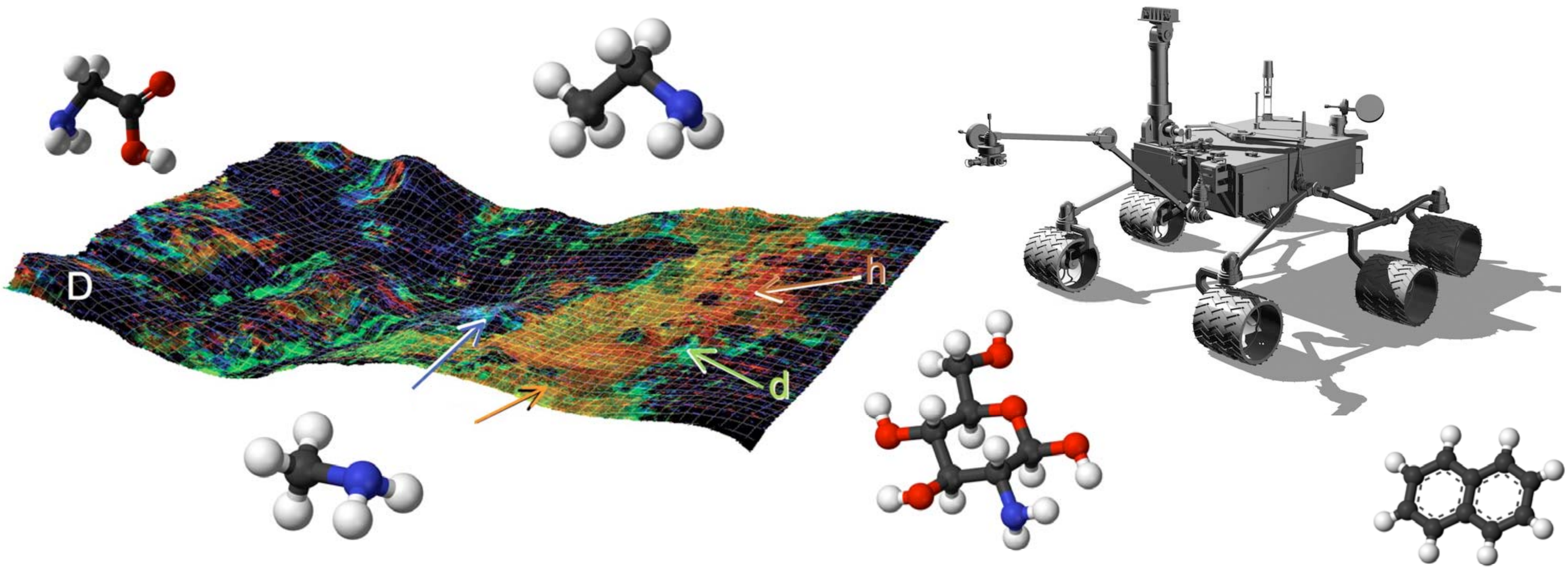
MSL Landing Site Selection & Organic Preservation



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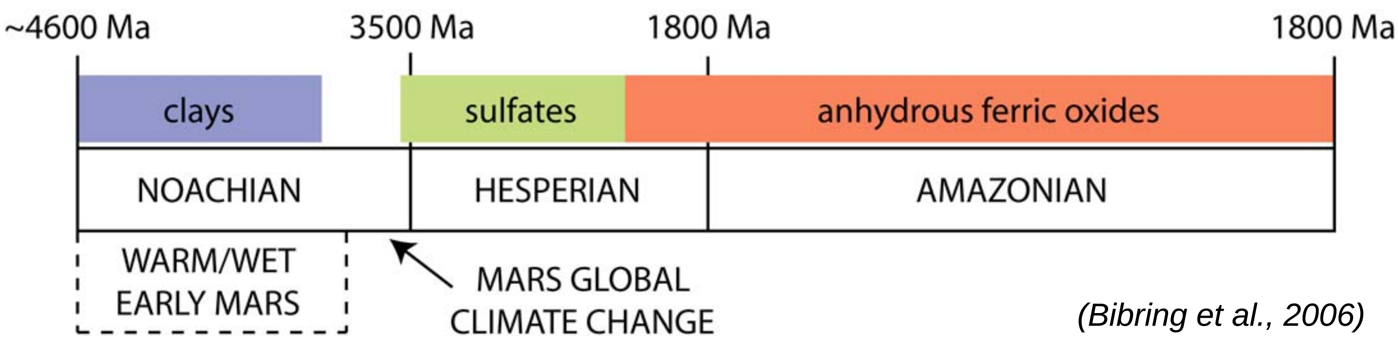
Factors to Consider in Site Selection

1) **MSL Payload Goals**
2) **Potential Molecular Targets (especially important for Life Detection missions)**
3) **Long Scales of Diagenesis over Ga timescales (Burial/Exposure)**



(Bibring et al., 2006)

4) **Facies Properties (Depositional Environment)**
   - ✓ **Specific priorities for Individual Instruments**
   - ✓ **Geochemical Targets of Interest**
   - ✓ **SPECIFIC MINERALOGY STILL HIGHLY UNCERTAIN!**

Factors in Biomarker Preservation on Mars

Current Environmental Conditions – Harsh Surface Conditions

- **Ionizing Radiation – Galactic Cosmic Rays (Kminek et al., 2006)**
- **UV-Radiation (Garry et al., 2006; ten Kate et al., 2005)**
- **Surface Oxidants (Viking; Phoenix – Peroxides)**

Mineralogical Concerns

- **Iron *in situ* catalysis-fenton chemistry (Sumner, 2004)**
- **Radiation attenuation of regolith or by minerals (Fe-rich, sulfates)**
- **Sequestration by minerals or adequate protection from oxidants**

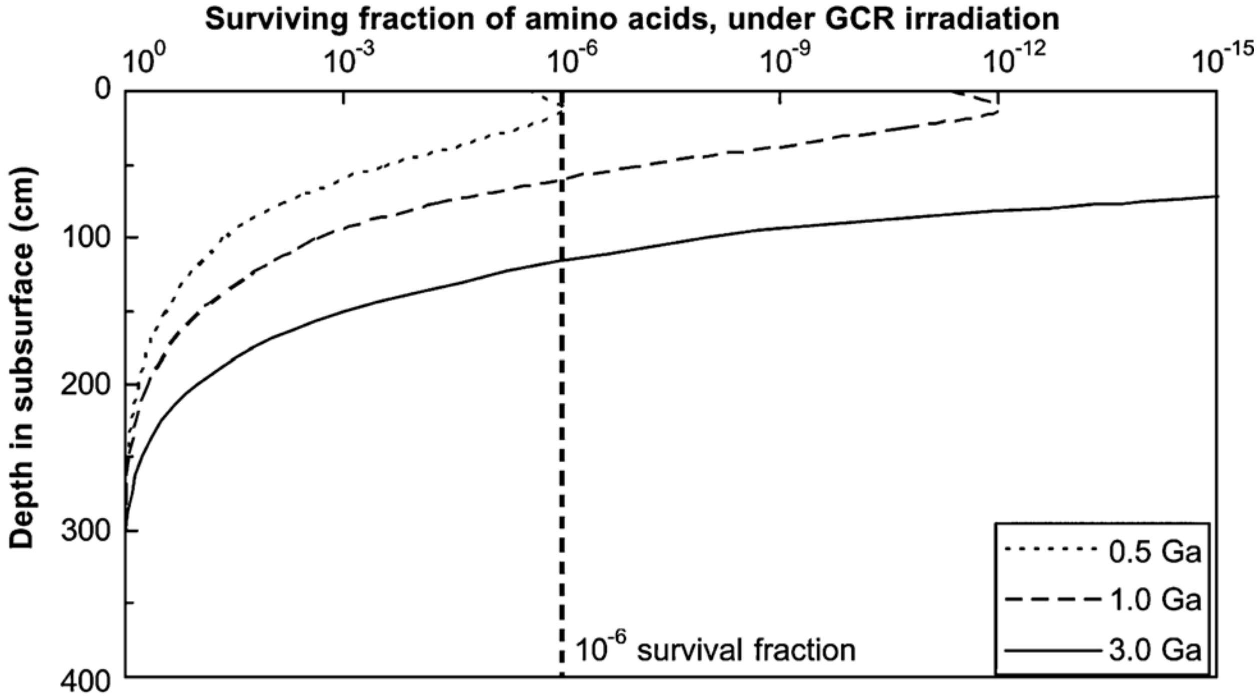
Past Environmental Conditions

- **Hypersaline water bodies on Mars (Tosca et al., 2008)**
- **Evaluation of stability issues with respect to preservation**

Galactic Cosmic Ray Spore Inactivation/Degradation

Studies reveal requirement for subsurface sampling in order to access organics sheltered from Mars' harsh surface conditions including UV radiation (ten Kate et al., 2005; Garry et al., 2006) and ionizing radiation (Parnell et al., 2007).

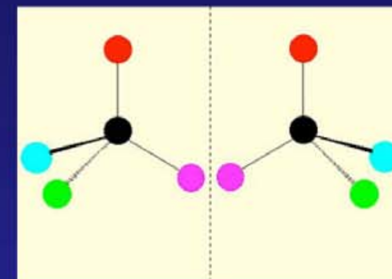
Organic Preservation via Burial
(Martian Regolith Model)

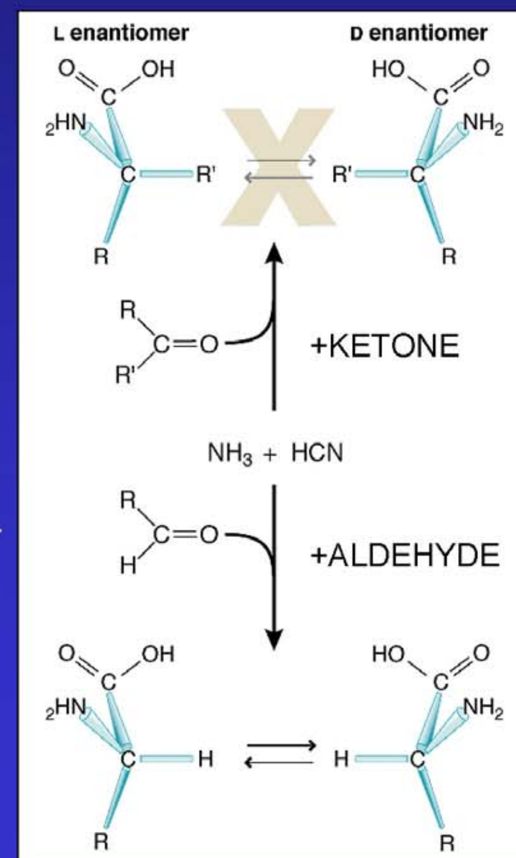


Model from Parnell et al. (2007)
Using data from Kminek & Bada (2006)

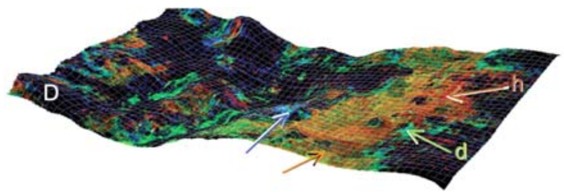
We have used amino acids as a measure of preservation

- Amino acids are ubiquitous in all forms of life.
- They compose 55% of dry bacterial cells by weight as a molecular class.
- Virtually all amino acids in bacterial cells are of the L-enantiomer.
- Amino Acids racemize, decarboxylate, and deaminate. These pathways may offer age information.
- Form abiotically by strecker-type syntheses and can offer evidence synthesis or external delivery to Mars.
- Easily tagged with fluorescent reagents for increased analytical sensitivity.

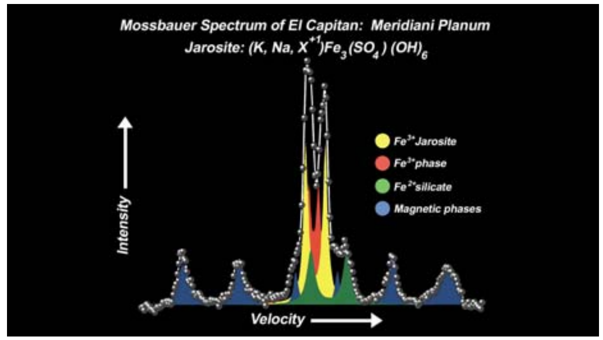




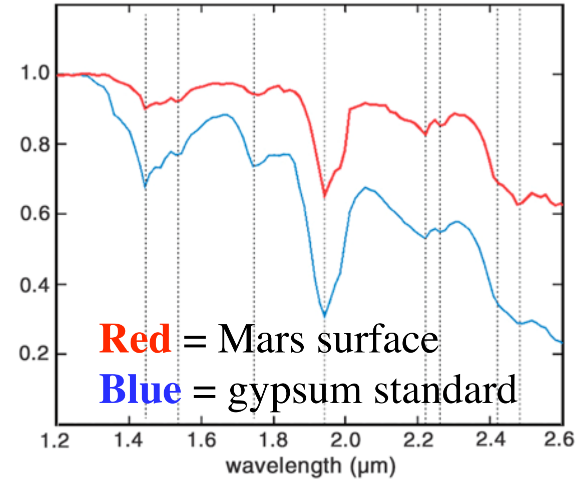
Amino Acid Diagenesis – Preservation on Mars



Phyllosilicate deposits, Mawrth Vallis (Bishop et al., 2008)



jarosite



- ✓ **Consider general classes of minerals detected on Mars & evaluate terrestrial analog locations in order to determine preservation potential.**
  - – ***Sulfates*** **– using geologic samples to evaluate preservation potential**
  - – ***Halites*** **– analyses of both pure halite and halite with evidence of bacteria**
  - – ***Phyllosilicates*** **– deep sea cores and petroleum rich clays**

- ✓ **Goal is to determine importance of depositional environment for biomarker preservation and relative preservation potential of various facies over geological time.**

TABLE 2. AMINO ACID CONCENTRATIONS OF VARIOUS SULFATE MINERALS

Location (Ma)	Asp	Ser	Glu	Gly	Ala	Val	MA	EA	Z*
South Bay Gypsum (0)	77.7†	1495†	176	1591	3172†	731	37.2	173	0.04
Anza-Borrego Gypsum (4)	137†	8.3†	116	10.3	30.0†	Trace	10.2	8.8	0.5
Haughton Crater Gypsum (23)	21.7	65.9	13.5	N.D.	6.7†	Trace	17.7	18.7	5.4
Panoche Valley Gypsum (40)	5.6†	3.3†	234	N.D.	2.9†	??	40.3	21.2	21.2
Panoche Valley Anhydrite (40)	55.5†	587	93.4†	N.D.	58.9†	46.2	72.4	7.9	1.4
Panoche Valley Jarosite (~40)	62.8	50.3†	39.0	28.1	120†	55.8	11.9	10.5	0.15

Note: All values are blank-corrected and reported in mass ppb. Uncertainties in the measurements are ±10%.

* $Z = \frac{MA + EA}{gly + ala}$

†D-enantiomer detected.

N.D. – Not detected above blank level.

?? – Valine is not possible to evaluate because of interference from an unknown component.

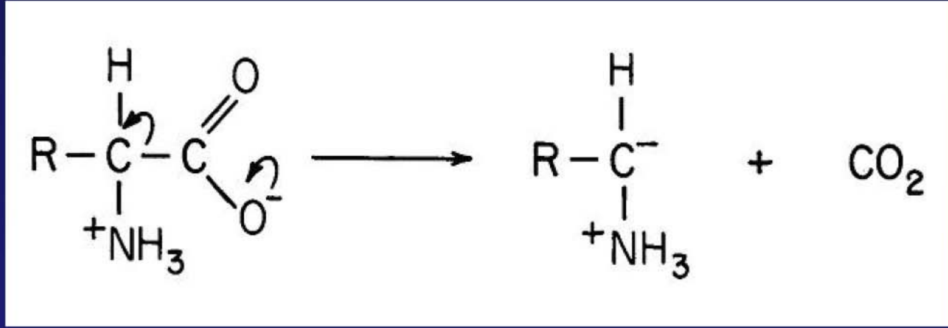
- ✓ Low Z values also found in modern gypsum samples from Australian Saline Lakes (Z_{MA} < 0.05; Z_{EA} < 0.03); Z increases with age in gypsum.
- ✓ The presence of the D-enantiomers of several amino acids imply they are ancient and not modern contamination.
- ✓ Amino acid distribution is different from that of extant bacteria.

Amino acid kinetic inferences from Amine Values

$$Z = \frac{(METHYLAMINE + ETHYLAMINE)}{(GLYCINE + ALANINE)}$$

- Amine concentrations in gypsum are negligible at age zero
- The source of volatile amines in sulfate matrices is from decarboxylation of their parent amino acids
- All amines are retained in the sulfate matrices
- The ratio Z, {methylamine + ethylamine} to their parents {glycine + alanine}, represents extent of decarboxylation

Decarboxylation Reaction



ASSUMPTION: $$AA_0 = AA_t + AMINES_t$$

FIRST ORDER RATE EQN: $$\ln\left(\frac{AA_t}{AA_0}\right) = -k_{DC} \cdot t$$

MODIFIED RATE EQN: $$\ln(1 + Z) = k_{DC} \cdot t$$

HALF-LIFE EQUATION: $$t_{1/2} = \frac{0.693}{k_{DC}}$$

TABLE 3. ESTIMATED RATES OF DECARBOXYLATION IN GYPSUM

Location	Average Exposure T (°C)	k_{DC} (years)$^{-1}$	$t_{1/2}$ (years)*	$t_{1/2}$ on Mars -20°C (years)	$t_{1/2}$ on Mars 0°C (years)
Anza-Borrego Gypsum	20	1.0×10^{-7}	6.8×10^{6}	2.2×10^{11}	8.5×10^{8}
Haughton Crater Gypsum	0	8.1×10^{-8}	8.6×10^{6}	2.3×10^{9}	8.6×10^{6}
Panoche Gypsum	20	7.8×10^{-8}	8.9×10^{6}	2.9×10^{11}	1.1×10^{9}

$^{*}\ t_{1/2} = \dfrac{0.693}{k_{DC}}$

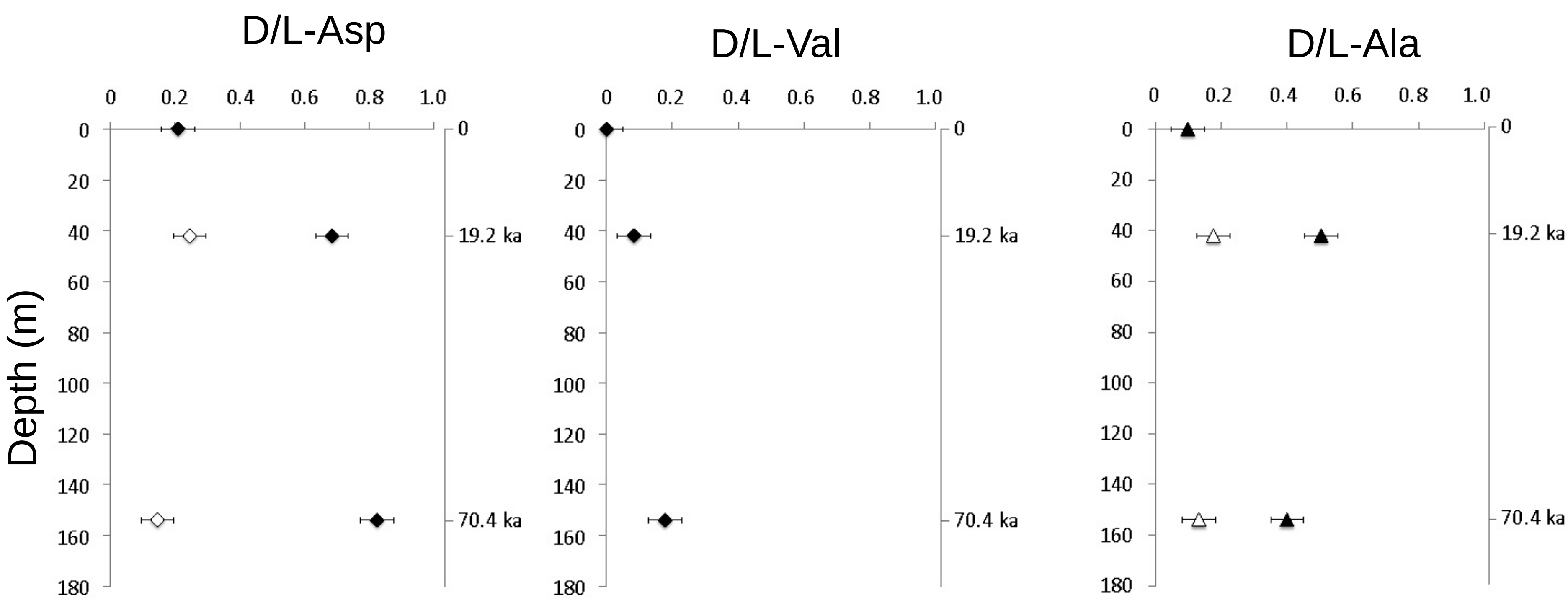
- **These half-lives indicate that amino acids and amines should be preserved in sulfate minerals on Mars for periods of billions of years.**

- **The corresponding half-lives for jarosite and anhydrite appear to be considerably longer**

Mars temperature (°C)	Anhydrite/jarosite decarboxylation half-life (yrs)
0°	1×10^{10}
-20°	3×10^{12}

Halite Core Sample Analyses

Cores samples provide information about diagenetic histories, geochemical/ chronological context and allow for kinetic determinations.
"Chronological snapshots"



Open symbols represent samples with visible purple inclusions of cyanobacteria. Data not reported for cyanobacteria-included samples for valine because of low degree of racemization). The presence of viable organisms can be easily detected!

Racemization/Degradation Rates in Halite

- **Kinetics of amino acid racemization determined for various amino acids in halite using depth profiles**
- **Amino acid racemization rates (assume T = 25°C)**

Asp	**2.4 x 10^{-5} yr^{-1}**	**$t_{1/2}$ ~ 3 x 10^{4} yrs**
Val	**6.5 x 10^{-6} yr^{-1}**	**$t_{1/2}$ ~ 1 x 10^{5} yrs**

- **Decarboxylation <u>at least</u> one order of magnitude slower than racemization reactions in geological samples**
- **Thus, conservative estimate for amino acid decarboxylation rate constant in halites is on the order of 10^{-6} to 10^{-7} yr^{-1}**
- **Extrapolating these rates to the temperature of Mars predicts amino acid survival in halites for billions of years**

$$\ln\left[\frac{1+D/L}{1-D/L}\right] - \ln\left[\frac{1+D/L}{1-D/L}\right]_{t=0} = 2 \cdot k_i \cdot time$$

Determined by Uranium Dating

A word on *Phyllosilicates-1*

Some of the amino acids detected in an aerobic core taken from a depth of 5344 m in the Pacific Ocean. The sediments consist many of red clay and some radiolarians. The top of the core is recent while the bottom is Pliocene to Miocene in age. Values are in nanomoles per gram. Data from Schroeder (1973)

	0-3 cm	**20-22 cm**	**40-42 cm**	**60-62 cm**	**80-82 cm**	**100-102 cm**	**120-122 cm**	**137-140 cm**
asp	250	2.4	-	1.2	-	1.2	-	0.6
gly	284	6.7	5.8	3.2	3	4.6	2.8	2.6
ala	179	4.2	2.9	1.4	1.5	1.6	1.1	1
val	102	1.5	0.8	0.4	0.3	0.6	0.3	0.4
β–ala	~400	107	96	77	94	82	46	32
γ-ABA	~140	98	122	62	92	67	31	28

β–ala = β-alanine

γ-ABA = γ-amino butyric acid

Below the first few cms there is poor preservation of amino acids other than those produced by bacterial degradation.

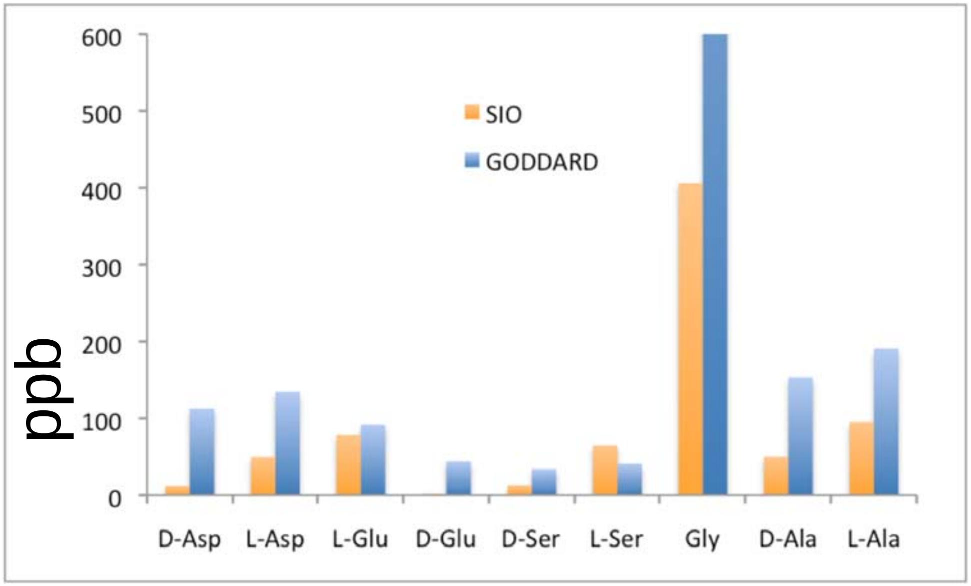
A word on *Phyllosilicates-2*

Green River Shale

43.8% Dolomite, 22.1% Quartz, 17.8% Albite, Smectite

Anoxic Depositional Environment

Label	Amino Acid	SCWE (ppb)
1	D-Asp	12.5
	L-Asp	50.1
2	D-Glu	2.03
	L-Glu	78.3
3	D-Ser	13.2
	L-Ser	64.7
4	Gly	406
5	D-Ala	50.4
	L-Ala	95.1
	TOTAL all	**772.33**



Conclusions

- **Sulfates appear to be good targets for organic preservation – fact that Mars' temperatures are extremely cold offers potential for preservation**

- **Halites also appear to be good targets for preservation of organics**

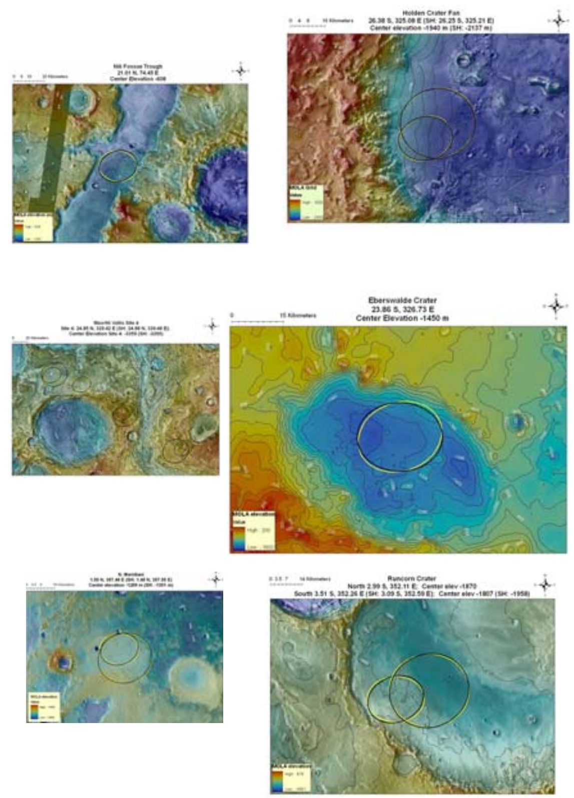
- **Clays provide for organic preservation only as long as they have had an anoxic depositional history**

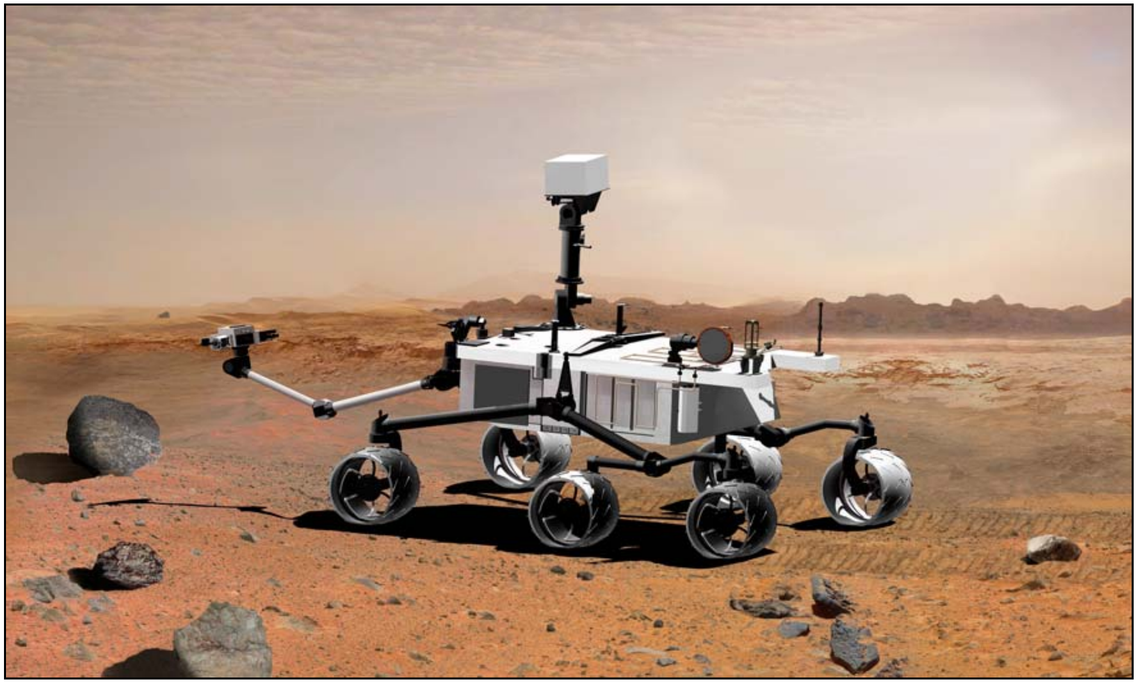
- **The best mineralogical matrix for organic preservation is within a mineral that offers protection from oxidants, UV and GCR-radiation**

Landing Site Candidates

- ✓ **Evaporitic sites (Sulfate/Halites) are primary for organic detection**
- ✓ **Represent evidence of standing water bodies – Biomarker Sequestration!**
- ✓ **Phyllosilicates may be less attractive because of oxidizing environmental conditions at their time of formation and at present**

Location	Latitude	Longitude	Elevation (m)	Mineralogy
Nili Fossae Trough	21.01° N	74.45° E	-608	-Phyllosilicates -Noachian
Holden Crater Fan	26.38° S 26.25° S	325.08° E 325.21° E	-1940 -2137	-Fluvial Layers -Phyllosilicates
Mawrth Vallis (7)	24.65° N 24.01° N 23.19° N 24.86° N	340.09° E 341.03° E 342.41° E 339.42° E	-3093m -2246 m -2187 m -3359 m	-Phyllosilicates (Layered) -Noachian
Eberswalde Crater	23.86°S	326.73°E	-1450 m	-Delta
Miyamoto (Runcorn)	3.51ºS 3.09ºS	352.26ºE 352.59ºE	-1807 m -1958 m	-Phyllosilicates ~~-Sulfates~~
S. Meridiani	3.1ºS	354.6E	-1589 m	~~-Sulfates~~ -Phllosilicates
Gale Crater	4.5S	137.4E	-4451 m	~~-Sulfates (Layered)~~ -Phyllosilicates





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REFERENCES:

Aubrey, A.D., *et al.* (2006) *Geology* **34,** 357-360.

Aubrey, A.D. (2008) UCSD Dissertation.

Bibring, J.P., *et al.* (2006) *Science* **312,** 400-404.

Bishop, J.L., *et al.* (2008) *Science* **321,** 830-833.

Garry, J.R.C., *et al.* (2006) *Meteorit. Planet. Sci.* **41,** 391-405.

Kminek, G., and Bada, J.L. (2006) *Earth Planet. Sci. Lett.* **245,** 1-5.

Parnell, J., *et al.* (2007) *Astrobiology* **7,** 578-604.

Schroeder, R.A. (1973) UCSD Dissertation.

Snider, M.J., and Wolfenden, R. (2000) J. Am. Chem. Soc. 122, 11507-11508.

Sumner, D.Y. (2004) *J. Geophys. Res.* **109,** E12007.

ten Kate, I.L., *et al.* (2005) *Meteorit. Planet. Sci.* **40,** 1185-1193.

Tosca, N.J., *et al.* (2008) *Science* **320,** 1204-1204.