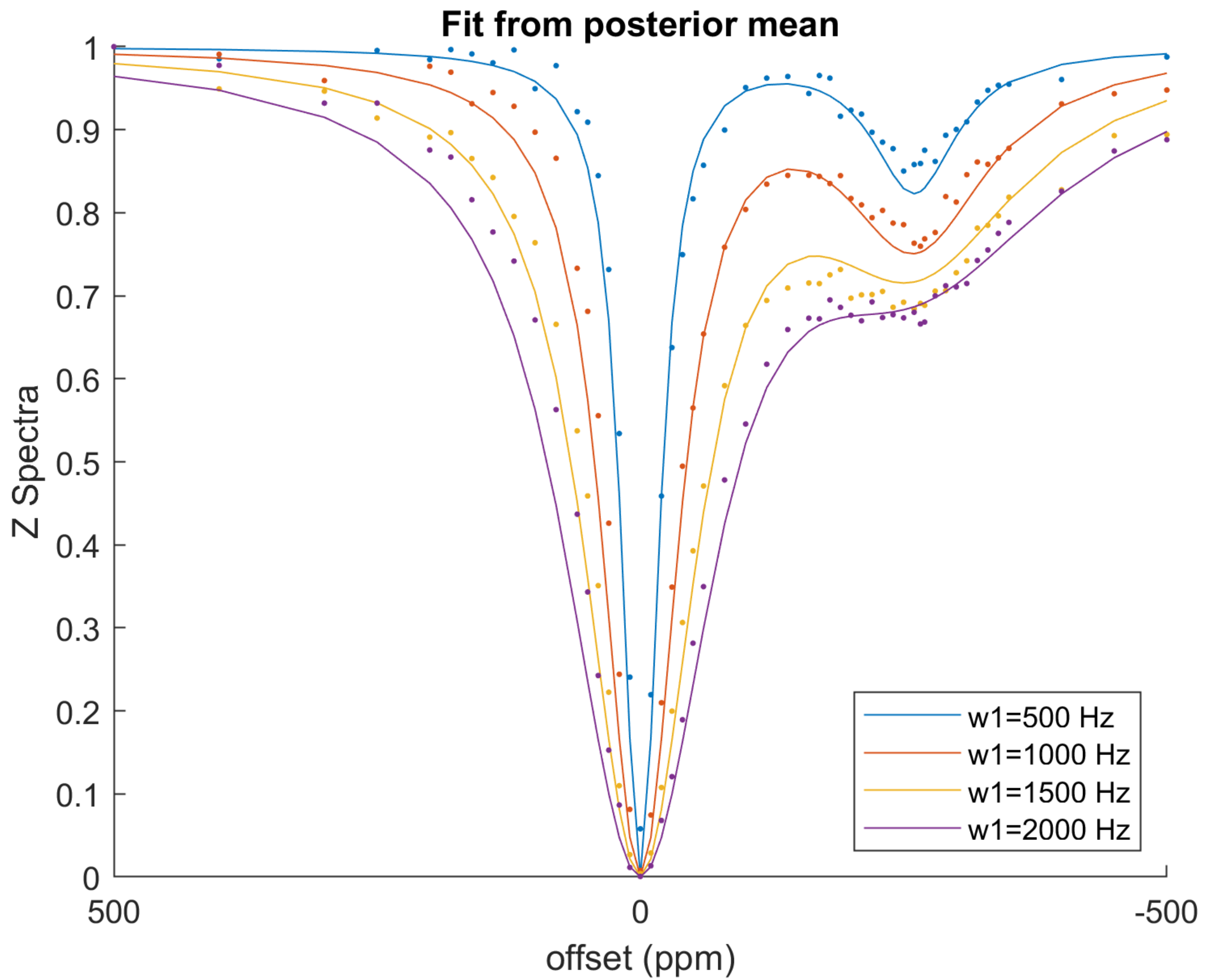
$$\sigma \sim \text{Half-Normal}(0, 0.05)$$



Results: Pair plot



Comparison of simulation from posterior mean and data



Limitations and plans

- Prior choice doesn't currently have mathematical or physical justification.
  - Possibility: usage of **maximum entropy** priors (E.T. Janyes)

- Complete pooling of multiple experiments into a single data set assumes measurements at the same offset but different B_1 are *uncorrelated*.
  - Possibility: Hierarchical modeling.