Studies of

Lanthanide complexes in a model ionic and photosynthesis environment by NIR, MRI and X-ray Imaging: *Subhendra Sarkar (Rad Tech), Chen Xu(CET) and Zoya Vinokur (Rad Tech)*

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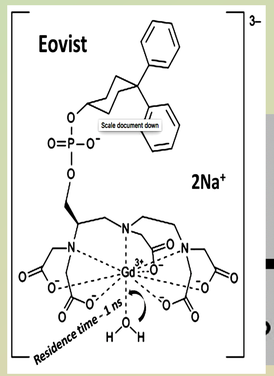
Abstract

This work explores the diffusivity of a lanthanide Gadolinium complex, Eovist (Gadolinium-Ethoxy Benzyl Diethylenetriamine pentaacetate) that is stable in neutral media but is not in acidic environment. An acidic fruit model like pineapple that is rich in transition metals was tested using x-ray and MR imaging. Another goal of this work was to perturb the photosynthesis systems that pineapple has maintained for millions of years during the evolution of circadian genes for efficient water conservation using dark photosynthesis. To detect such photosynthesis Near infrared reflection spectroscopy was used for pineapple samples to test if added lanthanide complex and pre-existing transition metals in pineapple can affect such photosynthesis processes. This is an ongoing project with potential medical and agricultural implications as well as impact on new solar cells and Lanthanide influenced bone regeneration.

Background

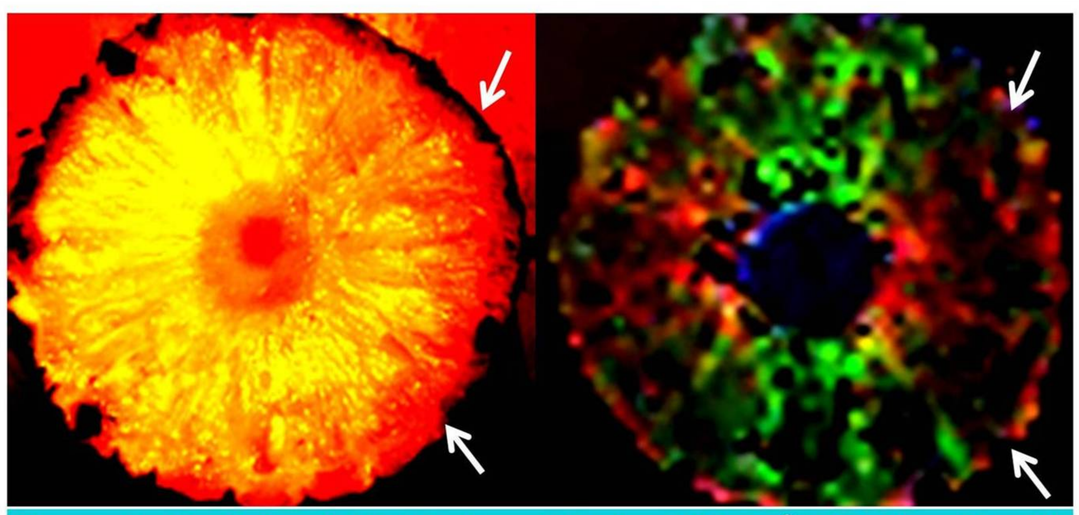
The pH distribution in the pineapple is heterogenous allowing perhaps different divalent and trivalent transition metals (Ca2+, Mg2+ and Fe3+) to partially remove one or more DTPA moieties from central Gd in Eovist antiprism allowing more water molecules to rush to the inner sphere.

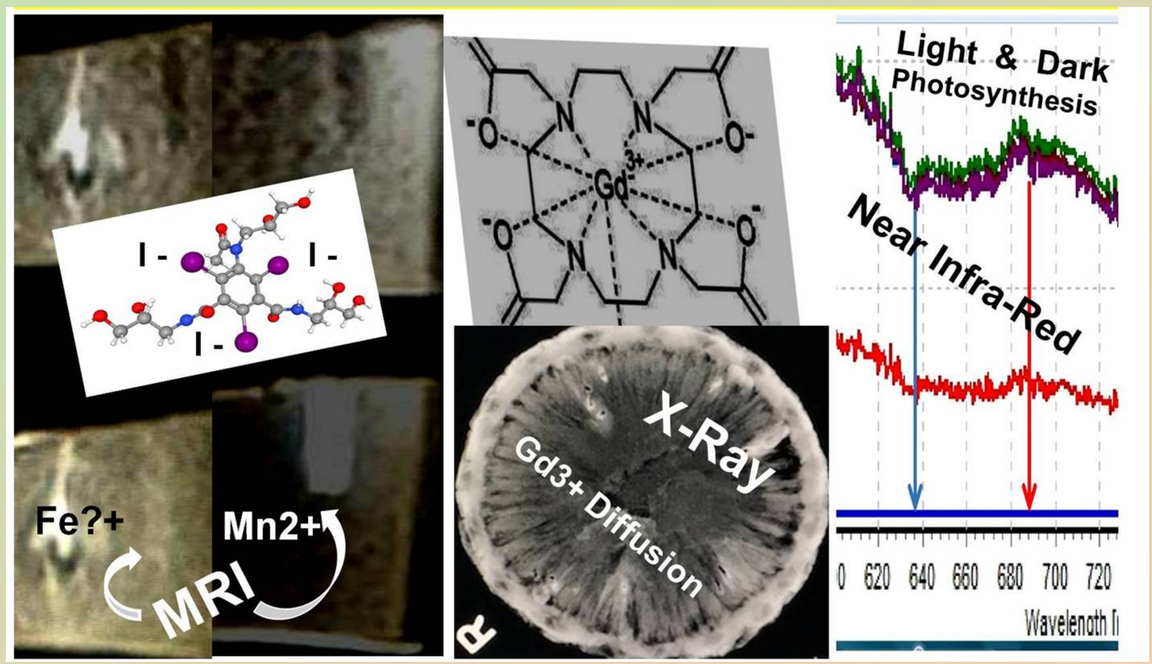
MRI contrast Eovist was used with Gd+3 atom loosely bound to other negative structures like phenol ring. Such complex structures supply or absorb electrons. We were able to observe spectral peaks that could be due to NIR driven photosynthesis at precise absorption wavelengths in cut pineapple.



The Eovist molecular structure with gadolinium at the center and negative ligands (all those chemicals surrounding Gd)

Diffusion MRI : Blunt injury causing metal ionic "flood" decreasing MR signal (arrows)





The MRI results **on the left panel show the effect of Omnipaque 300(an Iodinated contrast media, that should not produce any MRI activity). It was infused in apple, top; and in sweet potato, bottom. Note apple has a small amount of iron (0.2 ug/100g) that is present in biochemical pathways alongwith other ions including Mg, Na, etc. Iron can affect MRI signal generation by enhancing proton signals. Weak signal might be suggestive of low extraction of iron.**

Near Infra Red Reflection Spectroscopy (NIRS)

6-700 nm area shows the pineapple has peaks that may correspond to photosynthesis induced by NIR light. The implication of our work is: the pathway of photosynthesis may be accelerated or decelerated by injecting Gd and iodine complexes sensitive to L-edge x-ray absorption.

Discussion

❑ The MRI results on the left panel show the effect of Omnipaque 300(an Iodinated contrast media, that should not produce any MRI activity). It was infused in apple, top; and in sweet potato, bottom. Note apple has a small amount of iron (0.2 ug/100g) that is present in biochemical pathways alongwith other ions including Mg, Na, etc. Iron can affect MRI signal generation by enhancing proton signals. Weak signal might be suggestive of low extraction of iron.

❑ On the other hand sweet potato has most of those ions as well as a modest amount of Mn (0.25 ug/100g). We believe Iodinated nanoparticles are chelating iron (in apple) and Mn (in sweet potato, white arrows). There are no other MRI suitable ions other than Mn+2 to significantly enhance the MR signal, hence Mn seems to be fully extracted by iodinated nanoparticles.

Conclusion

- **X-ray imaging can directly show presence and diffusion of metallic or electron rich ions. It is a suitable probe for nanoparticle transport in fruits that could model physiologic behavior in biomedical applications including human tissues.**
- **NIR can map slow molecular dynamics modulated by metal ions, either contained in the fruit biochemical pathways or released by the nanoparticles infused. This may be able to detect modification of photosynthesis in fruit systems (PS-I and II) that involve charge transfer, and perhaps can be influenced by suitable nanoparticles.**
- **MRI seems to identify release of metal ions like Fe2+ or Fe3+ and, particularly Mn2+ due to electron-rich iodinated media and may be useful in monitoring bone regeneration , for example, with greater Ca+2 mobilization.**

Acknowledgment

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References

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Gadolinium Chemistry

- The ionic radius of Gd^{3+} is 0.99 Å, similar to divalent Ca^{2+}.
- If Gd^{3+} becomes fully hydrated, it is supposed to occupy the center of a square antiprism with 8 water molecules at the corners of this inner sphere with a residence time of approximately 1 ns for each eater molecule during which its electron lone pair engages with Gd^{3+} ion.
- Most Gd-DTPA complexes in biomedicine have one ligand available for water.
- Gd-EOB (Gadolinium-Ethoxy Benzyl) DTPA was chosen since it is an amphipathic derivative of Gd-DTPA (Gd-DTPA with a covalently bound lipophilic ethoxy benzyl arm).