CURJ

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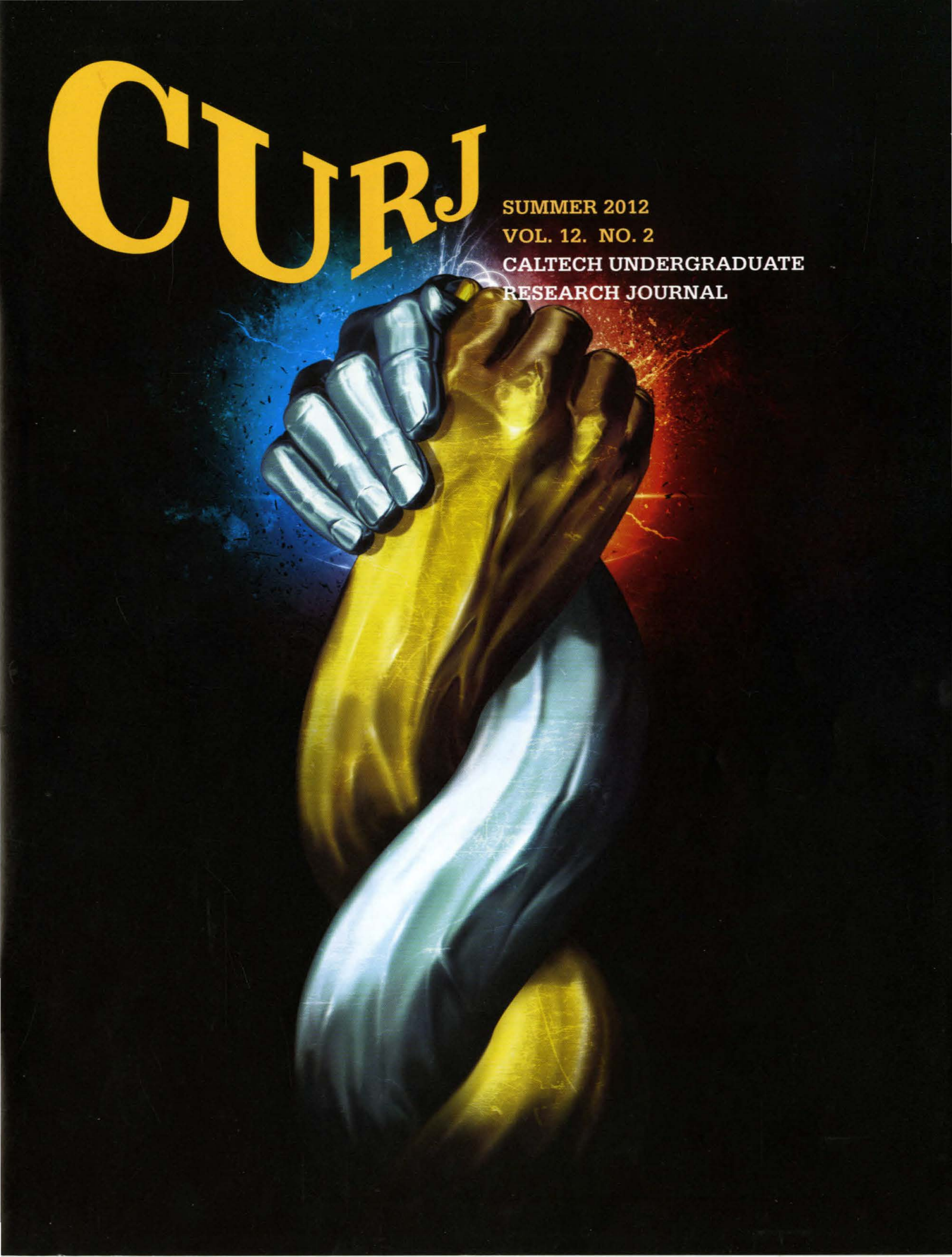
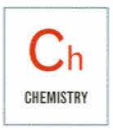
CALTECH UNDERGRADUATE
RESEARCH JOURNAL

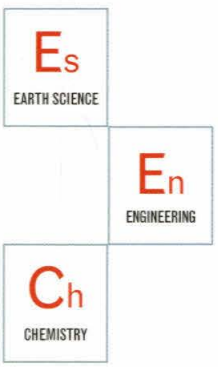


CURJ

Interview

Research





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CALTECH UNDERGRADUATE RESEARCH JOURNAL vol. 12. no. 2

From the editors

The Caltech Undergraduate Research Journal is designed to highlight the unique research at Caltech performed by some of the best and brightest students around the world. In coordination with the Summer Undergraduate Research Fellowship program at Caltech, hundreds of students can spend their summer doing what they love.

Students not only gain research experience, skills in laboratory procedures, and a keen eye for important issues in science, but a relationship with many of the undergraduate students, graduate students, post-doctoral fellows, and professors here at Caltech. It is the sum of all these parts that create a great scientific spirit at Caltech that is unmatched at any other institution.

It is a great honor to highlight some of the research done at Caltech by students from a diverse background. The Caltech Undergraduate Research Journal has selected four students: Deekshaw Agrawal, Tonia Ahmed, Marie Lau, and Alex Wang. Because of their outstanding progress in their own scientific fields, we are proud to include them in the Summer issue of 2012. These students have researched everything from structural and thermal properties of aluminum and titanium lattices to cloud thickness utilizing satellite imaging techniques.

Of course, research would not be possible without an outstanding faculty. The Caltech Undergraduate Research Journal thanks the faculty for their support in undergraduate research and in building a new generation of scientific leaders. Although we cannot thank everyone, we have chosen to highlight bioengineering professor Joel Burdick for his work in restoring circuitry in the spinal cord to patients that have lost vital functions through injury. We have also chosen to highlight geology professor Isaac Asimow for his work on understanding the effects of high pressures and temperatures on rock formation on Earth.

We thank you for picking up the latest edition of the Caltech Undergraduate Research Journal and hope that you continue to support undergraduate research at Caltech. Feel free to look at past issues of the Caltech Undergraduate research journal and find more content available on our website at curj.caltech.edu.

Best regards,

Granton Jindal and Marvin Gee

INTERVIEWS

Professor Isaac Asimow

Mahati Mokkarala

CURJ interview questions for Professor Isaac Asimow

Question: The Caltech Undergraduate Research Journal highlights undergraduate research opportunities and results throughout the school year. So we're wondering: Why did you decide to become interested in research and in particular geology research?

Answer: Well, I can begin with why geology. That's directly attributable to one great professor in my freshman year. I took a good mineralogy course in my freshman year at Harvard by James Thompson. The science I learned was amazing, something I never learned about before. In high school you never learn about geology much; geology doesn't seem like a science until you actually stumble onto it in college like I did when I took Professor Thompson's minerology class. Once I realized that geology is interesting, rigorous, involves math behind it, and consists of hard problems as the world is complicated. Also, geology departments are generally friendly, collegiate places and not terribly competitive.

I was lucky, as I found what I wanted to do, and I did it.

So why research?
Well, I like puzzles. Doing research, asking questions never asked before, is like solving puzzles. If you can do that for a living and get paid to solve puzzles, then that is just awesome.

Question: Did your undergraduate experiences define your ultimate career path? If so, why? What was your most memorable academic experience in undergraduate and graduate school?
Answer: Absolutely yes. I discovered what I wanted to do first semester freshman year at Harvard, and I never changed my mind. I know this is rare as people change their mind all the time. I was lucky, as I found what I wanted to do, and I did it. As for most memorable academic experience, I'd say my graduate interview here at Caltech turned out to be a remarkably influential moment, in that Professors Stevenson gave me an idea for a thesis project when I was interviewing that became my project for the next 3 years. Of course, that project didn't work, and I had to drop it for a theoretical thesis but it was a very influential moment. And as a geologist, it is easy to remember a lot of amazing field trips. In particular, for many years in this division, the high guru of field experience was Professor Bob Sharp and well into his 90's, Sharp was leading field trips around California for students. After going to Death Valley with Professor Bob Sharp, your eyes are opened, and you see the world for what it is. Professor Bob Sharp's field trips were definitely memorable experiences.

Most of my research involves the Caltech Shockwave Lab built by Caltech professors in the 1970s. . . . The Caltech Shockwave Lab allows me to access very high energies and pressures that enable me to measure properties of materials in high pressure, temperature environment found in the deep interior of the earth.

Question: What is your research on; can you explain what exactly it is you're working on and what is the next big discovery you want to find out in your field?
Answer: So, I work in several related areas; they are all related to melting rocks and the properties of molten rocks or metals. Most of my research involves the Caltech Shockwave Lab built by Caltech professors in the 1970s. The Caltech Shockwave Lab

is too large to be built on a college campus today, but since it's there, I will keep using the Lab. The Caltech Shockwave Lab allows me to access very high energies and pressures that enable me to measure properties of materials in high pressure, temperature environment found in the deep interior of the earth. I'm seeing what happens when rocks are exposed to extreme pressure (1 million atmospheres) found in lower mantle of the earth and then measuring densities of liquids under these conditions. So, I think about the melting lower mantle and figuring out whether the liquid rises up the surface or goes down towards the core.

I'm learning towards looking at metal liquids and its application with the Earth's core. We know that the Earth's core consists of iron and nickel, but its density is 10% lighter than traditional iron/nickel alloy liquids at that temperature. The core probably consists of about 5 elements such as silicon, hydrogen, sulfur, oxygen, nitrogen. If all you know is density, you'll never figure it out. So I'm working on an experiment measuring sound speed of molten alloy liquids under actual core temperatures. So, the hope is that if the measurements are precise enough and under same temperature/pressure measurements found in the actual core, the sound speeds would be a new constraint on what materials work or don't work/reside in the core.

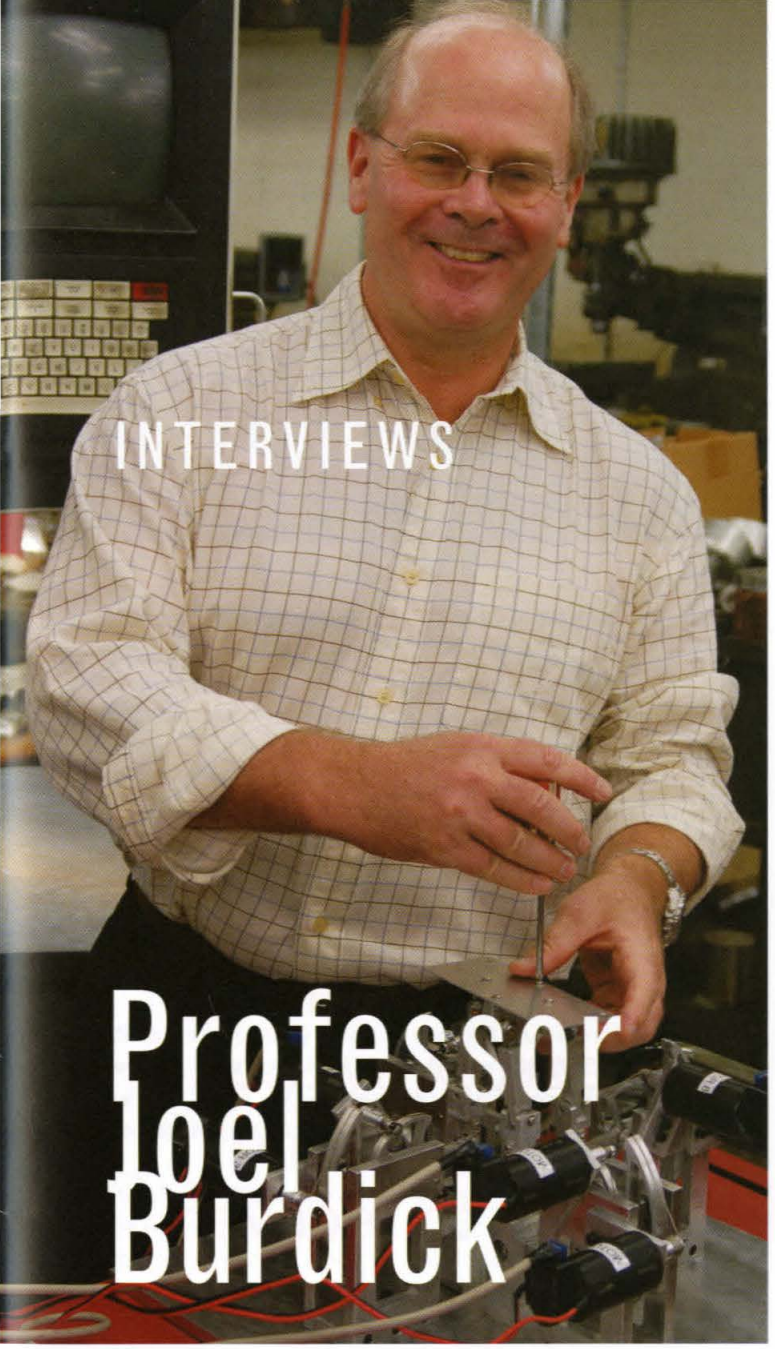
Question: Just this past month you won the Feynman Teaching Award for excellent teaching. Do you feel that professors should balance good teaching and research? Why is this important? What makes a good teacher.

Answer: Well yes, obviously. If we're been given the privilege to do our research in an academic environment, we don't have to base our salary on grants, which is a great privilege. What we're given in exchange is mentoring students and teachers. We are chosen for our research but we are paid to teach. I think it's important to pay attention to how one teaches and what one teaches. I think what fundamentally makes a good teacher is paying attention, and thinking about it, and putting some time and effort to teach well. The skill with teaching is remembering what people know and don't know at each level as the students grow. There are many skilled scientists who forget what it is like to not know all of the things they know. Being organized also makes all the difference in the world on whether a class works or not. In small class settings, where I've had the luck to work, I think all of the above matters. There are different skills involved with teaching big classes but we don't have any big classes in Geology.

I think what fundamentally makes a good teacher is paying attention, and thinking about it, and putting some time and effort to teach well. The skill with teaching is remembering what people know and don't know at each level as the students grow.

Question: From personal experience, what advice do you have for Caltech undergraduate students?

Answer: I guess in general, I think what's most important is that you go through finding a major, finding research opportunities, going to graduate school, or getting a job. I think the most important thing to do is to love what you do. Science is hard and incredibly tedious, and if you don't like it, science is not worth it. The earlier you figure out whether you like what you're doing and want to keep doing, the better. Your undergraduate time taking class and doing research is your best chance to really decide if science is sufficiently awesome to keep doing it. Graduate school is too late.



INTERVIEWS

Professor Joel Burdick

By Marvin Gee and Granton Jindal

You've become a well-established professor at a great institution. What was your path here including your interests in undergraduate and graduate school? What was your motivation?

My wife says I'm a fossil in training. It's not that interesting of a story, but it's rather roundabout. I actually finished my chemistry and engineering degree as an undergraduate at Duke. Then, I went to Stanford for graduate school. At the time, it was a couple of years after a major energy crisis.

There was a very hot topic called magneto-hydrodynamics. Basically, you turn coal to very high temperatures and you put the exhaust gas through a magnetic field to strip off electrons and generate electricity. Because I had both a chemistry and engineering background, I was suited for that, but when I got there, all the graduate students on the project had joined the project. The government killed the program in a year and shut down the MHD program.

On a whim, I had taken a control course, and I got associated with a robotics group there. This was when research in robotics wasn't necessarily a clear job path. You had to be kind of whacky to do robotics back then, and I switched advisors late in the game in my PhD career, which is an onerous thing. My first advisor was kind of pathological. In fact, the university took his lab away from him and demoted him.

When I had started robotics, it wasn't a career path, but when I finished, it was the tail end of the first big boom in robotics, and so, they were hiring in robotics. I got a position here; it was the best offer of the schools that I got, so I came here, and I still do robotics. But, starting 15 years ago, I started doing medical robotics. It's a very common topic in the robotics field, so at least I was sensitized to doing human related things.

A couple years ago, I started collaborating with Anderson at Caltech in neural prosthetics and I worked with him for about a decade. It was very satisfying work, but because of that work, I also met a guy at UCLA, Edgerton. He's working on spinal cord injury, and, over time, I felt that there were more opportunities in spinal cord injury than cortical prosthetics. It's a great team of people who are really terrific scientists and terrific people. We're working on a really interesting problem and one that's personally satisfying.

The advances you've made are quite incredible. Could you explain in very lay terms what your research is about and the significance of its impact?

It's a small step; let's be honest. Here is a little background about spinal cord injury. When you interact with your lower limbs, you have two features of the system that help guide the lower limbs. The first feature is a direct connection, direct muscles that tennis and gymnastics uses. And obviously after any spinal cord injury, that is completely cut off. The other system we know well has fast reflexes. When you hit a sharp tack, a sensory perception goes up your legs and up to your spinal cord, which goes up to your brain. But with a feedback loop, it goes right back to your muscles so that you minimize the time in contact with the painful material.

What we really use is a third system, which is less known outside of biology, something called a pattern generator. So, when you're walking down the hall and talking to someone or thinking about the set you didn't turn in or whatever, there's circuitry in your spinal cord that controls the limbic system. Obviously after a major spinal cord injury, that command signal is gone. All the feedback loops to make relatively complex decisions about movement are gone. The spindle centers of your muscles, your

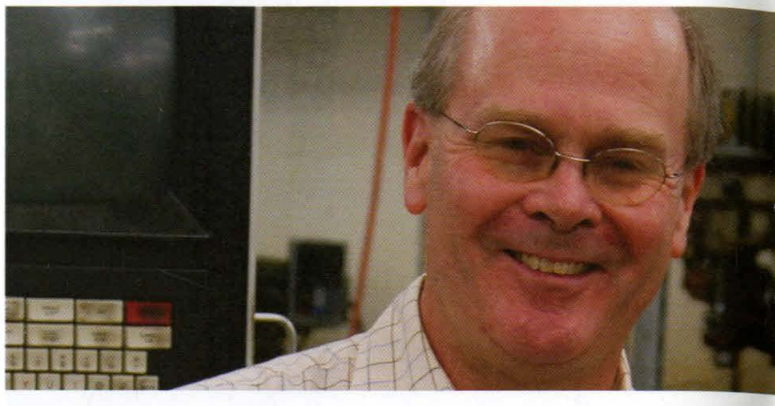
skin centers, and joint centers that you have, that information goes to the spinal cord. If you're standing at a party or something, you automatically know what to do. So what we try to do is to tap into that system. Since after they have a spinal cord injury, it is cut off from the circuitry that starts it, stops it, and modulates it.

There's also a chemical imbalance that happens after a spinal cord injury. There are key neurotransmitters, primarily serotonin, dopamine, and norepinephrine, which are largely synthesized in centers inside the brain and made available to the lower spinal cord via axonal projections. After spinal cord injury, those axonal projections wither away and die. Our strategy was to activate the lower spinal cord by spritzing it with drugs to partially replace the missing chemistry. The sexy part of it is developing electrodes to place over the spinal cord and good old-fashioned physical therapy. You'd say, what do you mean by physical therapy? What those electrode arrays do is hard to piece apart. One thing that they do is they replace the signaling from the brain, and it says, get going! The other thing is, between the drug therapy and the electric field applied by the electrode arrays, it gets the circuits kind of excited to work. So all of a sudden, they get a go signal by us, after which, they start moving.

The downside of that approach is why we call it therapy and not recovery. It's still not connected to a brain. It's just an outside on-off switch that we can use to turn it on to allow the patient to exercise, which gives them many positive benefits. It appears that by combining physical therapy and electrode arrays, we could rewire the neural circuits down there, build cortex by the spinal cord so that they start to recover voluntary motion. There are other collateral benefits in terms of bladder, bowel, and blood pressure.

Did you know that when you began your research that you would be so successful? How did you overcome hardships, if any?

Obviously, the patients take the hardship, not us. When you work with spinal cord injury, you see some really sad stories. The researchers don't really have hardships. In fact, this project hasn't been a hardship at all, it's been one of the most exciting things I've been engaged in my career, and we didn't expect to get these incredible results that we've had so far. If we look at what's ahead of us and how far we have to go to make a big impact on spinal cord injury, it's a pretty small step. What we do know now from our second patient is that it's not a mistake. It is going to be helpful. What we don't know is who can be helped, and how they can be helped. So, we see this as a circumstance of near-term potential, having these patients lead healthier lives;



It appears that by combining physical therapy and electrode arrays, we could rewire the neural circuits down there, build cortex by the spinal cord so that they start to recover voluntary motion.

in the long term, some biological solution, whether it's stem cells, neural transplants, and/or axonal generation mechanisms

What were your initial reactions at hearing your announcement about winning the Popular Mechanics Breakthrough Innovator Award?

It was a nice thing, but it's not the Nobel Prize. It's a fun little thing. I was pleased because having worked with Rob Summers, our first patient. He's truly an amazing guy, just amazing to work with. He's unstoppable. Every time I think I have a bad day, I think of what he's been able to accomplish, and that's very inspiring. What we appreciated was that it brought attention to the problem of spinal cord injury.

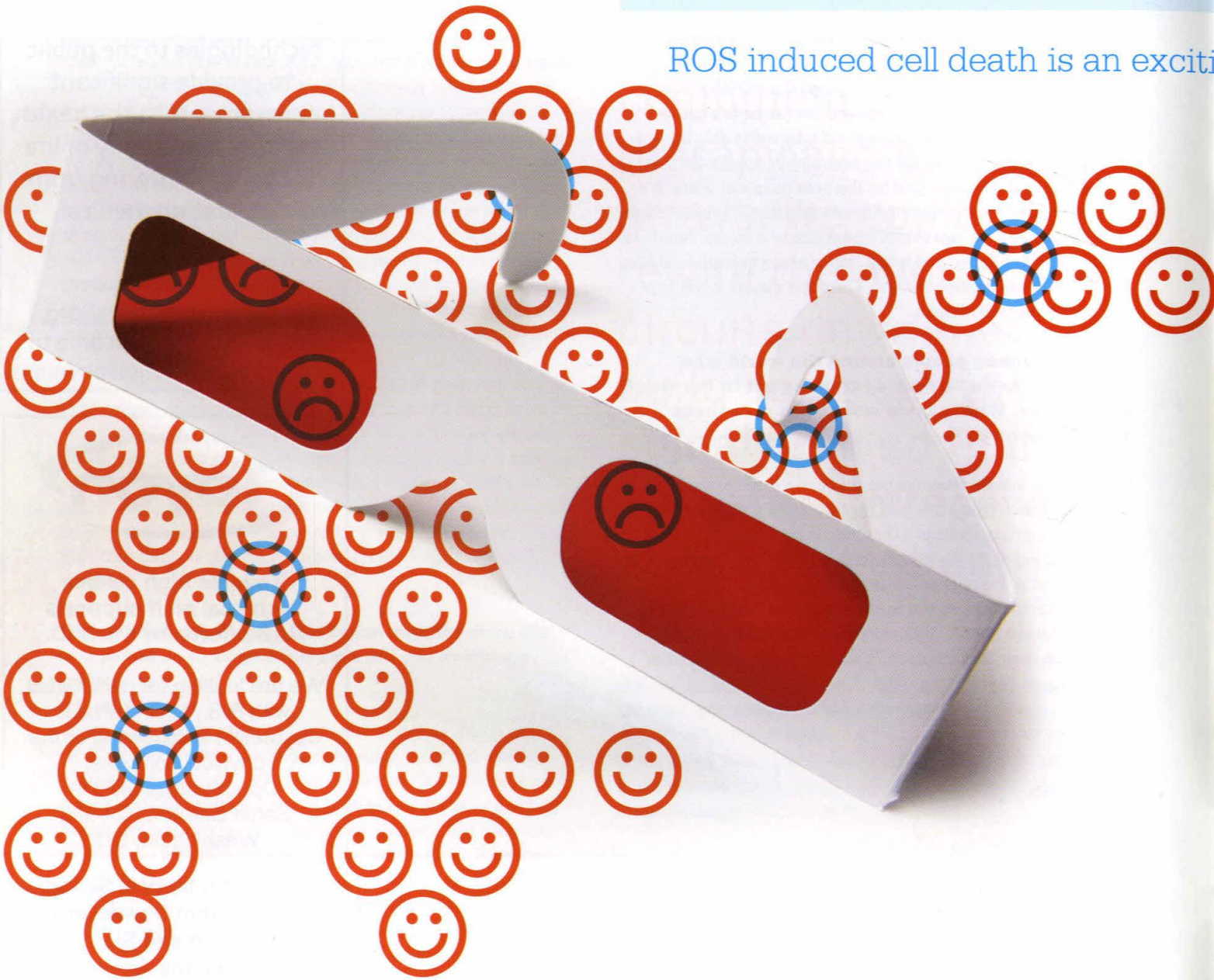
What are your hopes for your research in the future?

From the technical side, one of the things I'm working on is to understand how we can better allow these patients a greater range of mobility. If we can understand why we're able to induce voluntary motions, we can optimize or accelerate that. That's kind of the interim goal for the next couple of years. It's very scanty, but there's some evidence that this approach could work for people with loss of movement due to a stroke. But, how this is going to happen and when this is going to happen is hard to say. I'm pretty confident it will; I just don't know it will happen in my research lifetime.

There are young people around the world who would love to make such a large impact in the world as you have. What advice would you give these young hopefuls?

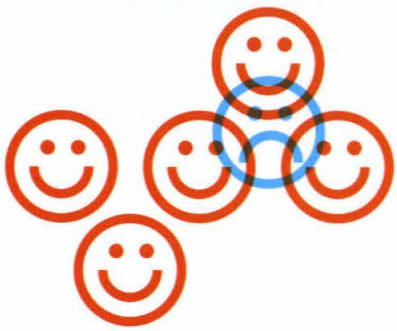
I think most Caltech students get this. I'm a slow learner. It took me some time to figure this out. I got involved in spinal cord stuff for all kinds of reasons. I didn't do it because of money. It's just something that I really wanted to do. It's an old saying; it's not new that if you're passionate about something, you'll do it better. Caltech works on the feudal fiefdom model, and Caltech is one of the last schools that works that way. Everyone sort of works on their own research. It works, though, on the most interesting problems in my mind today. This tends to be a tough project for undergraduates, since it has a high learning curve on the biology side. Then again, it's not as bad as you think. People can actually make a difference.

ROS induced cell death is an exciti



Characterization of Small-Molecules That Increase Reactive Oxygen Species

ing potential therapeutic pathway to target cancer cells.

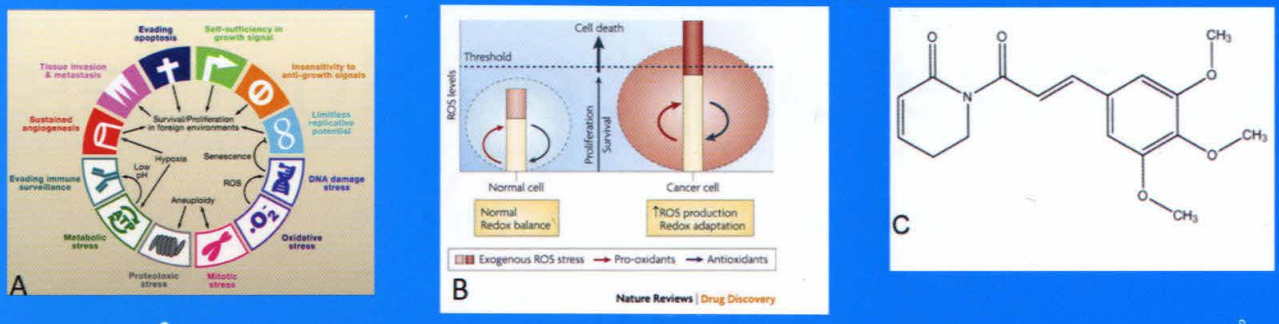


Author: **Alex Wang**
Hometown: Dallas, TX
College: Caltech
Major: Chemical Engineering
Expected Graduation Year: 2013
Hobbies: cello, running
Mentor: **Stuart Schreiber**
Co-Mentor: **Drew Adams**
Associate Mentor: **David Tirrell**

Introduction

Cancer is a leading cause of death worldwide, responsible for 7.6 million deaths in 2008 alone. Despite the common misconception, cancer is not a single disease, but rather an umbrella term for over 200 types of genetic diseases united by a set of common traits. One notable trait cancer cells share is increased oxidative stress because of elevated production of reactive oxygen species (ROS). ROS are essential for basic cell functions such as proliferation and differentiation at normal physiological levels, but excessive amounts leads to oxidative damage of DNA and proteins and ultimately cell death. ROS poses an exciting possible therapeutic pathway to target cancer cells specifically and scientists are researching methods to either directly increase ROS or indirectly raise ROS by removing cells' antioxidant capacities. [1,2]

Figure 1 | Oxidative stress in cancer cells



a, The hallmarks of cancer as adapted from reference 1. Increased oxidative stress and DNA damage stress are a direct effect of increased production of ROS.

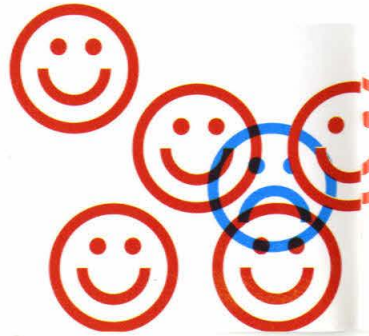
b, An increase in ROS would overload a cancer cell's already strained antioxidant capacity and kill them while normal cells without increased oxidative stress would be below the death threshold. (Figure taken from reference 2.)

c, The structure of piperlongumine, which selectively kills cancer cells apparently by increasing ROS levels.

The Pied Piper of Cancer

Recently, the Schreiber lab observed that piperlongumine (figure 1c), a natural product derived from the Piper longum L. plant, was able to selectively kill cancer cells by interacting with proteins that quench ROS3. It is thought to disrupt proteins that quench ROS through glutathione-based mechanisms, which selectively induces apoptosis in cancer cells because of their increased dependency on the ROS stress-response pathway. Piperlongumine and other small molecules capable of interfering with ROS homeostasis and other ROS stress-response functions are all exciting new potential cancer therapies.

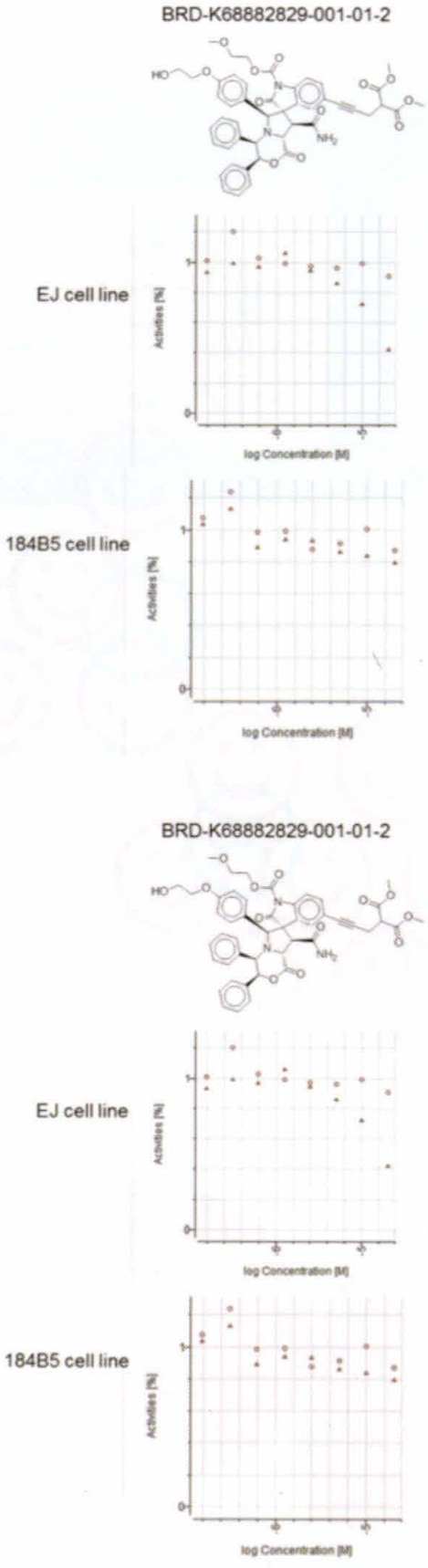
The Schreiber lab identified 902 novel compounds that were able to increase compounds in a screen of 40,000 small molecules. Our objective was to further characterize piperlongumine and the hit compounds to provide insight into their mechanisms of action and to confirm the correlation between ROS generation and cell toxicity. To realize these objectives, we conducted three different high-throughput experiments, including an enhancer screen, a bioactive rescue screen and an antioxidant rescue screens.



Enhancer Screen

The purpose of the enhancer screen was to identify which compounds were mechanistically synergistic with piperlongumine, which would provide insight into the biological mechanism of piperlongumine. These compounds kill cancer cells much more effectively with the addition of a sublethal amount of piperlongumine, implying a shared pathway. For this experiment, cells were grown onto 384-well plates, each well containing a different compound. EJ bladder carcinoma cells were pinned with the 902 ROS increasing compounds in 8 doses along with a sublethal dose of 2.5μM piperlongumine. To determine how many cells remained alive in each well, the amount of ATP in each well was detected using CellToter-Glo, an assay that lyses cells and causes ATP to become luminescent. The initial screen identified 12 enhancers; interestingly, these compounds show little to no toxicity alone, but show significant improvement when piperlongumine was added. Complementary molecules such as these could allow lower the effective cancer drug dosage and thus protect against toxicity risk.

Figure 2 | Piperlongumine enhancers



Two common groups of compounds isolated are shown in figure 2. The multi-aromatic ring structure and a 14-membered ring structure show clear enhancer property in the EJ cells, a cancer cell line, but no significant enhancer ability in 184B5 cells, a non-cancerous cell line. One hypothesis is that piperlongumine interferes with glutathione S-tranferase p1-1 (GSTP1-1), a ROS-quenching protein, but the enhancers may be able to directly quench ROS.3 In order to further clarify the mechanisms of piperlongumine and the enhancers, more characterization assays such as a superoxide screen needs to be done.

Bioactives Rescue Screen:

Complementary to the enhancer screen, a piperlongumine rescue screen in EJ cells was done for a group of 1280 bioactive molecules with known functions. As before, a high-throughput 384-well plate assay was performed where cell viability was tested after adding both a lethal dose of piperlongumine and a bioactive compound. Three bioactives (Table 1) were able to moderately rescue piperlongumine treated cells and were retested at different dosage points. Cells treated with these bioactives have a normal morphology and have higher density than those treated with piperlongumine only but lower density

These graphs depict cell viability plotted against compound concentration for two of the most promising piperlongumine enhancer compounds, which are pictured. Triangles represent samples with piperlongumine while circles represent the compound only. In the EJ cancer cell line, it is clear that cell viability is significantly reduced in the presence of piperlongumine. The 184B5 immortalized non-cancer breast line acts as the control and shows no enhancer effect, which suggests that the enhanced lethality is selective against cancer cells only. Plots generated by Condoseo.

relative to cells treated with only DMSO (Figure 3). Rescue data in figure 4 shows that the kinase inhibitors are strong rescuers of piperlongumine – up to 50% of cells were rescued. Lowering the concentration of piperlongumine, however, did not improve rescue percentage.

Interestingly, the bioactives may be directly inhibiting the mutated Ras pathway, thus preventing piperlongumine-induced cell death by making the cell exhibit less oxidative stress. This hypothesis could be tested by attempting to rescue cells with other Erk1/2 or Ras pathway inhibitors.[4]

Antioxidant Rescue Screens:

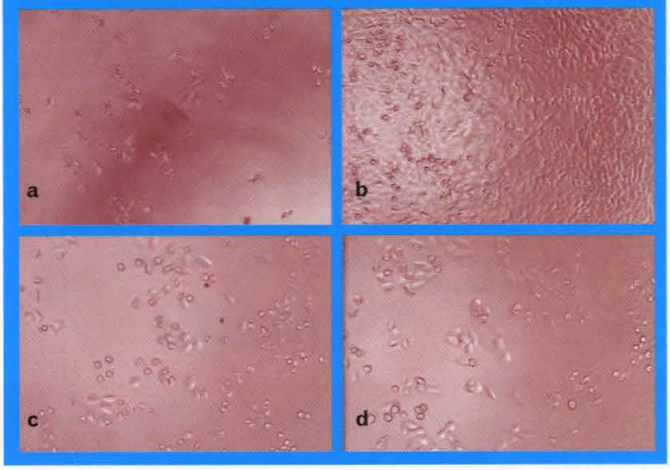
Preliminary antioxidant rescue experiments were performed on piperlongumine to confirm that piperlongumine was acting through a ROS-mediated mechanism. Of the two antioxidants tested, N-acetylcysteine (NAC), and beta-carotene, only NAC successfully rescued piperlongumine toxicity[3]. Unfortunately, this data does not definitely show that piperlongumine was acting through a ROS dependent mechanism. NAC may be interacting directly with the electrophilic site of the small-molecule to shut down its activity. Ultimately, it seems that only thiol-based antioxidants are effective, suggesting that piperlongumine's electrophilic conjugation to cellular proteins may play a larger role in cell toxicity than ROS stress, but more work needs to done.

Table 1 | Bioactive piperlongumine rescuers

Compound	Biological Function
Ro 31-8220 mesylate	Protein kinase C inhibitor, with activity at other protein kinases.5
Aminopurvalanol A	Cyclin-dependent kinase inhibitor.6
Mitoxantrone dihydrochloride	Type II DNA topoisomerase inhibitor. Disrupts DNA synthesis and repair and induces damage by DNA cross-linking.7

Table shows compounds that have been found to rescue piperlongumine and their most well-known biological effects.

Figure 6 | Microscope images of select wells.



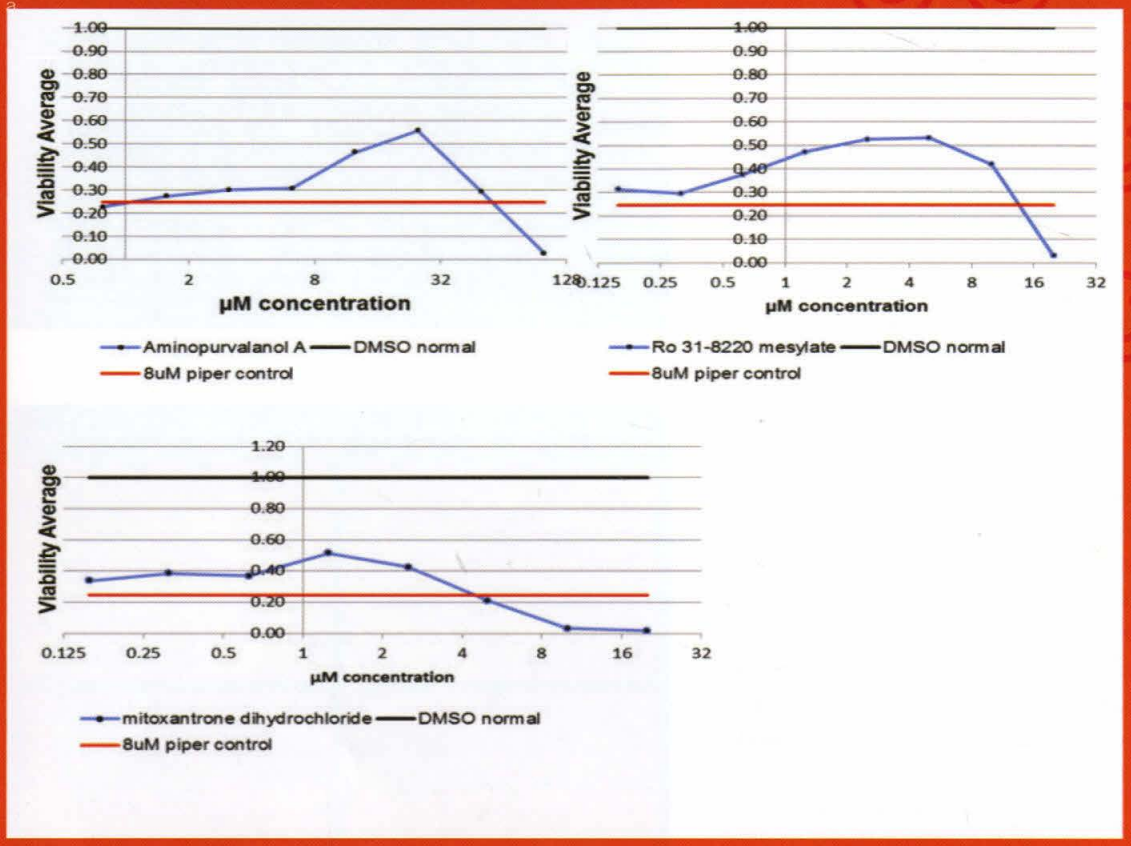
a, Control well of 8μM piperlongumine, a dose leading to 80% toxicity.

b, Control well of only DMSO. Note that the cells are almost confluent.

c, Well with 8μM piperlongumine and Ro 31-8220 mesylate.

d, Well with 8μM piperlongumine and Aminopurvalanol A. The images have been artificially colored red for better contrast

Figure 7 | Cell viability rescue



The graphs show viability of EJ cells treated with 8µM piperlongumine along with increasing concentrations of the bioactive compound. The DMSO control cells are normalized to a viability of 1. The kinase inhibitors aminopurvalanol A and ro 31-8220 mesylate show the most promising rescue activity. Each concentration was run in duplicate.

Conclusion

The hit compounds and Piperlongumine were further characterized, showing promising avenues of further pursuit in exploring ROS-mediated selective killing of cancer cells. Although it's inconclusive whether increased ROS is sufficient for cancer cell toxicity, data provides valuable insight into the mechanism of ROS death as well as opportunities to further follow up each small molecule individually.

Further research would involve resynthesis of interesting compounds and development of analogs of piperlongumine. Future work includes pursuing the bioactives rescue of piperlongumine further by testing more specific compounds inhibiting the Ras pathway as wlel as expanding the panel of antioxidants for the antioxidant experiments. When the most promising compounds are eventually found, mouse models will be necessary to test these small molecules in a more complete biological system. Ultimately, this project shows the potential for a non-oncogenic cancer drug target pathway through oxidative stress increase.

Further Reading

1 Trachootham, D., Alexandre, J. & Huang, P. Targeting cancer cells by ROS-mediated mechanisms: a radical therapeutic approach? Nature reviews. Drug discovery 8, 579-591, doi:10.1038/nrd2803 (2009).

2 Raj, L. et al. Selective killing of cancer cells by a small molecule targeting the stress response to ROS. Nature 475, 231-234, doi:10.1038/nature10167 (2011).

Acknowledgments

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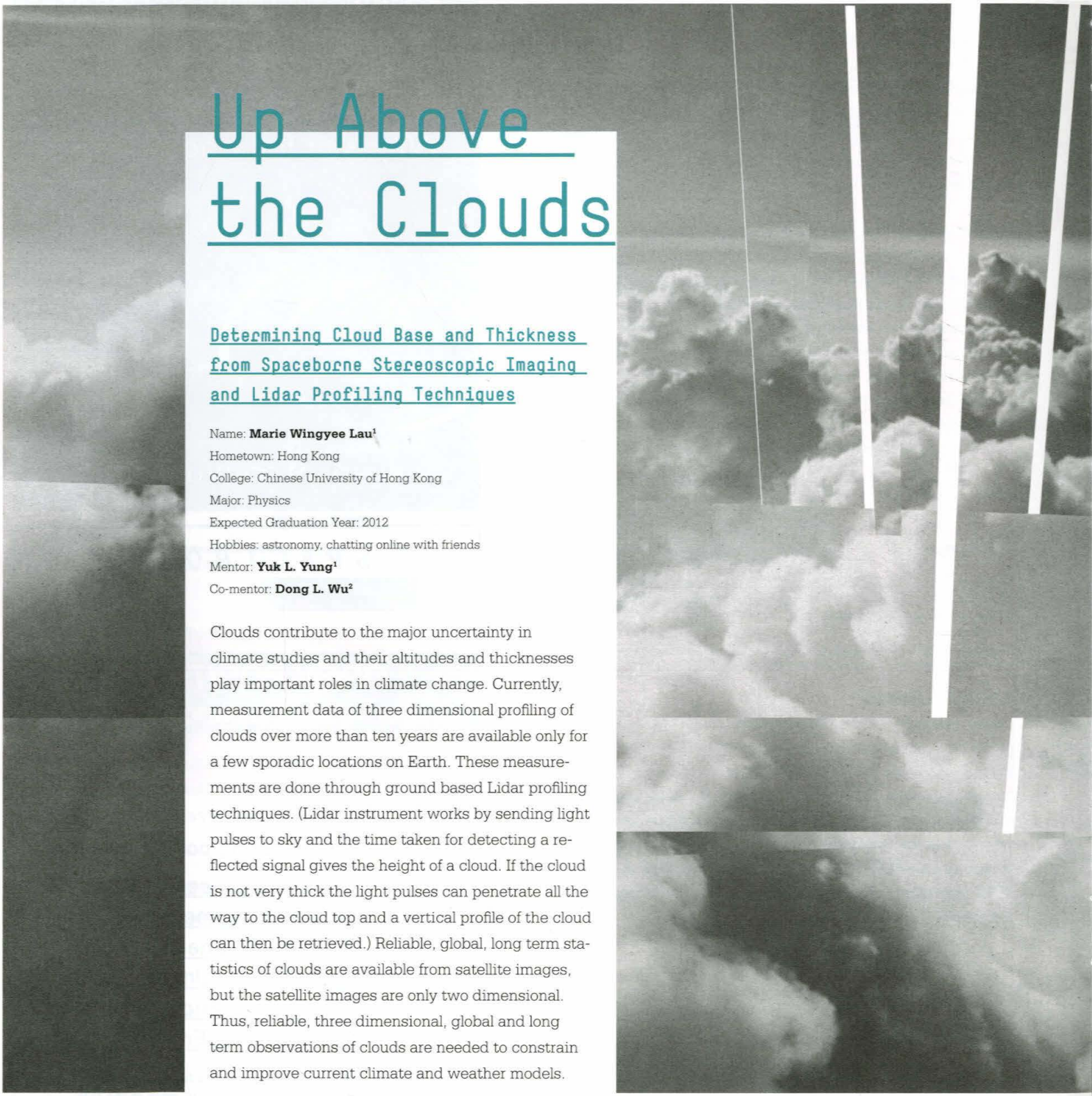


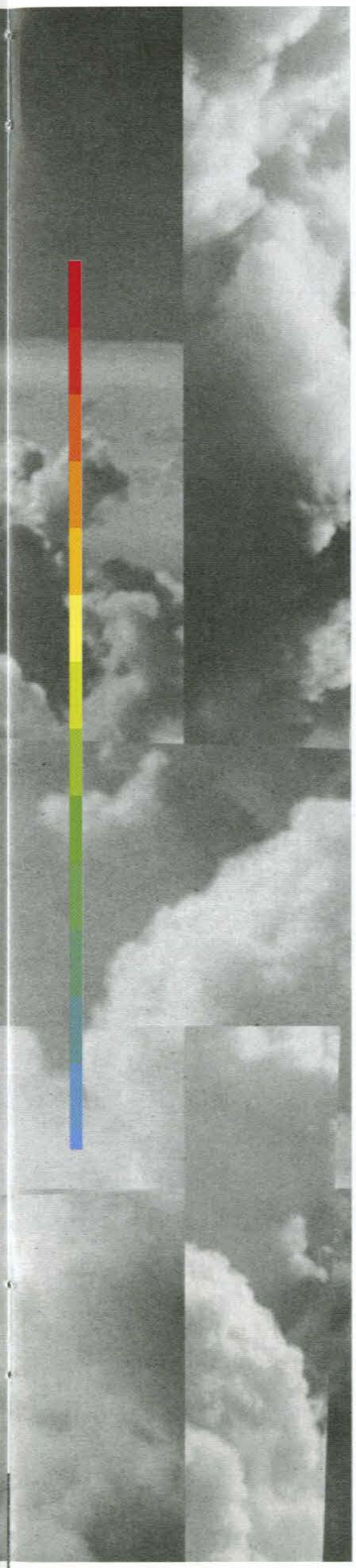
Up Above the Clouds

Determining Cloud Base and Thickness from Spaceborne Stereoscopic Imaging and Lidar Profiling Techniques

Name: **Marie Wingyee Lau**[1]
Hometown: Hong Kong
College: Chinese University of Hong Kong
Major: Physics
Expected Graduation Year: 2012
Hobbies: astronomy, chatting online with friends
Mentor: **Yuk L. Yung**[1]
Co-mentor: **Dong L. Wu**[2]

Clouds contribute to the major uncertainty in climate studies and their altitudes and thicknesses play important roles in climate change. Currently, measurement data of three dimensional profiling of clouds over more than ten years are available only for a few sporadic locations on Earth. These measurements are done through ground based Lidar profiling techniques. (Lidar instrument works by sending light pulses to sky and the time taken for detecting a reflected signal gives the height of a cloud. If the cloud is not very thick the light pulses can penetrate all the way to the cloud top and a vertical profile of the cloud can then be retrieved.) Reliable, global, long term statistics of clouds are available from satellite images, but the satellite images are only two dimensional. Thus, reliable, three dimensional, global and long term observations of clouds are needed to constrain and improve current climate and weather models.

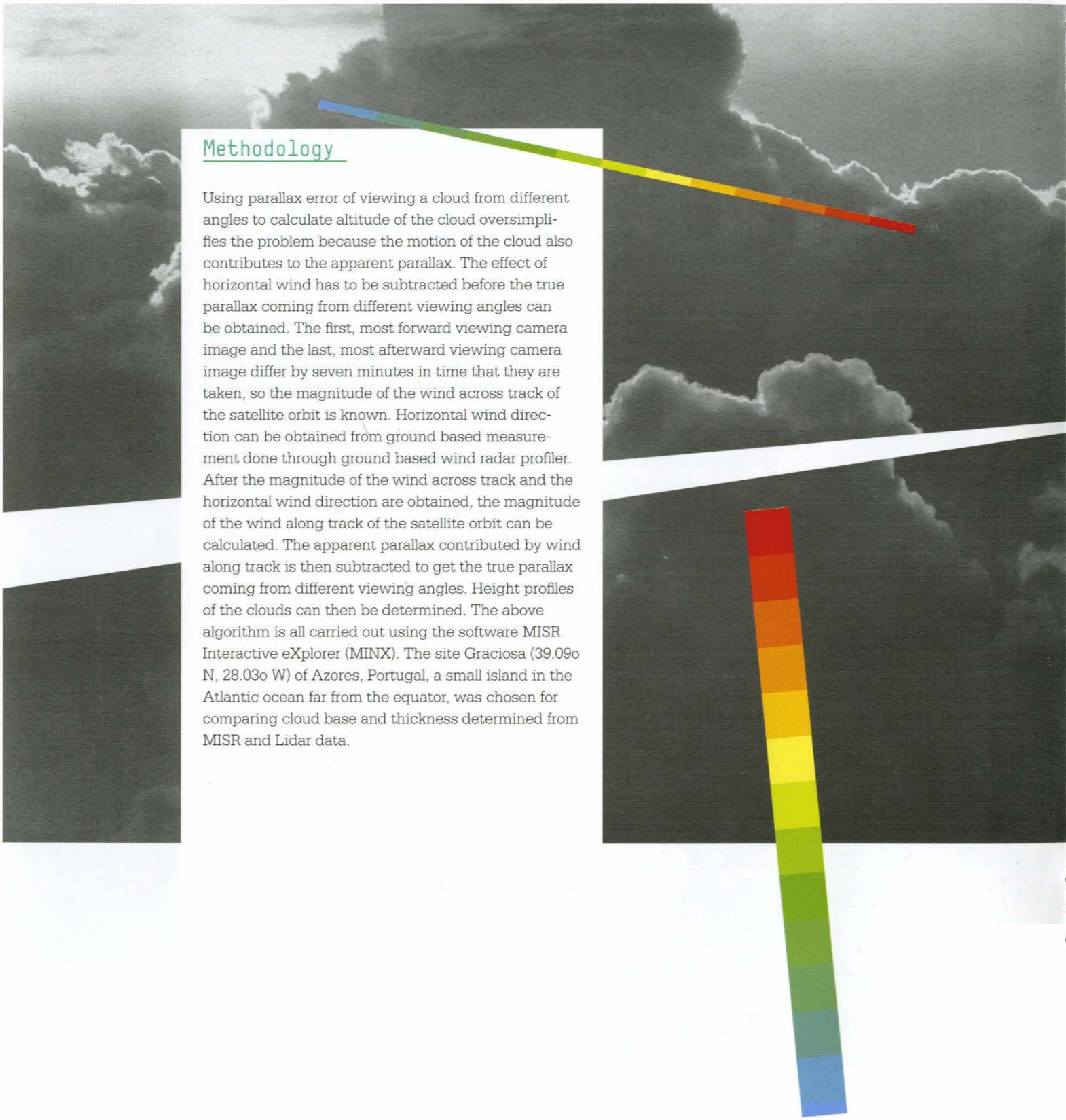
[1]California Institute of Technology. Pasadena, CA
[2]Goddard Space Flight Center, NASA. Greenbelt, MD



New Profiling Technique: Spaceborne Stereoscopic Imaging

New capabilities of the Multiangle Imaging Spectro-Radiometer (MISR) instruments which enable global wide cloud base height and thickness determination make such observations feasible. MISR is a space-borne stereoscopic imaging instrument which has nine cameras with nine different viewing angles at Earth surface. As MISR moves along its orbit, the foot-print of the nine cameras sweeps through the same region on Earth, one by one, from the most forward viewing camera, to the nadir viewing camera, and finally to the most afterward viewing camera. Vertical distance between MISR and any object in nadir view can be calculated from parallax. The satellite bearing MISR is tracked by the Global Positioning System so its height is known. These two combine to give the height of the top of the object in concern, which is, cloud top in our study. Because of the stereoscopic capability from cameras of large viewing angles, for isolated and only moderately thick clouds, MISR can see the cloud edge, whose height is close to the cloud base. Hence, cloud base and thickness can be determined from these cameras surveying from above. Finally, MISR can also see through windows in a relatively tight cloud layer to retrieve height profiles of features below.

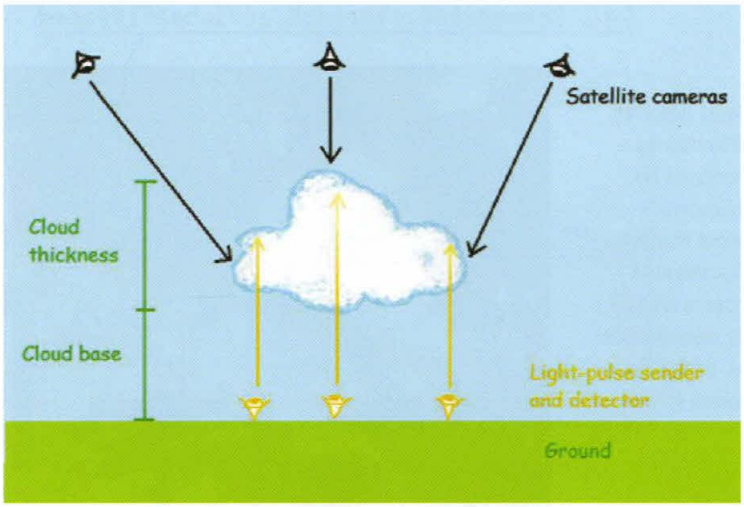
Our research goal is to validate cloud base and thick-ness determined from the image data of the space-borne MISR against those determined from the Lidar data measured by ground based instruments. Figure 1 gives a simple illustration of how MISR and Lidar are able to retrieve comparable height profiles.



Methodology

Using parallax error of viewing a cloud from different angles to calculate altitude of the cloud oversimplifies the problem because the motion of the cloud also contributes to the apparent parallax. The effect of horizontal wind has to be subtracted before the true parallax coming from different viewing angles can be obtained. The first, most forward viewing camera image and the last, most afterward viewing camera image differ by seven minutes in time that they are taken, so the magnitude of the wind across track of the satellite orbit is known. Horizontal wind direction can be obtained from ground based measurement done through ground based wind radar profiler. After the magnitude of the wind across track and the horizontal wind direction are obtained, the magnitude of the wind along track of the satellite orbit can be calculated. The apparent parallax contributed by wind along track is then subtracted to get the true parallax coming from different viewing angles. Height profiles of the clouds can then be determined. The above algorithm is all carried out using the software MISR Interactive eXplorer (MINX). The site Graciosa (39.09o N, 28.03o W) of Azores, Portugal, a small island in the Atlantic ocean far from the equator, was chosen for comparing cloud base and thickness determined from MISR and Lidar data.

Figure 1. A simple illustration of how MISR and Lidar retrieve the height profiles of the same piece of cloud.

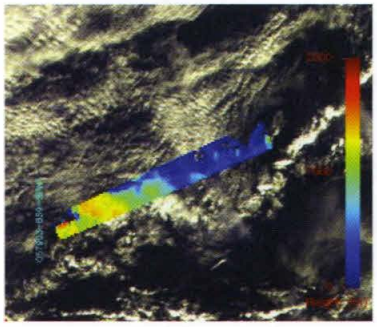


Results

We found 12 cases in which there are at most two tight layers of clouds, the weather is fine and stable, and the clouds are isolated and only moderately thick, over Graciosa. It is interesting to note how clouds with prominent vertical structures or multilayered clouds are manifested in MISR height profiles, showing promising future possibility of cloud analysis using MISR images that was not possible with our current two dimensional spaceborne imaging techniques.The following are two examples selected from the twelve cases. For each case, a contour map of MINX height retrieval results is shown. An image of the clouds studied is also shown, with a yellow arrow on it indicating the direction of wind inputted to the MINX program obtained from ground based wind measurement. Then, the MISR height profiles are shown and on the plot the cloud base and thickness determined are marked by two pink lines. After that, the Lidar height profiles are shown, and again on the plot the cloud base and thickness determined are marked by two pink lines.

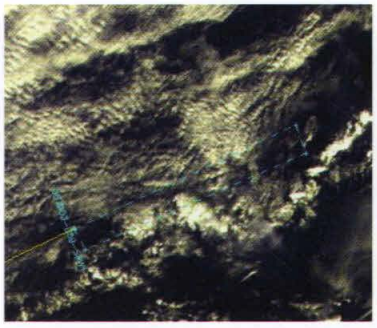
Example 1. Trade Cumulus

Figure 2A. Contour Map



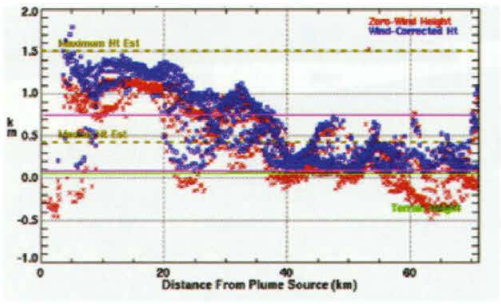
Features: vertical protrudings

Figure 2B. Wind direction given.



Height Profiles (ASL) for 057903-SPW1

Figure 2C. MINX retrieval of height profiles.
From MISR retrieval, cloud base ~ 50 m, thickness ~ 700 m



Results (Continued)

The 12 case studies of MISR and Lidar cloud height profiling comparison are summarized in Figures 4a and 4b. Figure 4a shows cloud base determined by Lidar against that by MISR and Figure 4b shows cloud thickness determined by Lidar against that by MISR. A line of y=x is plotted over both figures as a reference. It can be seen that our results deviate little from the expectation. Lidar systematically determines a smaller cloud thickness than MISR does, probably owing to the limited power of the light pulses to penetrate all the way to cloud top.

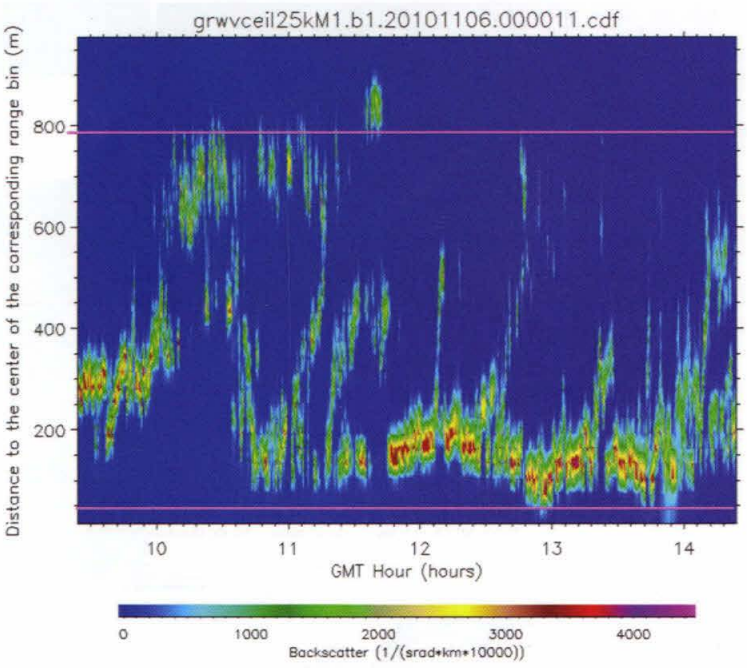


Figure 2D. Height profiles from Lidar measurement. From Lidar profiling, cloud base ~ 50m, thickness ~ 750m

Example 2. Through a higher layer

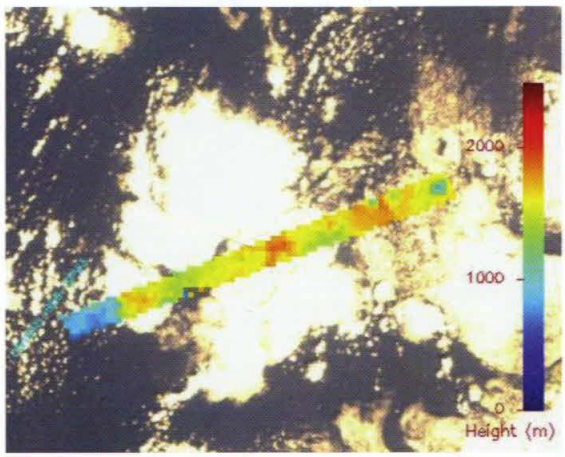


Figure 3A. Contour Map

Features: two layers, convection

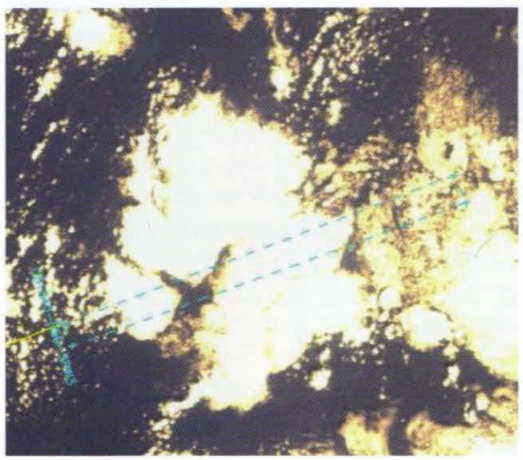


Figure 3B. Wind Direction given.

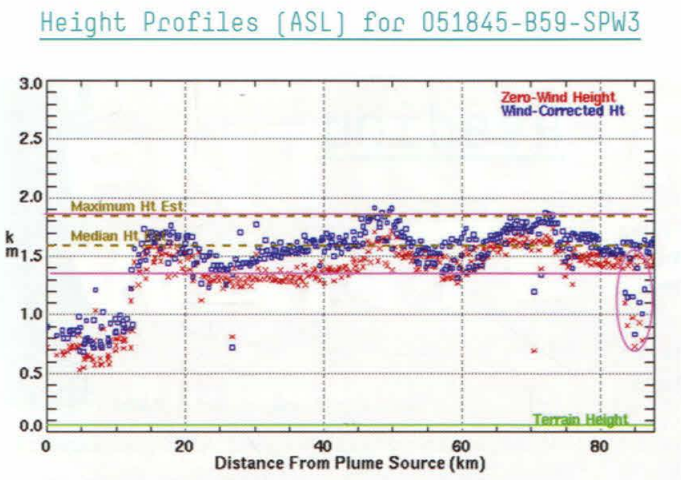


Figure 3C. MINX retrieval of height profiles.
From MISR retrieval, cloud base ~1350m, thickness ~ 500m

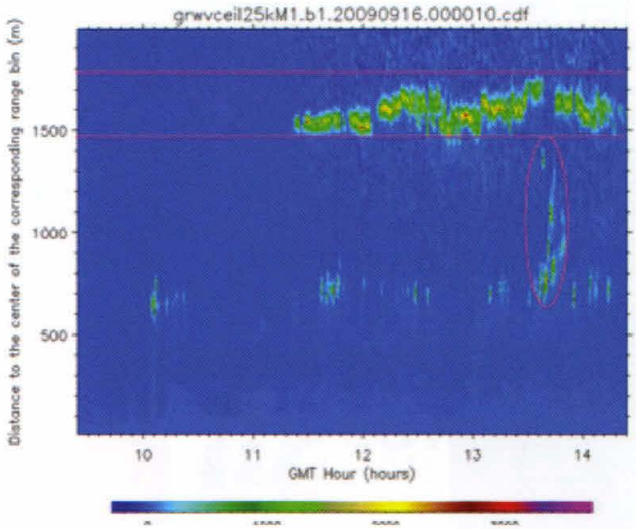
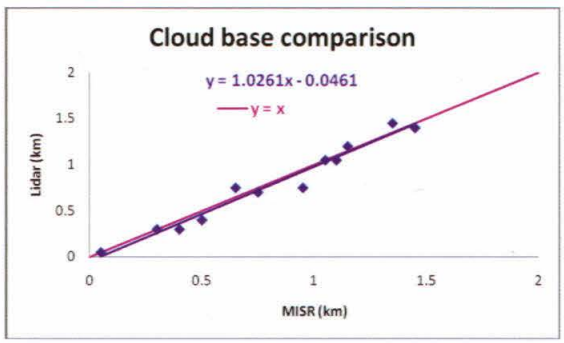


Figure 3D. Height profiles from Lidar measurement.
From Lidar profiling, cloud base ~ 1450m, thickness ~ 350 m



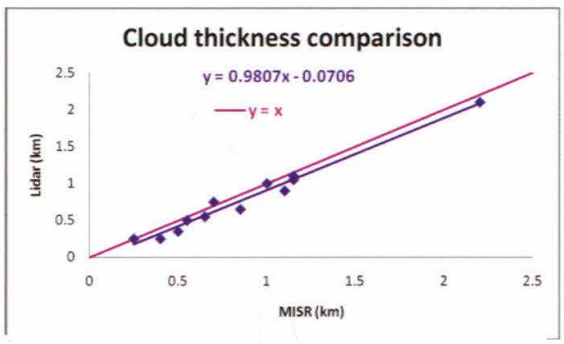
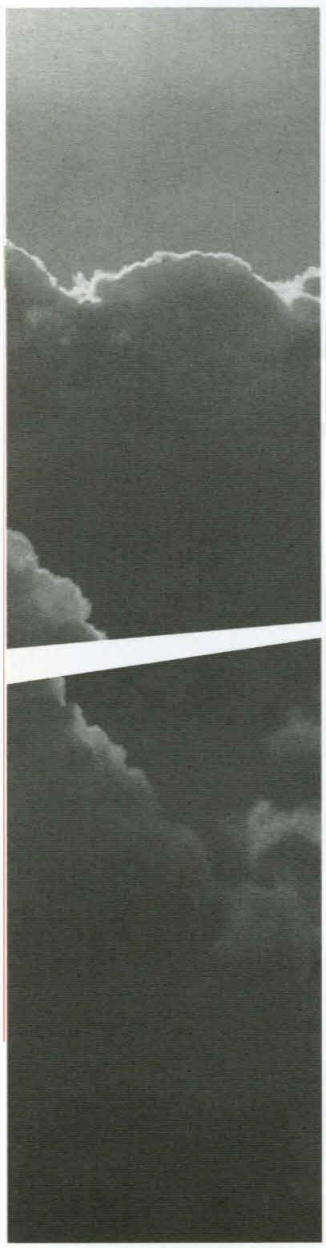


Figure 4A (top) and 4b (bottom). Cloud base (4a) and thickness (4b) determined by Lidar against that by MISR. A y=x line is plotted over both figures.



Conclusion

We have successfully validated the technique of determining cloud base and thickness from spaceborne stereoscopic imaging against the Lidar profiling technique. The good agreement between them opens up future possibilities of global, three dimensional and long term cloud analysis.

Acknowledgment

The MISR data were obtained from the NASA Langley Research Center Atmospheric Science Data Center, and the Lidar data were obtained from the U.S. Department of Energy as part of the Atmospheric Radiation Measurement Climate Research Facility. Due acknowledgement is given to these two parties.

Further Reading

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In-plane thin film lattices: Thermally Stable Mirrors

Name: **Deeksha Agrawal**
Hometown: India
College: California Institute of Technology
Major: Mechanical Engineering and Business, Economics and Management
Expected Graduation Year: 2015
Hobbies: Latin dancing, hip hop, swimming, surfing, dramatics, debating
Mentors: **Chiara Daraio, Eleftherios Gdoutos**

Many structural systems, such as high speed aerospace vehicles, require a material with high structural stiffness that is capable of experiencing large temperature changes. Otherwise, substantial thermal stresses develop when high temperature components are connected to lower temperature structures.

This leads to failure by yielding, fracture or fatigue, as well as the formation of gaps that require sealing and extreme forces on attachments to other structures. Composite bimaterial lattice structures, which combine low (or zero) thermal expansion with high stiffness, structural robustness over wide temperature ranges and manufacturing facility have been proposed for this application. To suppress the failures common in other materials, we fabricate and study expansion thin film bimaterial lattices with tunable thermal expansion. The lattice configuration is composed of Aluminum and Titanium which have different coefficients of thermal expansion (CTEs) and intervening spaces. According to theoretical predictions, the higher CTE internal Aluminum expands more rapidly and pushes outward against the lower CTE exterior lattice of Titanium. This causes the latter to rotate, thereby counteracting the lengthwise elongation of the material. We fabricated this lattice structure on a silicon wafer. The results were then verified by conducting experiments and finite element simulations to test the various thermo-mechanical properties of this lattice.

Figure 1:
Lattice structure proposed by Steeves:High CTE member in blue and low CTE member in red

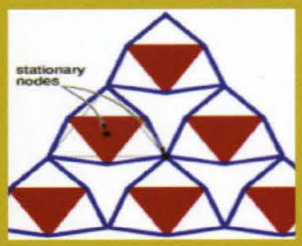
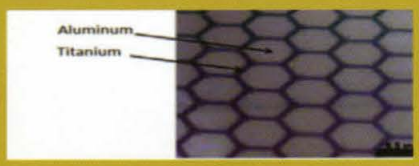


Figure 2:
Hexagonal lattice composed of Aluminum and Titanium used for our experiments



Background

In structural systems that experience large temperature changes and thermal gradients such as high-speed aerospace vehicles, heat pipes and space craft, large thermal strains can cause excessive geometric changes and substantial thermal stresses when high temperature components are connected to lower temperature structures. This is a significant impediment to successful design and implementation of small, thermally stable devices and the consequences include failure by yielding, fracture or thermo-mechanical fatigue, as well as the formation of gaps that require sealing and extreme forces on attachments to other structures. As a solution to suppress such failures, the material should have a low thermal expansion coefficient, over a wide range of temperatures combined with adequate stiffness, ductility and toughness to support heavy loads.

In the past, materials with some of these characteristics have emerged. For example, the bimaterial lattices presented by Lakes and Jefferson were designed to have zero expansion, but both had low stiffness and strength because of the bending of one of the sub-lattices upon mechanical loading. This stiffness deficiency was obviated by the Sigmund and Torquato design, obtained by optimizing for combined zero expansion and maximum biaxial stiffness. However, the limitation of this material was that it was geometrically too complex for manufacturing and had only modest in-plane uniaxial stiffness.

The Project

We aim at fabricating and studying for the first time, zero expansion thin film lattices with topologies amenable to manufacturing that are stretch- (not bending-) dominated upon mechanical loading, enabling them to achieve zero Coefficient of Thermal Expansion (CTE) while being relatively stiff and strong and resistant to thermal fatigue. This material has various applications in optics, micro- and nano-fabrication and aerospace industries.

Our lattice configuration will be composed of two materials with widely differing individual coefficients of thermal expansion (CTEs) and intervening spaces. When heated the higher CTE internal members expand more rapidly and push outward against the lower CTE exterior lattice. This causes the latter to rotate, thereby counteracting the lengthwise elongation of the members. The lattice described here will be stretching dominated and hence is approximately one order of magnitude stiffer than comparable bending-dominated structures. The lattice described by Steeves (Figure 1) was triangular. Here we plan to use hexagonal lattices with smaller gaps between the two metals making the lattice more mechanically intact and easier to fabricate (Figure 2).

We will also model the lattice using finite element simulations to study the various thermo-mechanical properties of the material. To validate the theory the lattice will be tested in different thermal environments and thermal expansion measurements will be presented. The finite element analysis will also

Figure 3:
Cross section view of the fabricated wafer with the Gold sacrificial layer

Figure 4:
Cross section view of the fabricated wafer with the Silicon sacrificial layer

be used to ascertain stresses induced around the bimaterial nodes during a temperature excursion to ensure that the lattice concept provides adequate resistance to thermal fatigue.

Fabrication of Bimetallic Lattice

We used two methods in the fabrication of the bimetallic lattice – one employing a gold sacrificial layer and the other using a silicon sacrificial layer.

In the gold sacrificial layer method, we fabricated this lattice structure on silicon wafer (4"). We coated the wafer with 5nm thick layer of Chromium to act as the adhesive layer and 50nm of Gold to act as the sacrificial layer. We coated HMDS on the substrate to promote the adhesion with the photoresist. We coated the substrate with photoresist AZ5214E using spin-coating, exposed it with UV and developed the pattern using commercial developer CD 26, coated with Aluminum by E-beam evaporation, lifted off the photoresist and Aluminum by acetone washes and then iterated the procedure with the second metal (Titanium). Therefore, two rounds of photolithography were used to achieve the pattern that we required (Figure 3). Then we tried separating the 1 micron thick layer of the Al-Ti lattice by using AU-5 (5% Iodine, 10% Potassium Iodide, 85% Water) to etch the gold layer. This is one of the most critical steps of the fabrication process. Upon investigating the success of separation by looking at the sample in SEM, we found that the etchant was unable to separate the lattice from the silicon wafer due to insufficient contact between the etchant and the Gold layer.

In the alternate method, we planned to directly etch the Silicon wafer instead of the Gold sacrificial layer (Figure 4). We followed the same procedure for lithography. In this method a ring of Silicon would be left unetched near the boundary to provide structural support to the lattice.

Figure 5:
For FEM Analysis four unit cells represent the whole lattice due to symmetry

the CTE of the lattice decreases as the ratio of the CTE of Al over Ti increases.

Simulations

We performed Finite element simulations using the commercial package ABAQUS 6.9-2 (HKS). Using the symmetries of the system, only four unit cells of the lattice were modeled (Figure 5). The temperature dependent elastic and thermal properties of the two metals such as thermal expansion (CTE), elastic modulus, thermal conductivity, Poisson's ratio, and bulk modulus were used for the analysis. We studied the changes in the CTE of the Al-Ti lattice due to changes in the CTE of the constituent metals, changes in the ratio of the CTE of Al over Ti and change in the amount of heat applied. We did a detailed study of the changes in the CTE of the Al-Ti lattice by further refining the mesh. After analyzing the data, we concluded that the CTE of the lattice decreases as the ratio of the CTE of Al over Ti increases. We verified these results by varying the CTE of Aluminum and Titanium individually and for different temperature ranges (Figure 6 and Figure 7).

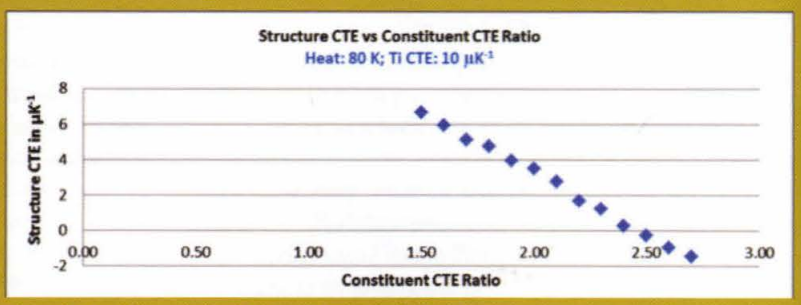


Figure 6: *Graph representing Structure CTE of the Al-Ti lattice vs Constituent CTE Ratio of Al over Ti with Ti CTE fixed at 10 μK^{-1} and the Heat applied 80 K.*

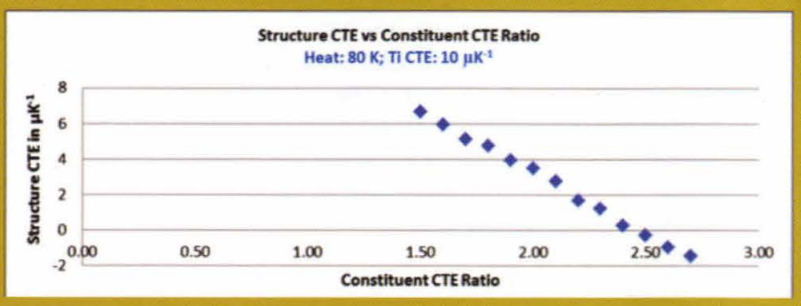


Figure 7: *Graph representing the Structure CTE of the Al-Ti lattice vs Constituent CTE Ratio of Al over Ti with Al CTE fixed at 22 μK^{-1} and the Heat applied 20 K.*

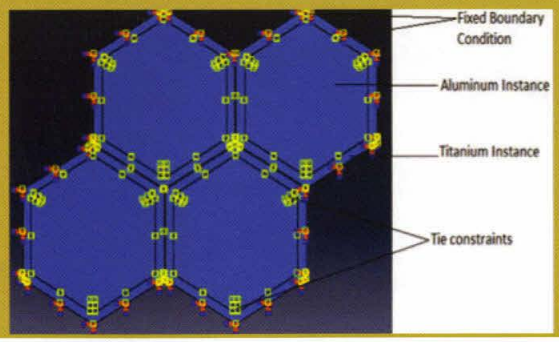


Figure 8:
Al-Ti lattice composed of four Ti and Al instances with the Tie constraints and Fixed Boundary Condition to study the CTE of the structure and the mechanical stress at the center of the structure as we increase the size of the lattice.

An increase in the lattice size from 4 to 10 hexagons was not sufficient number of unit cells to discount the effect of the fixed boundary condition.

We also studied the variation in the thermo-mechanical properties of the structure due to the growth of lattice, tie constraints and under specific boundary conditions. We studied the change in the CTE of the structure and the mechanical stress at the center of the structure upon increasing the size of the lattice. In ABAQUS, we defined the finite element model as an assembly of Aluminum and Titanium instances. We also applied a fixed boundary condition near the outermost boundary of the lattice as in the real world the lattice boundary is constrained to have zero displacement due to the low CTE Silicon ring maintained around the lattice for structural support (Figure 8). Hence this fixed boundary condition imposes the constraint of zero displacement at the boundary of the lattice throughout the analysis. Upon analyzing the data for the changes in the stress range due to lattice growth, we found that without the fixed boundary condition the stress range varies in no set pattern as we increase the size of the structure from 4 to 10 hexagons. From this we concluded that an increase in the lattice size from 4 to 10 hexagons was not sufficient number of unit cells to discount the effect of the fixed boundary condition since most of the unit cells had a part of their boundary constrained by the fixed boundary condition hence the data collected could not give accurate results.

X-Ray Diffraction Analysis

For the finite element simulations we plugged in various parameters in ABAQUS such as CTE, elasticity etc. of Al and Ti thin films to carry out the analysis and collect data. For most of these parameters we used the theoretical values. However, in order to get the exact values based on experiment for the physical properties of Al and Ti thin films we carried out X-Ray Diffraction. X-Ray Diffraction technique yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. It is used for differentiating between crystalline and amorphous materials, determining the structure of crystalline materials (crystal axes, size and shape of the unit cell, positions of the atoms in the unit cell), determining electron distribution within the atoms, and throughout the unit cell, determining the orientation of single crystals, identifying crystalline phases and measur-

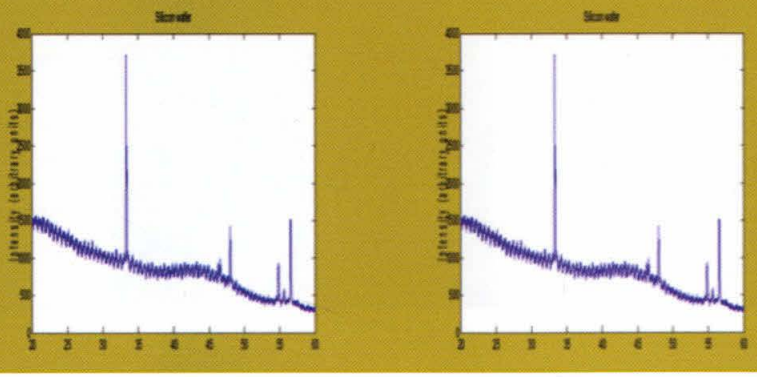


Figure 9:
The MATLAB plots for the X-Ray Diffraction data of just the silicon wafer (a) and the silicon wafer with the Al thin film fabricated on it (b)
(Units: Y axis – Intensity in Absorbance units (a.u.); X axis - Two theta in degrees)

We successfully fabricated zero expansion thin film bimetallic lattices composed of Aluminum and Titanium.

ing the relative proportions and determining phase diagrams, measuring strain and small grain size, measuring various kinds of randomness, disorder, and imperfections in crystals; and determining radial distribution functions for amorphous solids and liquids. These values obtained by X-ray diffraction of Al and Ti thin films can then be plugged in FEM in order to get more realistic results based on experiments for the thermo-mechanical properties of the Al-Ti lattice.

We collected two sets of X-Ray Diffraction data – one for just the silicon wafer which was the substrate on which the lattice was fabricated and the second for the silicon wafer with the Al thin film fabricated on it. We processed these two sets of data in order to get the X-ray diffraction data for just the Al thin film to obtain the information regarding the crystalline structure and physical properties of only the Al thin film without the silicon wafer substrate. For this we aligned two plots - one representing the X-ray diffraction data for the silicon wafer with the Al thin film fabricated on it while the other representing the X-ray diffraction data for just the silicon wafer using MATLAB and then subtracted the two plots.

The plot (a) in Figure 9 representing the X-ray Diffraction data for just the Silicon wafer was subtracted from plot (b) representing the X-Ray Diffraction data for the silicon wafer with the Al thin film fabricated on it to give the plot for the X-Ray Diffraction data of only the Al thin film (Figure 10). This data can now be processed to obtain the values for the various physical properties of the Al thin film.

Concluding Comments

We successfully fabricated zero expansion thin film bimetallic lattices composed of Aluminum and Titanium using two approaches – one employing a gold sacrificial layer and one a silicon sacrificial layer. In the first approach however after the successful fabrication of the lattice, we were unable to separate the lattice from the silicon wafer by etching the gold sacrificial layer. We now look forward to the successful separation of the lattice from the wafer using our second approach where we plan to etch the silicon wafer itself leaving behind a ring of silicon near the boundary of the lattice for structural support. The lattice materials introduced here provide the unique combination of low thermal expansion with high stiffness in an easily manufacturable, yet structurally robust, geometry.

We also modeled this lattice by performing Finite Element simulations using the commercial package ABAQUS 6.9-2 (HKS) to study the various thermo-mechanical properties of the lattice. We concluded that the CTE of the Al-Ti lattice decreases as the ratio of the CTE of Al over Ti increases. We verified these results by varying the CTE of Aluminum and Titanium individually and for different temperature ranges. We also studied the variation in the thermo-mechanical properties of the structure due to the growth of lattice, tie constraints and under specific boundary conditions. Upon analyzing the data, we

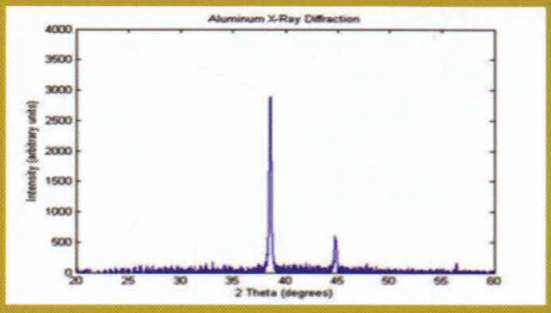


Figure 10:
The MATLAB plot for the X-Ray Diffraction data of only the Al thin film obtained by aligning and subtracting the X-Ray Diffraction plot of just the silicon wafer from that of the silicon wafer with the Al thin film fabricated on it.

concluded that an increase in the size of the lattice from 4 to 10 unit cells was not sufficient to discount the effect of the fixed boundary condition since parts of the boundary of most of the unit cells that we used to collect the data from were directly being affected by the fixed boundary condition hence the data collected could not give us an accurate result. In order to get an accurate result, we need several layers of unit cells so that none of the unit cells from which the data is being collected are directly involved in the fixed boundary condition.

We also managed to get the X-ray Diffraction data for only the Al thin film by processing the X-ray Diffraction for the silicon wafer and the silicon wafer with the Al thin film fabricated on it. This data can now be processed to obtain information regarding the exact crystal structure and the various physical properties of the Al thin films.

Acknowledgements

I acknowledge my mentor Professor Chiara Daraio and my co-mentor Eleftherios Gdoutos for their support on the bimaterial low CTE structure and the multilayer mirror stack design and fabrication. I also acknowledge support for this project by Brenda and Louis J. Alpinieri for funding this SURF project. I would also like to thank the Keck Institute for Space Studies for their research work in this project.

Further Reading

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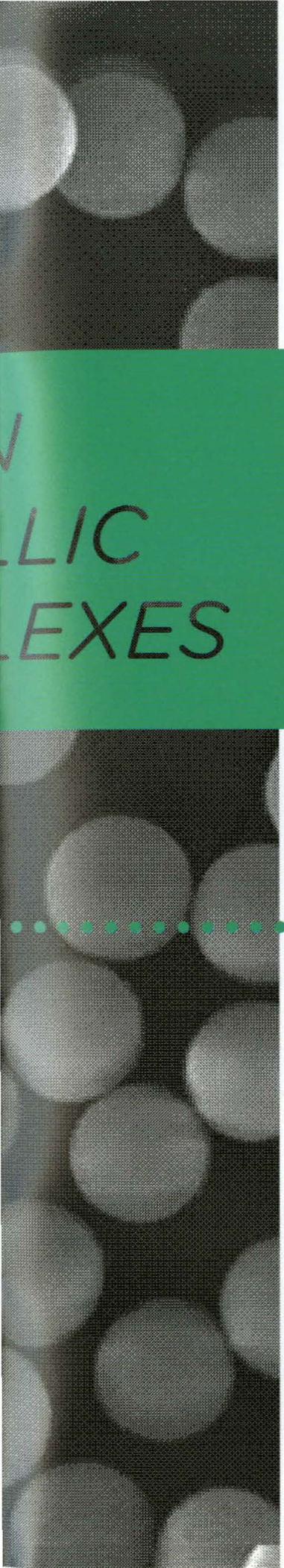
The lattice materials introduced here provide the unique combination of low thermal expansion with high stiffness in an easily manufacturable, yet structurally robust, geometry.

C-H BOND ACTIVATION USING ORGANOMETAL IRIDIUM METAL COMPL



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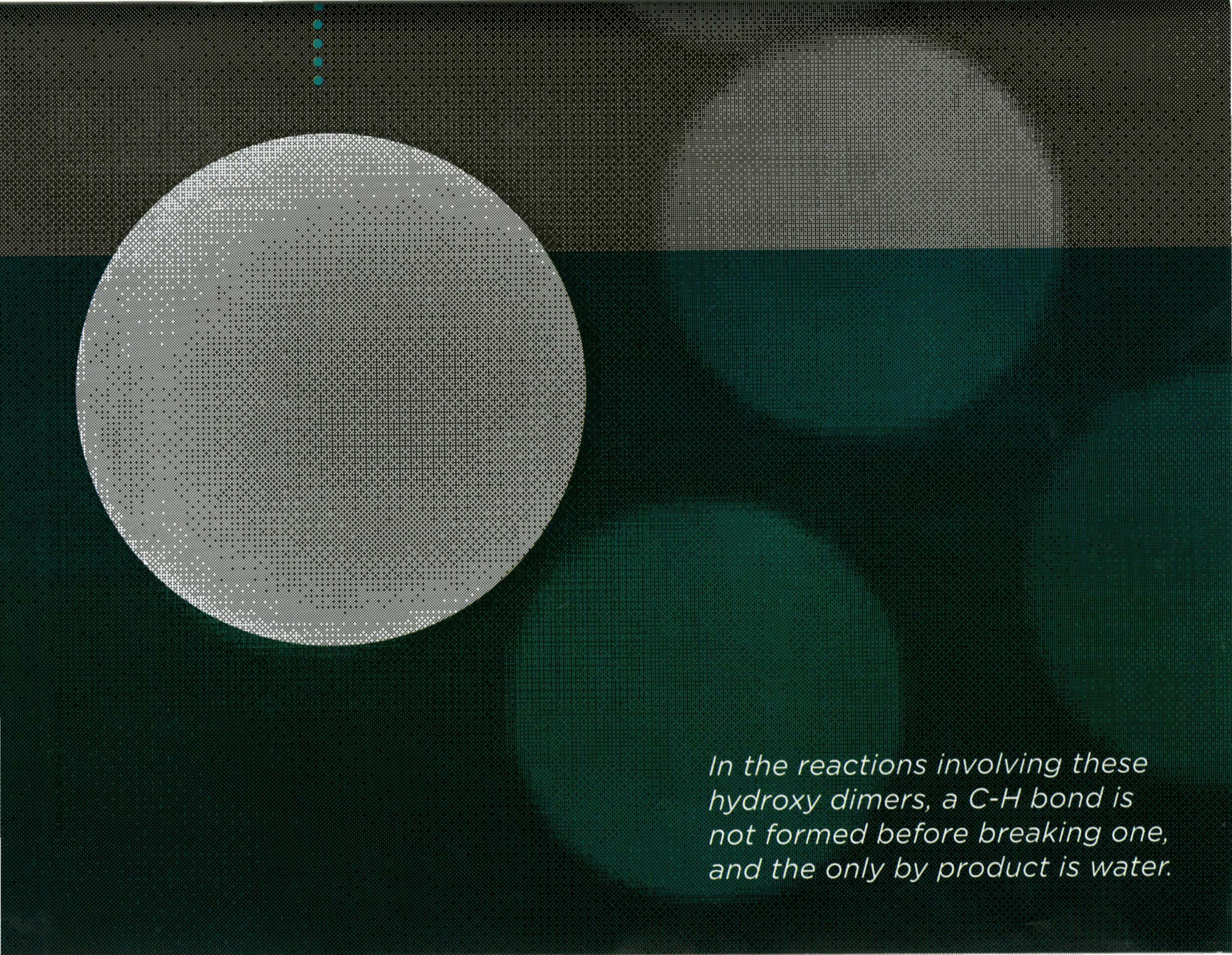
Author: **Tonia Ahmed**
Hometown: Morgantown, WV
College: West Virginia University
Major: Chemistry/Mathematics
Expected Graduation Year: 2015
Hobbies: Tennis, cooking, reading, traveling

Introduction: One Man's Trash...

A large part of the petroleum extracted for society's consumption is composed mainly of methane gas. However, few methods have been found to efficiently and selectively convert methane to other more valuable products. [1] Moreover, because of the cost and difficulty of transporting gases, oil companies generally resort to burning methane gas instead of utilizing it. As an alternative, methane could be converted to liquid methanol through selective C-H bond activation. One of the few processes found to convert methane to methanol is the Shilov Cycle (Figure 1). However, there are several drawbacks to the cycle. It is not especially selective for methanol, and it requires platinum (IV), which is very expensive as a stoichiometric oxidant.

The use of group 10 metal complexes for C-H bond activation has been studied extensively. Previous studies of C-H bond activation in the Bercaw group have focused on (diimine)platinum and palladium methyl complexes. However, these systems first make a C-H bond before breaking one. Recently, the group has studied successful C-H bond activa


In the reactions involving these hydroxy dimers, a C-H bond is not formed before breaking one, and the only by product is water.

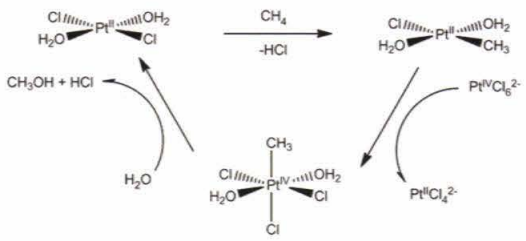


Figure 1:
One of the few processes known to transform methane into methanol, the Shilov Cycle.

$$\ln\left(\frac{k}{T}\right) = \left(-\frac{\Delta H^{\ddagger}}{R}\right)\cdot\frac{1}{T} + \ln\left(\frac{k_B}{n}\right) + \frac{\Delta S^{\ddagger}}{R}$$

tion using platinum, palladium[2], and rhodium[3] hydroxy dimers. In the reactions involving these hydroxy dimers, a C-H bond is not formed before breaking one, and the only byproduct is water. In this paper, we explored the possibility of using a different catalyst, an iridium dimer in place of platinum (IV).

Initial Results: To Kill a C-H Bond

C-H bond activation was studied using iridium hydroxyl dimers. The system that was primarily studied involved the activation of a test system, indene, with the $[(COD)IrOH]_2$ dimer (Figure 2). The reactions were performed in a mixture of deuterated dichloroethane and trifluoroethanol, and the formation of the product, (COD)Ir(3-indenyl), was detected using nuclear magnetic resonance.

Kinetics: Like Watching Chemicals Dance

Kinetics experiments were also performed to ascertain the rate dependence on the substrates of this reaction. It was determined that the reaction is first order in $[(COD)IrOH]_2$ dimer. There also seemed to be a first order rate dependence on the concentration of indene.
However, due to the insolubility of the hydroxy dimer in most common solvents, it was difficult to actuate the order of the reaction in terms of indene. Using Eyring analysis, the values of the enthalpy of activation ($\Delta H\ddagger$) and entropy of activation ($\Delta S\ddagger$) were found to be 12.0 kcal · mol^{-1} and -36.6 cal ·mol^{-1} · K^{-1}, respectively.

Eyring Equation: The value of $\Delta S\ddagger$ indicates that the reaction is a bimolecular process, which is consistent with our belief that the reaction is first order in indene. The reaction was also performed using 1,1,3-trideuteroindene. The value of kH/kD was determined to be 3.11±0.10, which indicates that the rate-determining step is C-H bond activation. Incidentally, the rate of the reaction increased as the concentration of deuterated trifluoroethanol increased, although this is likely due to the change of the dielectric constant of the solution rather than a mechanistic change.

The Road Maybe Taken

From the data collected through the kinetics experiments, we were able to produce a proposed mechanism for the process (Figure 6). Two equivalents of the product, the η^3-indenyl species, are formed from one equivalent of the hydroxyl dimer. The results indicate that the reaction proceeds through a deprotonation and dehydration to form the product. (NMR) spectroscopy (Figure 3). The characteristic peaks indicate that the indenyl product was indeed synthesized.
$[(COD)IrOH]_2$ was also able to activate cyclopentadiene almost instantaneously. The formation of the desired product was confirmed by comparing the NMR spectrum to that of CpIr(COD) prepared through a simple salt metathesis reaction of sodium cyclopentadienide (NaCp) with $[(COD)IrCl]_2$ (Figure 7). The identical spectra indicate that the correct product was indeed formed.

An Auspicious Cycle

Iridium hydroxy dimers have proven to be successful candidates as catalysts in C-H bond activation. The activation proceeds very rapidly under the chosen reaction conditions; at 60°C and 70° C the reaction goes to completion within 2 hours. Other iridium hydroxy dimers, $[(dppe)IrOH]_2$ and $[(COE)2IrOH]_2$ that could potentially be used for C-H activation studies were also synthesized. We believe that $[(dppe)IrOH]_2$ will perform C-H bond activation faster than $[(COD)IrOH]_2$ because it is more electron rich and susceptible to oxidation. The study of other ligands for the hydroxyl iridium dimer system is important in order to discover a catalyst that can activate more useful substrates at rapid rates. Future research of other iridium hydroxy dimers may yield fruitful results in the activation of C-H bonds and the conversion of methane to methanol.

The Approach

C-H Bond Activation Experiments: Due to the instability of the $[(COD)IrOH]_2$ in solution in the presence of air, most of the reactions were set up in an inert atmosphere glove box. For each experiment, $[(COD)IrOH]_2$ was weighed directly into a screw-cap NMR tube. After sealing the tube with a septum and screw cap, it was taken out of the glove box. The solvents and substrates were then injected throughthe septum. The tube was then sealed with electrical tape. After an NMR spectrum was taken, the tube was heated in an oil bath. The temperature at which the tube was being heated varied based on the experiment that was being performed. NMR spectra were taken after heating the tubes for every 30 minutes or 1 hour.

Salt Metathesis Reaction of Sodium Cyclopentadienide with $[(COD)IrCl]_2$: This reaction was performed inside the glove box. Two equivalents of cyclopentadiene was added to a solution of $[(COD)IrCl]_2$ in diethyl ether which was allowed to stir overnight. After removing the solvents in vacuum, the product was dissolved in deuterated methylene chloride and transferred to an NMR tube to take spectra.

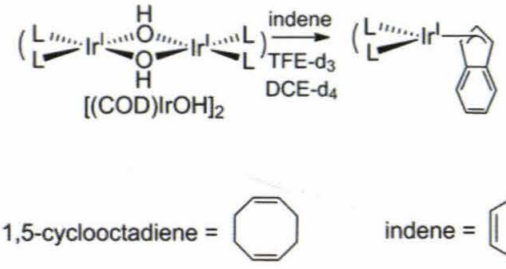


Figure 2:
The reaction of the iridium dimer with indene.

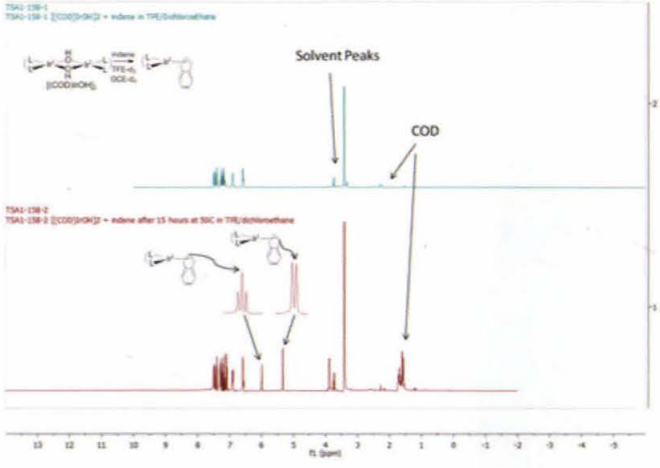


Figure 3:
The reaction was performed in NMR tubes and the formation of the product was verified via NMR.

For quantitative analysis, 10 mgs of the dimer were used in each reaction, and it was dissolved in 750 microliters of solvent consisting of 650 microliters of deuterated $C_2D_4Cl_2$ and 100 microliters of trifluoroethanol-d3.

Synthesis of $[(dppe)IrOH]_2$: After synthesizing $[(COE)2IrOH]_2$ using literature procedures, it was reacted with dppe in toluene under argon on the Schlenk line. Vacuum was used to remove the excess solvent. The product was then washed with pentane.

The value of kH/kD was determined to be 1.00±0.10, which indicates that the rate-determining step is substrate coordination instead of C-H bond activation.

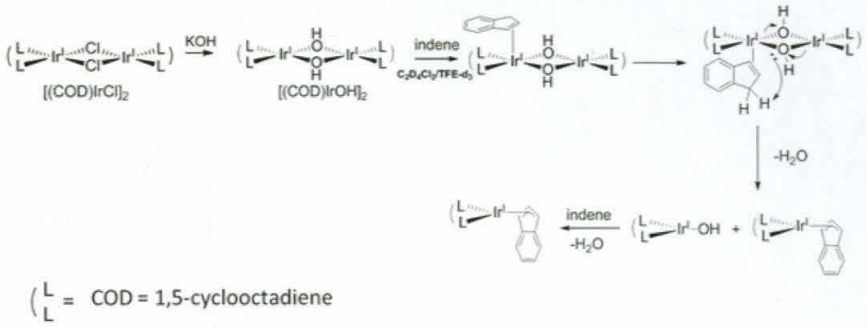


Figure 4:
Proposed mechanism of reaction between indene and iridium dimer.

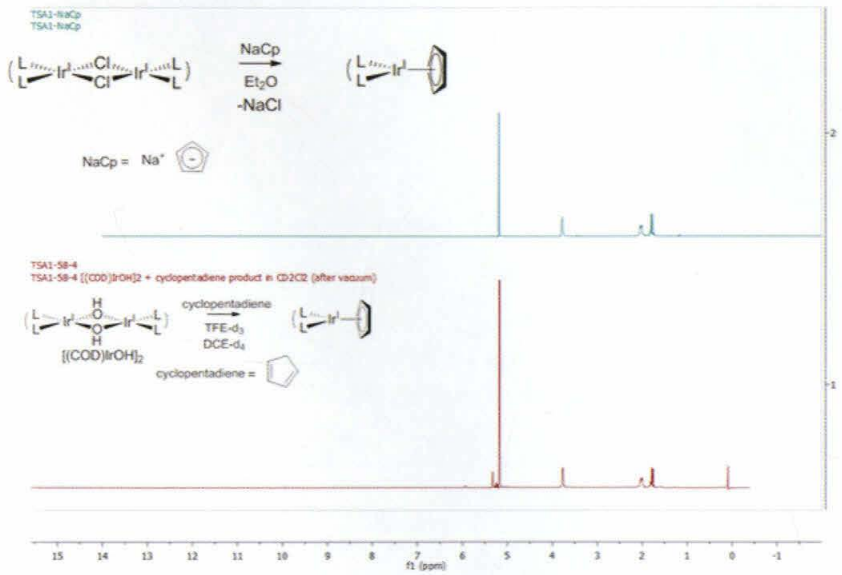


Figure 5:
NMR spectra confirming the formation of the activated cyclopentadienyl product.

We believe that [(dppe)IrOH]$_2$ will perform C-H bond activation faster than [(COD)IrOH]$_2$ because it is more electron rich and susceptible to oxidation.

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