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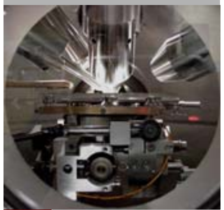

Surface Interactions

SI ontario

Newsletter of Surface Interface Ontario

Welcome

Chuck Mims (left) shares some thoughts with Jim Robinson of Datacomp during the visit to Thermo Electron in February. (See article on page 2)

Dear colleagues:

Along with Rana Sodhi and Peter Brodersen, it is my pleasure to offer our first newsletter from Surface Interface Ontario. The laboratory, established in 2002 with a Canadian Foundation of Innovation award, is now in the midst of a significant expansion of its capabilities and activities. This happy circumstance is the result of a second CFI award from the Leading Edge Fund, announced late last year. More details of this exciting initiative can be found below. Sample preparation and handling are critical aspects of the study of surfaces and hence, an important part of the expansion will be a user laboratory dedicated to sample preparation and handling. The high quality and wide-ranging impact of the research activities of you, our users, combined with expanding needs for high quality, collaborative surface analysis is the reason that CFI chose to invest further in SI-Ontario. Therefore, our success is really your success. We plan to bring you a newsletter several times a year in order to inform you of our operations and capabilities as well as to highlight recent advances. We hope that this will stimulate new ideas for our current users and trigger new research programs in the research community at large. We look forward to working on your problems in surface chemistry and of course, welcome your comments and suggestions.

News

SI-Ontario receives Canadian Foundation for Innovation award.

SI-Ontario will benefit from a $1.36 million investment by the Canadian Foundation for Innovation (CFI), as announced last November. The proposal, which was submitted to the Leading Edge Fund, was entitled "An Integrated Centre for Surface and Interfacial Analysis of Advanced Materials" and spear-headed by Prof. Charles Mims. The total budget, with in-kind and matching contribution, will come to $3.4 million. The award will not only allow SI-Ontario to upgrade its equipment but will greatly expand the scope of work it can currently undertake. The new infrastructure will allow Canadian researchers continued access to state-of-the-art surface analysis equipment and the related expertise, as well as comprehensive surface preparation facilities, thereby ensuring their position at the leading edge for years to come. See article on page 2 of this newsletter.

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Toronto to host SIMS XVII in 2009

Last Spring, a proposal was submitted to the SIMS International Committee at the bi-annual SIMS workshop in the US for Toronto to host the Seventeenth International Conference on Secondary Ion Mass Spectrometry (SIMS XVII). This is a joint venture between SUNY (Buffalo), Surface Science Western (UWO) and SI-Ontario (Toronto). Prof. Joe Gardella (SUNY) is the Conference Chair with Prof. Leo Lau (UWO) and Dr. Rana Sodhi (SI-Ontario) acting as co-chairs. The Committee enthusiastically supported the proposal and SIMS XVII will be held in Toronto in the Fall of 2009. A meeting management company has been chosen and work is underway already in securing a venue. The SIMS conference is held every two years. Manchester hosted SIMS XV in 2005 and SIMS XVI will be held in Kanazawa, Japan this Fall.

Enhancing the capabilities of SI-Ontario

The research supported by SI-Ontario is as diverse as its client base and is of high impact. A common thread is the need for the best available surface and interface chemical information. While the current facilities have provided a critical component to the supported research, advances in technology have necessitated further investment in the infrastructure to allow leading edge quality and fulfill needs currently unmet both regionally and nationally. The new CFI funding allows us to now meet these goals.

Four main categories have been highlighted for enhancement.

- **ToF-SIMS upgrade:** This is to include the new Bi cluster ion source, which will replace the present Ga source; a third ion gun column to house a new C_{60} ion source; pulsed secondary electron detection and associated data systems; and improvement to the sample-cooling system to -150°C.
- **Imaging XPS/AES system:** A small spot (~ 10 µm), monochromatic (angle-resolved) XPS with imaging capabilities, a sample treatment chamber, heating-cooling (-150° - 600°C), and Auger imaging with 100 nm spatial resolution.
- **Specialised sample treatment/ preparation facilities:** This will include a cryomicrotoming/freeze fracture, custom stand-alone preparation chamber; a vacuum suitcase and other (cryo and inert gas) transfer devices; a surface profilometer; polishing equipment; and a glovebox.
- **Expanded laboratory/user facility:** To house the expanded facility, lab space will have to be doubled. The new space will house the old XPS - for use on dedicated projects, preparation chamber/equipment, glovebox and space for visitors. In addition to more data stations in-house, the proposal also includes networking capabilities with other institutions.

Further details will be posted on our website - www.si-ontario.utoronto.ca.

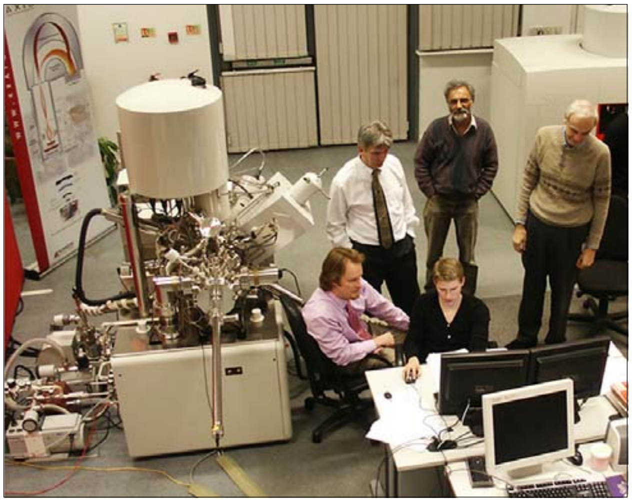
Visit to Thermo Electron and Kratos

In order to help decide which XPS fits SI-Ontario's user base the best, Rana Sodhi, Peter Brodersen and Chuck Mims visited both Thermo Electron (E. Grinstead, UK) and Kratos (Manchester, UK) in early February. Thermo offers 2 instruments of interest: the Thetaprobe and the Escalab 250, while Kratos' flagship - the Ultra, is also a leading contender.

Visiting the team at Thermo Electron. Thetaprobe is in the foreground, Escalab 250 is n the background.

The advantage of the Thetaprobe is its ability to do parallel angle-resolved XPS, negating the need to tilt the sample. By focusing its X-ray down to 15 µm, it is able to do small spot analysis, achieving good count-rate, while stage-rastering allows imaging capabilities.

Both the Ultra and the Escalab use a parallel imaging mode. By decreasing the aperture in the lens system, small areas of analysis can be defined. Scanning the plates allows both systems to generate a map. Both systems claim a spatial resolution of better than 3 µm. Angle-resolve XPS is done by tilting the sample.



The team at Kratos busy demonstrating the performance of the Ultra.

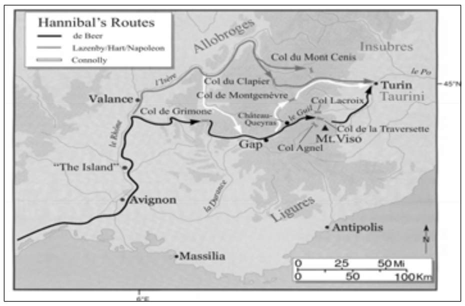
A final instrument, Ulvac-Phi's Versaprobe, has just come onto the market. Unlike the instruments above, it images by scanning a small spot X-ray.

All in all, it is going to be a tough decision! A comprehensive set of real samples was taken over to compare performance. Also, the ability to integrate sample preparation chambers is of importance. The good thing is that whatever our decision, we can't really make a mistake.

Hannibal's Possible Routes Invasion of Italy - 218 BC

Perhaps one of the more esoteric applications of SIMS presented at SIMS XV in Manchester in 2005 was entitled "ToF-SIMS applied to historical archaeology in the Alps" [1].

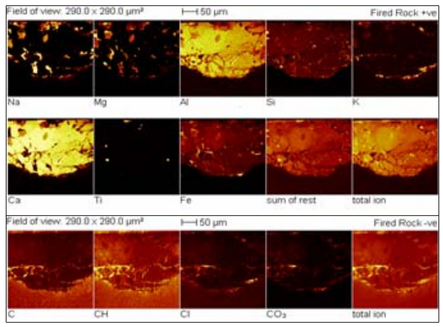
According to literature, there are 3 possible invasion routes followed by Hannibal during the second Punic War (see map).



While proof exists that he used the Col de le Traversette, ancient literature suggests that there should be burnt rock on the Italian side of the Alps due to his "firing" of the rocks. The Col du Clapier is the only pass where "fired" rock has been found.

The question is, is this due to timber being used as related to Hannibal, or is it more recent, say to a modern day road crew?

SIMS images for a cross-section of the burnt rock are shown here.



Of interest is the presence of K on the burnt crust and within the fissures. The presence of K has been attributed directly to the firing, resulting from the ash residue that would remain after firing with timber. This would not be expected if gasoline had been used for the firing.

Thus the SIMS results are in broad agreement with the historical literature which states that Hannibal did use timber to fire the rocks and clear his route. This alone is not positive proof that he indeed did this and used the Col du Clapier, however, it does confirm that timber was used in this case.

[1] R.N.S. Sodhi, W.C. Mahaney and M.W. Milner, Applied Surface Science **252** (2006), p7140

SOFCs—Isotope Exchange and Depth Profiling

Results from SI-Ontario's collaborative work with University of Houston (Chemistry & Physics) on solid oxide fuel cells (SOFCs) were reported at SIMS XV in Manchester (UK) in the fall of 2005. The presentation highlighted the ability of SI-Ontario's ToF-SIMS instrument to study the oxygen transport kinetics of newly developed mixed ionic electronic conductor cathode materials. SOFCs are highly efficient, non-polluting electrochemical energy converters, directly transforming chemical energy into electrical energy. For commercialization, operation of SOFCs at intermediate temperatures (500–700 °C) is desirable in order to reduce costs and enhance cell stability.

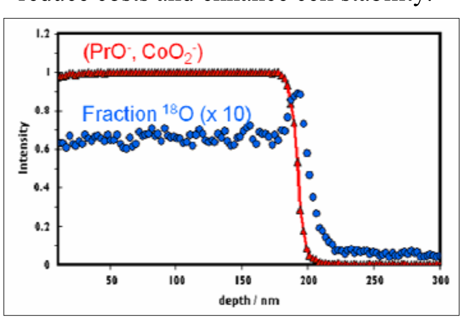


Figure 1 Dual beam depth profile of $^{18}O/(^{18}O+^{16}O)$ and other cathode ions

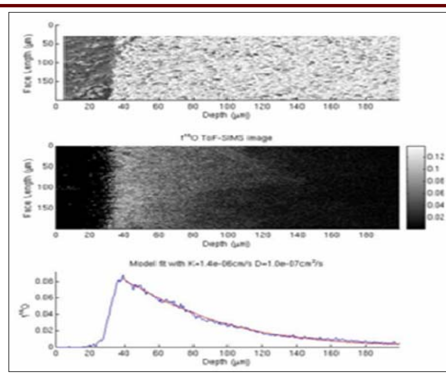


Figure 2 Depth profile (bottom) extracted from image (center) of area of interest (top)

At lower temperatures, cathode resistance becomes the limiting factor in overall cell performance. Current efforts focus on finding oxides that are electrolyte compatible and which have the high oxygen diffusion and surface exchange kinetics necessary for low electrode resistance.

Isotope exchange and depth profiling (IEDP) has been used to evaluate oxygen transport kinetics. Samples (both thin films and bulk) are equilibrated in oxygen (0.2 atm) with normal isotopic abundance and then exposed to ^{18}O (99% isotopic abundance) and rapidly quenched. The resulting ^{18}O profiles are determined via ToF-SIMS using either dual beam sputter analysis (thin film cathode - **Fig.1**) or imaging of cross sections (bulk cathode - **Fig.2**). The extracted profiles are used to determine oxygen surface exchange and oxygen bulk diffusion coefficients.

In this project, the imaging capability of our TOF-SIMS IV instrument has also proven useful for investigating profile phenomena, including lateral heterogeneities as a function of depth in thin films and gross distortions in ^{18}O profiles of cross-sections caused by e.g. cracks in the material (**Fig.3**).

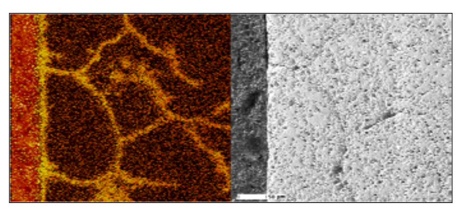


Figure 3 ^{18}O map (l) and secondary electron image (r) of coincident area

For further information on this project, see *Journal of Materials Chemistry*, DOI:10.1039/B618345J (2007)

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"Creating Partnerships for Innovative Research"

Surface Interface Ontario evolved from the Surface Science Unit of the Institute for Biomaterial & Biomedical Engineering (IBBME), moving into newly renovated office and lab space within the Department of Chemical Engineering & Applied Chemistry at the University of Toronto in Spring 2002. A successful CFI-LEF proposal in November 2006 now allows us to greatly expand the scope of the lab. This unique facility provides enabling information for a wide range of applications from many disciplines involved with advanced material research, both at the University of Toronto and beyond.

For more information and job request forms, please visit us at

www.si-ontario.utoronto.ca

Heating & Cooling

Being able to heat or cool a sample *in situ* can be very important. For example, certain polymers can restructure, showing different orientations between the wet and dry states. The ToF-SIMS has a special heating-cooling stage (below), which allows the temperature to varied between -130°C - 600°C in both the preparation and analytical chambers.

In a recent study, Sosnik [1] has looked at collagen/poloxamine hydrogels by a 'deep freezing' ToF-SIMS approach in order to study the availability of the collagen molecules at the surface of the hydrated polymer structure and consequently their ability to induce the attachment of cells on the designed matrices. Three matrices considered: collagen, poloxamine and poloxamine + collagen.

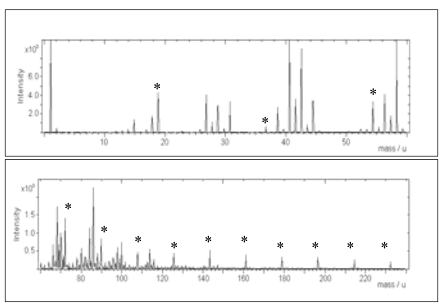


Figure 1

The samples were cast in a special Cu holder which was attached to the cooling stage and placed in the transfer chamber. This was flushed with dry N_2 and cooled down to -120° C at which point the vacuum was started. After placing in the analytical position, the sample was heated in 5°C increments until the H_2O sublimed off. Figure 1 shows the positive spectrum at -95°C and it can be seen from the marked (*) series of peaks due to $H(H_2O)_n^+$ fragments that the water has not totally sublimed off. Heating the sample drives this remaining H_2O. Figure 2 shows the positive ion spectrum of a collagen/poloxamine-methacrylate hydrogel heated to –65°, which shows peaks characteristic of both the collagen and the pure hydrogel.

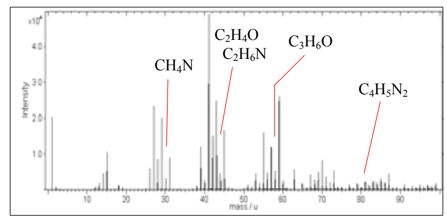
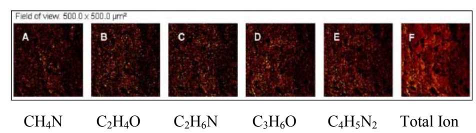


Figure 2

The work confirms the presence of collagen at the surface which is evenly distibuted as seen in positive ion image shown below.



[1] A. Sosnik, R.N.S. Sodhi, P.M. Brodersen & M.V. Sefton, Biomaterials **27** (2006), p2340

Some Recent Publications

Surface study of collagen/poloxamine hydrogels by a "deep freezing" ToF-SIMS approach. A. Sosnik, R.N.S. Sodhi, P.M. Brodersen and M.V. Sefton, Biomaterials **27** (2006), p2340

ToF-SIMS applied to historical archaeology in the Alps. R.N.S. Sodhi, W.C. Mahaney and M.W. Milner, Applied Surface Science **252** (2006), p7140

Imaging of aerosols using time of flight secondary ion mass spectrometry. C. Font Palma, G.J. Evans, R.N.S. Sodhi, Applied Surface Science (2007) in press

Shape-Controlled Bi2S3 Nanocrystals and Their Plasma Polymerization into Flexible Films. R. Malakooti, L. Cademartiri, Y. Akçakir, S. Petrov, A. Migliori, and G. A. Ozin, Advanced Materials **18** (2006), p2189

ToF-SIMS Analysis of PEG Penetration into Wood Cell Walls. D. Jeremic, P. Cooper, P. Brodersen, Holzforschung (2007) in press

Oxygen Exchange Kinetics of Epitaxial $PrBaCo_2O_{5+\delta}$. G. Kim, S. Wang, A.J. Jacobson, Z. Yuan, W. Donner, C.L. Chen, L. Reimus, P. Brodersen, C. Mims Applied Physics Letters **88** (2006), p024103

Polymer Multilayer Particles: A Route to Spherical Dielectric Resonators. I. Gourevich, L.M. Field, Z. Wei, C. Paquet, A. Petuhkova, A. Alteheld, E. Kumacheva, J. Saarinen, J. E.