

Secondary Ion Microscopy and Spectrometry. Explorer's notes over a half-century journey.

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Foreword

At the 20th Workshop last year in Key Largo, Peter Williams mentioned one of my papers back in 1958, nearly half a century ago! It was a shock, all the sudden I felt old and started to ask myself about the meaning of that long lasting activity. An answer came out: "I want to finish something I have started a long time ago" but it was foolish - there is no end to research. To exorcize that evil spell, I decided to make a list of things I wished to complete before stopping. Not really easy to make such a list, each time I dug out a piece of unfinished work it triggered new thinking and the strong desire to make new experiments, which I knew I had little chance to do. From there a subtle way of escaping those problems arose in my mind, I would just confess the "unfinished" things and let the scientific community "separate the wheat from the chaff". Not easy either to replace those unfinished things in their context without ending up in a "historical session" with the obligation to produce long lists of references trying to acknowledge anyone's work. A terrible task!

My fears were partly justified since I am in a "historical session" but I was given the freedom to break the spell by not making an historical account. It will just be a story about my own exploration of **Secondary Ion Microscopy and Spectrometry** over half a century. To put things in perspective, I want you to know that I am perfectly aware that if someone had undertaken an objective historical account, the story I am preparing to tell you would be only a small part of it, a small part of the amount of work done in fundamentals of ion emission and, in the field called **Secondary Ion Mass Spectrometry**, including depth profiling, surface analysis, organic samples and material science.

Whatever it may be, I just cross my fingers not to be too boring

Early days

As some of you may know my thesis adviser was Raimond Castaing. For younger people in the audience let me recall that Castaing was a brilliant physicist who, among the many things he accomplished, built the first electron microprobe (1952). He was a young Professor at the University of Toulouse when he asked me to make measurements on secondary electron emission of solid samples bombarded with keV ions. It was a piece of experimental work that I had to do as a postgraduate student. It's also the origin of the paper mentioned by Peter. With the experimental set-up I had designed, secondary electron energy distributions were measured by a counter field method and I did notice the appearance of a weak positive current when most secondary electrons were repelled. Many reasons could account for such positive currents, for instance tertiary electrons induced by fast sputtered neutrals or backscattered primary particles...

You may wonder why I mention such a "detail" and why it became so important. I reported my results to Castaing and we were exploring all sorts of explanations. When we started to speculate about the possible existence of sputtered positive ions he suddenly got excited. You may think that the excitement came from the hope to have discovered a new ion source for

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mass spectrometry. If it had been the case I wouldn't have any story to tell you since the discovery was already made by others as we learned later on from literature (Herzog, Vichboeck, Veksler, Benjaminovitch, Liebl, Honig, Bradley, Stanton, Cooper, ...). No, the origin of Castaing's excitement was that if positive ions were emitted from the sample surface he anticipated that ion images could be produced directly and that it would open a new way for directly mapping the chemical distributions of elements composing the sample!

Direct imaging with emitted charged particles.

Let's pause and explain why that idea of ion images looked so exciting. As you know, impacts of electrons with few tens of keV on solids generate X rays with wave lengths characteristic of the elements composing the volume under the impact area (Moseley's law). André Guinier proposed to Castaing for his doctorate thesis to explore the possibility of getting local chemical compositions by bombarding the sample with a finely focused electron probe. Distribution maps of various elements could then be obtained by scanning the electron probe. The alternative could have been to irradiate the sample with a broad electron beam and focus X rays generated in each point into X ray images but that working mode was out of reach because of the lack of adequate X ray optics. Castaing did not like the slow and tedious scanning procedure.

To complete the scenery, at that time a great development was going on in electron microscopy. On one hand transmission microscopy progress with thin sample preparation and on the other hand many attempts to find new ways for observing metallographic samples, for which it was only necessary to prepare a flat polished section from a piece of bulk material. In the later case, research was going on to get lateral resolutions much better than that of the light microscope. Different irradiation modes were used to produce electrons from surfaces: photons, fast electrons and ion bombardment. Then, emitted electrons were accelerated by a strong electrostatic field and focussed into an image of the surface by using what was called a cathode lens or else immersion or emission lens.

Now let's imagine that you replace secondary electrons by sputtered ions, you could directly get ion images instead of electron images. Then let's imagine a mass spectrometer able to mass filter ion images while keeping their optical quality and you would have an instrument providing directly elemental and isotopic maps. Who can think that we did not consider using an ion probe and making an ion version of Castaing's electron probe? But it looked so much more elegant to get directly mass filtered ion images and get rid of the scanning procedure that we had no hesitation on the direction to go. There were of course a few other arguments related to the state of art at that time that would be too long to develop here.

It was my first lesson about elegance in Physics, a lesson that I have tried not to forget "for better and for worse".

Roses and thorns.

Bright ideas give directions but then it remains to find ways. First, nobody had ever made a mass spectrometer with the capability of filtering ion images. Second, ion images were difficult to observe on fluorescent screens since there were no channel plates at that time. Castaing's guidance was essential in overcoming those difficulties with elegant solutions like the stigmatic magnetic sector coupled to the immersion lens in such a way that ion images were placed in an achromatic plane to avoid blurring by energy dispersion whereas mass

selection was performed at the exit of the magnetic sector, on the image of the illumination pupil (crossover) of the immersion lens. Besides, ion images could be converted into electron images and observed on a fluorescent screen by adapting a converter designed a few years before by Möllenstedt and Drücker.

But what would have been the use of those elegant achievements if it had turned out that secondary ion emission were not adequate for producing ion images? Indeed, our knowledge on ion emission was very limited. We were anxious about yields, initial energy distributions and above all about the exact origin of those ions. The way positive sputtered ions could escape neutralisation at the exit of a conducting surface was a kind of mystery because so many swift electrons were available at the Fermi level to follow slow positive ions leaving the surface. We were extremely worried by that last question.

If neutralization were the main phenomenon, the probability of getting ions would be very low and we could end up with vanishingly small ion yields. The fact that significant yields were reported in literature was not completely reassuring either since it could imply ionisation processes occurring outside but too far from the surface. The stressing question was how far from the surface?

Indeed, let's imagine that sputtered particles leave the surface as neutral and become ionized somewhere outside. Such ions would be created at some distance from the position they originate in the surface (**slide 1**). Thus, the position of an ion being registered in the ion image given by the immersion lens could be far from its initial position in the sample surface, far enough to prevent the production of an ion image with a decent lateral resolution. If it were the case, the bright idea of direct imaging would collapse! Only an experiment could answer the question and for that we had to build the whole apparatus. We lived a period of great suspense before we got the first evidence that we could get ion images in the micron range resolution (1960, 1962). In return, the result could be considered as an indirect proof that most ionizations occurred at a distance smaller than 1 μ m.

Let's have a look on the experimental set-up (**slide 2**).

I would like to mention that in the meantime a group of PhD students was working with Castaing on ionization processes when conducting samples were bombarded with noble gas ions and of course I was following closely their work. The general scheme was about auto-ionizing electronic states created during atomic collisions and their survival probability up to a point where they could escape neutralization. But this is another story.

The worrying side in retrospect.

You may think that I like to tell that episode to give a little spice to my story but the threat was real and no matter how elegant ideas are, they may fall on the wrong side of the road. Indeed, as I carried on my investigations further I found that our fears were partly justified. Yes, ions can be produced outside the surface far enough to kill any possibility to get a direct ion image with acceptable lateral resolution! Observation of direct images made that statement obvious in a few instances. For example, zinc targets bombarded with argon ions showed very fuzzy images. The recording of the initial energy distribution of Zn⁺ ions, showed what we named a "prepeak", that is ions appearing with energies lower than what they should have if they had left the sample as ions with zero initial energy (**slides 3, 4**). It meant that neutral particles may leave the sample and get ionized outside the sample at distances ranging from 0 to several tens of μ m. Similarly, at mass number 40, on samples

containing calcium one could observe a degradation of ion images by shifting the position of the energy band towards low energies. It was because at mass 40 there is a superposition of $^{40}\text{Ca}^+$ ions and $^{40}\text{Ar}^+$ ions. The vast majority of argon ions are produced outside the surface by charge exchange of the incoming primary beam with sputtered argon atoms previously implanted whereas calcium ions are produced much closer to the surface by other processes. Peter Williams and his group pushed those observations further and made beautiful work on that external and delayed production of ions. For instance, they have demonstrated the existence of ions like Mo_2^{++} produced outside and proposed a detailed ionization scheme, which has been successfully confronted with calculations on stability, life time and ionization energy of various molecular configurations by another group.

Now if you realize that many energy distributions exhibit a prepeak, a sizable proportion of positive ions are created at a few tens of μm from the surface, you may think that we were really lucky that other ionization mechanisms were occurring closer to the surface and had much higher probabilities.

Let me give you a last example with negative ions. It concerns a quartz sample bombarded with caesium ions. The surface of that insulating sample has been carefully kept equipotential at a constant value by using the normal incidence electron gun, which allows electrons to be reflected on the surface with vanishingly small energies as I described it in the last workshop in Key Largo². Neither the sample potential nor the electron beam were changed during the recording; only the electrostatic sector was scanned in synchronism with the electrostatic peak switching. As you can see prepeaks are present in various proportions for different ionic species (**slides 5, 6**). So, negative ions also can be produced outside the sample surface. By which mechanisms are those ions produced, are they proportional to the primary beam density, do they depend upon the beam density of reflecting electrons and can differences in the sharpness of direct images be observed? All those points remain to be explored and many assumptions that may occur to one's mind need to be checked... and are part of the unfinished work I mentioned

Impossible to miss.

The instantaneity of direct ion images made the observation of several secondary ion emission properties fairly easy. Two of them were quite obvious: the chemical and the lattice effects. Let me show you a few micrographs. The first example is about a sample of copper containing copper oxide nodules bombarded by an argon beam (**slide 7**). The image was made of Cu^+ ions, but similar images could be observed with CuO^+ and O^- ions. It showed that the oxide nodules emitted more Cu^+ ions than metallic copper itself. In general, it was observed that ion yields were order of magnitudes higher when metallic elements were associated with oxygen so that sceptical minded people were entitled to wonder if secondary positive ions would exist at all if ultra pure samples were bombarded with mass filtered argon ions in an ultra high vacuum! As a matter of fact, it was a hard blow for straightforward quantitative analysis.

I do not say that those effects were preventing us from getting valuable chemical information but you needed to be an expert and perform special studies in nearly each case! Let me just show a micrograph of a copper-beryllium (1.7%) alloy (**slide 8**). The penetration of oxidation along grain boundaries far beyond the oxidation front inside the grain is easily visualized. But

² A paper is in preparation.

saying that is anticipating on previous metallurgical knowledge about oxidation processes of those alloys. Indeed, you must realize that you are looking at a Cu^+ ion image and what you are actually observing is the enhancement effect on Cu^+ emission resulting from the presence of BeO oxide. For instance, the gradient being observed near the grain boundary is related to a lower concentration of Be, which has diffused towards the boundary during the oxidation process, and not to a lower concentration of copper. Images from other ionic species are also necessary before you can get a fair understanding of what you are looking at. However, the subject of interest here was the abrupt limit at the oxidation front and ion imaging offered a way of getting interesting information on slanted sections to stretch the zone of interest.

The second example is related to lattice effects. On **slide 8** one can see bands with different intensities inside a crystal grain that are related to the presence of twins. Similar observations can be made O^- ion micrograph from another section of the same alloy (**slide 9**). Grain boundaries can easily be observed, they appear bright because of BeO oxide segregation during the oxidation process. The twin structure inside grains is the other conspicuous feature. To explore a little further those orientation effects, with Marc Bernheim we have used a sample rotating stage derived from my thesis apparatus. For instance, **slide 10** shows how currents evolve with angular positions when an aluminium single crystal was bombarded with argon ions and Al^+ intensities recorded at each angular position. A simple glance to **slide 11** is enough for a first explanation of the phenomenon... Now when you have a polycrystalline sample, the lattice of each individual grain is oriented differently with respect to the primary beam direction and thus each grain has different sputtering yields. I do not remember precisely what the effects on elemental ratios were, it would be interesting to revisit that part of the work, but I know that proportionality was not strictly obeyed... Again we were far from the mere simplicity of electron microprobe analysis and it was another blow for straightforward quantitative analysis.

Struggling with complexity

If I had to plot our position at that time I would say that we did succeed in our first objective but the science behind those beautiful ion images was rather complex, probably too complex to become a universal tool for elemental analysis as the electron probe had become. From that acknowledgement of partial failure followed several attempts to overcome what was felt as a deadlock for a whole set of practical usage. Since the chemical effect could not be ignored, let's produce chemical effects intentionally! There were several ideas behind that attempt (i) the most obvious one was getting higher sensitivities, (ii) then came the hope that surface atoms could be reorganized in some kind of amorphous layer that would suppress lattice effects (iii) and last one could dream of some chemical reagent that would impose a single and simple ionization law for all elements or at least for a large category of them.

From time to time, we had the hope that we could succeed. For instance, when the previous aluminium single crystal was flooded with oxygen while being bombarded with argon ions, the lattice effects could be suppressed as it can be seen on the **slide 12**. But it did not work as well on other targets, depending on their reactivity to oxygen. Moreover, we discovered remarkable matrix effects on copper aluminium alloys and copper alloys with Be or Mg where small concentration of those elements were able to drastically increase the yield of positive copper ion emission in presence of oxygen (like in slide 8).

Another direction to go was obviously the bombardment with reactive ionic species. Oxygen ions were of common use. With Marc Bernheim we explored the capability of various

primary species to suppress crystalline effects. We have tried among others O^+ , O_2^+ , I^+ , I_2^+ , CCl_3^+ , SF_n^+ , ... with $n = 2, 3, 4, 5$. On a (100) aluminium crystal, lattice contrasts were reduced but not suppressed. Thus flooding seemed to be more efficient and the reason why was not simple to figure out. May be that according to experimental conditions, disturbed layers created by bombardment with reactive species were renewed too rapidly to allow those layers to become amorphous over thicknesses able to hide the underlying lattice completely. The dynamics that controls the renewal of implanted surface layers is another subject that would deserve more thorough studies.

We went on trying more exotic ionic species like WF_3^+ , WF_5^+ , TaF_3^+ , TaF_5^+ , For instance, with TaF_3^+ lattice contrasts were suppressed on aluminium and on zirconium (**slide 13**) but on copper they were reversed with less amplitude however. We also had a divine surprise with a set of samples containing oxygen in solution at various concentrations in zirconium: ZrO^+/Zr^+ ratios were linear with oxygen atomic concentration! (**slide 14**). Much later I came across a source of ReO_4^- ions by J. Delmore et al, I would have been delighted to try it, who knows!

All along that quest we behaved somehow like alchemists looking for the *philosopher's stone*, a universal solution for quantitative elemental analysis. But our quest with exotic ions stopped when the vacuum system broke down and we had to spend two months cleaning the apparatus. I am pleased to see that investigation with different primary ions is going on today, in safer conditions I hope, and with somewhat different objectives of course.

The other commandment: "Be useful".

I have to diverge from the main stream of my talk to go back to what has been the other guiding line inherited from Castaing. If I don't betray his thinking it went like this. "We, as scientific researchers, we enjoy what we are doing and we owe a return to the society supporting us". It could be teaching, it's why probably I became a professor, or when possible tried to help industry with our findings. Castaing had already an experience with the electron probe being commercialized by Cameca. He handed on the torch to me for the ion microscope and it was the beginning of a long interaction with Cameca.

Indeed, any scientist likes to share his findings by publications, in meetings or by teaching. When you have built an apparatus that could be useful for applications in other fields in research and technology you are facing something a little different. The medium is not a scientific journal but a group of people who will translate your ideas and experience into an instrument, that is into a tool that others will have to master and to use for solving their own problems. The other irreducible constraint is that the final product must fit a need and find buyers...

In that sort of translation things are lost and others are gained. I am grateful to those people in Cameca who have done their best over many years to improve the reliability and the ease of use of instruments and those who are daily in contact with users and do a difficult and often remarkable job in maintaining instruments in good working conditions and advising users.

Above all, I wish to acknowledge the creativity of users who got far reaching results, fulfilling my hopes beyond my expectations. I felt and still feel deeply moved and honoured when people choose instruments I have designed for their research, even though I don't know

them personally. My deepest desire would have been to design even better instruments for them.

Flashback on my involvement in applications

*My interest in applications received a paradoxical impulse during my post-doc at Stanford University (1964-65) in the Genetics Department. How did I land in that department? I do not remember exactly, my guess is that Elliott Levinthal, a physicist who was working with Joshua Lederberg (Nobel Prize for his work in bacteria genetics), attended a lecture given by Castaing mentioning the ion microscope. Lederberg, who was also involved in artificial intelligence and space exploration, thought that it was worth exploring the possibilities of the ion microscope in Biology. As I understood later, among many other things, he wanted to get information on the ratios of the four nucleotide bases in giant chromosomes like those observed in salivary glands of mature fruit fly larvae (*Drosophila melanogaster*). Even nowadays it seems an extremely ambitious program! Needless to say that our first results on organics were rather disappointing and Lederberg had that lucid but terrible sentence “well, you are looking at ashes”. He did not show the slightest sign of disappointment, it was just something that needed to be tried and it was done. Apparently, what I felt as a failure was just considered as a step in the general process of research: “now you know”. The approach of “success” and “failure” was very different: “let’s try” as opposed to the discouraging “it may not work”. Sometimes it sounded a little bit naïve or even crazy to me but, thinking about it again, I must admit that I liked that “craziness” and in a way I got contaminated.*

Of course, if I had been aware of such expectations before leaving I would probably have stayed home. It would have been a pity. The environment was extremely stimulating, it gave me the opportunity to be exposed to genetics and biochemistry with remarkable professors. Not to speak about my “discovery” of America! I should have told you also that I was working with another physicist, Sidney Liebes, and that our experiments were made on a set-up that we had put together in a few months. Among others, we discovered interesting oscillations in the yields of cluster ions Cu_n^\pm and C_n^\pm , oscillations of positive and negative ions being out of phase. Stupidly we made no publication but via “private communications” our spectra could be used by theoreticians to relate those oscillations to the stability of the ions. It was a period of intense activity and hard work that left me with a feeling of incompleteness when I went back home: Time had to pass before getting away from that narrow-minded failure/success reference and consider with other eyes the rich experience I had during my stay .

First commercial instrument, a digression on its “vertical” prototype!

The prototype of the first commercial instrument was a vertical instrument. The funny point is that one reason, among others, to make it vertical was that it would look like an electron microscope! It turned out that pumping with vertical oil pumps made that structure fairly inconvenient since we needed more pumps than in electron microscopes to produce a better vacuum, and these interfered physically with the many flanges and feedthroughs needed for the design. The commercial version, named SMI300 as some of you may remember, was horizontal. Let me say a few words about that instrument since it may not be very familiar to most of you. The magnetic prism was coupled with an electrostatic mirror. The incoming secondary ion beam made a first turn in the magnet and was reflected back by the mirror and made a second turn into the magnet bringing the final outgoing beam in continuation with the previous incoming beam (**slide 15**). The essential point was that high energy secondary ions

could touch the repulsive electrode, where their electric charge was lost, whereas low energy ions were reflected. The mirror was a kind of low energy pass filter and it was put there to improve mass resolving power.

Imaging capabilities were highly appreciated by users and played an invaluable role in selecting areas of interest on which measurements could be made safely. Other applications, in particular in biology and metallography, took more advantage of the available lateral resolution. From those experiments, I got the feeling that least lateral resolution had to be improved to make the method more attractive and competitive with other approaches.

In the meantime, depth profiling applications were growing very rapidly. Long before the great inflation of depth profiling in semiconductors I had used the progressive erosion provided by sputtering to record diffusion profiles mostly with isotopic labelling. It seemed such an obvious thing to do that I did not make a media hype with it. I believe that I was among the first, if not the first, to have done depth profiling measurements. (^{18}O diffusion in UO_2 in **slide 16**, Ta_2O_5 sandwich layers labelled with ^{18}O in **slide 17**, high resolution mass spectrum of the very first layers of Ta_2O_5 in **slide 18**). Then it became the playground of the semiconductor industry as you all know. Many people were involved who had means far superior than those I could expect in my lab at the university so that my added value would have been probably insignificant. I did not involve myself very much in the field, it was an error maybe since in an orchestra each instrument has its role³.

The main reason for recalling today the existence of the vertical version is that it gives me the opportunity to talk about observations made on liquid metals. That work remains one of the unfinished things I mentioned in the beginning of my talk.

I asked a student, Robert Laurent, to examine the temperature dependence of lattice effects from room temperature up to the melting point⁴. Aluminium was an ideal material because we could quite easily get large crystal grains and because, of course, the melting point was low (660°C). Laurent was a skilful and watchful experimenter. For instance, he discovered the oscillatory behaviour of argon cluster emission when the primary argon beam was aligned along high density atomic rows (low sputtering yields) and the temperature was suitably adjusted to help implanted argon gather into bubbles by diffusion (**slide 19**). It was really a beautiful experiment and I would be delighted to talk about it but I have to make a choice and what follows is even more exciting in my view.

After some time of practice our skills improved and it became possible to heat the sample close to its melting point and rely on the extra power brought in by the primary ion beam to “melt” the surface and only the surface! In fact our aluminium samples contained impurities and, as every one knows, impurities tend to segregate at grain boundaries with the effect of lowering their melting point. We were making our observations using Al^+ direct ion images just as if we were using a light microscope and often forgetting that it was not a light microscope (artist view in **slide 20**). The melting of grain boundaries was a grandiose and unforgettable spectacle. Rivers of molten metal seemed to run nicely around islands of solid metal! With very little power removed everything got suddenly still and with very little power added grains themselves were flooded by what looked as a veil of molten metal. Another

³ For instance, there were problems with measurement repeatability, which I have encountered later with isotopic ratios. Besides, I was offside when shallow profiling problems arose...

⁴ It was in the context of a kind of master degree called 3rd Cycle Thesis (nov 1973).

striking thing I remember was that scratches on a grain could disappear under “liquid metal” and reappear unchanged at the same place when a little power was removed. A true enchantment that left us like under a spell! When we recovered our spirits it was time for the student to pass his exams and he didn’t want to stay for a PhD. He was a kind of practically minded guy and he wondered if it were reasonable for grown-ups to make a living by blowing argon bubbles in metals or by watching rivers of molten metal run.

Of course it was not unknown that surfaces melted before bulk material but what was the exact origin of contrasts on ion images that gave us the impression that we were literally “seeing” it? Something was happening at the level of ion emission but what exactly? The question remained unanswered. We had no movie camera so that only remains the testimony of eyewitnesses and there are not so many left. Of course, I promised myself to redo the experiments but I never did it. May be I was unconsciously reluctant to propose such a frivolous subject to another student? Be wiser, try it and don’t forget to tell me about it!

The second instrument and a few innovating features

The mirror was a low energy pass filter so that prepeaks could not be eliminated. In some cases their presence could prevent the detection of elements at low concentrations, in others case higher mass resolution was required to separate atomic from polyatomic ions on images like for $^{56}\text{Fe}^+$ and $^{40}\text{Ca}^{16}\text{O}^+$ in minerals. Besides, as applications to semiconductors were progressing it became urgent to solve the problem and an electrostatic prism was added to get high mass resolution whichever energy band was selected. It was a temporary solution because ion images at high mass resolution could not be obtained with that set-up.

Fortunately I had in my drawer the optical scheme of more classical instruments that I had designed with Castaing some time ago, basically the IMSXF series. In short, by coupling an electrostatic sector ESA and a magnetic sector MS via a unipotential lens, it was possible to get mass filtered images at high mass resolution. Cameca decided to replace the IMS300 by an instrument built according to our design.

In the mean time I was working on a side project which was to replace a spark source by a sputtering ion source on a Mattauch Herzog spectrometer (built by a British company AEI). It gave me the opportunity to think about the general problem of ion source matching in mass spectrometry. Returning to the ion microscope it led me to the concept of transfer optical systems able to match the acceptance of the mass spectrometer, working at a given mass resolution, with the secondary ion beam extracted by the immersion lens. The Workshop on “Secondary Ion Mass Spectrometry and Ion Microprobe Mass Analysis”, held at NBS in Sept 1974, gave me the opportunity to set out the basic ideas, which were resting merely on the optical invariant concept. Experiments to check the feasibility were made in our lab by transforming our SMI300 and the paper describing the first experiments was presented at the 8th International Congress on X-Ray Optics and Microanalysis in 1977⁵. The paper was lost and I realized that when I read an ad for the Proceedings in a journal. The editor felt very sorry of course. He managed to include the paper at the end of the proceedings but he could not include it in the contents page. For mysterious reasons those proceedings were published in 1980, 3 years later. As a result the paper is never cited because it is too difficult to find. But it is not the end of the story.

⁵G.Slodzian and A. Figueras, “A transfer Optics for Micronanaysis by Secondary Ion Emission”, pp 659-665 in 8th International Congress on X-Ray Optics and Microanalysis (Boston, Aug 1977). Ed.D.R. Beaman et al, Pendell Publishing Company Midland Michigan 1980 ISBN 0-87812-180-3

Cameca knew what I was doing, they got interested and they wanted to include the transfer optics in the IMS3F that was under construction⁶. Writing a patent in our country was a real burden and the person who was technical director at Cameca at that time convinced me somehow that it may not be worth to spend time and nerves applying. So the transfer optical device became a pure Cameca product and brought a lot of praise to Cameca for the incomparable flexibility of the instrument. It was good for my modesty. Having a philosophical discussion on the matter with Castaing, his conclusion was “You should be happy about Cameca doing well owing to you”. Retrospectively, it remains a funny anecdote to tell with a pinch of humour about our naïve and exaggerated fears to see Cameca fail and our will to help at any price... It must be placed in the context of the sixties, twenty years after the end of the Second World War, where some people believed deeply that it was their duty to help in the reconstruction of an industrial environment of good quality in France.

Concerning the transfer optics let me mention a dynamic working mode that allowed keeping the secondary ion beam motionless with respect to the spectrometer while scanning an ion probe over the sample surface. Properly used it gave the instrument a remarkable “transmission” at high mass resolution.

At about the same period, I was involved in pluridisciplinary applications. In particular, I was working with geochemists and petrologists. The problems which confronted us in isotopic ratio measurements were insulating samples and repeated peak jumping with the magnetic field. Besides, oxygen isotope ratios were very popular but ionization yields of oxygen in the positive mode were low.

It was easy to decide that a better choice would be to use O^- secondary ions, because of better ionization yields, but then a solution for sample charging up had to be found. It gave me the opportunity to design and experiment the coaxial electron gun. Last year in Key Largo I made a presentation revisiting the immersion lens working as an electrostatic mirror so that it may not be necessary to remind you the principle (see slide 5). Again the first experiments were made on our SMI300. That time I worked with an engineer who accepted to spend time on taking a patent. When Cameca learned what we were doing that they wanted to incorporate the device in the IMS3F. However, the instrument was almost completed and it would have been too much work redesigning the whole system. Compromises were necessary so that the position of the electron gun was not the most adequate one. Nonetheless it worked and as you know “it works” is a magic sentence, it stops any objection. The other magic sentence is “nobody complains” with the understatement “except you”, which leaves you alone with your inability to understand or to operate the instrument. The other version is “stop being obsessed by academic perfection”. Much later, when a IMS4F was installed in our lab, I understood better why people were trying to temper my enthusiasm about the electron gun by saying that it was certainly nice in principle but rather difficult to adjust. In our lab, after a while, I managed to make the mirror a pleasant game again but with little success among those who already knew better ...

Peak switching was the last of the designs oriented towards isotopic ratio measurements I made during that period. The choice was to use an acceleration deceleration electrostatic system that we called the “tube”. Recently in Palm Springs I presented a revised and updated version to extend the mass range as you may remember. A patent was taken, Cameca got the rights but something went wrong in the way the device was accommodated and used. It’s a complicated story I don’t have the time to lay out, full of lessons about an unsuccessful transfer to industry. I regret very much that this wonderful device was not made broadly available.

⁵ A paper presented by Cameca can be found in the Proceedings already cited.

In brief, you may see that interaction with people working in other fields was a strong stimulation for creativity.

Striving for higher lateral resolution.

As I already suggested, one of my obsessions was better lateral resolution for ion images. The more I thought about the more it convinced me that the best solution would be to use ion probes in a clever way. The reason was simple. To improve lateral resolution in direct ion imaging one must reduce aberrations of the image forming system, which can be ultimately achieved only by reducing the collection solid angle of ions stemming from each object point. It follows that the better the resolution, the lower the signal. Intrinsically, there is a loss of information due to the instrumental process and not to physical features involved in secondary ion emission processes. On the contrary, when ion probes are used, it is possible to disconnect lateral resolution (size of the probe) and collection efficiency of secondary ions. Of course, there are physical limitations related to useful ion yields and to the number of available atoms in submicron volumes, not even speaking about the dispersion of collision cascades in the target putting some blur on the spatial origin of emitted particles. It is not my purpose to revisit the whole matter since it has been done fairly recently at the Workshop held in Hilton Head.

Although I had to give up the use of direct imaging, the concept in itself remained a powerful tool for conceiving high collection efficiency of ions emitted from a point and for extending that efficiency all over the surface with a scanning probe in operation (dynamic transfer). Naturally, I could not help making an attempt to push a little bit further the lateral resolution as it is shown in **slide 21**. Among the many questions in suspense was the best direction to take concerning parallel detection. Indeed, the method is destructive and one cannot redo twice an analysis on the same volume so that ions emerging from a sub micron volume must be detected in parallel channels. It looked easier to achieve it with a scanning ion probe than with direct imaging but the full discussion of those points would take too much time and send us back to the Hilton Head presentation. I promised myself to go back to direct imaging later, hoping to find suitable conditions where it might be valuable to use it, for instance with low energy primary ion bombardment. But until now I had no opportunity to try it nor either to explore with more insight the nature of various contrasts that ion images exhibited when different initial energies were selected.

Now let's say a few words about the nanosims adventure, which began in the late seventies. I had a few basic ideas in mind and a few estimated performances with possible set-ups in my files when I started hunting for room, people and funding. Of course, I also had all sorts of possible applications in my pocket that could entice supporters to contribute to the project. Knowing the difficulties of quantitative analysis, the emphasis was put on isotopic applications. Indeed, I knew the role played by isotopic labelling in biology, in material science for diffusion work for instance and in general the interest of isotopic determinations in terrestrial geochemistry and in planetology with anomalies occurring in small dust grains. Oxygen, carbon, nitrogen seemed to cover wide fields, so that I decided to start with negative secondary ions and Cs bombardment.

The most important thing was to find a place where to work and people with whom to work. If I had the talent of a good humorist I could tell you the journey in my lab, in my University and in some other places. Finally, it was Castaing who was the saviour, he told me that at ONERA two very good engineers were completing their job and that they might be free soon to undertake something else. ONERA is a government agency devoted to aeronautics and space research depending upon the Defence Ministry.

It was not too difficult to convince Bernard Daigne and François Girard of the interest of the project. With the recommendation of Castaing, the management accepted to host the project on the condition I would manage to get funded. It was a first and important step. I could not imagine a more auspicious start since the project was going to be hosted in a department with a good experience in instrumentation where, if you believe in symbols, Castaing made his thesis and built the first electron probe.

Surprisingly, it was less difficult to raise funds. The people I met were trained to resist the appeal of inspired professors but listened with cautious sympathy. Five or six public agencies joined to contribute to the project, to share the risk in case of failure I guess. And finally we were ready to start in 1980. It took about ten years to get the first published micrographs and twenty years before the first commercial instrument was delivered at Bob Walker's lab at Washington University in Saint-Louis (**slide 22**).

When a project is stretched over such a long period there is a risk that it will sink as the promoters' enthusiasm wanes. The other fear is that by the time it will be completed it will be completely obsolete. Some days I was discouraged by the slowness of progress and ready to give up but the good point when you work in a group is that all members do not get discouraged at the same time. We suffered from an obvious lack of man power although we had hired a good PhD student Fabrice Boust. But there were days of collective discouragement. On one of those days of bad mood, I made a last effort to find help and I phoned to the CEO of Cameca. Our relations were not excellent but the situation looked desperate. Within 24 hours he gave me his agreement to hire an engineer of our choice to work with us on the project. Despite our differences I am grateful for his shrewd business intuition that made him take a fast and helpful decision. A few months later we were lucky to find somebody of the quality of François Hillion, who is presently in charge of the nanosims at Cameca.

We started from scratch and we had to build almost everything: the ion source, the primary column optics, the extraction optics and the mass spectrometer with the multi detection,... The first prototype had also a scanning electron microscope incorporated in situ (and plans were ready for incorporating a scanning transmission microscope!). I must say that the SEM observation of the ion probe impact with the primary beam on was absolutely fascinating. The ion impact area had a different secondary electron/electron yield than the surroundings so that we could adjust the focusing of the primary ion beam and follow the displacement of the probe quite easily; it was like playing with a video game. Of course, it was not that easy to align both ion and electron beams. I remember that one day the beams were lost and it took one month before getting them back!

Fortunately I was working with practical people who made me understand that the theoretical and playful advantages of a dual instrument could not overcome the disadvantage of down times and of much higher building costs. The acquired experience made us confident in our ability to build a Scanning Ion Microscope and Spectrometer rather simpler, robust and easy

to run. The best was to postpone more sophisticated set-ups until it became obvious that they were needed. In other words, it was foolish to anticipate too much. So we decided to design a simpler version, the second prototype later named Nanosims 50, using parts of our first prototype. The foolishness of the beginnings was exhilarating but following that road would have been running to our ruin.

My direct involvement in the nanosims stopped soon after the instrument was completed. The political world had changed in the meantime. The Berlin Wall was down, the Soviet Union was breaking up and was no more considered as a threat to the Western World. As a result military budgets started to shrink in France. ONERA being ruled by the Defence Ministry wanted to get rid of their involvement in civilian programs to keep running their other programs. It was not a good time for starting an application group and go on with instrumental and other academic studies. The second prototype was lent to Cameca, not a bad return for them indeed and better than to see the instrument rust in a corner. The research group broke up.

Of course, it was sad to stop working with the Nanosims, as sad has it can be when somebody prevents you from playing with your own toys! But it was the best move for making the instrument available to other researchers. Look! Beautiful results have been established in planetology and cosmochemistry by Bob Walker's group, followed by others in that field. Claude Lechene in biology showed how isotopic labelling could be made quantitative inside a single cell. He renamed the method MIMS (multi imaging mass spectrometry) and applied it in many biological situations of interest. It has been a great pleasure to cooperate with him reviving my past incursion in the biology world. I hope that he will have many followers and that biology will become one of the major applications. And there are many other examples in different fields that I have no time to mention...

Among a few others things going on.

In parallel to my work on the nanosims at ONERA, I was exploring in my lab at Orsay isotopic fractionation problems. I wanted to find out why isotopic measurements were not repeatable beyond a given precision. I took the simplest possible system, a wafer of silicon bombarded with Cs ions for measuring silicon isotopes in the negative emission mode. I was aiming at precisions in the range of 0.1%. It seemed to me that instrumental reliability was a prerequisite for tackling the difficult problem of isotopic fractionations related to ionization processes with matrix effects.

It gave me the opportunity to learn about the art of high precision measurements. We spent days and days hunting for artefacts and we had to drive them out one after the other, the last but not the least were those related to the electron multiplier. It's again a long story⁷. The reason to mention that work here is that in many respects it belongs to the unfinished things although I succeeded in getting reproducibility in the rang I was aiming at. I would be delighted to tell you about the directions planned to improve the electron multiplier measurements but after attending the Workshop in Phoenix in 2001 and listening to Bonner Denton's presentation, it became obvious that there were also other directions to explore. Peter Williams, Bonner and I worked together for a time on a project of charge measurement with tiny Faraday cups that should have the potential to bridge the gap between the usual current measurements with Faraday cups and ion counting with EMs. We are still carrying on

⁷ I had the opportunity to talk about a little bit as a keynote lecturer at SIMS XIV.

with the project in cooperation with a Czech researcher Jan Lorincik. It's the case of unfinished work going on at a slow pace but with great hopes of promising outcomes.

Since I moved to the lab hosting me presently at Orsay, a study on silicon isotopic fractionations in various mineral samples has been started with Cécile Engrand. We got interesting results which could mark the beginning of a new phenomenological approach on matrix effects. The work is in progress, which is another way of saying that I don't know if it will be finished soon. My first idea was, before I got involved in the present talk, to report on its present unfinished state at this Workshop.

Let's dream for a while

When you do not perfectly understand a foreign language you pick up sentences that ring in your head because they concentrate in a few words a lot of things. For instance "I want my money back" (like Margaret Thatcher claimed) or more commonly heard "not in my backyard". I may understand that if you wake up with a windmill in your backyard you may not be happy. Waking up with a nanosims in your backyard has a vanishingly small probability. Nonetheless, in case it happens to you, before you blow up, let me suggest a few things you could try.

Electron / ion images. First, why should you blow up? You can use it or make happy a few friends by lending it to them. If you are fond of beautiful images and since you heard me talk about a scanning electron microscope that was built-in with the first prototype, you may want to try scanning ion microscopy using secondary electrons generated by ion impacts. Well, you know that it already exists in the instrument but may be you would like better resolution with smaller probes. A friend might have told you that he heard about a scanning ion microscope using He^+ ions, Orion made by Zeiss. That would be great! Just put their source on your instrument and it will work. You could observe high resolution images without sputtering too much the sample and choose exactly the place you want to analyse. You could also manage to record backscattered helium ions with specific energies, which might give you some insight on the elemental composition of the outermost layer of the sample. Beautiful but maybe a little bit expensive....

Bombardment at low energy. Let's forget about the glamour of high resolution images what else could you do? Maybe you are more on the basic side of interaction of ions with solids? Let's have a look at the heart of the instrument, I mean the objective lens. Primary ions travel along the optic axis normal to the surface sample and sputtered ions are accelerated in the opposite direction. Presently those beams are made with particles of the opposite sign and get separated by an electrostatic splitter. Let's then play with particle signs and with voltages to have primary ions decelerated by the sample while sputtered particles of the same sign are extracted. How could you separate beams made of particles of the same sign with the electrostatic splitter? Imagine that you direct a short pulse of primary ions on the sample, you could then switch on the splitter at appropriate times just before sputtered ions triggered by a primary pulse reach the splitter. Taking into account flight times, the duty cycle would be about 1/10... (**slide 23**) You would have a system allowing to bombard the sample with very low energies at normal incidence in a context where secondary ions would be collected efficiently. A lot to experiment with, a lot to play with,...

Images by mechanical scanning. Could we try something conceptually simpler? OK. The ion probe is scanned over the sample surface. There are always small imperfections with scanning: field curvature of the last condenser lens, slight astigmatism due to the scanning plate, adjustments of the dynamic transfer to rectify the direction of the extracted ion beam before entering the spectrometer,... Of course those defects are small, moreover some of them may be corrected electronically while scanning and you may like to work on that. You may also want to try something else for instance scan mechanically the sample. Here I can't help you any further you would have to explore the state of art of mechanical displacements by yourself. If you succeed you may have simplified image acquisition, improved image quality over the whole area being explored and got a bonus by being able to extend the field of view nearly at will.

Image contrasts. I can see that you don't like my suggestions too much because you are afraid to touch the basic structure of the instrument. You want to use the instrument as it is and do something that could just improve your understanding of how it works. It looks modest but it might be tough! You will have to immerse yourself into ion optics, know a few things about ion implantation and ion emission and prepare adequate test samples. But let's try.

For instance, implantation of primary Cs⁺ is necessary to increase emission yields of negative species. Concentrations at equilibrium of implanted particles depend on the local sputtering yields and in return caesium concentrations may control sputtering yields and ionization probabilities. You may wonder which effects it might have upon image contrasts for different grain orientations, for surface relief, for various materials,... One should also have in mind that, at equilibrium, atomic concentrations of implanted Cs may easily reach 20% so that superficial layers are quite different from the underlying bulk. Besides, you might be interested in studying the dynamics of the transient phase before equilibrium is reached. Again a lot of amusing things to play with! Moreover, caesium primary ions should not limit your horizon, you may explore other ion sources and the optical structure of the instrument is very friendly to such moves.

The other question I might suggest you look into is the origin of some image contrasts. In the nanosims, the optical system collecting secondary ions works in a non Gaussian mode with the waist of the beam being placed on the entrance slit of the spectrometer. The illumination of the waist depends upon local angular and energy distributions of emitted particles and local disturbance of the extraction field. Thus, when for one reason or another local distributions are disturbed, rays of different categories are rejected by the slit, which may have an influence on locally collected intensities and on the recorded image contrasts. What are the amplitudes of those effects? What does happen to ratio images? There are a few other suggestions I could make on the way of adjusting ion optics if one accepted to work with less collection efficiency and have some control on the crossover but may be it's too much in one time...

If none of those suggestions is appealing to you, let's forget about it and remember that it was only a dream!

**Thanks to the organizers for having invited me so often
Thanks for helping me understand
why I have been working so long,
why I may work a little longer.**