I. General
A.Time range

- Depends on: temperature, amino acid, taxon
- For isoleucine in the Arctic = 3-5 Ma
- For aspartic acid in tropics = few 1000 yr with annual resolution
- Resolution is higher during early stage of the equilibrium reaction

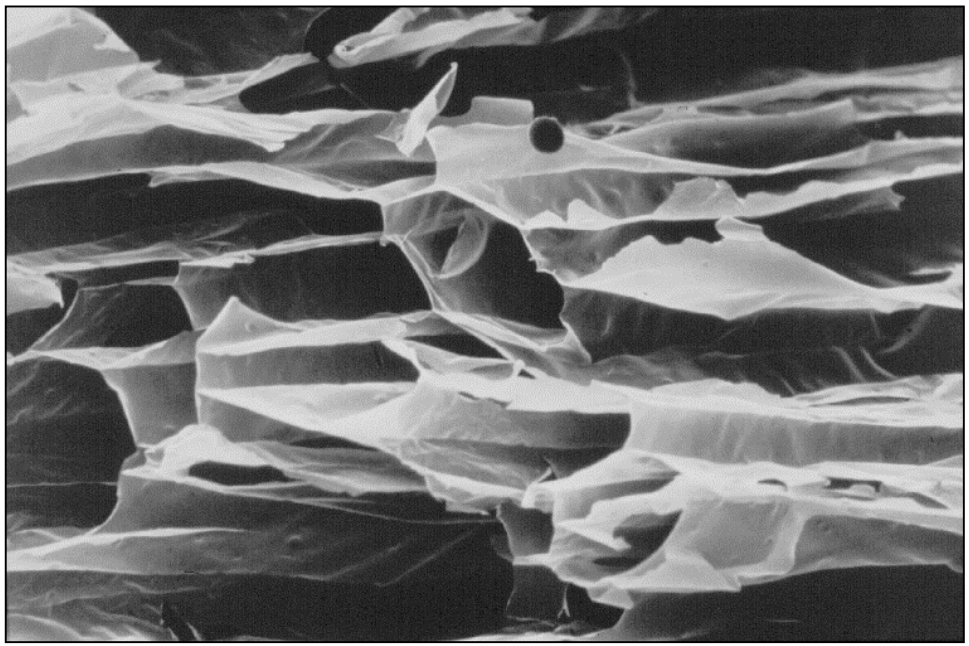
I. General
B. Materials

- Molluscs most commonly used
- Also other carbonates: braciopods, eggshells, oolites, whole rock beach sand, otoliths, ostracodes, speleothems, corals, foraminifera
- Has also been tried on wood, soils, meteorites

II. Principles
A. Amino acids

- All living organisms contain amino acids (~20 common in protein)
- Molecule contains an amino group (NH_2) attached to central C
- Amino acids link together by *peptide bonds* to form *proteins*

Decalcified eggshell



II. Principles
A. Amino acids (*cont.*)

- Amino acids are asymmetric or *chiral*
- D and L are *isomers* (same compound; different configuration)
- Exist in two different configurations which are mirror images = *enantiomers*
- Amino acids are *optically active* (= rotate polarized light)
- Levorotary = rotate light to left (L)
- Dextrorotary = rotate to right (D)

II. Principles
B. Racemization

- All amino acids in living organisms are Levo (except in some bacteria)
- After death, L is converted to D by reaction called *racemization*
- Extent of reaction is defined by D/L ratio (ranges from 0 to 1.0)
- Rate of reaction depends on amino acid
- Aspartic acid is among fastest; isoleucine is relatively slow

II. Principles
C. Epimerization

- Several amino acids contain two chiral C atoms (isoleucine)

- Racemization about one atom produces a new, non-stereo image isomer = *diastereomer*

- *D-alloisoleucine* is formed by *epimerization* of L-isoleucine

- *A/I* ratio equilibrium = ~1.3

II. Principles
D. Temperature

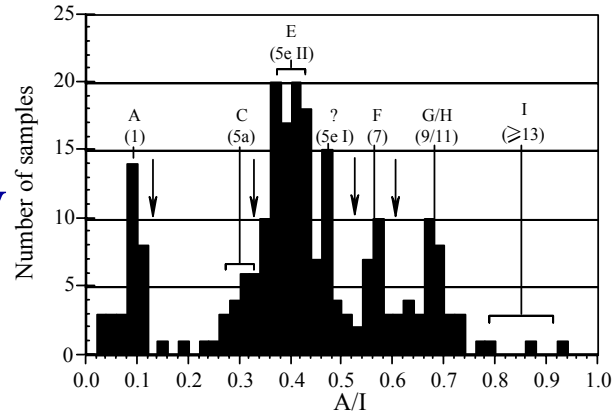
- Rate of racemization is highly dependent on temperature

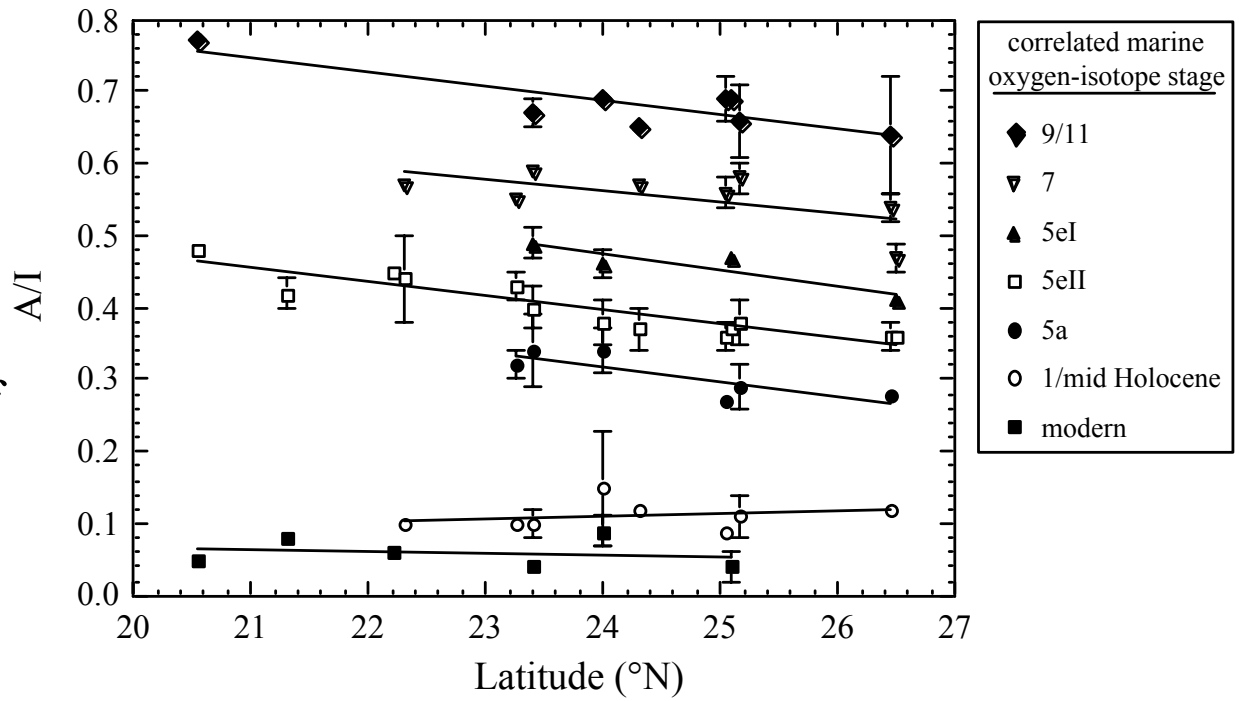
- Rate approximately doubles for each 10°C increase

III. Age determinations

A. Relative ages: aminostratigraphy

- D/L ratios are used as a relative-age index
- Used for correlation between sites
- Cluster of ratios (aminogroups) imply intervals of deposition
- Also used for general age approximation



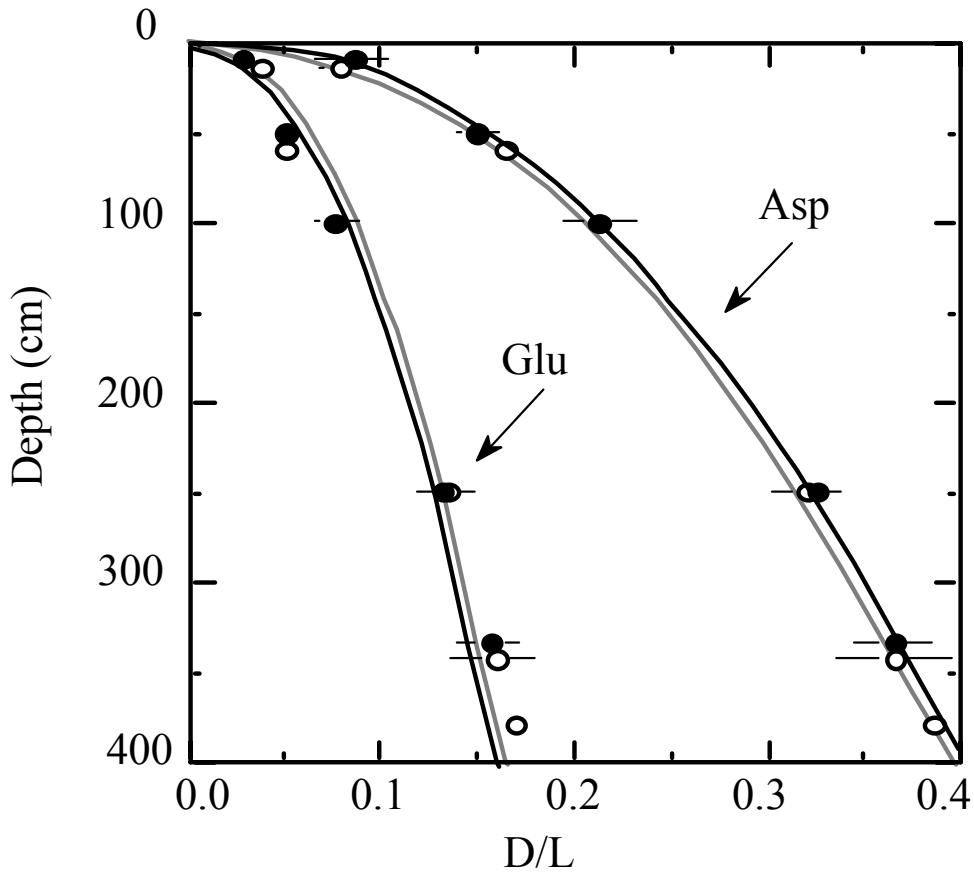


From Hearty and Kaufman, 2000

III. Age determinations

A. Relative ages: aminostratigraphy (*cont.*)

Extent of racemization (D/L) for aspartic acid (Asp) and glutamic acid (Glu) in foraminifer from two marine cores off NE Australia. The cores are located 80 km apart



V. Procedures

A. Sampling

- Use multiple shells per horizon (>5 shells per "sample")
- Shell size is typically a 10's of mg (although smaller will work)
- Typically 5-10% variability among shells from single stratigraphic unit
- Sample from at least 1 m below ground surface
- Samples sensitive to contamination; don't handle

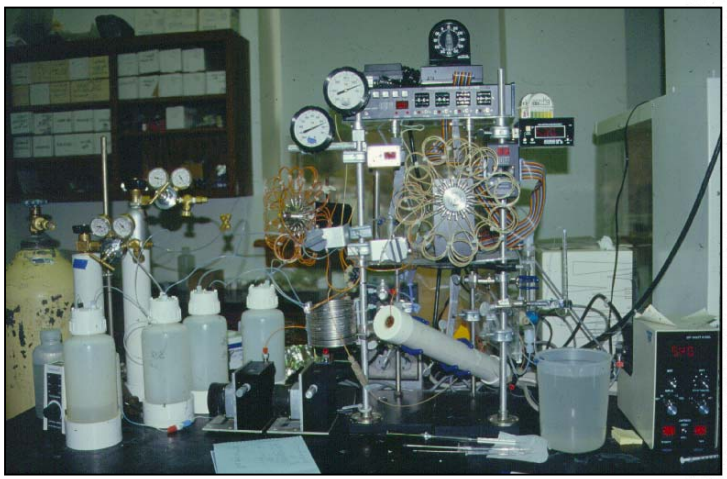
V. Procedures

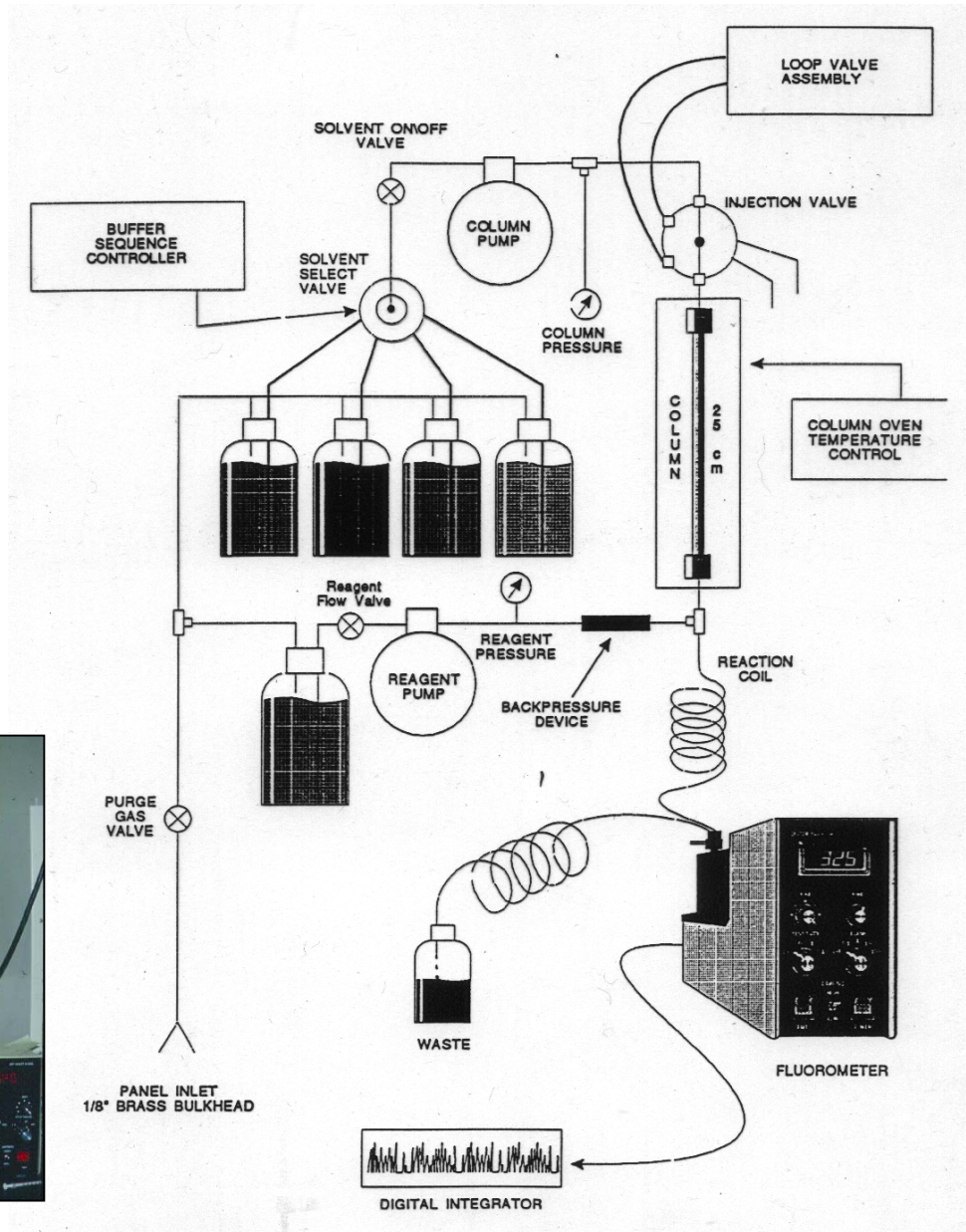
B. Laboratory

- Shells are subsampled in same position, or entire shell is used
- Protein composition and therefore rates of racemization vary within a shell
- Samples are cleaned, dissolved, hydrolyzed in laboratory

V. Procedures
C. Analytical

- Amino acids are separated on a high-performance liquid chromatograph (HPLC) using either ion exchange (IE) or reverse phase (RP) procedures

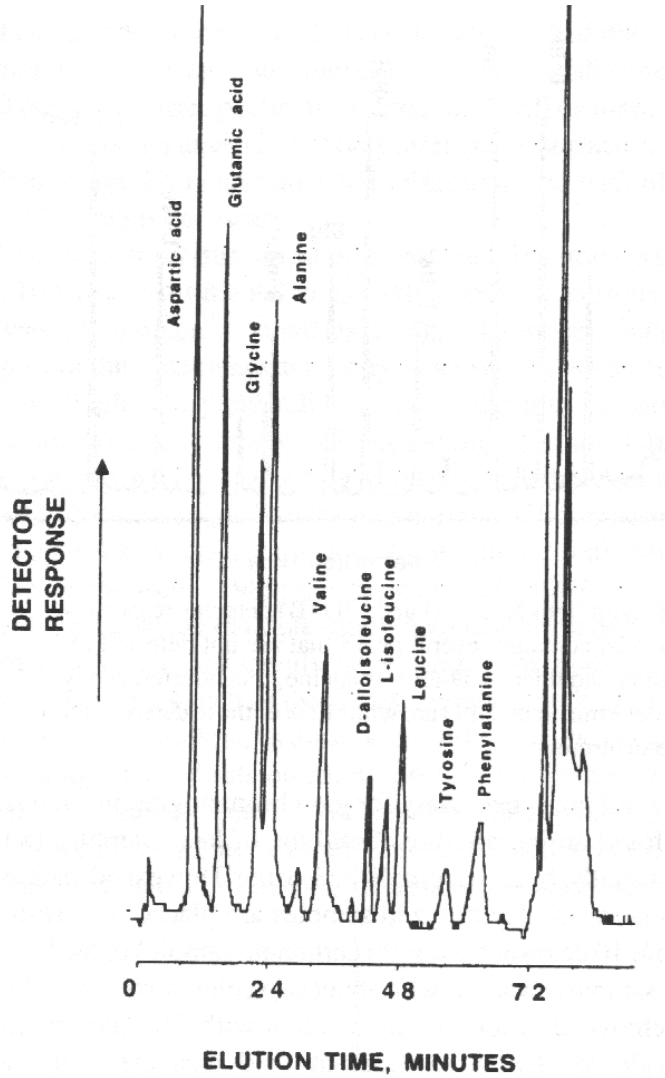




V. Procedures

C. Analytical (*cont.*)

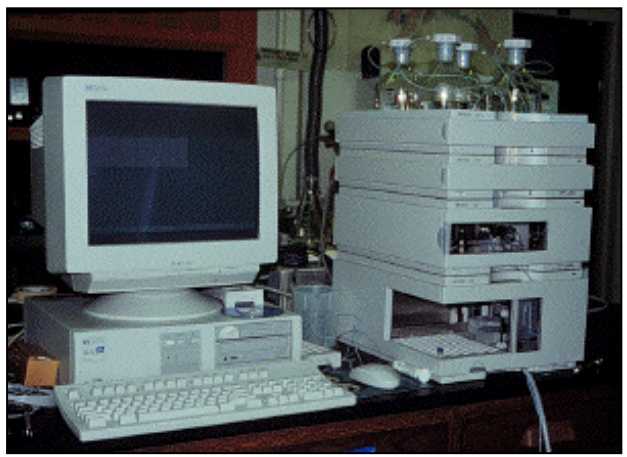
- IE is used most commonly
- Resolves individual amino acids, but not enantiomers (D from L), only diasteromers (isoleucine from alloisoleucine)
- GC separates D/L isomers for multiple amino acids
- Analytical procedure is more complex; difficult to automate
- Requires larger sample sizes

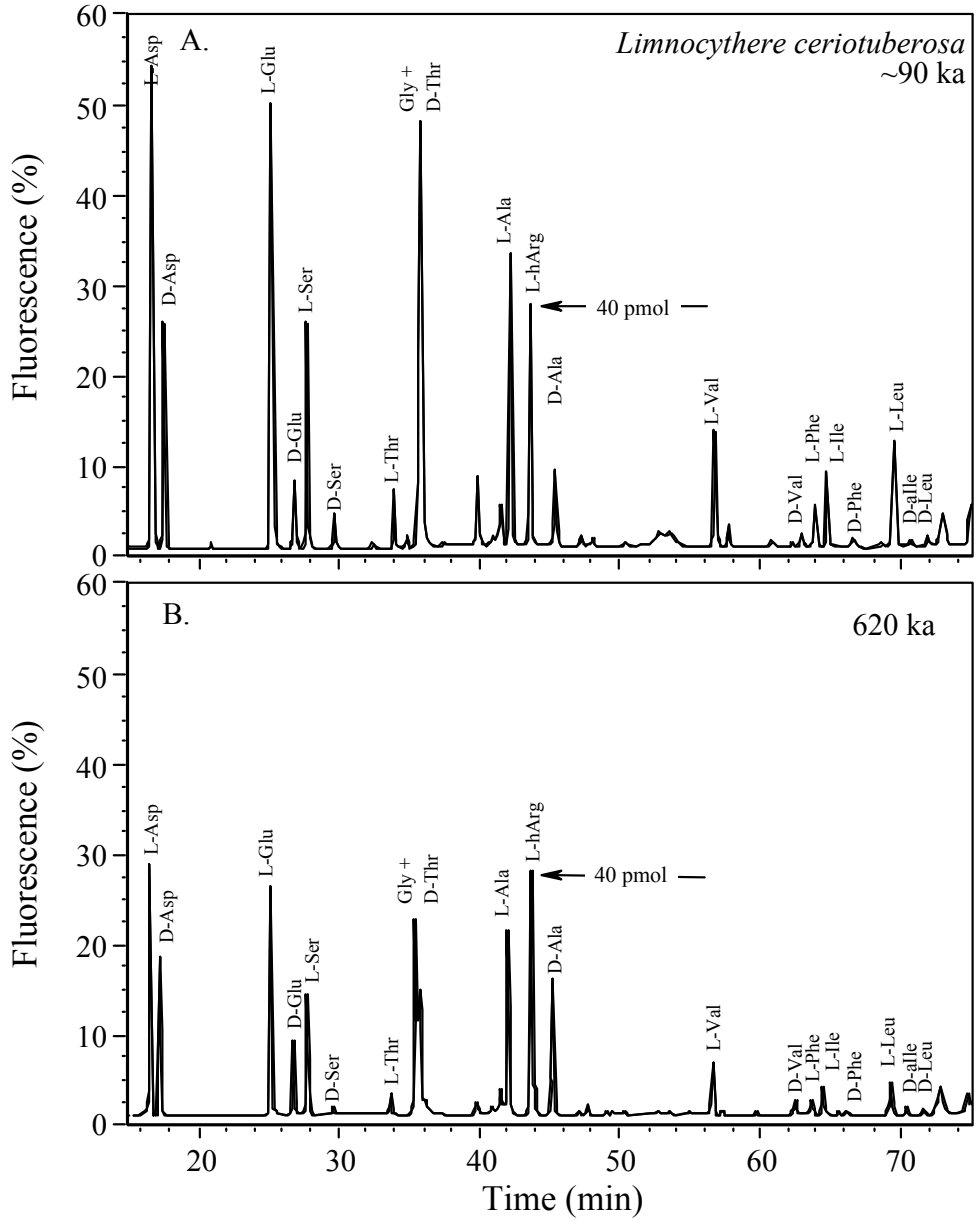


V. Procedures

C. Analytical (*cont.*)

- RP combines advantages of HPLC and GC
- Separates D/L ratios for multiple samples; simple; small samples





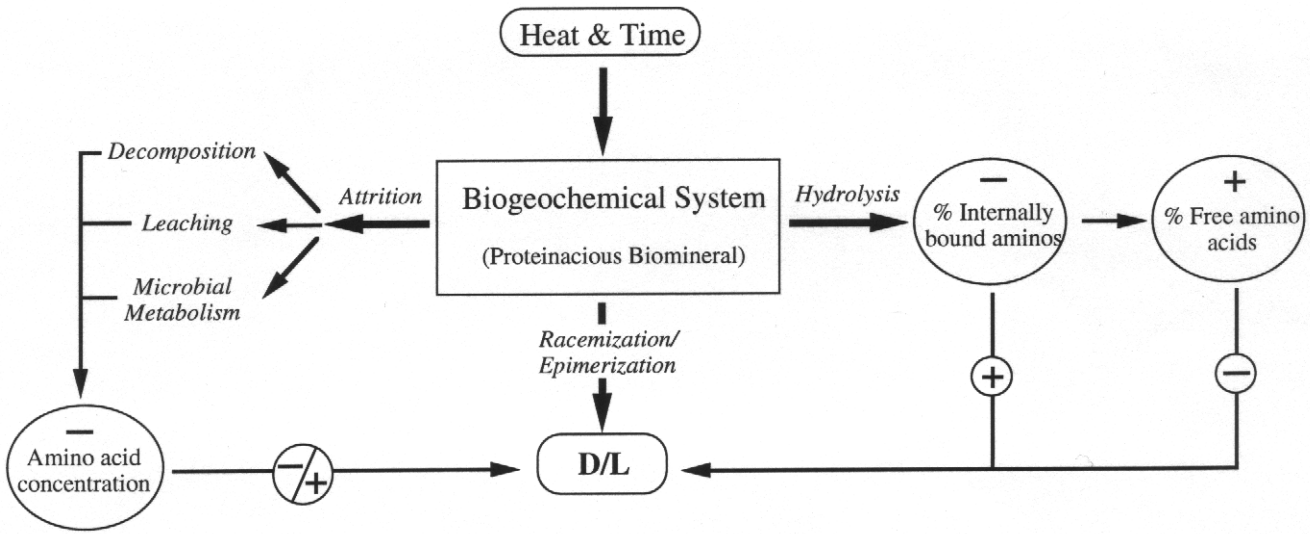
V. Procedures

C. Analytical (*cont.*)

- Sample solutions are typically analyzed more than once
- Values for inter-laboratory standards are reported with results
- Analytical precision based on repeat measurements of same solution is usually 1-5%

VI. Challenges

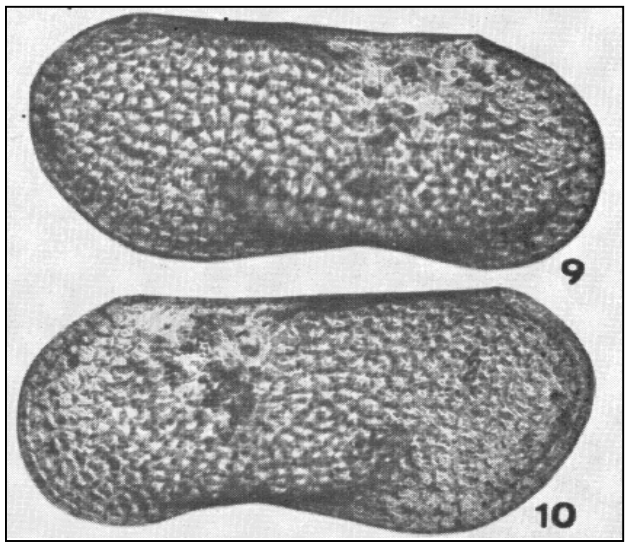
- Protein diagenesis is infinitely complex
- Reaction rates are highly temperature sensitive
- Racemization rate depends on taxon
- Need to use multiple genera for splicing together a stratigraphy
- Analytical procedure is tricky; can lead to laboratory biases
- No convention for reporting uncertainties in age estimates



VII. Opportunities

A. Reduced sample sizes

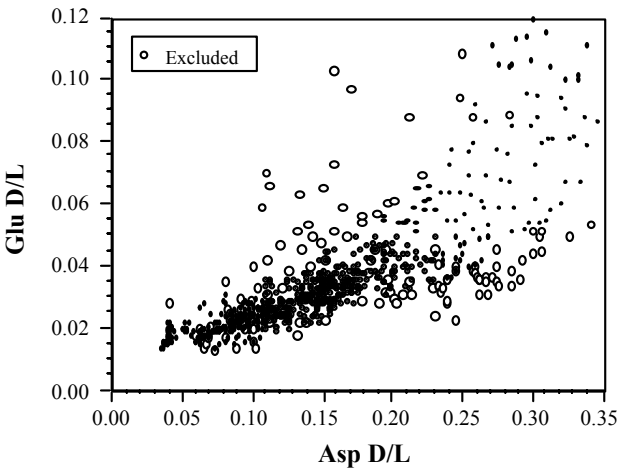
- Integrate amino acid geochronology into studies of lake and marine cores

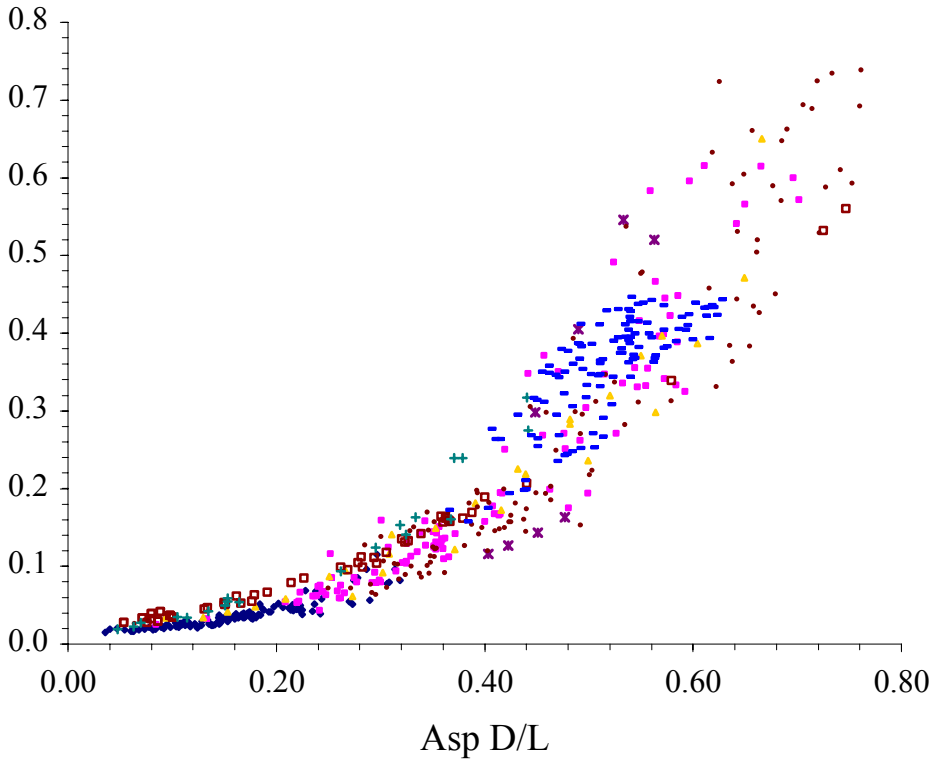


Limnocythere cerituberosa

VII. Opportunities
B. Improved screening criteria

- Aberrant samples can often be recognized by amino acid signatures
- Modern contamination exhibits abundant unstable amino acids





VII. Opportunities

C. Intra-crystal fraction

- Extract and analyze the best-protected fraction of protein
- Preliminary results indicate that intra-crystal fraction behaves as a closed system