**METEORITIC ISOLEUCINE EPIMERIZATION IN THE CHRONOLOGY OF ASTEROIDAL PARENT BODY FLUIDS.**

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**Introduction:** Meteoritic amino acid abundances and abundance ratios have been diversely applied in cosmochemistry. Abundances have gauged the duration of experimental heating of Murchison [1], and abundance ratios have exhibited differences according to meteorite classification group and the extent of asteroidal parent body aqueous and thermal alteration [2-5]. Enantiomeric excesses (*ee*s), expressable as amino acid enantiomer ratios ≠ 1, also have been shown to correlate with aqueous alteration. The *ee* of L-isovaline, a non-protein, α-methyl amino acid, increased with aqueous alteration in several meteorite groups [6,7], and the *ee*s of L-isoleucine (L-Ile) and D-*allo*-isoleucine (D-*a*Ile), α-H amino acids, decreased with aqueous alteration in a suite of CR chondrites [8]. Meteorite Hills (MET) 00426, a minimally altered CR 3.0 chondrite [9], contained the largest *ee* of a non-protein amino acid to date [8,10]. The capability of amino acids to racemize (or epimerize) and undergo a reversal of configurational symmetry is fundamental to discussions about the effects of aqueous alteration on meteoritic amino acids, but this same capability also allows applications to sedimentary geochronology.

Geochronometers based on amino acid destruction or racemization use naturally occurring amino acids in fossils [11] and in some cases can approximate ages of fossilized sediments younger than several $10^5$ yr [12]. Two amino acids used for this purpose, L-Ile and D-*a*Ile, interconvert via α-epimerization following loss and acquisition of protons on opposite sides of the molecule and undergo a chiral reversal at the α-carbon, known also as C2. D-Ile and L-*a*Ile, two other isoleucine stereoisomers of four total, also interconvert via α-epimerization. The kinetics of this process are described by isoleucine epimerization rate constants, experimentally shown to vary with changes in pH, temperature, and whether isoleucine is "free" in solution or chemically bound in peptides or proteins [13-21]. Published rate constants have been combined here to establish the average and range of rate constants to estimate possible timescales for isoleucine epimerization in asteroidal parent body fluids at constant temperatures.

We present kinetics calculations using stereoisomeric amino acid disequilibria (abundance ratios) to constrain the total residence time of these amino acids in their parent body fluids. Mineral and isotope analyses provide the chronological context to which these model calculations are compared.

**Methods:** $10^3$-$10^4$ amino acid concentration changes for each reversible, first order reaction were calculated by the finite difference method with Euler's approximation, a standard approach for modeling reactions governed by simultaneous, differential rate equations [22]. In any given time step, concentration changes due to α- and β-epimerization are calculable from rate constants $k_1$ and $k_2$ (α-epimerization) and $k_3$ and $k_4$ (β-epimerization) and the initial concentrations of amino acids during that step:

$$\frac{d[\text{D}-a\text{Ile}]}{dt} = k_1[\text{L}-\text{Ile}] + k_3[\text{D}-\text{Ile}] - (k_2+k_4)[\text{D}-a\text{Ile}]$$

$$\frac{d[\text{L}-a\text{Ile}]}{dt} = k_1[\text{D}-\text{Ile}] + k_3[\text{L}-\text{Ile}] - (k_2+k_4)[\text{L}-a\text{Ile}]$$

$$\frac{d[\text{D}-\text{Ile}]}{dt} = k_2[\text{L}-a\text{Ile}] + k_4[\text{D}-a\text{Ile}] - (k_1+k_3)[\text{D}-\text{Ile}]$$

$$\frac{d[\text{L}-\text{Ile}]}{dt} = k_2[\text{D}-a\text{Ile}] + k_4[\text{L}-a\text{Ile}] - (k_1+k_3)[\text{L}-\text{Ile}]$$

The number and duration of steps varied by calculation according to the total duration required to reach (1) the historical boundary condition where $[\text{L}-a\text{Ile}]$ or $[\text{D}-\text{Ile}]$ equals zero and (2) the duration of future alteration required to reach chiral equilibrium wherein $[\text{D}-a\text{Ile}] = [\text{L}-a\text{Ile}]$ and $[\text{D}-\text{Ile}] = [\text{L}-\text{Ile}]$.

**Results:** Isoleucine epimerization **k**inetics calculations using published abundances of D-isoleucine and its α-epimer, L-*allo*-isoleucine, in a suite of CR chondrites (Elephant Moraine 92042, LaPaz Icefield 02342, Graves Nunataks 95229, and MET 00426) indicate that the residence time of these amino acids in an aqueous phase ≥ 25 °C was short: < 8 x $10^4$ yr at 25 °C, < 2 x $10^3$ yr at 50 °C, or < $10^2$ yr at 75 °C.

Rate constants from epimerization studies were combined (Fig. 1) to allow extrapolation with error to lower temperatures relevant to the asteroidal parent bodies. Errors from Arrhenius parameters, if not published, were calculated by a least-squares fit and propagated to define the error of the average curve.

Epimerization was modeled in historical time at temperatures from 253 to 348 K (-20 to 75 °C) to identify the maximum possible total duration of aqueous alteration after the formation of these amino acids: Fig. 2 depicts results for MET 00426 at 25 °C. In these calculations, amino acid synthesis is assumed to occur before aqueous alteration at constant temperature, and concentrations measured in the laboratory are assumed to be equal to the concentrations when aqueous alteration ceased (considered $t = 0$).
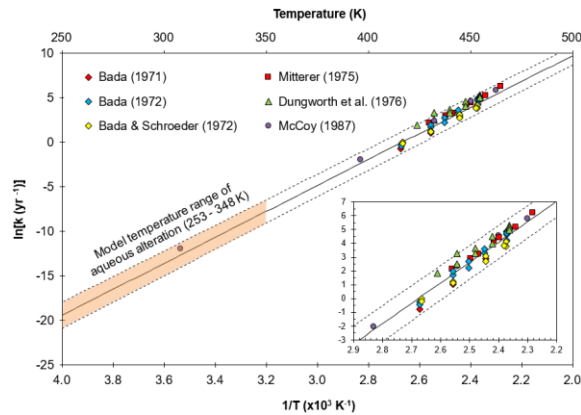
**Figure 1**. Combined Arrhenius plot of six isoleucine epimerization studies. The solid line is the average of slopes and intercepts; dashed lines bound error. All studies measured epimerization of isoleucine bound in a protein form except [13], which included "free" (unbound) isoleucine in the presence of metal cations.
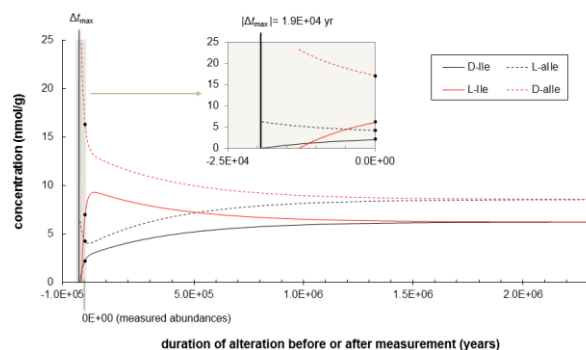


**Figure 2**. Concentration vs. duration plot depicting the historical limit for aqueous alteration of MET 00426 at 25 °C. The epimerization equilibrium constant of 1.38 and α-/β- epimerization rate ratio of 30 were used [19,21]. The α-epimer pair in red (L-Ile/D-aIle) is contaminable by terrestrial L-isoleucine. On the x-axis, historical alteration is negative, future alteration positive.

**Discussion:** We conclude that these meteoritic amino acids were not participants in aqueous alteration with sufficient conditions to fully α-epimerize and note that these maximum durations at a given temperature may be combined with other chronometers and thermometers to link amino acid formation or residence with dated, aqueously-formed mineral phases. In cases of multiple episodes of aqueous alteration, formation or emplacement of this subset of the organic suite cannot by any known means predate certain episodes according to episode duration and temperature. Therefore [L − aIle]/[D − Ile] may exclude duration and temperature combinations for aqueous alteration.

Uses of reversible, first order kinetics and the presented rate constants with error are justified: on the basis of reaction progress, historical isoleucine epimerization in these CR chondrites would have proceeded according to reversible, first-order kinetics [23], and the error considered in our calculations arguably includes settings [12,13] even less kinetically favored than the parent body. Future determinations of epimerization rate constants in the presence of meteoritic materials may reduce estimable durations.

Quantitative consideration of isoleucine epimerization is newly applied here to estimate maximum possible total durations of aqueous alteration in the presence of the isoleucine stereoisomers at a given temperature. These durations were calculated using α-epimer abundances not able to be contaminated by any known means and are shorter than durations among the shortest presently determinable by Mn-Cr isotope chronology within error (e.g., ~2-4 x $10^5$ yr [24]). This method may allow chronological constraints presently unachievable via isotope chronometry in the study of asteroidal parent body processes.

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