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Microscopy AND Microanalysis

Today's and Tomorrow's Instruments

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Abstract: This article will discuss the importance of Raimond Castaing's thesis on the genesis of a nondestructive and truly quantitative microanalytical method that assisted the scientific community in moving forward in the development of microanalytical instruments. I will also share with you my recollection of the decades of improvement in the electron probe microanalyzer (EPMA), that has allowed us to reach our present level of instrument sophistication, and I will explore with you my thoughts on the future evolution of this technique. To conclude, I will present the current status of related microanalysis techniques developed under Castaing in Orsay in the 1960s, as Castaing's interest in microanalysis was not limited to electron probe microanalysis alone.

Key words: R. Castaing, CAMECA, electron probe microanalyzer, virtual microprobe, secondary ion mass spectrometry, electron energy loss spectroscopy, NANOSIMS

INTRODUCTION

When Raimond Castaing presented and published his thesis in 1951 at the University of Paris (Castaing, 1951), the wheels of electron probe microanalytical instrumentation were put into motion. His ideas for a nondestructive and a truly quantitative microanalytical method were simple in concept and principle, yet proved challenging when it came to the translation of those ideas into operational instrumentation. To understand the progress accomplished since then, a quick flash back to the "Elvis years" is worthwhile.

THE "ELVIS YEARS"

It was indeed at about the same time that Elvis Presley was redefining Rock 'n Roll that others were busy developing the electron microprobe. Among them was Raimond Castaing[1] who, thanks to outstanding and simple ideas, devised means for an absolute calibration. He developed the theory and demonstrated that nondestructive quantitative microanalysis was possible because one could use pure standards and because the X-ray signal coming from a micro volume of material would be sufficient. He fully understood the power of his new tool, built an instrument, and started to solve metallurgical problems with it.

Finally, in the late 1950s, with the urgent need for microanalytical tools in metallurgy and sufficient advances in instrument design, the first commercial electron probe microanalyzer (EPMA), the CAMECA MS 85 model (Microsonde for EPMA, in French, built in 1958) was produced (Fig. 1). It was the first electron probe not built in an academic environment and available for sale to the public.

This instrument had two wavelength dispersive spectrometers at an 18° take-off angle, with one crystal each

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[1] In 1947, James Hillier patented an electron beam column and an X-ray spectrometer but did not pursue his project. At the same time and independently, R. Castaing and A. Guinier were setting the base of electron probe microanalysis.

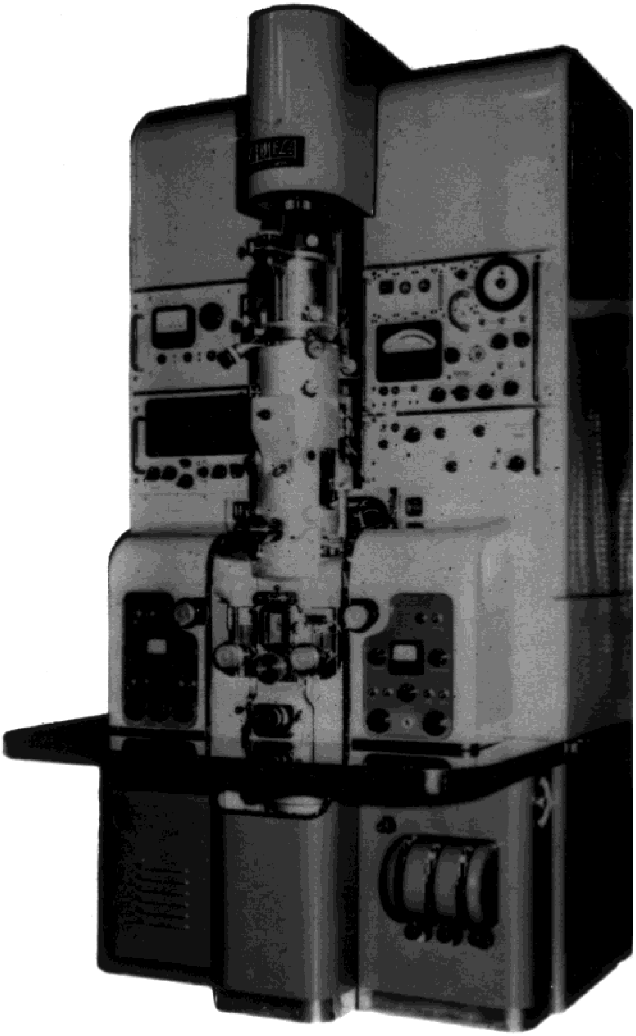

Figure 1. The first commercial electron probe, CAMECA MS 85.

(quartz and mica), and no computer. Light elements were beyond the reach of that existing technology. All controls, stage and spectrometers, were manual. Back then, a microprobe was run by tactile feedback and intuition. The maximum sample size was a quarter of an inch in diameter, and computing was performed with a slide rule. This instrument had excellent wavelength resolution and a good optical microscope. A hard workday could produce outstanding analysis on, at best, 10 points of interest.

From what has been just said, it might look as though the pioneers had a limited vision of the future application and development of the electron microprobe. But this was not the case at all. While preparing this article, I read a few older publications (Castaing, 1960) that were available in the late 1950s and early 1960s. I was surprised at the seemingly modern features and capabilities, many of which we are still discussing today. Light element analysis, quantitative energy dispersive spectrometer (EDS) analysis, X-ray mapping, analysis of insulated material, and field emission gun technologies were hot topics even then.

At this point, and because this symposium is dedicated to the father of electron probe microanalysis, I would like to share with you one of my early personal experiences with Raimond Castaing, that occurred in 1963. I was a green engineer at Cameca when Raimond Castaing received funding for a commercial microprobe of his own design. Like most young technical graduates, I was daring and naive and saw no reason to refuse the directive to install and pass the acceptance test of the microprobe purchased by Castaing. Even today, I am still wondering why this job was offered to me. Was it a test, someone at Cameca trying to get rid of me, or was it just a lack of volunteers? I will never truly know, but I am thankful today for the following experience.

In 1963, Castaing's laboratory was extremely active. This was when Georges Slodzian (Slodzian, 1964) was busy developing the secondary ion mass spectrometry (SIMS) technique and Lucien Henry (Castaing et al., 1967) was working on magnetic high-energy electron filtering known today as electron energy loss spectroscopy (EELS). Also present during this period were Jouffrey, Derian, Henoc, Bernheim, Blaise, Colliex, Hennequin, and El Hili. El Hili, who later ended up as the Dean of the University of Tunis, Tunisia, was in charge of setting up the probe in Castaing's laboratory. With his help, the probe was quickly installed and running and the usual tests passed successfully. But I was soon to learn with dismay of Castaing's high expectation for acceptance tests. These consisted of nothing less than running some of the same experiments published in his thesis, something I was not made aware of. It took us quite a while to set up and run those experiments. Often in the evening, Castaing returned to the laboratory. We could always hear him coming, his powerful voice, a unique voice with a friendly southern French accent, echoing in the corridors of the university. We knew, before he even reached the door, if he had had a successful day or if an experiment performed by one of his students had been flawed.

Raimond Castaing was a forceful and passionate person and his mood could turn from enthusiasm to despair in a second. Another trait of Castaing was that he had a constant fear of making mistakes. He was always cross-checking his own results or asking his students, "êtes vous sûr?" (Are you sure?)

At some point we came up to the task of measuring the

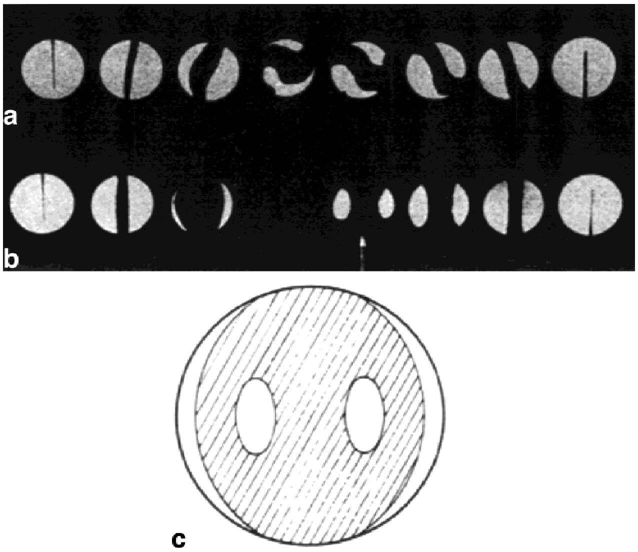

Figure 2. Experimental results (reprinted from Castaing, 1951, p 22, with permission). **a,b:** Shadows of the wire observed on a fluorescent screen placed in the lower part of the instrument, when varying the excitation of the probe forming lens. **c:** Computed image of the shadow when the Gaussian diameter of the probe nearly covers the wire.

spherical aberration of the final lens, that consisted of occluding the electron beam with a 1-µm diameter metallic wire. The difficulty was not the measurement or the computation but the fabrication of the small, perfect metallic wire.

Castaing assigned the task to El Hili, and I went back to Cameca to wait. One week passed, still no news. When I called El Hili, he explained that he was having difficulties with the fabrication of the wire. Two weeks, then 3 weeks passed and still no metallic wire. Finally after suggesting to El Hili that we should call Castaing, the wire was mounted in the probe and I was back in Orsay. I looked in the microscope eyepiece and I saw a straight line about 1-µm wide. I immediately carried out the experiment, took pictures, and later that afternoon we had them developed (Fig. 2). With our slide rule, we started to compute the spherical aberration. We expected an aberration of 3.6 cm and, at the first measurement attempt, we found something over 1 m! We spent the rest of the day recomputing without much success. The next day we took more pictures and we computed the spherical aberration in the afternoon. The computed values were reproducible but wrong. After a few more days of unsuccessful attempts, I decided to talk to Castaing against everybody's advice, the most vocal being El Hili himself. Our appointment was fixed at the instrument for 5:30 p.m. At 5:00 p.m., everybody in the laboratory who had no reason to hang around had left. Castaing arrived, concerned that we could not duplicate an experiment he himself had performed successfully over 10 years earlier. He looked at the pictures and under his swift direction I ran the calculation several times on a now "smoking" slide rule with the same deceptive result. Finally, Castaing moved to the instrument and peered into the eyepiece. Within a few seconds the lab was filled with a loud roar. Castaing's expertise and careful eye had immediately realized what I had not seen. El Hili could not build a small wire and had easily fooled me with a huge rod of 20-µm diameter. What I thought was the wire was in fact the reflection of the light on the top of a relatively large cylinder! Needless to say, the lecture I received that evening was a tough one to bear, but the positive side was that if you listened well and learned from your mistakes, you were accepted into his innermost circle for life.

From Early Models to Present Microprobes

In the early 1960s, the number and variety of electron probes increased rapidly to reach the incredible number of 12 companies, all offering a microprobe of more or less conventional design. The less conventional was the Elion probe with a so-call beam compression or afocal electron optics. Early microprobes were developed after WWII, in a world driven by metallurgy. These early EPMAs usually had few wavelength dispersive spectrometers (WDS) at low take-off angles (Fig. 3). Why is this? It was mostly for practical and economical reasons, especially for the laboratories, which were converting an electron microscope column into a microprobe. It was also easier to combine a large numerical aperture optical microscope, a magnetic lens, and WDS. But a low take-off angle is less tolerant to a small change in the sample orientation. It was shown that at a low take off-angle, a variation in the specimen surface of 1° could change the relative intensity by 10% compared, in most cases to 1% when the take off-angle was above 30°. In addition, the need for light element analysis and the fast growing use of EPMA in the geological field, where more WDS were needed, sent the manufacturers back to the drawing board.

The design of modem microprobes was then a compromise between light optics, electron optics, and higher take-off angle WDS (Fig. 4). There were three possible de-

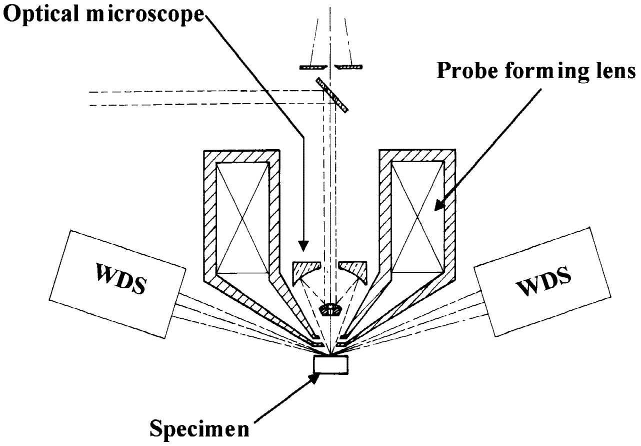

Figure 3. Early electron probe microanalyzer (EPMA) cross-section: final lens arrangement of an early EPMA model. WDS, wavelength dispersive spectrometers.

signs of X-ray path geometry: X-rays through the final lens, X-rays through the pole piece, and X-rays outside the final lens, hence three major suppliers arose based on those concepts. (The three EPMA manufacturers were: ARL, CAMECA, and JEOL.)

FUTURE EPMA IMPROVEMENTS

I would suspect, as the past has shown, that two engines will drive future improvements in EPMA. These engines are the need to explore new research fields, and the eternal human quest for "ease of use." For both, the technology is certainly within present reach. With regards to new research fields, it is interesting to note that in the last 50 years, we have primarily followed the path opened by Raimond Castaing, namely, to develop the quantitative capability of the technique. This has been perfected to a level that is unique in the entire instrument business. However, X-rays excited by electrons carry a lot more information than just elemental concentration in a few cubic microns. In addition, it is a nondestructive technique—that is a very important feature.

I think that the EPMA of the future will boldly traverse research fields that are barely being explored at present. These include: small volume analysis, nondestructive quantitative multilayered structure analysis, patterned material analysis, geochronology, and chemical bonding analysis. New applications mean new required specifications. Let us explore how these new applications will be translated in future EPMA hardware and software development.

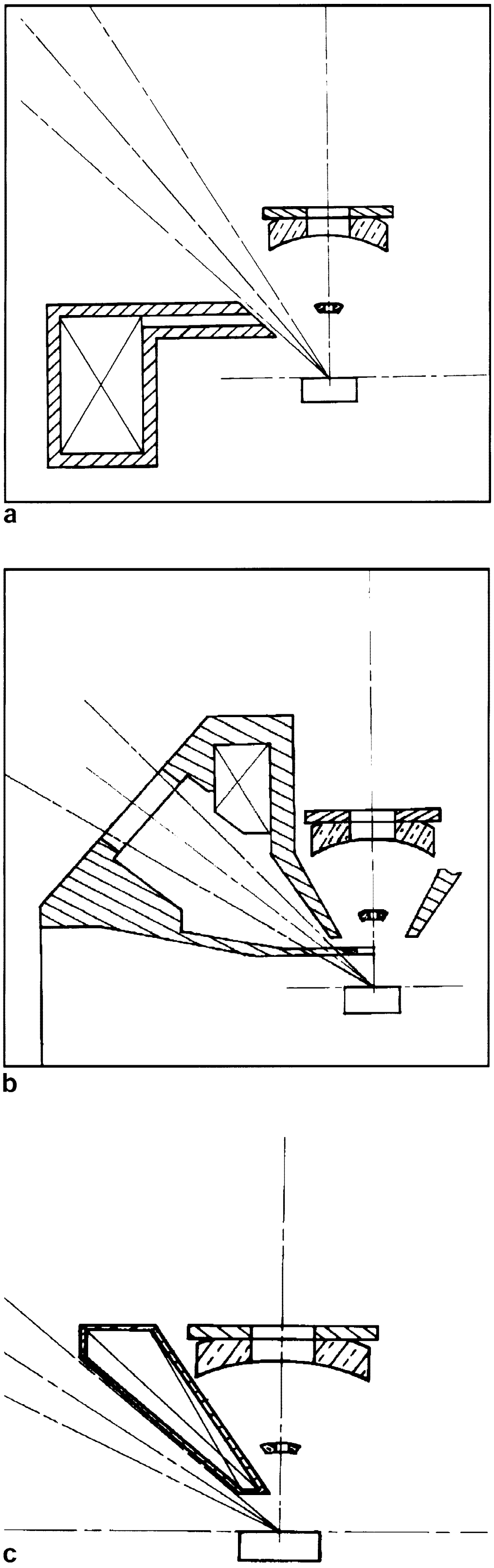

Figure 4. Modern X-ray path geometries: cross-section of three probe forming lenses (PFL), optical microscope, and WDS arrangements. **a:** X-ray path through the PFL; **b:** X-ray path through the pole pieces; **c:** X-ray path outside the PFL.

SMALL VOLUME ANALYSIS

It is common nowadays to analyze features of 2 to 3 μm^3 in volume on bulk samples. Although the EPMA will never compete with the scanning auger microprobe (SAM) or the transmission electron microscope (TEM) with EELS or EDS, or beat the tomographic atom probe for the smallest analyzed volume, one can expect to quantitatively analyze submicron volumes in a better and easier way with EPMA than with the other techniques just mentioned.

Small volume analysis requires working at low voltage and using soft X-ray lines. Success in this area will depend upon improved physical parameters (e.g., mass absorption coefficient) for the transition metal *L* lines. This is not trivial. The low voltage work can be successful, but it is not yet robust. It is worth mentioning that when this capability is finally attained, high spectral resolution spectrometers will be mandatory in order to differentiate between the *L* and *M* lines unambiguously.

In the meantime, however, hardware component performances required for small volume analysis are progressing steadily. New crystal technologies are under development and new ways to profit from Bragg's Law are still being conceived. I also foresee more progress in crystal sensitivity.

High beam brightness at low voltages is already possible with LaB_6 and field emission (FE) guns. Beam tracking systems, which keep the focused beam stable with great accuracy, on tiny particles, typically within 0.1 μm, are becoming available, and this is probably the next important progress toward small volume analysis.

ANALYSIS OF MULTILAYERED STRUCTURES

Analysis of multilayered structures a long time ago was considered a novelty concept; it is now a well-entrenched application. Pushing the "depth resolution" of the technique to its limits, people are now addressing the characterization of surface and interface concentration gradients buried below the surface of the sample. However, the quantitative interpretation of the X-ray intensities requires appropriate models for describing the electron–matter interaction in the low energy region and at low overvoltages. Conventional models do not work well under those circumstances. Thus, a new model, called IntriX, was developed by P. Staub (Staub, 1995) for his thesis. Incidentally, Castaing was a member of Pierre Staub's examination board.

PATTERNED MATERIAL ANALYSIS

More and more devices such as sensors, integrated circuits, and medical implants are being patterned in some fashion at a micro-scale level to achieve their desired characteristics. This means that excitation volumes may include more than one material, not only in the Z-axis but in X and Y as well.

One of the easiest examples is the case of porous materials where the second phase is simply *not* present (i.e., void space). Current microprobe methods do not account for changes in the back-scattered coefficient of porous materials. A new software approach based on Monte Carlo modeling and experimental data may some day allow us to explore more of these types of complex geometries and phases.

GEOCHRONOLOGY

The high sensitivity and extreme stability of modern WDS instruments have allowed a new and unexpected EPMA application in the geosciences: direct age dating of monazite and other minerals (Montel et al., 1994; Williams et al., 1999). The method involves direct measurement of U, Th, and Pb concentrations in the target mineral grain. It is assumed that the initial isotopic ratios for these elements were typical for the earth's crust, so the EPMA-measured chemical concentrations may serve as a proxy for the actual isotopic abundances. Radiometric ages are then calculated in the conventional manner using these proxy isotopic data, and are subject to the usual considerations such as closure of the mineral system and the accumulation of measurable daughter Pb.

Dating of monazite has been very successful, with an accuracy near that of conventional isotopic techniques. The EPMA method has advantages in that the technique is nondestructive, has high spatial resolution, and may be applied to mineral grains in situ with normal sample preparation.

CHEMICAL BONDING ANALYSIS

The natural ability of WDS to provide good spectral resolution, with typically ($\Delta\lambda/\lambda$) better than 10^{-2}, is not only beneficial to avoid peak overlaps, it can also be used to distinguish between several chemical states of the same element. Hence, localized chemical bonding analysis can be performed. Although it has been around for some time, localized chemical bonding analysis with an EPMA has not been used much until now.

Because it is a nondestructive technique, which allows one to analyze buried features such as metal/oxide interfaces, metal/polymer interfaces, and interfaces in semiconductors, EPMA could help solve problems found in modern microelectronic devices. These applications will probably require higher spectral resolution spectrometers. It will also require the development of tables showing the value of the shift associated with various chemical bonding types, for each element, as they already exist for the infrared wavelength range.

Earlier in this article, we have seen that in the old days EPMA users played with just plain hardware. After 50 years of progress in automation, who can appreciate these days the feeling of setting a spectrometer on a peak with thick metal knobs? Computer sophistication makes the virtual microprobe a possibility and *C*omputer *A*ided *M*icro *E*lectron probe *Q*uantitative *A*nalysis a reality.

VIRTUAL MICROPROBE

Nowadays, an EPMA is primarily a keyboard. The trend is obviously for the analyst to be distanced from the hardware, thanks to the software. It is not hard to predict that the next step will be to forget both hardware and software, and to fully focus on the application. The EPMA as we know it today will be somewhere in the background, out of sight, maybe even on the Internet, maybe a little more compact with more advanced specifications and new spectrometers such as microcalorimeters. But except for loading of the sample, the analyst will ignore its presence.

Looking into my crystal ball, I see the analyst seated with a 3-D helmet and touch-sensitive gloves. An enlarged image of the sample is displayed in front of him or her. He or she selects a point or an area to analyze with a virtual pen and so on (Fig. 5).

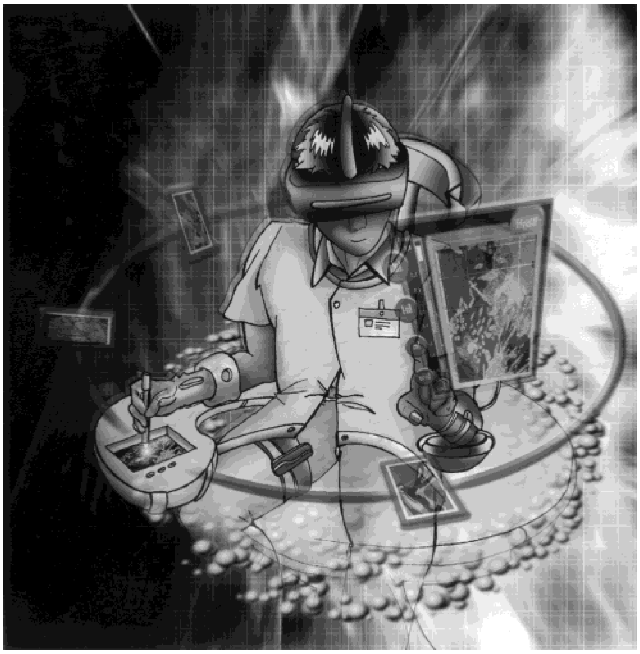

Figure 5. The virtual microprobe.

COMPUTER AIDED ELECTRON PROBE QUANTITATIVE MICROANALYSIS

Analysis with an EPMA requires the analyst to master a considerable amount of knowledge and to deal with numerous parameters for the optimum set-up of the instrument. Computer Assisted Systems are being designed (Fournier, 2000) to help EPMA analysts define the optimal analytical strategy. The result is faster analysis, better accuracy, and ease of use for novice users as well as for experts. Each analytical parameter (peak position, intensity, high vacuum (HV), current, crystals, standards, etc.) is modeled by specific algorithms. The Computer Assisted Analysis Program selects the parameters by minimizing, at every stage, the statistical error predicted by the algorithm. The accuracy of the results is guaranteed by the statistical error calculation continuously carried out while the program is running. New Computer Assisted Analysis programs are coming fast. One was actually presented at this meeting in Portland at the poster session (Fournier et al., 1999).

CASTAING'S LEGACY

Raimond Castaing's interest in microanalysis was not limited to EPMA. In the early 1960s, students at Orsay were investigating, under Castaing's strong direction, many different ways of enhancing image contrast and conducting microanalysis in solid materials. The most notable projects in addition to the electron microprobe were the energy

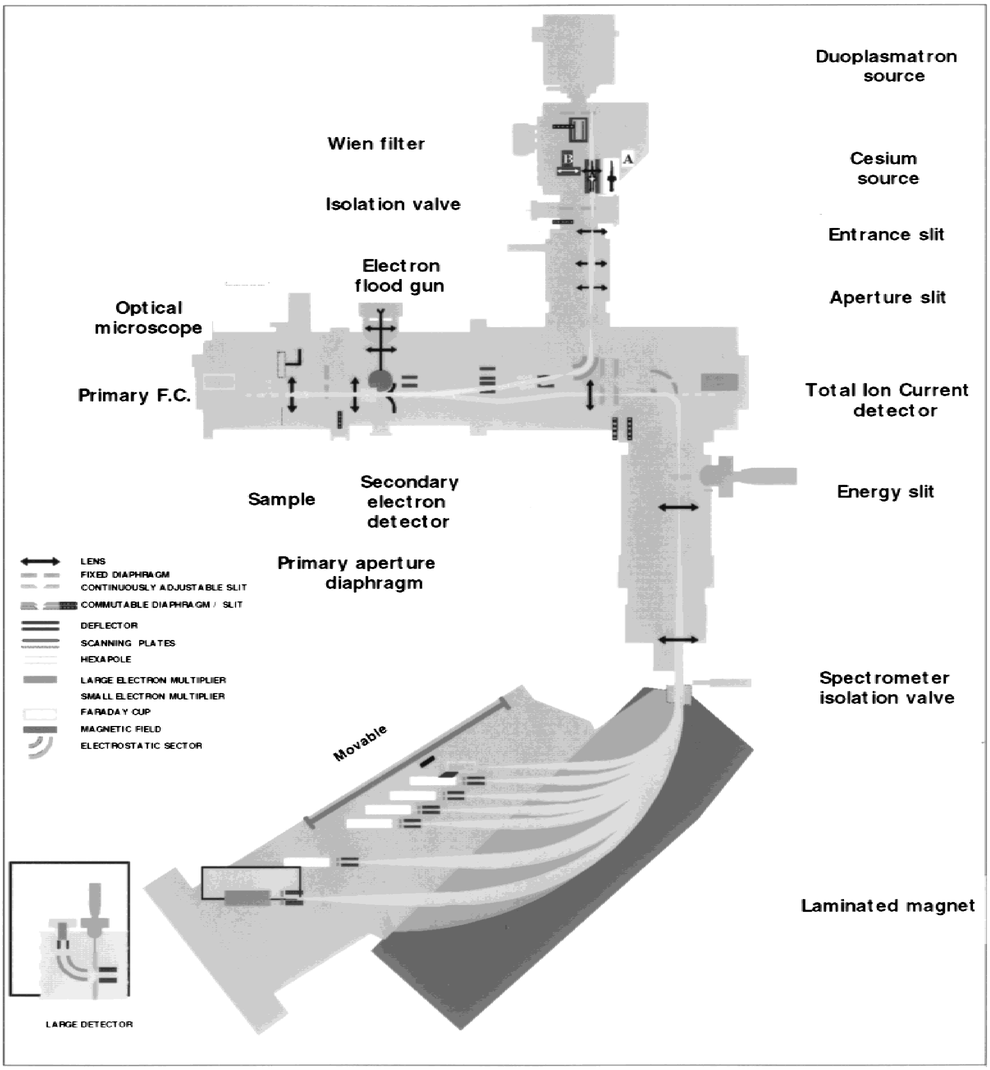

Figure 6. The NANOSIMS 50: a new ion optic design.

filtering technique by Lucien Henry, now offered by all TEM manufacturers, and the SIMS technique developed by Georges Slodzian. It is worth noting that the legacy of Raimond Castaing includes three modern techniques: EPMA, SIMS, and EELS.

I will close my article by discussing tomorrow's magnetic SIMS instrument, as it was under Raimond Castaing's direction that Prof. G. Slodzian so successfully developed this technique. The contribution of magnetic SIMS sectors instruments has been essential in planetary sciences and geochemistry. In the semiconductor industry in both research and development (R&D) and Fab-lines, it has been the tool of choice to monitor the in-depth distribution of dopants and to monitor contaminants at trace levels. Most of the computer chips we are using today, for instance to replace our slide rules, have achieved their level of performance and reliability thanks partially to the SIMS. Recently, Prof. G. Slodzian (Hillion et al., 1993) conceived and designed a new high mass resolution submicron ion probe (Fig. 6).

This NANOSIMS 50 features both a very short working distance (WD) and a multicollection mass spectrometer. The small WD is obtained thanks to the colinear design of the primary and secondary ion optics. A short WD provides both low lens aperture aberration and high signal collection resulting in the capability to analyze submicron volumes easily, typically in the 100-nm range with high sensitivity. A parallel multicollection mass spectrometer ensures perfect image superimposition of up to five masses and allows measurement of isotopic ratio, from the same small volume.

This new tool has already provided extremely valuable data in material research, in biology, and in planetary sciences. We can certainly say, in summary, that Raimond Castaing's contribution to his era went far beyond just

Figure 7. Raimond Castaing, a revolutionary figure.

physics and instrumentation. Thanks to the tools he developed or initiated, we can now better grasp and understand our world. He was a truly revolutionary figure (Fig. 7).

ACKNOWLEDGMENTS

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