Organosilicates as Potential Biosignatures

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General Objectives

- Can we detect and identify organic material on meteorites without demineralizing the meteorite?
- Can we use the IR technique to identify the organic material in the meteorites while it is bound to the mineral component?
- Do important biomolecules give useful biosignatures while bound to the mineral component?

Significance of our Research

- Future Missions to Mars or meteorites
  - Preservation of biomolecules could serve as an indication of past or present life
- NASA's "Stardust" Mission
- Geology: study of rock coatings and desert varnish

Organic Substances Studied

- Amino Acids
- Sugars
- Maillard Products
- Metal complexes of Maillard Products
- Acid Halides
- Alcohols
- ATP/AMP

Modes of interaction of biomolecules with silicate

Biologically relevant compounds can be preserved as silicates by two mechanisms:

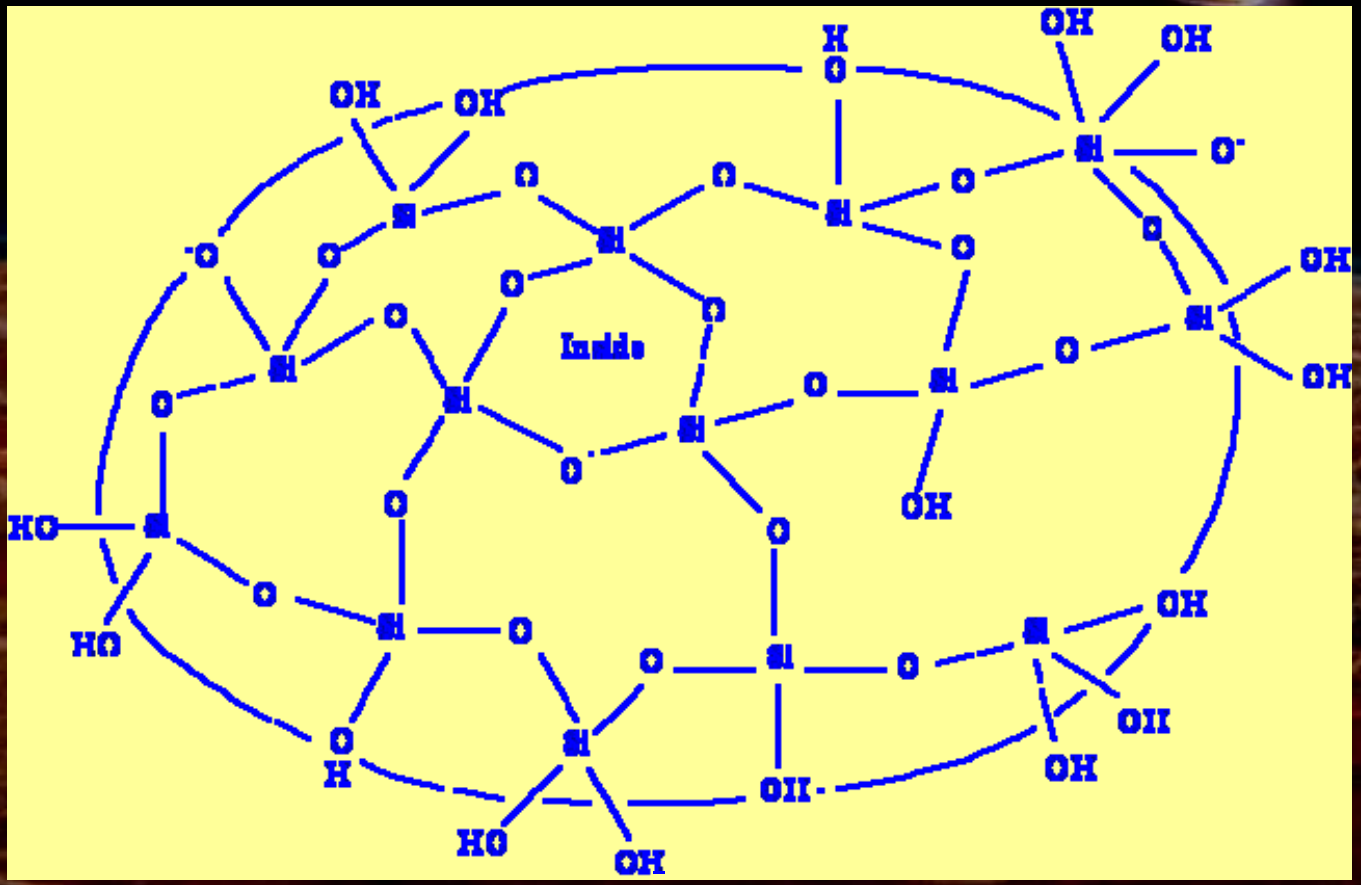
A) Entombment

B) Chemical Bonding

A) Entombment

In the first mechanism, these biomaterials cause polymerization of silicic acid and become entombed in the silicic acid polymer (silica gel). In this mechanism we would observe only the Si-O-Si bonds in the silica gel.

Entombment of organic material in polymerized silicate (silica gel)

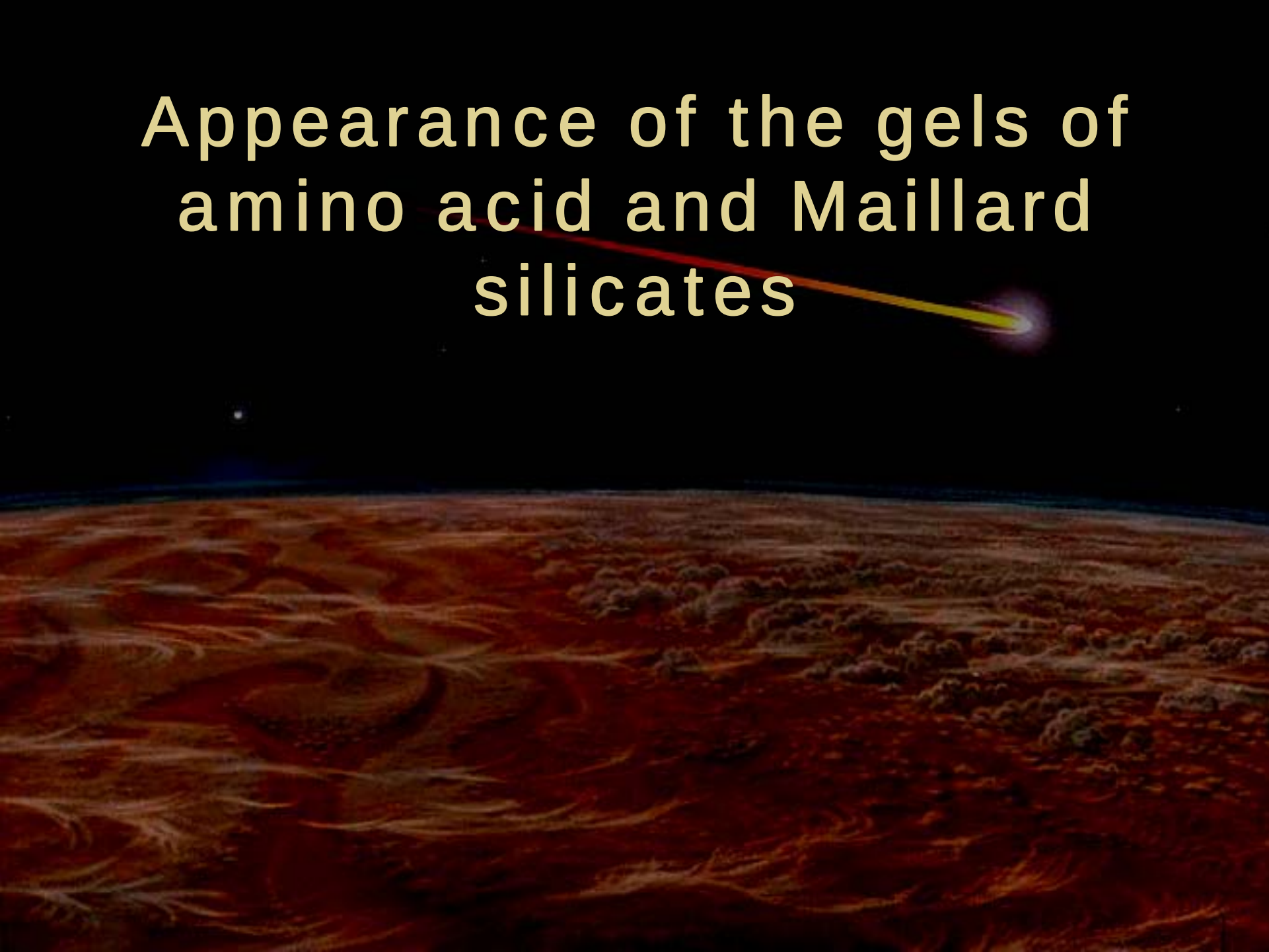


B) Covalent bonding to give organosilicates

In the second mechanism, the bio-molecules make chemical bonds with the silicic acid, to create organic silicates, which would have the Si-O-C bonds.

We are investigating these two mechanisms by the Infra-red (IR) spectroscopy.

Appearance of the gels of amino acid and Maillard silicates



Gel formation between amino acids or amino acids + ribose and Na-silicate:

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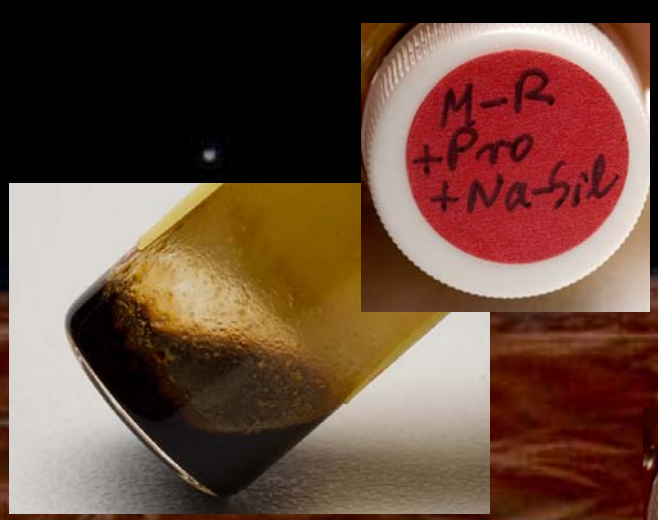
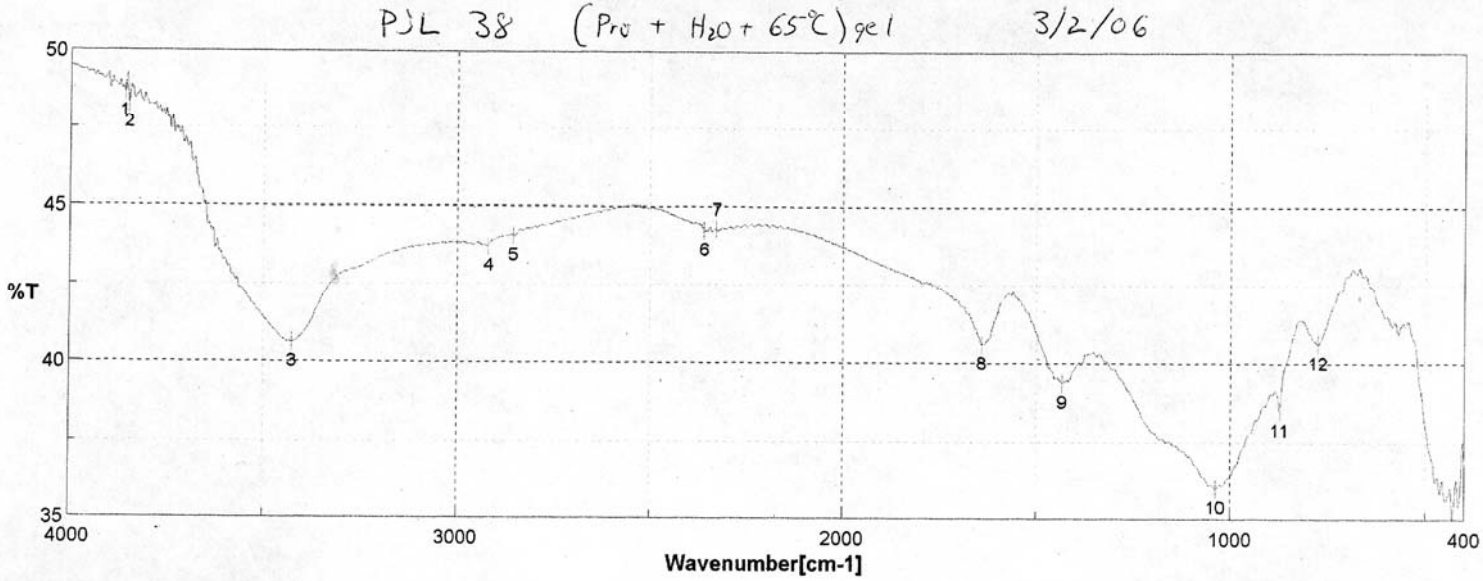


Gel formation between amino acids or amino acids + ribose and Na-silicate:

The IR spectra of isolated silica gels

- Only examples of amino acid gels are shown
- Features of the IR: intense bands in the Si-O-Si/Si-O-C region are observed
- Small amount of entombment is noticed

Examples of our IR Spectra



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Sample Name			
Comment			

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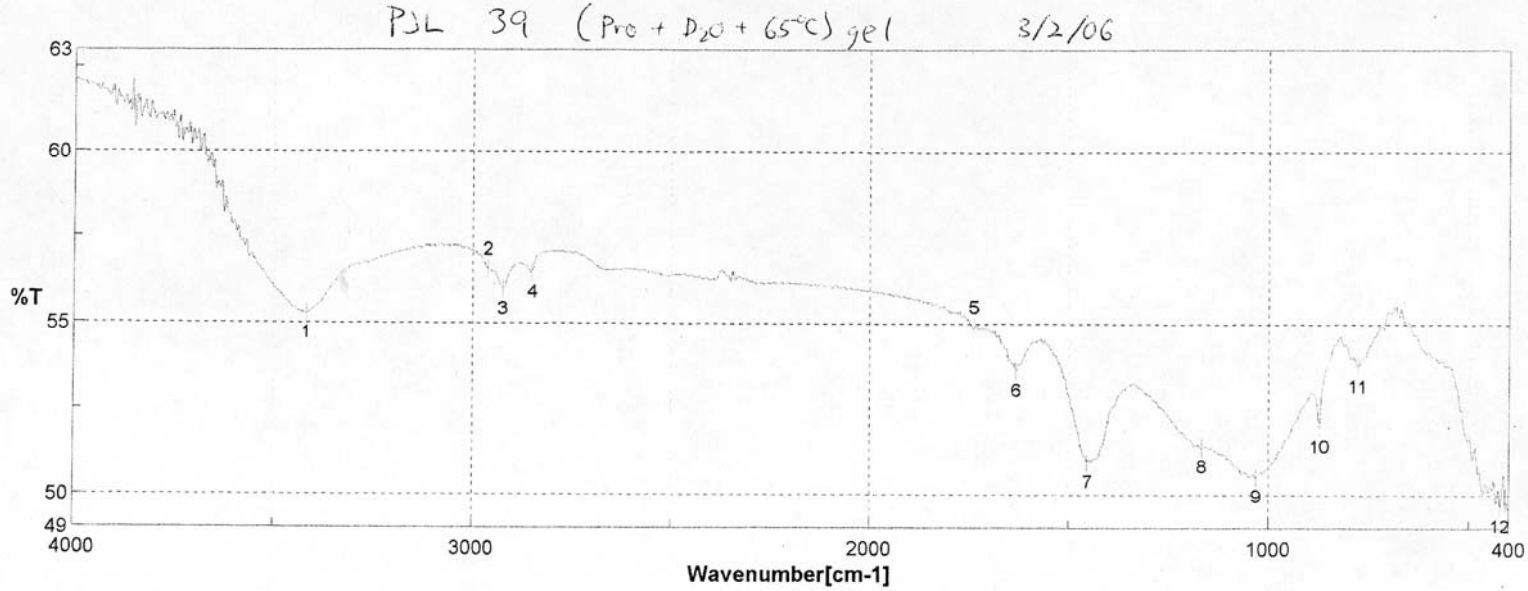
6	2359.48	44.2331	7	2328.62	44.2825	8	1640.16	40.6086	9	1432.85	39.3902	10	1037.52	36.0081
11	872.631	38.5112	12	774.279	40.6219									

Examples of our IR Spectra



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1	3417.24	55.2918	2	2961.16	56.5749	3	2923.56	55.9953	4	2850.27	56.4978	5	1735.62	54.9218
6	1631.48	53.643	7	1453.1	50.9845	8	1164.79	51.4197	9	1030.77	50.5439	10	872.631	52.0237
11	776.208	53.7626	12	421.37	49.6613									

The analysis of the IR frequencies

Selected literature values in cm-1:

- **Si-O-Si** antisymm. str. at 1100-1000 (Bellami, the values depend on cyclic/open chain structure); **Si-O-C** antisymm. str. in the same region (Bellami);
- **Si-O** stretch at 950(Hino, by deuteration);
- **Si-OH** bend at 870 (Hino, by deuteration);

The problem

- The Si-O-C band in the IR overlaps partially with the Si-O-Si band.

- IR absorption bands arising from linkages involving Si atoms are ~ 5x more intense than the bands corresponding from the C-linkages.

Our deuteration method

The deuteration method should lead to the differential shifting of the bands in question.

Two methods for deuteration:

- Forming gels, then treating with D_2O at 65° C
- Using D_2O to initially prepare the gels

Differences in IR peaks upon deuteration

- **One relevant band shifts towards higher frequencies upon deuteration**

- **The bands position is influenced heavily by hydrogen bonding; this quality changes upon deuterium substitution**

Conclusions

1. Amino acids, alcohols, and acid halides appear to follow the entombment mechanism.

2. Sugars point to organosilicate formation (in solution)

3. The amino acids and their Maillard products catalyze the D/H exchange in the manner which is specific for these bio-molecules.

4. Tentative IR band assignments:
   - Si-O-Si ~1100-1000 cm^{-1}
   - Si-O-C ~1250-1100 cm^{-1} (slightly higher)

Acknowledgments

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Research Presentations, Abstracts, and Publications

1. V. M. Kolb and P. J. Liesch, “Organic Silicates as Biosignatures”, Astrobiology, 6, 223 (2006).
2. V. M. Kolb and P. J. Liesch, “Role of amino acids and their Maillard mixtures with ribose in the biosilicification process”, in “Instruments, Methods, and Missions for Astrobiology IX” R. B. Hoover, G. Y. Levin, and A. Y. Rozanov, Eds., SPIE, Vol. 6309, 63090T(1-8) (2006).
3. V. M. Kolb, M. Bajagic, P. J. Liesch, A. Philip, and G. D. Cody, “On the Maillard reaction of meteoritic amino acids”, ibid, 63090B (1-13).
4. V. M. Kolb and P. J. Liesch, "Organic Silicates as Biosignatures", Astrobiology Science Conference, March 26-30, 2006, Washington, DC, Abstract No. 15.
5. V. M. Kolb, P. J. Liesch, M. Bajagic, and A. Philip, "Role of the Maillard Reaction in the Biosilicification Process", Instruments, Methods, and Missions for Astrobiology X, SPIE 200 August 13-17, 2006, San Diego, CA, Abstract 6309-16.
6. P. J. Liesch and V. M. Kolb, “Organic Silicates as Potential Biosignatures”, 7th Annual UW Syste Symposium for Undergraduate Research and Creative Activity”, UW-Stout, Menomonie, WI, May 5, 2006, Abstract PO44.
7. P. J. Liesch and V. M. Kolb, “Organic Silicates as Potential Biosignatures”, Posters in the Rotund A Celebration of Undergraduate Student Research, Capitol Rotunda, Madison, WI, April 25, 2006, Abstract 63.
8. P. J. Liesch and V. M. Kolb, “Organic Silicates as Potential Biosignatures”, 1st Annual Showcase Student Scholarship, UW-Parkside, Kenosha, WI, April 17, 2006.

Current Work (Submitted Abstracts for Publications and Presentations)

1. V. M. Kolb and P. J. Liesch “LIVING STRATEGIES OF UNUSUAL LIFE FORMS ON EARTH AND THE RELEVANCE TO ASTROBIOLOGY” (submitted to SPIE)
2. V. M. Kolb and P. J. Liesch “THE IMPORTANCE OF THE MAILLARD-METAL COMPLEXES AND THEIR SILICATES IN ASTROBIOLOGY” (submitted to SPIE)
3. P. J. Liesch and V. M. Kolb “IMPORTANCE OF THE INTERACTION BETWEEN SODIUM SILICATE AND ORGANIC MATERIALS TO ASTROBIOLOGY: EXAMPLES FROM OUR LABORATORY” (submitted to SPIE)
4. P. J. Liesch and V. M. Kolb, “Silicates of Alcohols as Potential Biosignatures”, 2nd Annual Showcase of Student Scholarship, UW-Parkside, Kenosha, WI, April, 2007.
5. P. J. Liesch and V. M. Kolb, “Silicates of Alcohols as Potential Biosignatures”, 8th Annual UW System Symposium for Undergraduate Research and Creative Activity”, UW-Stout, Menomonie, WI, May 5, 2006, Abstract PO44.