Optical Activity as a Biosignature in the Search for Extraterrestrial Life

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Outline of this talk

- **Science**
  - How will we detect life on other planets?
  - Some proposed biosignatures
  - Biomolecular structure, chirality, and circular dichroism spectroscopy

- **Conjecture**
  - What happens if there's something in the ice?

- **Exploring the possibilities**
  - Steps to take to explore frozen biosignatures
Life- How will we know it?

Perhaps the most central of Astrobiological questions is: How will we know life when we see it?

It is almost impossible to simultaneously frame this question without terrestrial bias and think of ways to explore the solar system for life. Consideration of biosignatures relevant to Astrobiology must be made with the fewest terrestrially-biased assumptions to decrease the ambiguity in finding a positive result.

Image from: http://commtechlab.msu.edu

Image source: http://library.thinkquest.org
Biosignatures - Immunology and Biomarkers

Biochemical tests which are used to study terrestrial biological molecules have been proposed to study other planets.

Immunological Studies

- Use of antibodies to detect proteins

Fluorescence probes

- Use of fluorescent probe molecules to detect biomolecules

While a positive result from biochemical tests on another planet would be a unambiguous detection of life, a negative result would be ambiguous e.g. Mariner experiments.
Isotope fractionation for several elements is known to occur and may be taken as a possible biosignature.

- Sulfur is fractionated by sulfate reducing bacteria.
  
  \[ ^{34}\text{SO}_4^{2-} \rightarrow ^{34}\text{SH}_2 \]
  \[ ^{32}\text{SO}_4^{2-} \rightarrow ^{32}\text{SH}_2 \]
  
  Leads to an enrichment of \(^{32}\text{S}\) in inorganic sulfates.

- Iron may be fractionated by iron reducing/oxidizing bacteria.
  
  \[ \text{Fe(aq)} \rightarrow \text{Fe(aq)} \]
  
  Research being worked on by NAI.

- Carbon is also fractionated by organisms that use \(\text{CO}_2\) or carbonates as a carbon source.

- We don’t really understand how isotopic fractionation occurs so its hard to know if it is a ubiquitous sign of life.

- Some abiological processes can also lead to isotopic fractionation.
Biosignatures- Complex organic molecules

- Complex organic molecules are often thought of as being signs for life:
  - Polycyclic Aromatic Hydrocarbons (PAHs) are found in oil deposits and are the result of decaying biological matter
  - Amino acids (AAs) are a fundamental component of terrestrial life and are the building blocks of proteins
  - Since both have been found in meteorites and ISM, complex organic molecules are considered ambiguous biosignatures
**Biosignatures- Chirality**

 chúrality may be an ideal biosignature since it makes only one assumption

Though chiral organic molecules occur both as a result of biological and abiological processes, only in the case of biological origins is one form of a chiral molecule selected almost completely over the other.
What is Chirality?

The classic definition of a chiral object is one which is not superimposable with its mirror image.

Hands are an example of chiral objects.

In chemistry, a pair of molecules whose mirror images are nonsuperimposable are known as enantiomers.

When there is more of one enantiomer than the other (like amino acids in proteins), an enantiomeric excess (ee) occurs.

When “chirality” is heralded as a biosignature of life on other planets, what we are really looking for is a case where there is an enantiomeric excess of chiral molecules.
Chirality in organic molecules

Organic molecules can be chiral due to the spatial arrangement of bonds around a carbon center:

In tetrahedral carbon (a carbon that has four single bonds to it), when there are four chemically distinct atoms that the central carbon is bound to, then that carbon is a **stereogenic center** and the molecule is chiral.

Stereogenic centers exist in amino acids and sugars used in DNA.

Biomolecules are made from exclusive enantiomers of these components.
Other aspects of biomolecular structures are also of a chiral nature.

Most duplex DNA exists in the “B”-form where the helix has a right-handed twist.

In proteins, nearly all of the \( \alpha \)-helices are right-handed.

Image source: http://www.bmsc.washington.edu
Studying chirality with spectroscopy

Circular dichroism (CD) spectroscopy is used to study chiral molecules

- “R” and “L” designations of molecules indicates that the molecule absorbs more right or left circularly polarized light at a given wavelength

CD spectroscopy utilizes circularly polarized (chiral) light since you need a chiral test to study a chiral system

Measuring a CD spectrum

- A CD spectrum is measured by looking at the difference in the absorption of left and right circularly polarized light by a sample as a function of wavelength.

Spectrum calculated as: 

$$CD = A_l - A_r = \frac{\theta}{32982}$$ at each wavelength.

Image source: http://www.umassmed.edu/
UV-Vis CD

Most biological work is done in the UV-Vis (190-800 nm) spectral region.

UV-Vis looks at electronic transitions.

In proteins, UV-Vis CD can provide information about secondary structure.

Example of a UV-Vis CD spectrum for the protein myoglobin.
Vibrational circular dichroism (VCD)

A recently developed technique is VCD which can be used to examine the infra-red spectral region.

IR spectroscopy looks at bond vibrations, stretching, etc.

This not only gives a wide variety of things to look at but also provides more information about the molecule.

VCD is a relatively new technique and commercial machines have only been available for a couple of years: much to be done.

How can CD be used to detect life?

One major problem with using CD as the basis of detecting extraterrestrial life is that it assumes chemical similarity. Since we don’t know what an extraterrestrial biomolecule will be made of, we may or may not be able to use these methods, but...

In UV-Vis CD and the primary bond detected is:

- Amide carbonyl bond, protein backbones, two transitions from 190-240 nm
- Nucleobases have several transitions from 197-298 nm

VCD looks for bond stretches, and signature bands for biological molecules include:

- **Carbonyl**: 1600-1800 cm\(^{-1}\)
- **Amide NH**: 3300-3500 cm\(^{-1}\)
- **Alcohol OH**: 3590-3650 cm\(^{-1}\)
- **Various CH**: 2835-2962 cm\(^{-1}\)
Terahertz circular dichroism (TCD)

TCD is still a developing technology but could be useful in describing whole molecule vibronic modes.

Illustration of the atomic motions of bacteriorhodopsin at 0.498 THz

Simulated bacteriorhodopsin TCD spectrum

When fully developed, TCD will be a powerful tool for Astrobiology, but until then…

Xu, J. et al. Astrobiology 2003, 3, 489-504
Induced circular dichroism (ICD)

- In some situations, a CD spectrum can be measured for an achiral molecule
  - When an achiral molecule becomes physically (not chemically) attached to a chiral molecule, then it is in a chiral environment

An ambidextrous latex glove is achiral until...

...it is placed on one hand or the other and then is a left or right handed glove

- In a chiral environment, an achiral molecule will become CD active
Example of ICD effect

One example of this is the insertion of achiral chromophores into DNA films:

So, to use ICD for Astrobiology, we need to identify a simple, ubiquitous “probe” molecule that can be studied by either UV-Vis or IR and that is expected to be intimately associated with biological molecules.

Follow the water…in the cell?

While we are on the topic of water and ice in the solar system:

Water is, of course, a primary component of living systems:

- Cells are made primarily of water
- *E. coli* composition: water (70%), proteins (15%), RNA/DNA (7%), polysaccharides (2%), lipids (3%), inorganics (3%)
- About 5% of the water in a cell is coupled to biological molecules
- Even in the liquid state, this water is tightly coupled to the biomolecule such that molecule-associated water exchanges very slowly with bulk water
Clathrates beyond methane

- Clathrates are the cages that water forms around a nonpolar molecule in water
- Clathrates form to minimize interaction of a nonpolar molecule with polar water
- The same is true for biomolecules, where water is intimately associated with the molecule.
- You can see where this is going...

*Image from: http://www.brookscole.com/*

*Image from: http://www.imb-jena.de*
ICD in bioclathrates?

- Here is the conjecture: is the water that surrounds a biological molecule ordered enough to exhibit ICD?

- This biosignature may be found as a result of frozen extraterrestrial cells or biological molecules trapped in the ice layers around the planet, especially in an active environment like Europa.

- On an icy body in the solar system, there may be evidence for life in the ice itself.

- It may be possible to detect life in these places by using VCD to study the ice.

Photo: Kjell Ove Storvik/AMASE

Image source: NASA

Image source: http://images.cambridgesoft.com/
Molecular modeling

- Computer simulations could be used to understand water/ice assembles around biomolecules.
- These studies could be used to predict whether or not the clathrate structure would be chiral.
- Predictions could also be made as to how strong this ordering would be and therefore what kind of signal to expect.
- Could also look for temperature variations.

Image from: http://www.isbu.ac.uk
Laboratory studies

The next step is to actually take a look at VCD of water in biomolecule liquid/frozen solutions.

- Commercially available VCD spectrometer
- Effects to look for: biological source (whole cell/individual molecules), concentration, temperature effects
Space mission

To get to the final target, flight mission would be needed

A flight mission is needed to carry a specially designed spectrometer

The mission would go after planetes/moons with surface ice that has been clearly observed

Here, reflectance VCD would be used to study water ice spectra
Summary

There are several biosignatures we can look for
- Probably no one single technique will tell the whole story
- Looking for high degrees of enantiomeric excess in molecules makes the least number of life assumptions and may provide the most unambiguous life detection technique

Circular dichroism is the best way to look for ee
- Molecular CD can be studied at several wavelengths thus can be used to look at several different types and aspects of molecules

“Bioclathrates” may hold the key
- Clathrates formed around biological molecules may be the most straightforward thing to look for
- This biosignature requires only two assumptions: that water is the medium of life and the ee is a signature of life
- Molecular modeling and simple VCD studies would provide a look into this possibility