Chapter 1

A History of Cameca (1954–2009)

Emmanuel de Chambost

Contents

49, rue des Cendrières, 91470, Limours, France, http://siteedc.edechambost.net/Histoire_de_Cameca/History_of_Cameca.html

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1. GENEALOGY OF CAMECA

1.1. Scope of Electron and Ion Optics from the Origin to 1945

1.1.1. The Early Electron Microscope

It is well known that research on electron microscopes began at the Berlin Technische Hochschule at the turn of the 1930s. As he was finalizing his thesis on cathode ray tubes (1924–1926), Denis Gabor became interested in electron beam focusing. Then, Hans Bush investigated more thoroughly the working of what would be called *magnetic lenses.* Introducing the concept of lens in the field of electron physics opened the road toward electron microscopy. This was the road taken by Ruska, under the supervision of Max Knoll (Ruska, 1980, p. 13).

Ruska wrote that he failed to relate his own research to Louis de Broglie's theory until attending a conference in 1932 (Ruska, 1980, p. 29). As he discussed this issue with Knoll, the possibility that an electron wavelength could limit microscope resolution troubled him. It is only

after he computed the Abbe formula with a 70-kV electron wavelength that he concluded he could obtain a resolution fairly better than the light microscope.

In 1932, Ruska obtained a grid image resolution as good as that with light microscopes and left the Technische Hochschule for another job. Colleagues improved the intrument according to the recommendations of Ruska and finally, Friedrich Krause demonstrated a resolution of 130 nm for real biological images only in 1937. Ruska was then involved in the development of the electron microscope manufactured by Siemens & Halske, which was marketed in 1939.

In North America, James Hillier and Albert Prebus at the University of Toronto completed a prototype of an electron microscope with resolution that was also better than that of light microscopes. Later, Hillier joined RCA to develop an electron microscope that would also be marketed.

In all three cases, the instruments were transmission electron microscopes (TEMs). Scanning electron microscopes (SEMs) were first investigated in 1938 in Berlin by Manfred Von Ardenne, but several projects were abandonned since the obtained resolution was not as good as with the TEM. SEMs were eventually produced in great numbers in the 1960s only after a secondary electron detector was proposed by Everhart and Thornley at Cambridge.

1.1.2. Early Mass Spectrometry

Before any e-beam devices or instrument developments were available, Joseph J. Thomson and other scientists had pointed to evidence of electrons at the turn of 1900. Thomson had also highlighted ions in tubes under vacuum; by applying a magnetic field onto moving ions, he succeeded in characterizing the m/e ratio. In 1912, he demonstrated that elements such as helium or neon could have several isotopes.

Mass spectrometry was therefore born, and it appeared that an applied magnetic field was insufficient for precisely measuring m/e as soon as the ion energy spread to some extent. Different methods of compensation involving an electric field were proposed by Thomson and then by Francis W. Aston, who had helped Thomson design his instrument at the Cavendish Laboratory and who won the Nobel Prize in Chemistry in 1922 for identifying 212 isotopes of the 267 so-called stable isotopes—or in other words, existing at the natural state.

In the United States, the University of Chicago became a holy place of mass spectrometry. Arthur J. Dempster took advantage of the magnetic field boundary effects to focus on an ion beam homogeneous in mass. Some years later, at the Vienna University, Joseph H. E. Mattauch and R. F. K. Herzog combined Aston energy focusing and Dempster aperture focusing to design, in 1932, a "double-focusing" mass spectrometer (Mattauch and Herzog, 1934).

During the same period, Herzog understood that the magnet boundary tilting angle with respect to the beam axis has a balance effect on focusing effects in both the transverse and radial planes and that a "magic" angle exists—close to 27°—that would allow giving a magnet the same properties as a stigmatic lens.

From the end of the 1930s to the beginning of the 1950s at the University of Minnesota, O. C. Nier and some of his students improved the technique of mass spectrometry, the services of which would later be called upon for the Manhattan Project. In 1953, they published a sketch of a double-focusing spectrometer slightly different from that of Mattauch and Herzog.

1.2. What Happened in France?

1.2.1. French Science in the Interwar Period

Until the beginning of the Second World War, apparently there was no instrumental project for electron microscopy or mass spectrometry in the framework of any French university, research institute, or private company research lab. Generally speaking, the first half of the twentieth century was a period of decline for French science, particularly physics, and this decline was aggravated by WWII and the Occupation. Four French physicists won the Nobel Prize between 1900 and 1929, which is not many, but French physicists were entirely absent as winners between 1930 and 1965.

Independent of this issue of the decline of French science over a given period, the science historian Dominique Pestre has highlighted some of its distinctive features during the interwar period and until the end of the 1940s:

French science is the kingdom of a small group of members of University whose symbolic status is high and who are often considered as "intellectuals" whose mission is the scientific truth but also the progress of social justice. They are living in a world apart from the one of engineers and businessmen. The academic physicist etablishment is dominated by the so-called "Normaliens", i.e. alumni of the École Normale Supérieure de la rue d'Ulm (ENS-Ulm), the most highly regarded course of study within the French academic world, typical of academic elitism. In the industrial field, the French system of innovation is based on a continuous process of adaptation rather than integration of scientific knowledge and in electrical industry where knowledge is completely new, the strategy of French firms generally consists of purchasing patents and licences in order to have them adapted by engineers (Pestre, 1996).

So far it can be considered that the French scientific decline was curbed, the beginning of this revival arises probably during the thirties with a dramatic increase of the public funding of research (Pestre, 1980).

1.2.2. The Compagnie Générale de la Télégraphie Sans Fil (CSF)

According to Dominique Pestre again, only two French companies can be considered exceptions since they developed basic research laboratories. One of these two companies was the Compagnie Générale de la Télégraphie Sans Fil (CSF), whose workforce was slightly larger than 4,000 in 1939. "Sans fil" means "wireless." SFR (Société Française de Radiotéléphonie), the predecessor of CSF, was founded in 1910 to provide French administrations (namely, the army) with systems and devices for radio communications. After World War I, CSF was created to deal with the civilian radio broadcasting market. It should be noted that this company was small compared with other similar foreign companies, such as Telefunken in Germany, Marconi in the United Kingdom, RCA in the United States, or Philips in the Netherlands.

In 1929, the chairman and founder of CSF, Émile Girardeau, entrusted to a young 27-year-old physicist, Maurice Ponte, the leadership of both the department of vacuum tubes originating from SFR and a new research lab, the Laboratoire de recherches generals. Pointe was given carte blanche to appoint young physicists specializing in electronics and electromagnetic radiation. As a matter of fact, Ponte was an alumnus of the École normale Supéririeure (ENS)-Ulm. According to Pestre (1990), at the end of the 1940s, some fifteen men controlled appointments to the main academic chairs and the primary positions in big research labs in the field of physics. Among them, half a dozen controlled electronic and solid-state physics. Three were alumni of both ENS-Ulm and CSF laboratoire général: Maurice Ponte, Yves Rocard, and Pierre Grivet.

Yves Rocard, one of the fathers of the French atomic bomb, joined CSF during the same period as Ponte. Grivet was appointed by Ponte during WWII to the research lab of Levallois-Perret, the historical plant of CSF, in the Paris area. He was involved in a project of a 60-kV oscilloscope required for studies related to television (Grivet, 1985). This project led Grivet to develop some skills in electron optics and to get an order for an electrostatic electron microscope to meet the needs of different French administrations (Brenot, 1945). I am quite aware that it may seem surprising that in this period, during German occupation, a rather small company would have enough resources to initiate such a project. The history of CSF during German occupation is a very complicated issue, all the elements of which are not yet perfectly clear.

1.2.3. Radio-Cinéma

Before it was called *Cameca,* the company based at 103 boulevard Saint-Denis at Courbevoie, some kilometers from the center of Paris, was named *Radio-Cinéma.* It was not involved in scientific instrumentation but both

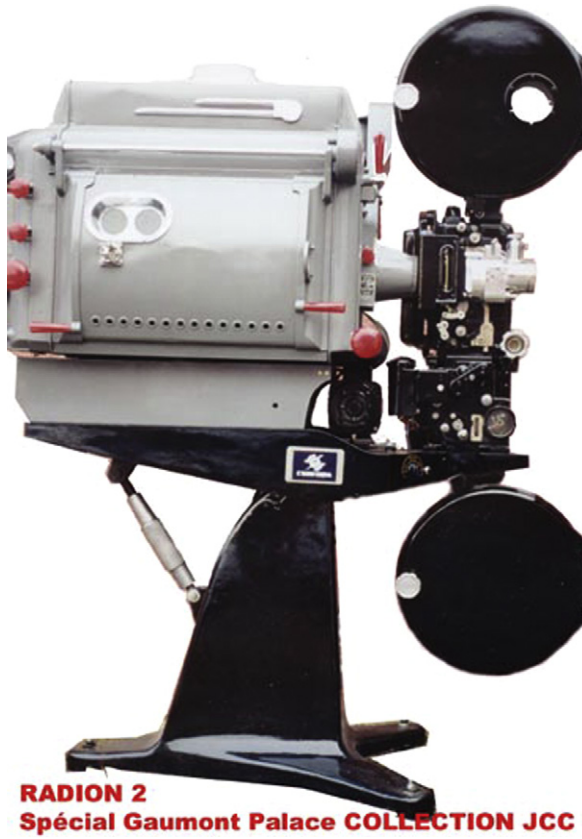


FIGURE 1 The Radion 2 film projector of Radio-Cinéma.

hardware for big cinema screening rooms (Figure 1) and 16-mm projector for more modest rooms such as parish halls.

Since its inception (June 21, 1929), Radio-Cinéma was a subsidiary of CSF. Of note, the year 1929 coincides with the beginning of the talkies. The name *Radio-Cinéma* is composed of "Radio," which is the prefix for all subsidiaries of CSF at that time, and "Cinéma," which is the specific trade of this subsidiary. At its very beginning, Radio-Cinéma's job consisted of installing sound systems in cinemas. Frédéric Mathieu, who was still technical director of Cameca in 1960, was reported to have been at the origin of the talkies in France. The head office of Radio-Cinéma was at the same address as CSF's head office—boulevard Haussman in Paris—while the first workshop was located in the 20th arrondissement, 17–19 villa Faucheur. After the Second World War, it moved to Courbevoie (see Figure 10), close to Levallois, an area where CSF has several factories.

In the early 1950s, Radio-Cinéma took over the company of André Charlin, a gifted sound engineer with recognized experience in the talkies, loudspeakers, and stereophony (de Chambost, 2009, p. 44).

1.3. The Castaing Thesis (1947–1951)

At the end of the 1940s in France, the revival of physics occurred mainly in recently created research organizations such as CEA, an agency devoted to nuclear science, or Centre National d'Etudes de Te'lecommunication (CNET), devoted to telecommunications. These organizations were not controlled by the university but directly by the government. Their creations were approved by all political sides, which had some strength after the Liberation of France, including the Gaullists and the Communists (Pestre, 1996). Raimond Castaing's thesis work took place in one of these agencies, Office national d'études et de recherches aérospatiales (Onera), devoted to aerospace.

1.3.1. The Discovery of X-Rays and the Early Development of X-Ray Spectroscopy

Very shortly after their discovery by Wilhelm Röntgen at the end of the nineteenth century, X-rays were used in the medical field. Since their wavelength is of the same order of magnitude as the interatomic distance, they were then integrated into early atomic physics but their main application field was crystallography, a science of interest for metallurgy people who are not very concerned by modern physics. Max von Laue, who was awarded the Nobel Prize in Physics in 1914 for his work on X-ray diffraction, continued his research about interactions between X-rays and crystals at the University of Berlin after 1919; this was the same topic that Lawrence Bragg and his father pursued at Cambridge and Henry Moseley pursued at Oxford. Both the son (Lawrence) and the father (Sir William Henry Bragg) were awarded the Nobel Prize in Physics in 1915.

In 1913, good use was made of the Bragg diffraction to measure the wavelength spectrum of X-rays emitted by different samples impinged by an electron beam. The so-called Moseley law, which stems empirically from the father's observations, states the frequency ν of the characteristic X-ray's spectrum peak depends on the atomic number Z of the measured sample atoms. The square root of the frequency is proportional to the atomic number increased by a constant.

$$\sqrt{\nu} = k_1 \cdot (Z + k_2)$$

Moseley died during WWI. Before his work, "atomic number" was merely an element's place in the periodic table and was not associated with any measureable physical quantity. The so-called Bragg's law (Figure 2),

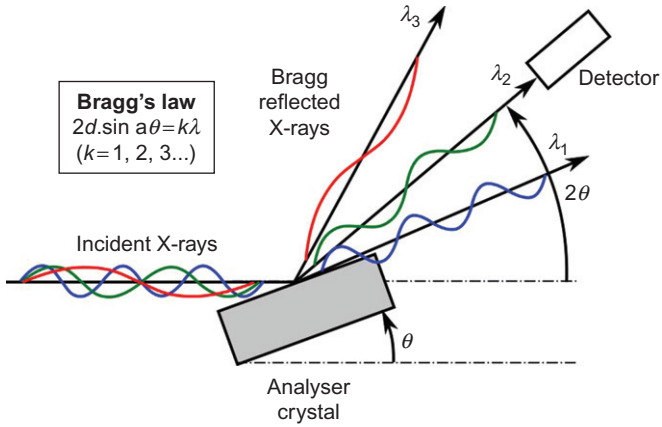


FIGURE 2 Bragg's law sketch: Bragg reflected X-rays are those verifying the Bragg relationship where *d* is the interatomic distance.

established in 1915, states that X-rays of wavelength λ hitting a crystal are reflected providing the angle θ between the incident ray and the scattering plane verifies the condition:

$$2d \sin\theta = k\lambda$$

where k is an integer ($k = 1$ or 2 or 3) further giving the "order" of the reflection, and d is the spacing between the planes in the atomic lattice. As is well known, it can easily be demonstrated that this apparent reflection stems actualy from a diffraction phenomena.

After the work of von Laue, Bragg, and Moseley on X-ray emission and diffraction, other researchers attempted to focus X-rays in the same way light rays are focused by glass lenses or charged particle trajectories are focused by magnetic or electrostatic lenses. They found a solution by using curved crystals.

Curved crystals have been proposed for refocusing X-rays emerging from a point. The names of Johann (in 1931) and Johansson (in 1933) are associated with two types of slightly different geometries (Figure 3): Johansson geometry crystals are more difficult to make because they are curved with a $2R$ radius, as for Johann geometry, but they must then be cut because the inner radius is only R. The advantage of Johansson geometry is that it makes possible the use of large crystals (i.e., to capture X-rays with a large aperture angle and refocus them without too much aberration; see Heinrich, 1981).

1.3.2. Castaing Thesis Adventure

Raimond Castaing (Figure 4) was 26 years old when he joined ONERA in January 1947 with the position of research engineer to prepare a thesis

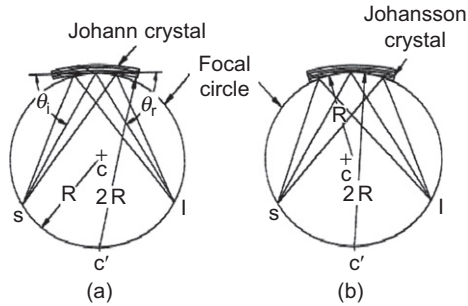


FIGURE 3 Curved crystals for X-ray spectrometers. In the case of Johann geometry (a), a crystal layer is curved with a 2R radius and in the case of Johansson geometry (b), it is also curved with the same 2R radius but also cut with an R radius. The "focal circle" is also called the "Rowland circle".

FIGURE 4 Raimond Castaing (1957).

under Professor Guinier. Castaing entered ENS-rue d'Ulm in 1940 and finally left the university to avoid the so-called STO (Service du Travail Obligatoire—the Compulsory Work Service) in Germany. He took up his studies again after the Liberation of France and passed the *agrégation,* a high-level civil service competitive examination for the recruitment of teachers (Castaing, 1975).

André Guinier, Castaing's professor, was born in Nancy in 1911. He was also an alumnus of ENS-rue d'Ulm and presented his thesis on crystallography in 1939. While studying crystalline defects, Guinier discovered (at the same time as George D. Preston) what would later be called *Guinier-Preston zones,* which are actually zones of concentration for one type of atom that make up an alloy (the first example was Al-Cu). These Guinier-Preston (G-P) zones are of great interest in metallurgy.

The ONERA is a government research institute devoted to aeronautical applications created by a law of May 3, 1946, under the Communist minister of the Air Minister Charles Tillon (Rossi, 1995). In 1947, ONERA had just been endowed with two electron microscopes. As Philibert (2001) wrote, it was a real luxury in 1948. Guinier used the first one, an RCA instrument, to investigate the G-P zones, which were known only by their diffractograms and which Guinier hoped to observe in the real space.

Castaing was therefore asked by Guinier to consider the possibility of bombarding an alloy specimen with electrons and detecting the X-ray's resulting signal. Castaing reported he replied that "It was very easy to do and it was surprising that no one had done it before" (Castaing, 1975). Castaing was actually partially right. Hillier had filed a patent in 1947 (Hillier, 1947) without attempting any project. In the U.S.S.R., it seems that Borowsky had the same idea as Guiner and Castaing. He produced an apparatus, RSACh-1, and claimed to have published it in 1951 (Borowsky, 1953, 1959; Borowsky et al., 1956).

The first problem to be solved was producing a fine electron probe. Castaing did not hesitate to tinker with the second electron microscope. It was actually a CSF, designed by Grivet, with electrostatic lenses (Figure 5). For dealing with lens aberrations, he learned the basics of electron optics in Zworykin publications, but he would have to learn by himself and solve all the practical problems more or less related to vacuum technology (Philibert, 2001).

At the beginning of 1949, Castaing obtained a few nanoamperes in an electron probe of 1 μm in diameter. Note that since 1939, there had been several projects of electron probe instruments and that five times finer probes had already been demonstrated.

Then, Guinier provided Castaing with a precious quartz crystal, especially cut and ground of the Johansson type. This Johansson crystal allowed him to build a spectrometer (Figure 6) that fit well on the outside of the main column. With this setup Castaing obtained his first X-ray data which were presented at Delft at the First European Conference on Electron Microscopy (Castaing & Guinier, 1950).

The setup consisting of the cannibalized CSF microscope and the Johansson spectrometer allowed Castaing to accumulate an impressive series of data so that he could submit his thesis in 1951 with the

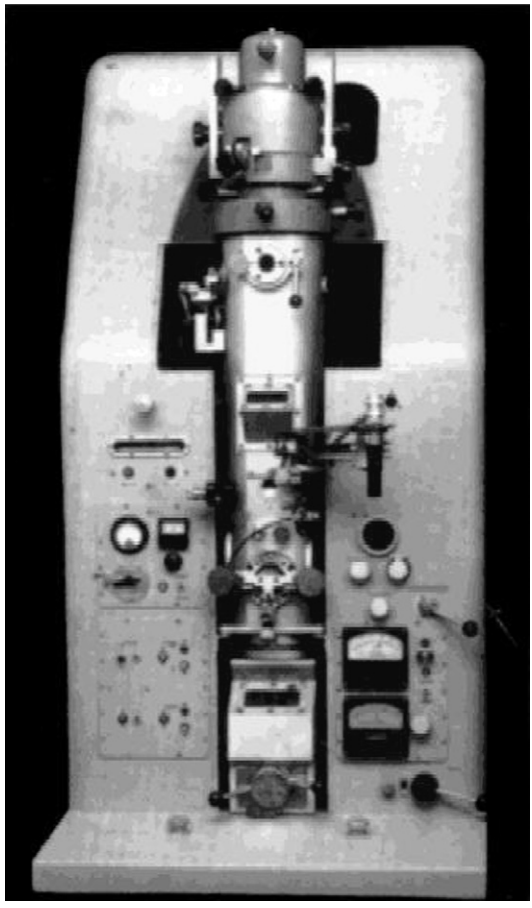


FIGURE 5 Castaing thesis CSF microscope.

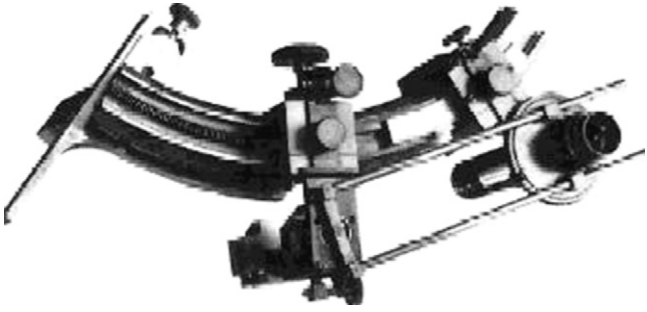


FIGURE 6 Thesis spectrometer equipped with the "Johansson"crystal.

title "Application des Sondes Électroniques à une Méthode d'Analyse Ponctuelle, Chimique et Cristallographique" ("Applications of the Electron Probes to a Localized, Chemical and Crystallographical Analysis Method"). This thesis covered both instrumental issues, such as lens aberrations and optimization of the electron probe, and more fundamental issues, such as X-ray emission modelization, correction calculations, some applications to metallurgy, and some Kossel diagrams (Castaing, 1951).

All the bases of what would be called EPMA are contained in the 1951 thesis, which was very rapidly translated into English by David Wittry. The modelization proposed by Castaing for the different physical processes involved in EPMA—namely, the electron penetration, the emission, and absorption of X-rays—have not aged after 60 years. The power of EPMA lies in the fact that it makes it possible to measure the concentration of a given element in a sample by simply calibrating the instrument with a bulk sample. A presentation of the implementation of the Castaing principles in the future EPMA instruments at Cameca is detailed further in the first appendix.

2. FROM RADIO-CINÉMA TO CAMECA (1954)

In 1954, CSF subsidiary Radio-Cinéma became C.A.M.E.C.A. (Compagnie des Applications Mécaniques et Électroniques au Cinéma et à l'Atomistique) (see Figure 7; the 1954 logo includes both names). While keeping to its core business, Cameca diversified toward precision engineering for aerospace radars and scientific instrumentation. Indeed, as early as 1947, the first project in this field, the Spectro-Lecteur, was initiated at the request of Pechiney, a French metallurgical company (Télonde, 1956). We owe to Maurice Ponte, director of CSF and a future member of the French Academy of Sciences, the entry of Cameca into scientific instrumentation.

2.1. The Spectro-Lecteur

In 1955, Cameca was organized into three departments: Cinema with both the Radio-Cinema and Charlin film projectors, mechanical production done on a contract basis with CSF business units, and last, scientific instrumentation. This last department was engaged in the Spectro-Lecteur (de Chambost, 2009, p. 49). A medium-sized building had recently been built on the spot where the two-tower bulding was later erected, with a view to hosting the production of electron microscopes based on studies directed by Pierre Grivet at CSF. However, the electrostatic microscope failed to be developed because it was found to suffer a definitive handicap with respect to the magnetic microscope.

FIGURE 7 The Cameca logo in 1954 still contained the old logo of Radio-Cinéma.

An article published in January 1954 by a German review documents the delivery of a Cameca Spectro-Lecteur before 1954 (Rosendahl and Kaiser, 1954). The photographic spectral method was frequently used for the analysis of alloys in the metallurgical industry. This method—still used in the twenty-first century—involves bringing forth a succession of sparks between two electrodes in metal collected for analysis. The radiation is dispersed by a prism into its spectral components. Before 1951, the spectrum was simply recorded on a photographic plate.

Cameca's "Spectro-Lecteur automatique" (Figure 8; "Lecteur" means "Reader") introduced new devices that allowed nearly automatic measurement. A pair of photomultipliers (PMs) was substituted on the photographic plate and the ratio of the intensity of rays received by the two PMs was recorded continuously.

In the Spectro-Lecteur, the optical spectrometer was provided by Jobin-Yvon, a French company specializing in optical spectrocopy, which was bought by Japanese Horiba early this century. The mechanical movement of this spectrometer was developed thanks to Cameca's expertise gained from the projection apparatus.

The Spectro-Lecteur was given a code name, SL15, which suggests that it could have been developed in 1951 (Mathieu, 1950). Its design was the work of Dr. Orsag at the Pechiney Research Lab in Chambéry, Savoie (Orsag, 1948). Cameca patented the PM amplifier (Radio Cinema, 1951) and 120 to 130 copies were delivered to foundries for "good/not good" manufacturing control. It took two to three weeks to achieve the installation.

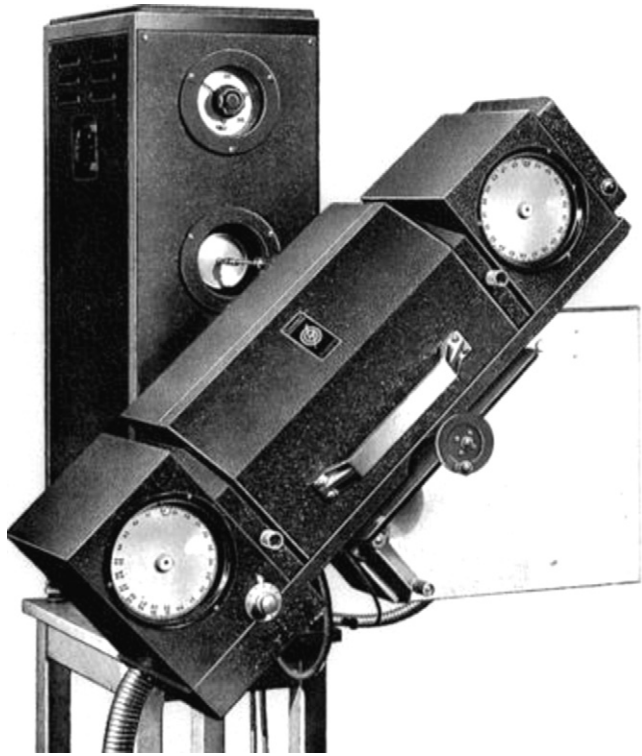


FIGURE 8 The Spectro-Lecteur (1954).

As it became involved in the Spectro-Lecteur, Cameca met for the first time with Applied Research Laboratories (ARL), which remained its most ferocious competitor until the late 1970s. The two companies shared the market almost equally. The difference between their products lay in the choice of measurement, which was either direct or integrated. The fact that, ultimately, a significant portion of the added value lay in the Jobin Yvon spectrometer, which also aimed at developing such products, penalized Cameca and led to its decision to exit this market (de Chambost, 2009, p. 47).

2.2. The Aftermath of the Castaing Thesis

During the years following Castaing's thesis, ONERA developed a scientific instrument based on the experimental setup that had been used in the thesis. Two identical prototypes were built (Figure 9a); the first one was delivered to ONERA's and the second one to Institut de Recherches de la Sidérurgie (IRSID), a French research institute for metallurgy, which was

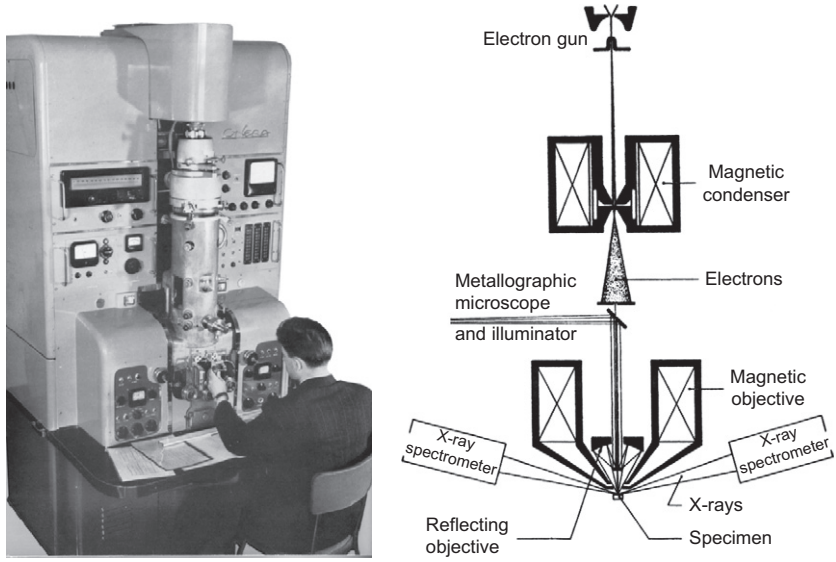


FIGURE 9 (a) The 1958 ONERA prototype operated by Castaing. (b) The MS85 schematics.

FIGURE 10 The Cameca plant in Courbevoie, as it is on the picture, with two towers, was built in 1956. The photograph dates from 1960.

convinced by Guinier to fund the project. Within IRSID, Jean Philibert, who had developed metallurgical applications under Charles Crussard, was in charge of this operation (Castaing, 1960). Different from the experimental setup of Castaing, which was electrostatic, the electron microscope was magnetic (Agar, 1996).

At the same time, the company built five CAMECA copies, which were available in 1958 and delivered, respectively, to International Nickel in Elizabeth, New Jersey; CEA-Saclay (French civil nuclear research center); CNET (French Telecommunication research Institute); CEA-DAM (French military nuclear center); and BRGM (French geological survey institute). Then, 24 other machines would be delivered by Cameca until 1964, when it was replaced by a new model. In 1960, the CNET machine was borrowed for exhibit in Moscow.

In addition to the two prototypes built by ONERA, 29 copies were produced by Cameca between 1958 and 1964. The plans developed by the department of mechanical engineering of ONERA are quite comprehensive and testify to a very high quality of execution. Unfortunately, the drawings of the electron gun originating from CSF were lost and had to be redrawn.

The most remarkable feature of the microprobe developed in the engineering department of ONERA is probably the light microscope with the Cassegrain mirror objective, crossed by the electron beam, allowing precise viewing of the area analyzed (Figure 9b). Designed by Castaing and Georges Nomarski, Institute of Optics, this very original provision was replicated by major competitors of Cameca, including ARL and JEOL as no patent had been filed.

2.3. MS85, the First Castaing Microprobe at Cameca

Maurice Ponte, general director of CSF at that time, was well connected with Guinier and they discussed the Castaing microprobe. Ponte introduced Castaing to Mathieu. The latter served as a director or technical director and had pioneered the development of projection of talkies in France (CSF, 1955).

In the mid-1950s, Jacqmin, CEO of Cameca and commercial director at CSF, appointed Jean Michel Rouberol, a graduate of École Centrale (an elite engineering school) to strengthen its engineering team. After successfully completing various tasks of minor importance, Rouberol was in charge of the developement of the MS85, which was actually a copy of two machines that Castaing had developed for ONERA and IRSID. In 2009, Rouberol remembered to personally bring the records of the MS85 from ONERA to Cameca (de Chambost, 2009, p. 48).

A little later, Rouberol was joined by Mathias Tong, who shared a similar background (he had studied in a Jesuit college in Shanghai) and became the project manager of the MS46 that replaced the MS85 in 1964.

Rouberol quickly became responsible for research and development (R&D) and, starting in 1964, was personally in charge of developing the ion analyzer. At that time, the head of mechanical engineering was Jacques Guernet who, in the sixties, filed several patents for the improvement of the Scopitone, which is mentioned a little later.

Although very different from each other, Rouberol and Tong formed a team that lasted from 1964 until 1988, when Rouberol left Cameca. During these 24 years, Rouberol seamlessly slipped into the role of a classic technical director of CSF and of Thomson-CSF, a Responsibility that Tong was unable to play because of the apparent confusion of his speech. This impairment, which hid a very imaginative spirit, was accepted by those who knew that he never made a mistake in his calculations.

The mechanics of the test batch of five instruments manufactured by Cameca was a true copy of the two prototypes designed by the mechanical engineering department of ONERA. The electronics were rather radically changed by Tong to improve performance and to take into account the evolution of components.

In 1960, Frédéric Mathieu, who never held the position of CEO, served as technical director of Cameca, and Jacqmin headed CSF's "Consumer Electronics" department, which controlled Cameca. From 1962 onward, Jacqmin was actively involved at Cameca. According to a legend, during the French debacle in 1940, Jacqmin (Figure 11), who was an employee, was noticed by the president of CSF as they all fled somewhere south of the Loire as he proposed to convert factories in the manufacture of bicycle carrier.

2.4. The Scopitone

In the late 1950s, Cameca was no longer involved in upscale movie projectors, but a 16-mm cinema projector (Figure 12a) was still manufactured until 1962. At this date, the final product more or less connected to the cinema was the scopitone.

The scopitone (Figure 12b) was a type of jukebox that featured a 16-mm film component. It was actually a forerunner of music video. Its inventor is not known. Presented to the press on March 28, 1960, and at the Paris fair in May, the STl6 model was based on a patent of the Italian Dessilani (Cameca, 1959; Dessilani, 1958) and the continuous motion was based on a previous Radio-Cinéma patent (Radio-Cinéma, 1934).

Two models were launched, the ST16 and ST36 (the 16 and 36 designated the number of movies that each scopitone model could handle). The scopitone activities were located in the basement of the factory in Courbevoie. It was a large machine shop, as most mechanical parts were made locally.

Since the scopitone offered huge benefits to Cameca, the CEO, René Jacqmin, searched for investment ideas in order to pay less tax. Rouberol,

FIGURE 11 The management team of Cameca in the United States in 1963, who negotiated with Bowmar for the scopitone and with Acton for the MS46. From left to right are Janichewski, the Bowmar chairman, Jacqmin, a Swiss businessman, and Mathieu, Rouberol.

(a) (b)

FIGURE 12 (a) 16-mm film projector (1960); (b) ST16 Scopitone (1960).

who had just seen at the Salon de la Physique a poster on the Centre National de la Recherche Scientifique (CNRS) "ion microscope," proposed investigating this matter. Castaing judged the ion microscope was

not sufficiently mature to be transferred to Cameca (de Chambost, 2009, pp. 51–52).

The scopitone was a movie viewer. In the sixties, Cameca developed another viewer that targeted U.S. supermarkets. This apparatus was named Came-Scope. It was intended to pass in a loop mode a movie singing the praises of the product exposed on the same stand.

Sales of the scopitone collapsed and the activity ceased in 1968. It could not compete with television and color CRT. Production of the Came-scope, which had never really started, was discontinued in 1968.

3. THE MS46, FIRST MICROPROBE DESIGNED AT CAMECA (1964)

3.1. The Pack of Castaing Microprobes

Castaing's thesis had a high profile. Many teams in the world were ready to embark on similar research. The American David B. Wittry, who translated the dissertation of Castaing, built a slightly different spectrometer within the framework of his own thesis. The American company ARL, which was seen above as competing with the Spectro-Lecteur and already was proposing instruments involving XRF, operated some Wittry patents to develop a machine competing with the Cameca MS85. The model EMX was marketed in 1960. A few years later, ARL eventually recovered the SIMS project that Liebl would develop on the East Coast, at GCA (Geophysics Corporation of America, Bedford, MA).

In the early sixties, 12 different models of Castaing microprobes were offered on the market, targeting primarly metallurgical applications (Conty, 2001). Soon, three actors shared most of the market: Cameca, ARL, and the Japanese company JEOL, which launched into the electron microscopy field in the immediate postwar period and marketed its first microprobe in 1960. This marked the beginning of a fierce competition with Cameca that lasted over 40 years, but in the early sixties, ARL remained the No. 1 enemy of Cameca.

3.2. The Competition with ARL (1960–1974)

Shortly after the marketing of the MS85, ARL released its own model, the EMX (Davidson et al., 1964). It was more efficient than the MS85, which was simply the industrialized Castaing prototype. The ARL instrument had four or six wavelength-dispersive spectrometers (WDS), while the MS85 only had two. The emergence angle of the EMX was 52.5°, while that of the MS85 was 18°. For years Cameca would fight with ARL about the angle of emergence, but Cameca reacted immediately to the EMX by releasing the more modern MS46, with four WDS instead of two but still an emergence angle of 18°.

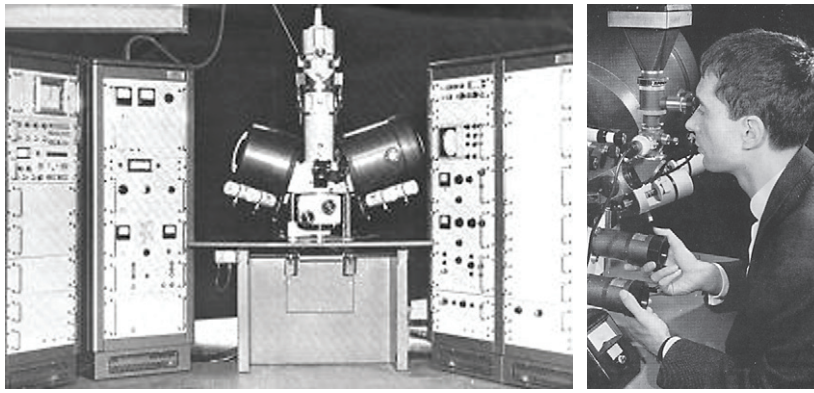
For years the angle war would continue for both overt and unacknowledged reasons. Cameca proclaimed that a too-low emergence angle limits the depth of analysis and reduces the uncertainties due to fluorescence caused by elements not belonging to the analyzed point and developed beneath the surface, and therefore not visible. Castaing developed such an argument that is true in the case of analysis of elements of medium atomic number—typical of the metallurgical applications at the time—but he did not say that the choice of emergence angle was a mechanical puzzle: Virtually, either X-rays pass under the pole piece, at less than 18°, or they go inside, at more than 52.5°. ARL's choice was risky with regard to the metallic samples but provided a more intense signal for analysis of lighter elements (typically, geological samples), which also posed a lower risk of errors due to fluorescence emission. As long as the market for steel industry and nuclear research was still developing, Cameca was evenly matched with ARL and even better if one includes the U.S.S.R. (de Chambost, 2009, p. 54). Behind the technical problems that could be solved lay a problem of industrial property: ARL had patented the solution to get the X-ray beam through the lens (Wittry, 1960).

During the same period, JEOL and Cambridge Instruments were developing SEMs. Before launching its first scanning microscope—the famous Stereoscan—in 1965, Cambridge Instruments released the Microscan, which had mediocre X-ray spectrometers but the capability of achieving images with a fast and automatic scanning mode. To counter Cambridge Instruments, Tong and Rouberol successfully adapted the MS85 with a moving mechanical stage propelled by speaker electromagnets that allowed fast motion without play by rastering the stage over a frame size of several hundreds of microns. This ensured achieving mechanical scanning X-ray images without defocusing spectrometers.

3.3. 1964: The MS46

In November 1960, Claude Conty, just graduated from the École des Arts et Métiers, had done an intership of six months at Cameca. He returned two years later after his military service in Algeria and was appointed to draft the electron probe MS46, which was planned to replace the MS85. This project had been overseen by Tong and Rouberol. Everybody at Cameca was convinced that a market actually existed in the United States for an electron microprobe, but in view of its competition with ARL, the MS85 was unsellable there, penalized by its design principles that prohibited, for instance, having more than two spectrometers or improving the vacuum quality. The design of the MS46 originated from this assessment (Figure 13).

The MS46 had four spectrometers. First, MS46 instruments were not automated, but some customers such as Claude Lechêne at Harvard had



(a) (b)

FIGURE 13 (a) The MS46 (1964); (b) Claude Conty operating the MS46.

achieved their own automation. In its 1964 version, no energy-dispersive spectrometer (EDS) accessory was included in the MS46 since the EDS was arising, coarsely, at the end of the 1960s. Some 220 MS46 models were eventually produced by Cameca between 1964 and 1974.

One of the findings of Cameca was the window of separation between the analysis chamber and the spectrometer, which allows the spectrometer to be under a primary vacuum (Rouberol & Guernet, 1963). As shown in Figure 14, the "linear" goniometer imagined by Rouberol Tong could easily include several vertical spectrometers, but since the X-photon counter was not on the Rowland circle, the window needed to remain broad.

In 1965, the production department was separated from the R&D department, on the occasion of the release of MS46. The so-called platform (i.e., the hall where the instruments are assembled and tested) was not yet located at its 2005 site but remained confined where there would later be both electronic testing and mechanical assembly. Philippon, a young engineer graduate of Supélec and assigned to the Scopitone, became responsible for the platform, but according to an official note written by Jacqmin, "Philippon continues to participate in studies conducted by Mr. Guernet and Mr. Rouberol." As a matter of fact, before the creation of the platform in 1965, the so-called Electronics Lab (i.e., R&D without the mechanical engineering department), was dealing with the development and installation of instruments and also secured the service of what was later called the Application Lab. This reorganization was roughly concomitant with the departure of Mathieu. Both Guernet and Rouberol reported directly to Jacqmin. In 1969, Rouberol assumed the title of "Directeur technique" (de Chambost, 2009, pp. 56–57).

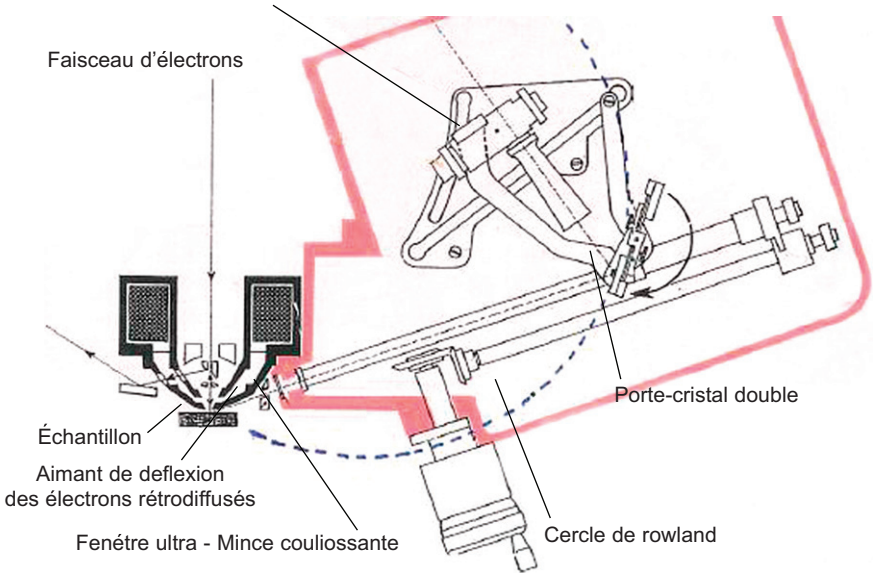


FIGURE 14 MS46 Spectrometer. (*Échantillon:* Sample. *Aimant de déflexion des electrons rétrodiffusés:* Backscattered electron deflection magnet. *Fenêtre ultra-mince coulissante:* Sliding ultra-thin window. *Porte-cristal double:* double crystal holder.)

At that time, Jacqmin was in the habit of saying that Cameca must rest on three legs: cinema, mechanics, and scientific instrumentation. In fact, with the departure of Mathieu and assigning Guernet and Philippon to instrumentation, there was really a switch from cinema to scientific instrumentation, despite the presence of artists such as French humorist Fernand Reynaud or singer Henri Salvador, who still attended the "plateau" (film set) in the basement to shoot for scopitone what was not yet called pop video. For Rouberol the MS85 project was a purgatory, as would be ten years later, the SMI 300. These projects consisted of copying instruments, the defects of which were already known. In contrast, the MS46, as would be the case ten or twelve years later of the IMS 3F, was an opportunity for talented engineers to give their best in solutions in which they believed.

The MS46 was so called because it was released in 1964, the same way that the MS85 was released in 1958. Immediately after the MS46 release, the sales manager Janichewski granted a license to manufacture and market the microprobe to Acton Laboratory, a U.S. company located near Boston in Massachusetts. In the United States, the probe was marketed under the name of MS64. Acton Laboratory manufactured and sold between 20 and 40 MS64s and then business faltered, mainly

because of competition from ARL. Acton Laboratory was acquired by a large company located in Los Angeles, CEC, a subsidiary of Böwe Bell & Howell. CEC, which was also granted the SMI 300, continued for some time to work with Cameca and finally threw in the towel in 1971. Then, Cameca decided to establish a subsidiary in the United States.

4. LAUNCHING THE SMI 300 (1968)

4.1. The Slodzian Thesis

In 1956, Castaing was a professor at the University of Toulouse and Georges Slodzian (see Figure 50) was one of his students of DES (a diploma that is passed before the thesis). Castaing gave him work on the secondary electron emission excited in metals by ion bombardment. Slodzian observed a positive current where a negative current was expected. Both the professor and the student searched for possible explanations and finally identified the origin of the current positive: It came from the ion-bombarded sample. This phenomenon was known in literature as *secondary ion emission* (Castaing, 1975; Slodzian, 2008)

Castaing seized the opportunity to make an ion microscope that could provide quantitative information on the elementary chemical composition, as well as its electron microprobe, but offering the possibility to directly produce a complete image, while the mapping of the sample could be obtained on the electron microprobe at the price of "one sweep," he thought long and tedious. Castaing was then appointed to the new University of Orsay and he offered Slodzian the opportunity to join him there for a doctoral thesis on this subject (Castaing, 1975; Slodzian, 2008).

Castaing asked two DES students to investigate specific aspects of the device: Hennequin for the magnetic sector and Jouffrey for the display device that was based on the principle of the "Möllenstedt converter." Slodzian designed the plans for the ion microscope, which was presented in the 1962 show of the French Physical Society, and defended his thesis in December 1963. By 1960 he had already acquired data with a relatively simple experimental setup (Figure 15) that nevertheless allowed beautiful images separated in mass (Castaing & Slodzian, 1962a). After his thesis, Slodzian had the opportunity to work in a laboratory at Stanford in the United States in what would later be called a "post doc" position (Slodzian, 2008).

Beginning in 1956, Duncumb and Cosslett worked to develop an imaging system by scanning the electron beam in a Castaing microprobe type (Cosslett & Duncumb, 1956). In 1962, in the *Journal of Microscopy*, Castaing described the limitations of the electron microprobe, denying

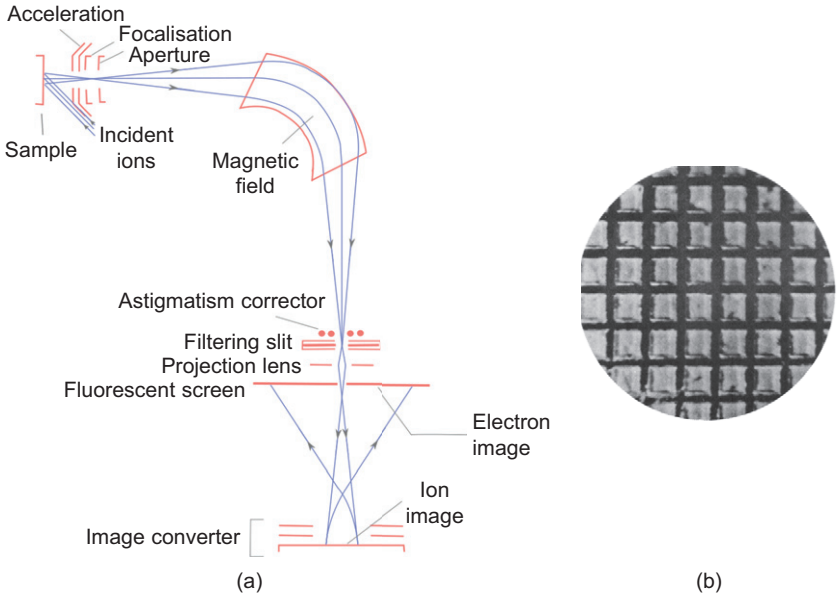


FIGURE 15 Sketch of the Castaing–Slodzian ion microscope (a) and image of a copper grid (in black) deposited on an aluminum substrate when the magnet is tuned on mass 27 achieved with the thesis setup (b). The grid step is of 25 μm. At the center of the image, there is a black hole, inherent in the ion imaging device and hidden by the grid bars.

the legitimacy of the competitor and boasting the benefits of the new ion analyzer:

> . . . However, applying this method to the lightest elements whose characteristic rays are highly absorbable, is quite difficult. Moreover, obtaining the distribution map of an element leads to a tedious operation, or requires the use of an electronic (ref to Duncumb) or mechanical (ref to Philibert) scanning device. We propose to describe here a method of microanalysis which seems to overcome these disadvantages. It is an entirely different principle, the basic phenomenon is the secondary ion emission. . . (Castaing & Slodzian, 1962b).

Thus, Castaing put the new analysis technique into perspective by comparing it with an electron microprobe and not with secondary ion mass Spectrometry (SIMS), which had existed since at least 1949.

The earliest history of SIMS can be traced to 1949 (Herzog & Vieböck, 1949). At that time, in Vienna, Austria, Professor R. F. K. Herzog, who had proposed the famous Mattauch–Herzog spectrometer a few years earlier, and his student, F. P. Vieböck, had constructed an instrument the principle of which consisted of primary ions that sprayed a sample. The atoms that were sprayed were further accelerated into a mass spectrometer.

Following Herzog and Vieböck, research on secondary ion emission was conducted in various places and even in France, in Lyon, by the team of Bernard Davoine, who had worked with Leauté at the "école Polytechnique" (Hawkes, 2004). Castaing was then professor of mechanics and thermodynamic physics at the University of Toulouse. He was unaware of this work.

As explained previously, Cameca had earned nice profits from the scopitone, and Jacqmin decided to invest this money in a new project. The ion analyzer was quite timely.

4.2. The Castaing Ion Microscope (1965)

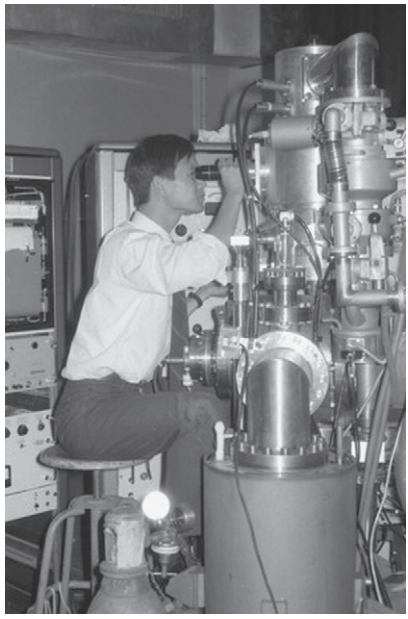
It was clear that the experimental setup of Slodzian lacked energy focusing—that is to say, a compensation of the magnet energy dispersion absolutely required for SIMS—because the secondary ions may have a wide energy spread. From the market of cinema projectors and especially from the scopitone, Cameca was naturally very sensitive to the issue of industrial property, and specifically, as discussed later, two patents filed by Liebl and Herzog and owned by GCA were a serious obstacle.

To circumvent these patents, Cameca asked Castaing for an alternative. While Slodzian did his thesis on the ion analyzer, another of Castaing's students had done another thesis on an energy filter for electron microscopy. This device could be adapted to the ion microscope, where it could solve both the issue of mass separation and compensation of energy dispersion. This seemed very clever.

The contracts between the CNRS and Cameca were completed promptly. As a result, a Castaing and Slodzian patent was filed by on November 28, 1962, jointly by the CNRS and CSF, claiming "a device for microanalysis by bombardment of primary positive ions…and a system of electron optics with a mirror…eliminating electrostatic too fast ions, and reflecting the other ions" (Castaing & Slodzian, 1962c).

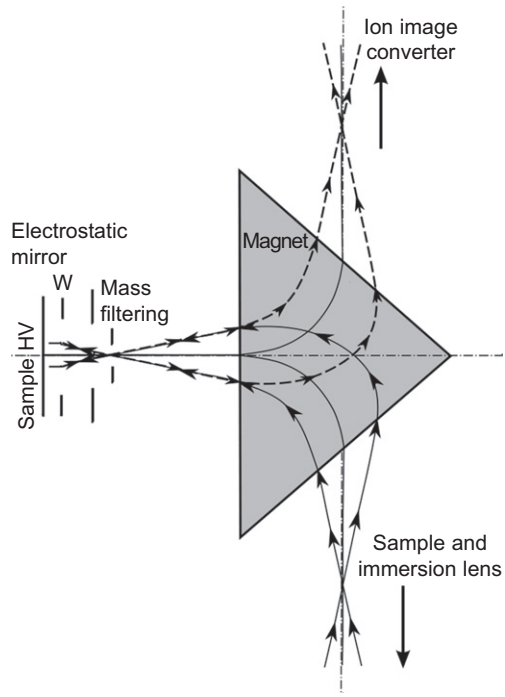
In fact, Castaing reiterated what he had done previously with its electron microprobe: After the thesis, an improved instrument was made in his laboratory of Orsay with the participation of a mechanical engineer named Dagnot. According to Castaing's wishes, this instrument was vertical (Figure 16a and 16b), like an electron microscope, but this setup was not convenient at all because the operator had to lie down to watch the picture.

The energy compensation was achieved by the so-called Castaing–Henry filter. The sketch in Figure 16c shows that it included both a magnet and an electrostatic mirror (a plane biased at the same voltage as the sample). Depending on the excitation of the magnet, a given mass passed online through the device. The most energetic ions were less deflected by the first part of the filter, but they were also less in the second half. The



(a)

(b)



(c)

FIGURE 16 The vertical ion microscope duplicated at Cameca and its Castaing–Henry filter (1965). Note that the energy focusing achieved by the filter is not illustrated in the sketch (16c).

optical sketch corresponds to the first instrument constructed in Orsay, with the source at the bottom, while the photograph shows the second instrument, duplicated at Cameca, with the source at the top.

A second instrument was duplicated by the engineering department of Cameca. Rouberol re-turned the column to bring the source to the bottom and the image at the top. Incidentally, he changed the image converter (Rouberol, 1967). The pole pieces could be rotated. In fact, on the one hand, it was somewhat easier to watch the image once it was formed at the top of the machine, but on the other hand, the unfortunate Dagnot, who had followed the project from Orsay to Cameca, was obliged to remove his shoes to play with the buttons at the tips of his toes while watching the image. The second version, installed at Orsay, was as unmarketable as the first. Commercial exploitation would come with the SMI 300. This time, Castaing would be persuaded to install the device horizontally (de Chambost, 2009, p. 66). A presentation of the implementation of the SIMS principles in the future instruments of Cameca is further described in the second appendix.

4.3. The Liebl and Herzog Ion Probe (1963)

At the same time, one of the 1949 pioneers—Herzog—teamed up with Liebl at the American company GCA (in Bedford, near Boston) to develop an ion probe based on the principle of scanning microscopy. This project was funded by the U.S. National Aeronautics and Space Administration (NASA). Also in the 1960s, the project of a magnetic mini-SIMS was proposed to be sent to the moon within the framework of the Apollo project (Benninghoven, Rüdenauer, & Werner, 1987, pp. 559–567).

Liebl and Herzog were at least one year behind the Castaing–Slodzian project. Their first publication presenting the IMS101 dates from 1963 (Liebl & Herzog, 1963), while the first images of Slodzian were obtained in 1960. However, they were formidable competitors not only because of their experience, but also because the economic and political climate was very favorable: support from NASA and direct involvement of a manufacturer, namely GCA. Compared with the Slodzian-Castaing instrument, the IMS101 had the big advantage of including a double-focusing spectrometer, therefore incorporating both a magnet and an electrostatic sector, while the French instrument had only a magnet. The IMS101 primary ion source was a duoplasmatron invented by Manfred von Ardenne and published in 1956.

A patent filed in 1958 claimed a double-focusing spectrometer and stigmatic properties (Liebl, 1958) and another by Herzog in 1959 claimed a device with a primary source of ions bombarding a sample and a double-focusing spectrometer (Herzog, 1959).

Helmut Liebl was among the toughest opponents of Cameca. He defended a thesis at Munich in 1956 and since then had been working in the field of ion optics, joining GCA in 1959. Around 1964, Liebl left GCA for ARL in California and in 1967 presented a new instrument, the ion microprobe mass analyzer (IMMA), that was the continuation of the GCA IMS101 (Liebl, 1967). In 1968 he returned to the Max-Planck Institüt in Munich to develop various projects (Liebl, 1974). Within the COALA project, the sketch of which was published in 1974, Liebl proposed the use of the same objective for both the primary and secondary ions. Later, the Cameca NanoSIMS would be based on the same principle (Liebl, 1972, 1974). After the first experimental data published in 1976 (Liebl, 1978), there was no publication of analytical data that would have been obtained with the instruments developed in Munich. After 1978 Liebl no longer attended SIMS conferences but continued to file patents for ion optics.

In designing his first ion microscope, Slodzian had paid special attention to the so-called extraction lens and matching the extraction conditions with the magnetic sector. Truly innovative in the Castaing–Slodzian draft was the idea that it is possible to take advantage of the magnet's stigmatic properties in achieving microscopy and, therefore, to combine the instrumental toolbox of electron microscopy (namely, the electrostatic lenses) with the toolbox of mass spectrometry (namely, magnets and electrostatic sectors). Paradoxically, in the 1930s Herzog was a pioneer in the field of magnet ion optics.

4.4. The Patent War

Released in 1968, ten years after the Castaing electron probe, the ion analyzer had to wait ten years before it weighed heavily in the turnover of Cameca. From 1968 to 1978, in a context of competition with ARL, between twenty and thirty SMI 300 models were eventually produced (de Chambost, 2009, p. 71). Before the release of the SMI 300, which was difficult as for every new model, a battle that was not won in advance had been waged from 1962 to 1970 in the field of patents.

In 1962, when Cameca became interested in the Slodzian–Castaing ion analyzer and negotiations with the CNRS led to a license agreement, Jacqmin realized that the CNRS had filed only one French patent (Castaing & Slodzian, 1959) and the time to make extensions abroad arose. Jacqmin then put pressure on inventors to be imaginative because the competition had not forgotten to undermine the field by patenting a mass spectrometer with double focusing applied to SIMS (Liebl, 1958; Herzog, 1959).

Castaing then proposed to patent a primary source of neutral atoms analyzer and "double-filtering" with two possible modes: a double magnetic sector (Castaing–Henry-like) and a more conventional arrangement (Nier–Johnson-like). This second patent (Castaing & Slodzian, 1962c)

was the basis for all future SIMS devices at Cameca. The extension of this patent in the United States was a bit painful; the examiner at the patent office repeatedly refused to issue a patent despite correspondence exchanges in which Cameca expanded all possible arguments. In fact, to circumvent the Liebl and Herzog patents, the Cameca strategy consisted of introducing in this Castaing–Slodzian patent (filed jointly by the CNRS and CSF) a new concept, that of the spectrometer analyzer, which corresponded to the ion microscope mode, and this remained somewhat obscure to the reviewer, Lundquist. It is true that the conceptual design and description of the embodiment of a "spherical condenser filter" was very vague and it was precisely in this embodiment that Cameca based more hope for post-SMI 300. To go fight the war in the New World, Miss Bodin, the patent representative of CSF, suggested to use for filing the U.S. patent the "continuation in part" procedure, which can benefit from the filing date of the original patent while adding material and even claims (de Chambost, 2009, p. 72). In that context, Rouberol wrote a note in which he described in a canonical way the various forms of achromatic spectrometer suitable for transferring the ion image of the sample. As discussed below, the sketch of the IMS 3F is found in this note. This note was the basis of a new French patent (Castaing & Slodzian, 1968) whose inventors were always Castaing and Slodzian, the same as those of the patent of 1962, which is not strictly required by the "contination in part" procedure which states that at least one of the inventors must be common to the two patents. With the help of Miss Bodin, Rouberol also wrote a note to challenge the examiner's arguments. They crossed the Atlantic to defend their case before the US Court of Customs and Patents, which by Appeal No. 8287 of August 13, 1970, eventually vindicated the complainants and disavowed the examiner Lundquist who had considered it obvious to those skilled in the art to introduce an ion mirror in the scheme of the double-focusing spectrometer of the Herzog patent (U.S. Court of Customs and Patent Appeals, 1970). It was actually obvious to nobody to think of something as complicated as the Castaing–Henry filter to achieve an ion analyzer. Due to her legal expertise, Miss Bodin opened a breach in the enemy system by taking advantage of the complexity of the mirror device, thereby opening the way for the IMS 3F which actually did not include the mirror.

But in 1970, the time of the IMS 3F had not yet arrived; it was still in the infancy of the SMI 300.

4.5. 1968: Launching the SMI 300 (or IMS 300)

The vertical microscope, unmarketable, had not even been exploited commercially. Cameca found itself lagging behind ARL. Five years of developments led to the SMI 300 (Figure 17), submitted to the 1968 X-ray

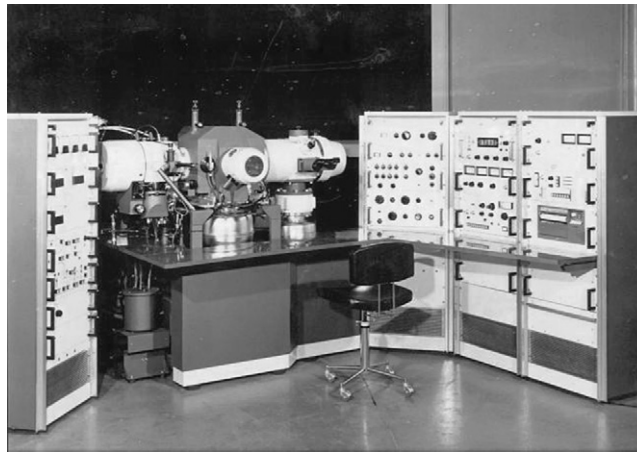


FIGURE 17 SMI 300 photograph (1968).

Optics and Microanalysis conference in Tübingen (Rouberol et al., 1969). Thirty-seven SMI 300s were produced from 1968 to 1978.

As the sketch in Figure 18 shows, the SMI 300 is actually derived from the results of the theses of two Castaing students: Slodzian (ion gun, primary column, and extraction) and Henry (magnet mirror). The Castaing–Henry filter, which combines the mass discrimination (the magnet) and compensation in energy (the mirror) is a very clever device, but it would prove to be more complicated than the Nier–Johnson system developed in the early 1950s and subsequently adopted by the IMS 3F. The Cameca engineers provided the primary probe with the possibility of electronic scanning, which would be an asset to depth profiling.

The SMI 300 was still an ion microscope that transferred the entire image in parallel. This was the essential difference from the Liebl probe, which had imaging capability but with the "artifice" that Castaing despised—scanning. The strength of the SMI 300 lay in its relative reliability due to the professionalism of the Cameca engineers: Guernet for mechanics and Guyon de la Berge for electronics.

Rouberol (Figure 19) had assimilated all the expertise in ion optics design. During the French strikes of May 1968, Cameca was closed for a few weeks like most companies in the Paris area, but that did not prevent some managers or engineers from working. During these weeks, Rouberol had plenty of time to play with the instrument. He checked that the properties of the instrument were consistent with the description given by various theories. He also noted that in its calculations, Henry has missed the overall astigmatism on both axes. Castaing, to whom he expressed his

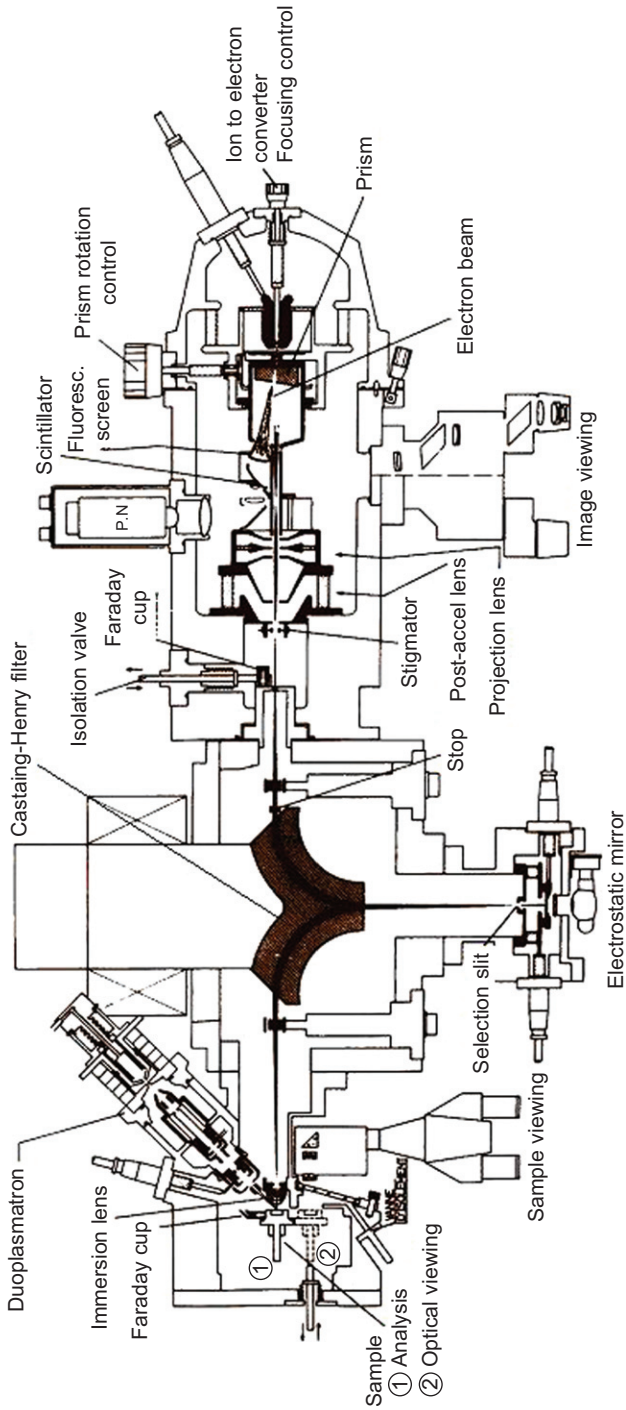


FIGURE 18 SMI 300 sketch.

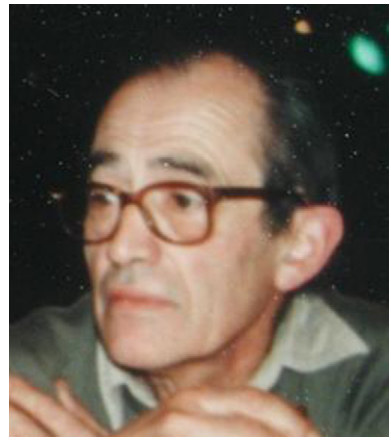


FIGURE 19 Jean-Michel Rouberol in 1980.

remark, found it interesting but noted in pencil on Rouberol lab notebook that this was the consequence of the symmetry in XY (see the copy of the Rouberol notebook in Figure 20).

4.6. The First Steps of the SMI 300 and the Early Development of Semi-Conductor Applications (1970–1971)

When the SMI 300 was marketed in the late sixties, the game was not won. The IMMA, the rival model from ARL, had been released a year earlier and produced good results—for example, in 1969, the pioneering analysis of lead in zircons (Andersen, 1970). It is true that the analysis was not performed at high mass resolution, as would be done fifteen years later with the IMS 4F. In the early 1970s, Cameca was not the favorite in the competition against ARL; even so, the SMI 300 could still find a market among metallurgy people due to the good reputation of the MS46 electronic probe, which had opened the way in France and abroad. The unexpected market for the semiconductor implantation test was like manna from heaven. The traditional method of measuring the doses and profiles of dopants in semiconductors was to grow an oxide and then deposit a metal layer and measure the capacitance, depending on the applied voltage, which had an effect on the depletion layer thickness.

So, the SMI 300 could be sold to some research labs that used the instrument for producing quantities of "depth profiles" (Rouberol & Basseville, 1972) (Figure 21). This new application was a real godsend for Cameca, because it turned out that the "true" ion microscope, dear to Castaing and Slodzian, was far better suited to depth profiling than the ion probe,

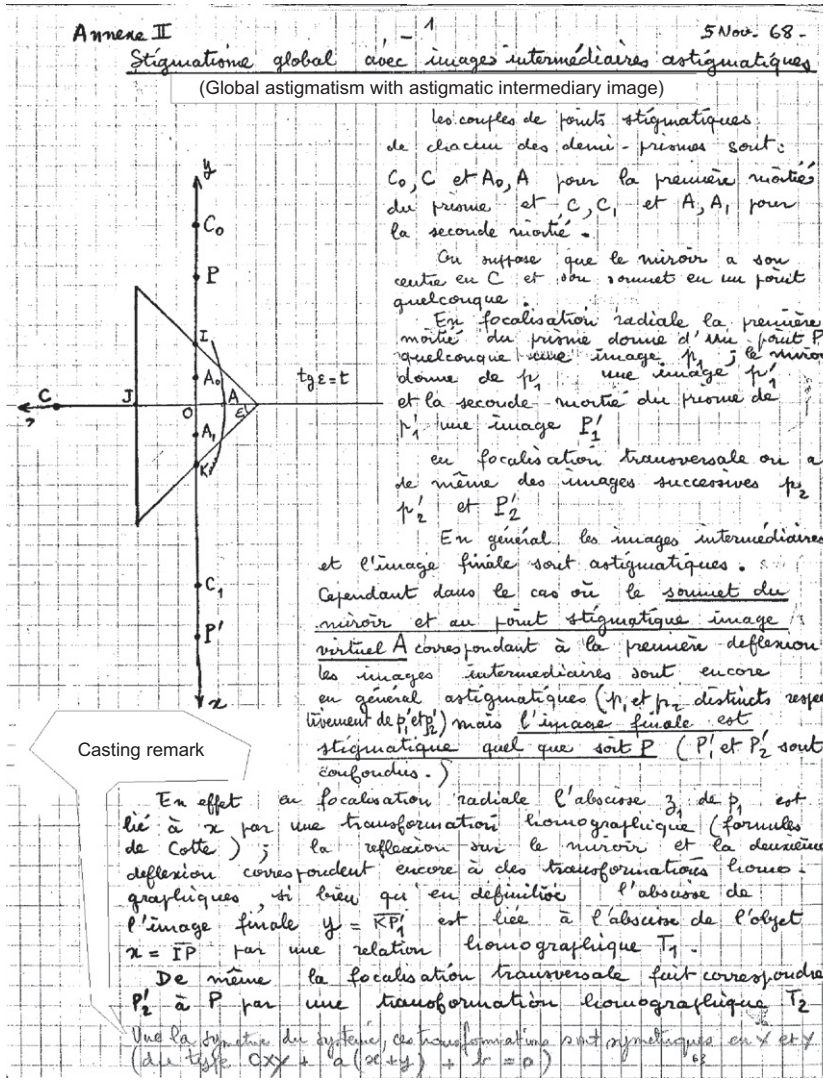


FIGURE 20 Rouberol notebook.

dear to Liebl. Transferring images in parallel made easier the implementation of the "optical gate" function, familiar to Cameca instrument users. A stop aperture was inserted within a plane where the sample image was formed so as to pass only ions emitted from the crater bottom. In principle, this spatial filtering could also be achieved with a fine scanned probe, but in fact, primary probes produced with a duoplasmatron were rarely well defined.

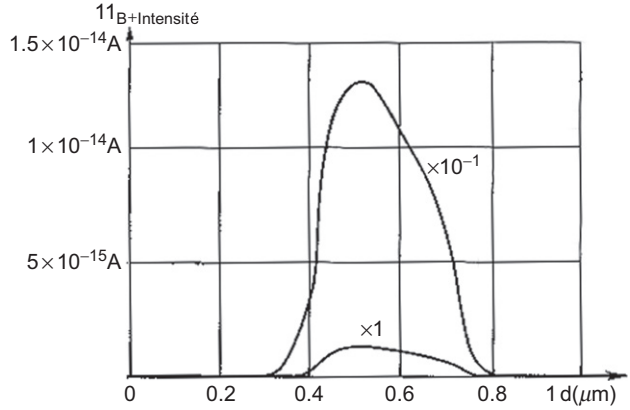


FIGURE 21 Boron in epitaxial silicon depth profile with the SMI 300 (Rouberol & Basseville, 1972).

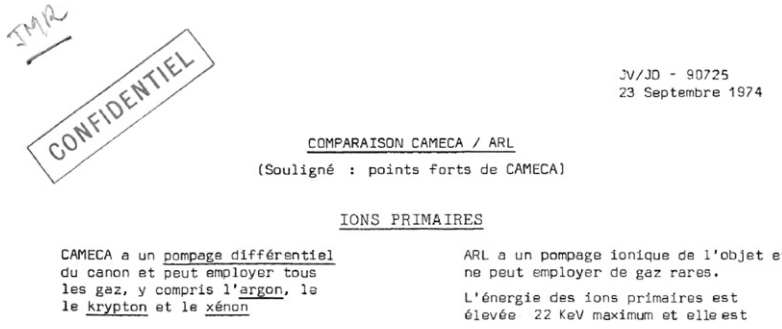


FIGURE 22 Copy of a sales note (1974).

The principle of the true ion microscope was also likely to secure the loyalty of customers. The complicated SMI 300s may have often shut down, but when they were working, the user could recover each morning his "aluminum grid" image and this ion image put his mind at rest.

4.7. The Performances of SMI 300 in 1974

In 1974, according to a sales note (Figure 22) dealing with competition with ARL, the main performances of SMI 300 could be listed as follows:

- The duoplasmatron can be operated with oxygen, nitrogen, and noble gases.
- Oxygen probe density as high as 50 mA/cm^2.
- Primary probe diameter can be varied from 10 μm to 300 μm.
- Scanned field area up to 1 mm × 1 mm

- Both primary and secondary ions can be positive or negative.
- An airlock makes possible to load a new sample within 3 minutes.
- An optical microscope allows direct viewing of the sample.
- Mass resolution as high as 1000 with the basic model can exceed 3000 with the ESA (Electrostatic Sector Analyser) accessory (see Section 4.8).
- Acceleration voltage: 4500 volts
- Transmission of 10% with a mass resolution of 200.
- Image resolution with the microscope mode as fine as 1 μm, not depending on the primary probe size.
- Mass drift less than 0.1 amu within 24 hours.
- Ion detector (scintillator + photomultiplier) noise: a few counts per second (cps).

Compared with the competition, the strength were the mass resolution that could be obtained with the ESA accessory and the image resolution with the microscope mode. On the other hand, weaknesses were the primary probe resolution, the accuracy of the sample stage, and the lack of primary filtering. ARL was also well liked because of the convenience of operating the instrument.

4.8. Through the Other Side of the Mirror

The Castaing–Henry filter that formed the core of the SMI 300 achieved energy focusing but did not include an energy slit—the means to select any energy bandwidth. The Castaing–Henry filter was strictly a low-pass filter. This was a real issue for a SIMS instrument, since depending on the considered ion species, a significant proportion of secondary ions are emitted with an initial energy ranging from tens to hundreds of electron volts. The capability of selecting the fastest ions allowed Andersen to solve with an ARL IMMA the interference issue for measuring zircon lead isotope ratios (Andersen & Hinthorne, 1972).

Without limiting the energy dispersion, it turns out that the mass resolution of the SMI 300 is limited to 1000. The solution is to "pass through the other side of the mirror"—that is to say, to further complicate the instrument by piercing the electrostatic mirror to replace the missing part of the magnetic prism by an electrostatic sector flanked by two slits, the energy slit and the output slit (Figure 23).

The ESA accessory was released in 1973. It allowed the mass resolution to exceed 3000. The project manager of this final version of the SMI 300 was Jean Vastel, a very high-level engineer nearing retirement who transferred to Cameca from the CSF mass spectrometry division. Ultimately, this "wart" mounted on the SMI 300 as an accessory constituted with the half Castaing–Henry magnet a type of Nier–Johnson spectrometer. The regular on-axis detection line was still required to achieve microscope

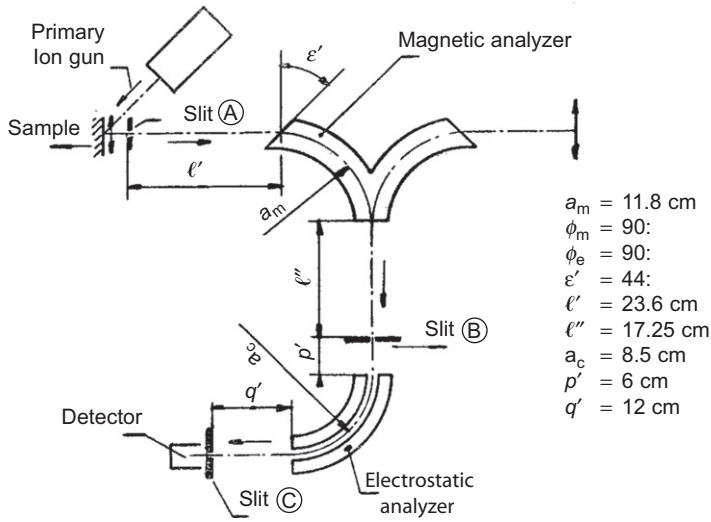


FIGURE 23 The SMI 300 ESA accessory (1973).

mode, but the part of the SMI 300 where the ions fly through the mirror and the ESA foreshadowed the IMS 3F, which was eventually released a few years later.

5. THE ADULT AGE (1975)

5.1. The Camebax (1974)

The decline of the MS46 started with the development of the geology market and the analysis of very light elements in the field of metallurgy. To make things worse, JEOL launched a new model equipped with a column derived from a SEM and with a WDS emergence angle of 40° made possible by a so-called minilens. At this time, Cameca was putting the finishing touches on the Camebax, which also had an emergence angle of 40°. Finally, in order to circumvent the hellish alternative—less than 18° or more than 52.5°—Guernet and Conty imagined an arrangement where X-rays pass through holes drilled in the pole pieces. This arrangement was technically satisfactory but presented great risks in terms of industrial property. The ARL patent (Wittry, 1960) claims "x-rays that pass through the electron lens." ARL could possibly argue that the Cameca sketch was infringing on the first claim of the patent. When asked about this, the patent attorney at Cameca was not very reassuring. Finally, after the launching of the Camebax, ARL did not move.

The angle of 40° provided an excellent compromise. On the one hand, it met the need of Castaing to reduce the analysis uncertainties due to fluorescence. On the other hand, X-rays of low and very low energies were not absorbed too much. It allowed freeing the bottom of the pole pieces, which made room for the secondary electron detection and permitted a more economical design of the microprobe while with the EMX, the device was in a large pot under secondary vacuum. Suddenly the players changed: ARL lost its advantages while accumulating disadvantages and was finally pushed out of the market. Cameca came to fight a duel with JEOL, whose intrument (the JXA-3A) had features similar to the Camebax with slightly worse mechanics but with a sales network and customer service certainly more developed than Cameca.

The Camebax (Figure 24), equipped with a novel spectrometer designed by Guernet, was presented in 1974 in New Orleans at the MAS (Micro Analysis Society) exhibition. The first Camebax was delivered to Dow Corning; 322 Camebaxes were produced by Cameca between 1974 and 1986 (de Chambost, 2009, p. 80).

Another difference between the MS46 and the Camebax was that the last aperture stop, which was located below the last lens pole piece with the MS46, was shifted above the Cassegrain microscope with the Camebax. This made it possible to observe the sample during analysis and fully achieve magnetic scanning as was usual with SEMs. The Camebax also inherited many improvements developed for the MEB07, a SEM

FIGURE 24 Camebax (1974).

TABLE 1 Comparison between the MS46 and the Camebax

Feature	MS46	Camebax
WDS	4	4 + EDS
Emergency angle	18°	40°
Sample diameter	25.4 mm	25.4 mm
Sample airlock	No	Yes
Electron gun valve	No	Yes
High voltage	30 kV	50 kV
Mechanical scanning	Yes	Yes
Electronic scanning	Electrostatic	Magnetic
Backscatter and secondary electrons detection	Coarse	Yes
Vacuum	10^{-4} T	10^{-5} T
WDS crystal	Pressed	Stitched
SEM resolution	0.1 μm	0.01 μm

launched by Cameca in 1970, the story of which is written below. Table 1 provides a detailed comparison between the MS46 and the Camebax.

The Camebax spectrometer goniometer was based on a very bright idea patented by Jacques Guernet (Guernet & Boissel, 1972), a mechanical engineer who was undoubtedly a star in the 1960s and 1970s at Cameca. He was a leader of men endowed with great charisma. He is more or less the father of the machanics of MS46 with the thin window separating the spectrometer and the electron chamber, the overall mechanics of the SMI 300, the mechanics of Camebax, and namely, the WDS spectrometer and finally the mechanics of IMS 3F. He eventually left Cameca around 1980.

The Camebax WDS (Figure 25) implemented an entirely mechanical solution to achieve the Rowland condition. The great advantage of the proposed arrangement was that the center of the Rowland circle was completely free from the goniometer mechanics, giving the sample stage enough room. Guernet had also imagined a solution for arranging the spectrometer in either a vertical or inclined position. Also of note with the new spectrometer was that the counter was located on the Rowland circle, so that the X-ray beam was focused on the counter, which allowed the size of the window to be reduced. Implemented in 1974 on the Camebax, the Guernet spectrometer was still mounted on the SX100 and the instruments of the shallow probe family in 2010.

It was possible to mount on the Camebax an EDS supplied by Tracor Northern (later renamed NORAN). The Camebax was the first electron microprobe to be partially computer controlled (namely, a PDP11). In fact, in 1974 the first Camebax did not include any computer but some years later, data acquisition hardware from Canberra was adapted to the instrument and interfaced with a SR33 teletype, which could be programmed by using the "Class" language. Analysis recipes could be stored on a punched

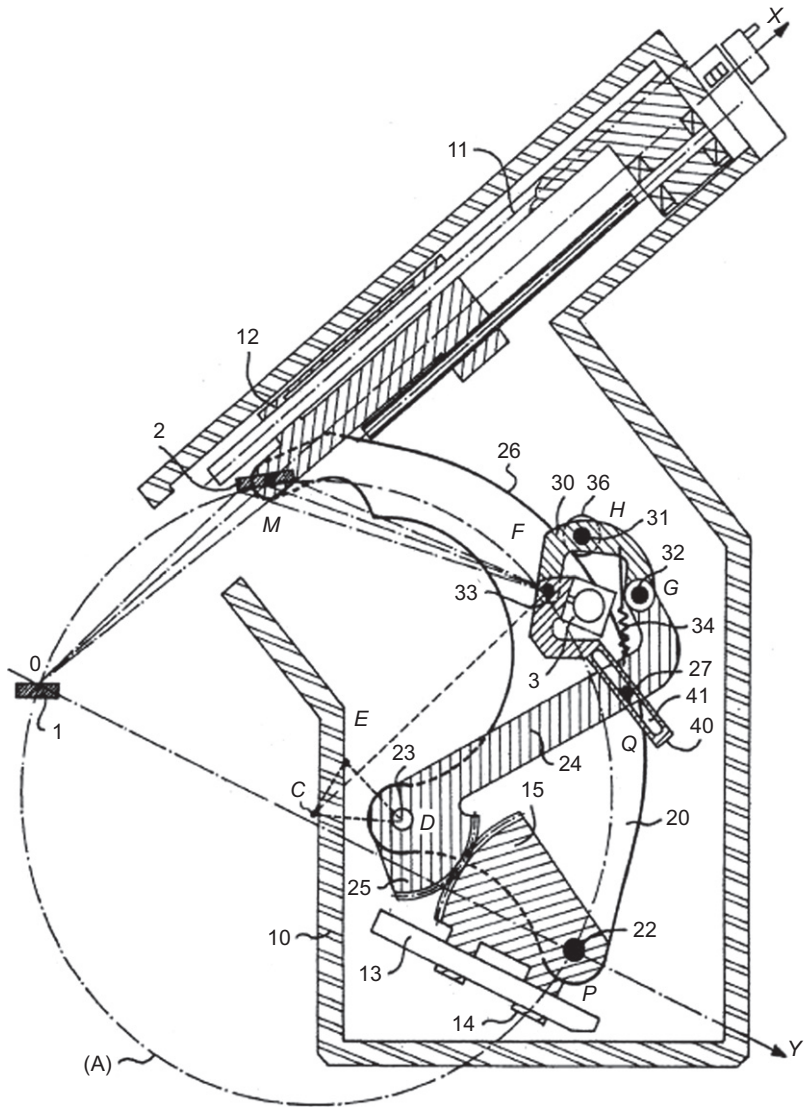


FIGURE 25 Guernet goniometer, patent drawing (Guernet & Boissel, 1972).

tape. At the very beginning of EPMA, the MS85 operator had to record data in a paper notebook, and during the evening, the operator transferred the data by hand onto punched cards that were brought to the plant computer center to be processed overnight.

Many accessories were developed for the Camebax. In addition to the cathodoluminescence device (which already existed for the MS46), Cameca proposed a TEM accessory (Figure 26) purposed for observing

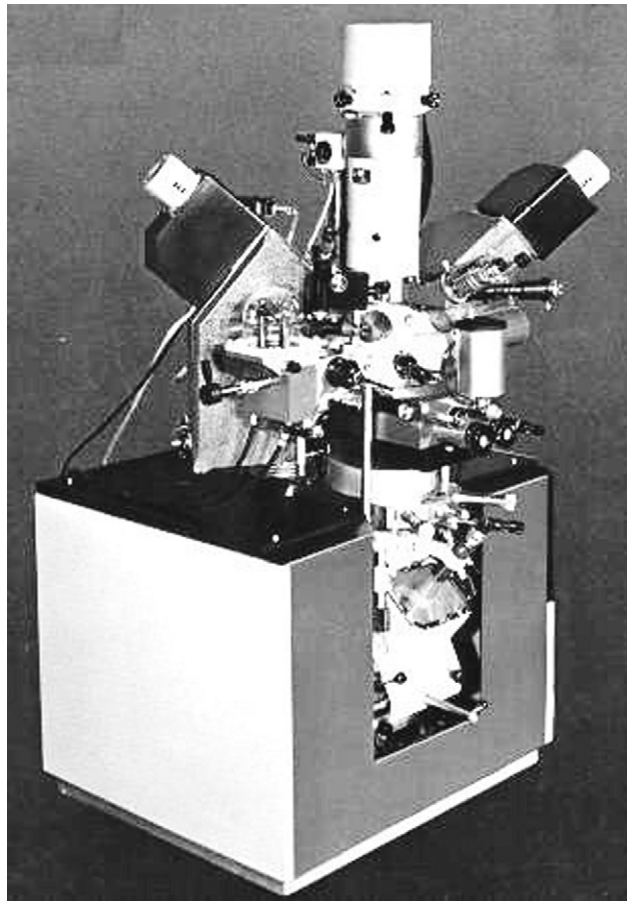


FIGURE 26 "Biology-Camebax" with a "TEM" accessory.

Kossel diagrams as far as the regular high-voltage level of 50 kV could be obtained. About ten of these TEM accessories were delivered. Other accessories were proposed for heating or cooling the sample (de Chambost, 2009, p. 83).

5.2. The IMS 3F

5.2.1. Genesis of IMS 3F

The introduction of the IMS 3F was a crucial moment in Cameca's history. The IMS 3F went on the market in 1978 and since that date, Cameca enjoyed a profitable product line due to a virtual monopoly on the magnetic SIMS.

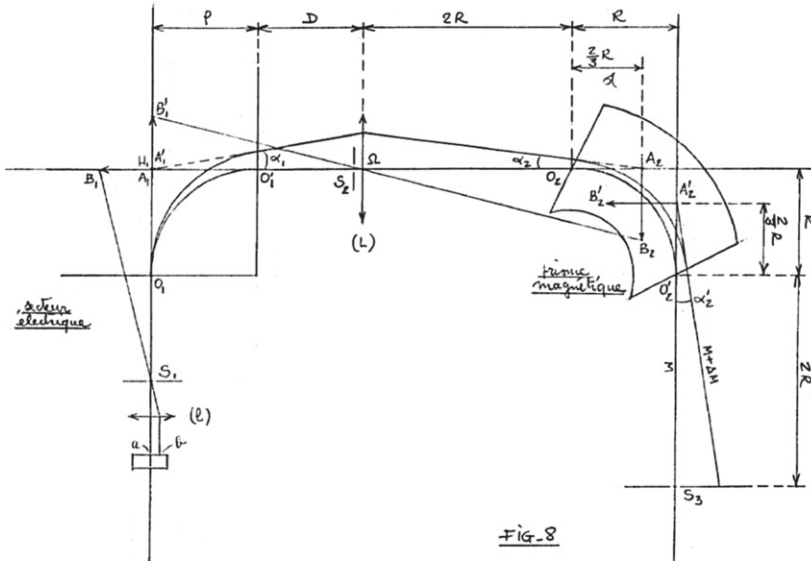


FIGURE 27 Sketch of a "C" double-focusing spectrometer as candidate for the "ionic analyzer." Rouberol, handwriten note November 3, 1967.

The idea of replacing the SMI 300 mirror filter with a more conventional double-focusing spectrometer had been in the air since 1967, when in the patent war against ARL (see Section 4.4) Rouberol had to compile an exhaustive list of all spectrometer structures. A handwritten note dated November 3, 1967, (Combined spherical condenser and magnetic sector ionic analyser), contains the IMS 3F spectrometer sketch shown in Figure 27. In this note, Rouberol considered all the configuration meeting achromatism conditions while transferring both the slit image and the sample image. From then on, achromatism became a key concept of the Cameca SIMS instruments, contrary to the 1962 patent, which considered only a low-pass filter (Castaing & Slodzian, 1962c).

From the launch of the SMI 300, it had been proven that its principle was unnecessarily complicated. The explanations above detail how attempts to improve the energy filtering and mass resolution led to another complication. In 1974, Rouberol was working daily to prepare the preliminary draft of a successor to the SMI 300, and in a particular meeting involving Rouberol, Guernet, and Lepareur, it was decided to launch the project, which would be known as the IMS 3F. The C structure was chosen because it was one that Guernet felt was the best from a mechanical point of view: The operator could have access to all machine settings from a single place. The machine was more compact and could be based on three points, like a marble for optical setup.

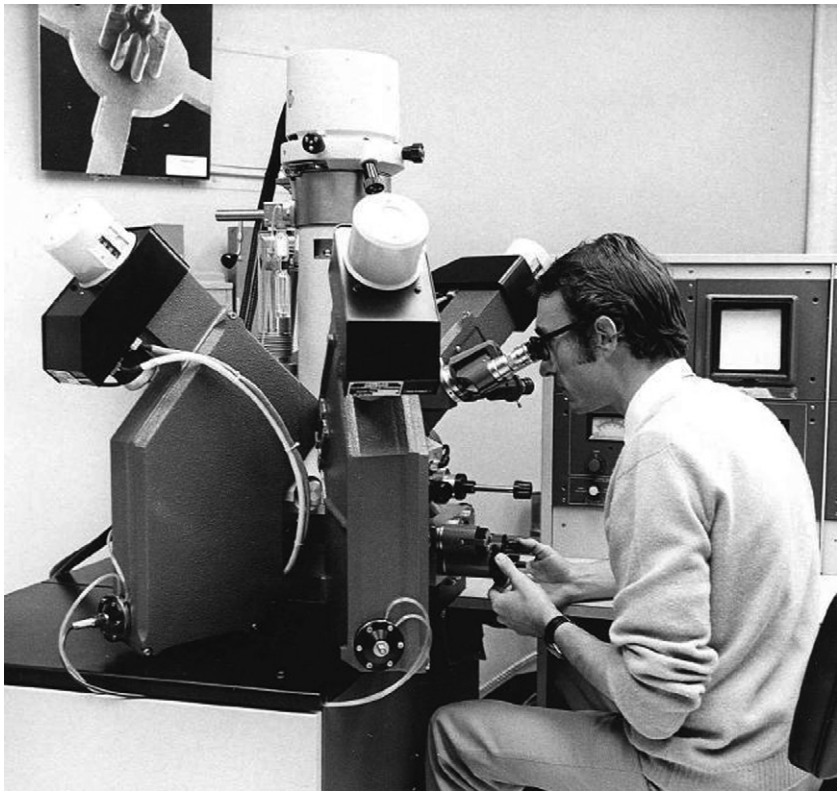


FIGURE 28 Michel Lepareur playing with a Camebax.

Michel Lepareur (Figure 28), appointed as project leader, now had all the cards in hand. Lepareur started his career with Cameca in the sixties as a field engineer. We was often selected for difficult tasks, such as installing an electronic probe MS46 at an exhibition in Beijing right in the middle of the Cultural Revolution.

The theoretical sketch proposed for filing was transformed to a draft to be calculated carefully, as shown in the notebooks of Rouberol and Lepareur (Figures 29 and 30). The spectrometer coupling len- focusing properties and chromatic aberration were estimated based on a model given by Grivet.

Two other novelties were included in the IMS 3F: The final image converter was based on a multichannel plate (MCP) device and so-called transfer optics. Before replacing the Möllenstedt converter with an MCP, a light intensifier including an MCP was adapted for the SMI 300 phosphorus screen. Light intensifiers (Figure 31) had been developed for military applications such as night vision. Rouberol had the idea of implementing

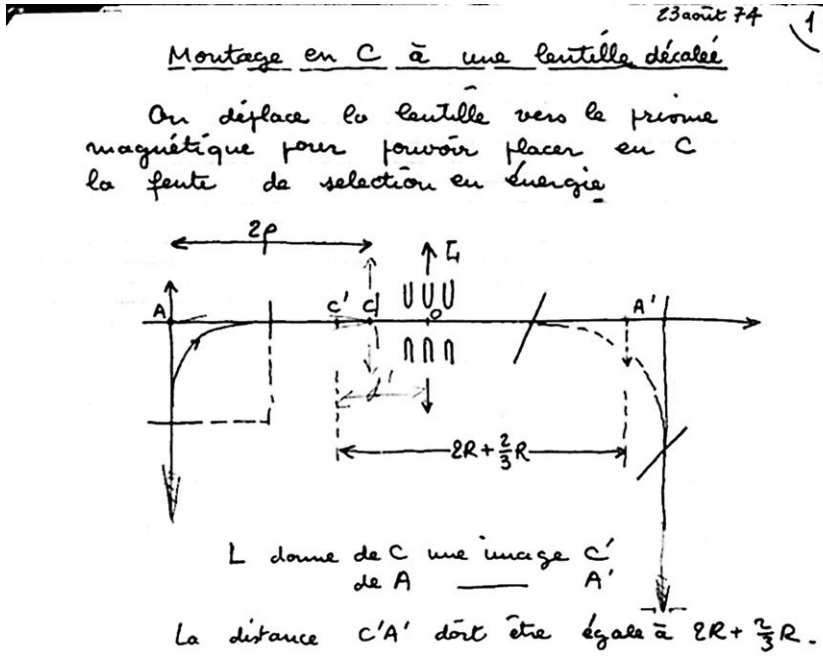


FIGURE 29 Rouberol notebook (August 1974) takes into account that the energy slit cannot be located exactly at the same plane as the spectrometer coupling lens. This results in a 3/2 magnification between the exit slit and the entrance slit.

the MCP directly in the ion analyzer. It served the function of ion-to-electron converter, while a simple acceleration space between the MCP and the phosphorus screen functioned as an electron-to-photon converter. The overall device was extremely compact—only a few millimeters—and ensured the conservation of spatial information.

In 1975, it was still highly hazardous to use the MCP directly with ion beams. Experience would demonstrate that incident ions can be converted in several secondary electrons identically to incident electrons and that they were not damaging the MCP very much. In fact, such an arrangement had already been used converting ion images: In 1967, Müller used an MCP for his field effect microscope (see Section 9.2), but in 1974 Cameca's personnel did not follow the progress of atom probe. Lepareur designed and tested the MCP-phosphorus unit just in time to mount it in the IMS 3F prototype in early 1977. During the same period, at the Slodzian laboratory, a more exhaustive study served as a dissertation for an engineering degree (Chaintreau, 1978).

The other novelty of the IMS 3F was "transfer optics," later known as "emittance matching optics" (Benninghoven et al., 1987): An arrangement

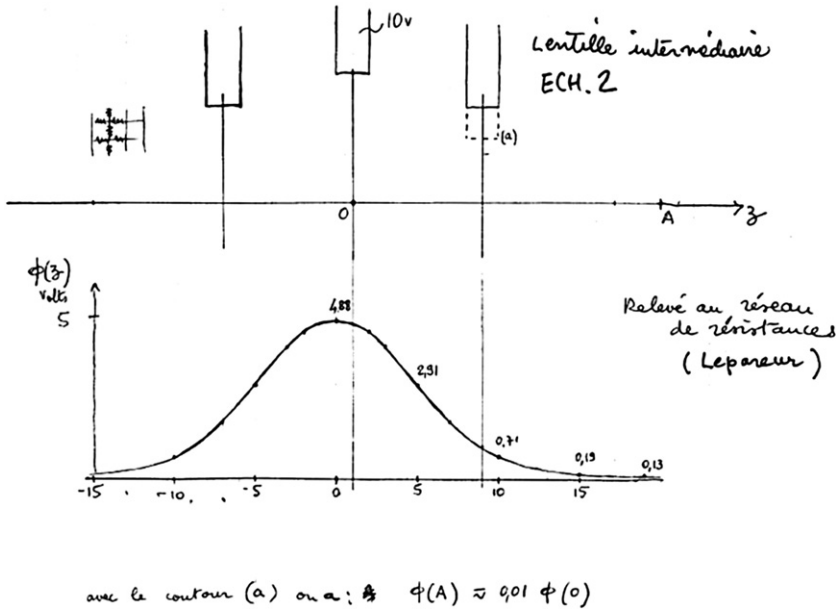


FIGURE 30 In the Rouberol notebook, an analog calculation of the coupling lens with a resistor network achieved by Lepareur (1975).

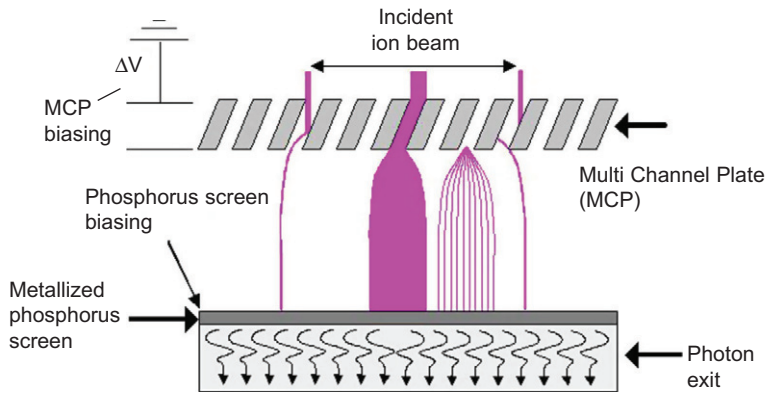


FIGURE 31 MCP integrated in an ion image display device.

of electrostatic lenses (Figure 32) is used to select a given area of the sample or, in other words, to vary the magnification between the sample plane and the MCP while keeping the same field aperture (Rouberol et al., 1977; Slodzian & Figueras, 1977). This idea came to Slodzian in 1970 at ONERA, when he had the occasion to couple a Mattauch–Herzog spectrometer to a

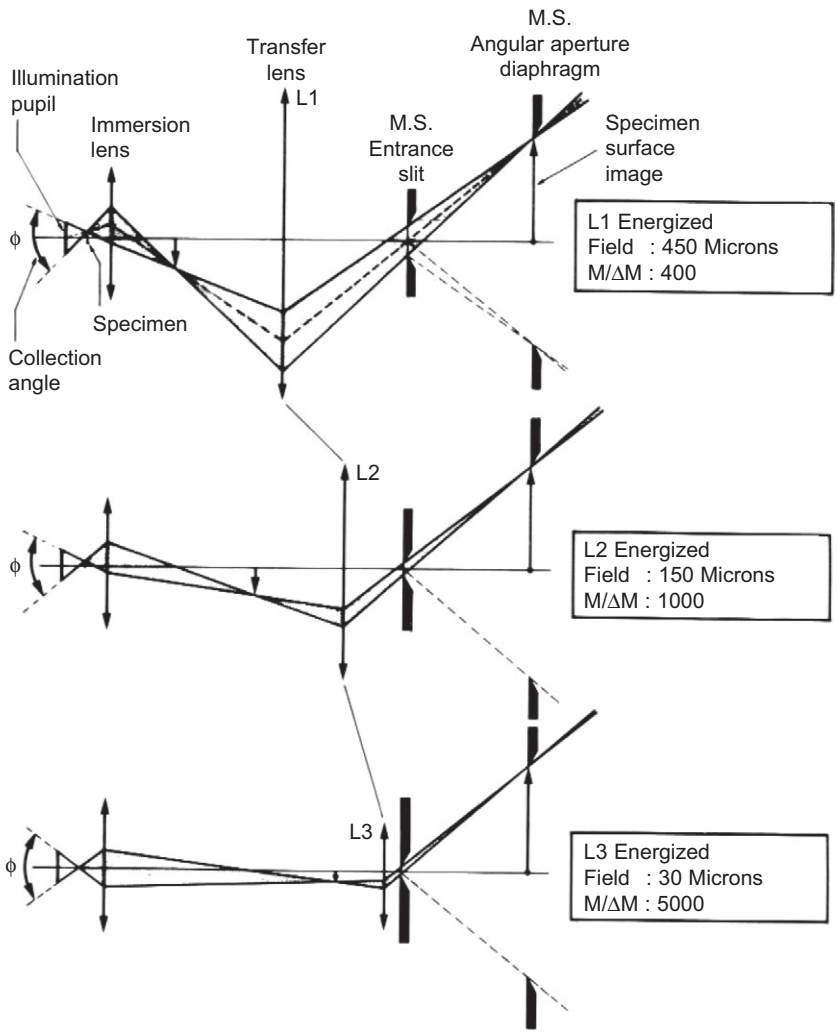


FIGURE 32 The IMS 3F Transfer Optics and the three possible magnifications of the sample image. This sketch was included in the presentation paper given at the conference of Boston in 1977.

SIMS instrument. Electrostatic lenses were required for matching the ion source. In the following years, Slodzian (1974) developed a theory about the concept of transfer optics. When Slodzian proposed implementing transfer optics in the IMS 3F, Rouberol was somewhat reluctant toward what he considered to be useless sophistication that could slow down the project. Nevertheless, he accepted it providing that Lepareur tested it, not directly with the prototype but with a separate setup. Fortunately, after

FIGURE 33 Max Sarfati in 1982.

this preliminary test, transfer optics could be mounted in the prototype in time for the final setting-on of the IMS 3F (de Chambost, 2009, p. 89).

Later the Cameca IMS, IMS4-5-6-7F, IMS Wf, IMS 1270, and IMS 1280 would still be equipped with this transfer optics, but after the IMS 6f in 1995, the three discrete lenses were replaced by a continuous zoom achieved with only two lenses.

Early in the project, Lepareur had a polystyrene mockup made only for an ergonomics test. The spherical electrostatic sector was forecast to be the trickier device to set on. In practice, it turned out that the physical device was not really an issue, contrary to its electronic supply, very long to meet its stability specifications.

Since the delivery of the SMI 300 to the Orsay university, Castaing had been given many different responsibilities, particularly in ONERA management, and Slodzian had become the academic partner of Cameca. Actually, among the Castaing team he was the only person still involved in SIMS. The relationship between him and Cameca was good and fruitful when Lepareur implemented transfer optics in the IMS 3F, and they would remain close a few years later, when the normal electron gun studied by Slodzian would be transferred to the IMS 4F. The NanoSIMS story, initiated by Slodzian, is another example of pleasant cooperation between public research and the private company Cameca.

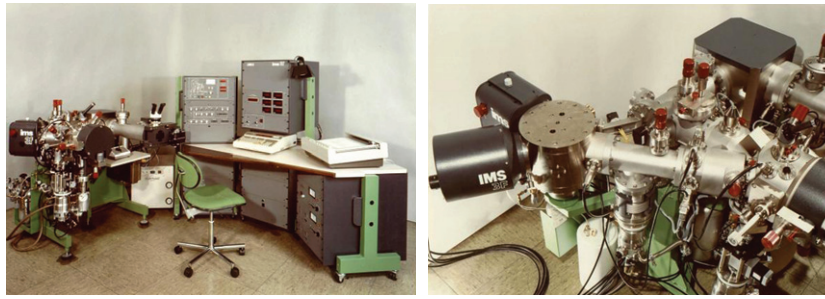
5.2.2. The Situation of Cameca in 1976

In 1976, Cameca's situation was critical: Despite the commercial success of the Camebax, the company had lost a lot of money. The SMI 300 was probably more prominent than its ARL competitor for the semiconductor application, but precisely in this field, the magnetic SIMS had been deeply challenged for a few years by far simpler instruments: The quadrupole SIMS consisted of only four parallel rods suitably excited with a radiofrequency (Benninghoven & Loebach, 1971; Maul et al., 1972). ARL proposed a quadrupole SIMS and at Cameca, QUASIMS was the code name for such an instrument.

The IMS 3F project, which started in 1974, was also the source Jacqmin's dismissal. Since Cameca lacked the ressources to develop this project, the CEO had to beg for grants from the Thomson-CSF headquarters, who were led to pay some attention to the bad health of the subsidiary. Finally, Jacqmin was allowed to continue the project but was punished for his poor financial handling. Max Sarfati, an executive of Thomson-CSF previously involved in radiotelephones, was designated as Jacqmin's successor with a single mission: to get Cameca out of the red. Sarfati carried out mass layoffs after Cameca withdrew from marginal business (such as subcontracted mechanical work) but confirmed the priority of the IMS 3F, believed to be promising for Cameca.

5.2.3. The Release of IMS 3F (1978)

The IMS 3F (Figure 34) was presented in August 1977 at the 8th Congress of X-ray Optics and Microanalysis with some very early experimental data (Rouberol et al., 1977). The first instrument was eventually installed at NEC, in Japan, by Lepareur and Robert Charron. Successively, Jacqmin and Sarfati had both believed in this project and made it possible.



(a) (b)

FIGURE 34 (a) IMS 3F (1978). (b) Improved IMS 3F (1982).

A prototype was installed at the exhibition, held in Boston simultaneously with the conference. Before shipping, the instrument was packed in a panic since Rouberol had broken the new MCP by lending a hand. The day before the show opening, the duoplasmatron supply failed. Bernard Autier, transferred to the United States for a few years, had to purchase the spare parts at a broker overnight.

The IMS 3F project had been promptly led and would be a great commercial success. Nevertheless, its birth was painful. It was the early time of complementary metal-oxide semiconductor (CMOS) circuits, and they were particularly sensitive to the flashes produced from time to time by the high voltages. Lepareur and his colleagues worked on Easter weekend to honor the delivery schedule of the Japanese customer (de Chambost, 2009, p. 95).

As Figure 34a and 35 show, the IMS 3F was equipped with a single ion source, a duoplasmatron. The operator, seated in the rolling swivel chair, can turn the buttons of the electronic crate while observing the ion image with the binocular microscope. The operator can also play with the keyboard of a HP9825 computer featuring a RAM of 8 kilobytes to launch automatic acquisitions. The IMS 3F structure, its size, and even some mechanical parts would last from 1977 to 2010 and probably beyond.

The name *IMS 3F* refers to the three different types of focusing: In addition to the aperture and the energy focusing that characterize any "double-focusing" spectrometer, imaging the sample plane at the MCP plane is the third type of focusing.

The success of the IMS 3F was striking not only in terms of technical performance but also from a commercial point of view: The competitor would be completely ousted from the magnetic SIMS field. Between the installation at NEC in 1978 and 1985, 100 instruments were delivered—an annual production four times higher than the SMI 300.

After NEC, Drew Evans was among the first customers of the IMS 3F. He left the University of Illinois to found CEA (Charles Evans and Associates), a company pioneering analysis service for semiconductor applications. CEA purchased five IMS 3F or IMS 4F models during the 1980s. Since analysis service allows SIMS analysis without the need to invest in a costly instrument, a company like CEA tends to spread the technique. Customers of CEA may become future customers of Cameca.

During the 1980s, some improvements were implemented on the IMS 3F (Figure 34b). A primary magnet called a primary beam magnet filter (PBMF) afforded the capability of mounting two ion sources—a duoplasmatron and a cesium source—and selection of the more-suited source for the analysis. The cesium source was manufactured by a small company, General Ionex, and later, Peabody Scientific.

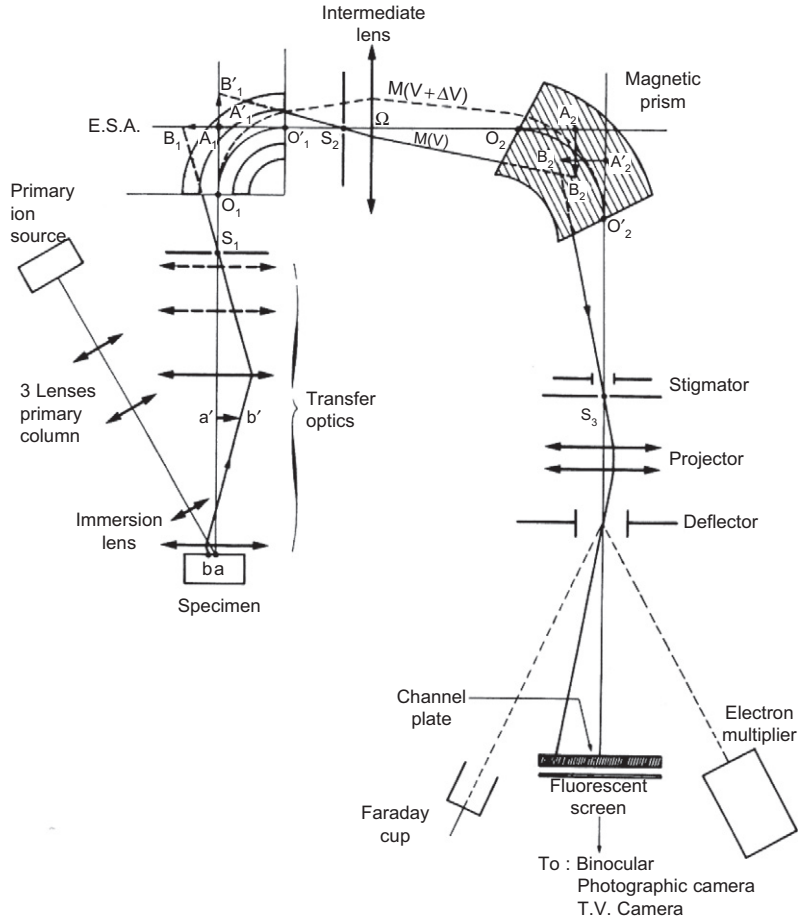


FIGURE 35 IMS 3F ion optical sketch (Rouberol et al., 1977).

5.3. Cameca International

5.3.1. The U.S.S.R.

Until the end of the 1970s, the U.S.S.R. was the primary source of Cameca's international business though at the early time of the Spectro-Lecteur and MS85 (in the 1950s) some instruments were also delivered to the United States and Japan. The first Camebax was installed in Moscow by the end of 1973, and during the first three years of this instrument's life, 34 Camebax instruments were shipped to the U.S.S.R., slightly more than to France (25)

but far more than to European countries (10) or North America (7). At this time, the world of Cameca was therefore Franco-Soviet. The MS46 had already been a great success in the Soviet Union, but their interest for the EPMA technique dated back to pioneer times.

Russian I. B. Borowsky led research work identical to that of Castaing and at the same time. In 1959, he published in a Soviet review a paper entitled "Practical Progresses of Science: The Method of Microanalysis." In his paper, he reported the data obtained with an instrument named "RSAIII-2" achieved at the Metallurgical Institute A. A. Baïkov. A small batch of RSAIII-2 instruments was to be produced that year, Borowsky wrote before concluding "It is of the highest importance that our economy can equip as soon as possible the laboratories of the institutes and of the factories with RSAIII-2 and RSAIII-3 instruments for studying the chemical composition of materials."

Professor Borowsky, who would soon be familiar to the engineers and salesmen of Cameca, was surely an influential member of Soviet society since his recommendations were good for Cameca business, since the U.S.S.R. paid "cash on the barrelhead."

The U.S.S.R. had the skills for creating huge metallurgical conglomerates, and undoubtedly, creative scientists were working within its prestigious institutes such as Baïkov, but this society was absolutely incapable of generating small business units such as Cameca and thus definitively unable to produce small batches of electron microprobes that worked properly. The Urals would become the El Dorado of Cameca, and its technicians and service engineers would spend a part of their lives there. They learned to work there in somewhat difficult conditions with few contacts aside from their Courbevoie base.

Shortly after the MS85 was launched, Jacqmin tried hard to break into the Soviet market. A good relationship between Borowsky and Castaing made this task easier. The first MS85 was installed in the U.S.S.R. in 1960 after a "metrology" exhibition organized to promote French products. SORICE, an export-import agency linked to the French Communist Party, acted as a go-between. Its employees, convinced Communists, were also excellent sales representatives. Joseph Astruc, the Cameca salesman, succeeded in establishing a friendly relationship with the members of the Soviet central purchasing agency and could hold his vodka well enough to get signatures on fantastic contracts. From the 1980s on, Cameca had its own business premises (de Chambost, 2009, p. 100).

The Soviet market collapsed in 1990 at the same time as the overall Soviet Union. A few months before this collapse, the SIMS salesman Jean-Jacques Le Goux received a group order of seven IMS 4Fs, only two of which were canceled. Sarfati estimated that Cameca would lose 15% of its turnover with the drying-up of the Soviet market and scheduled a layoff program.

5.3.2. The United States

Executives of Cameca had long entertained the American dream before it became a reality measurable in dollars. And yet, one of the first five electron microprobes MS85 was ordered by the U.S. company INCO as early as 1958. In 1963, it was thought wiser to conclude a manufacturing license agreement with a local company, Acton Lab, a subsidiary of Bowmar Instrument Corporation. Under this agreement, Cameca provided the mechanical parts of the MS46 and Acton was to add the U.S. electronic hardware. It was also more or less agreed that later Acton would manufacture the entire instrument.

This concept would never be very convincing. Nevertheless, about twenty microprobes were sold by Acton with the name of MS64 instead of MS46. The issue was not only to tackle the American market, but also to face ARL, a big player in the United States. After the launching of the SMI300, Cameca turned to CEC, a subsidiary of Bell & Howell, with whom an agreement was signed. Six SMI300s were delivered in the United States between 1970 and 1974. These successes were encouraging, but the American dream was actually fulfilled only from 1977 with the collapse of ARL and the success of the Camebax; forty instruments were installed between 1977 and 1982 (de Chambost, 2009, p. 102).

The U.S. subsidiary Cameca Inc. was created in 1971 with a French Cameca engineer, Bernard Authier, as chairman and Bob Hessler appointed as salesman. Both were based in rented premises in Elmsford, New York. The first Camebax, which had been presented at the MAS exhibition, would be installed there in a demonstration lab. Some months later, a Camebax was sold to Dow Corning. In 1976, Cameca Inc. was transferred to Stamford, Connecticut. Around 1982, after the resignation of Bob Hessler, Claude Conty was appointed first as vice chairman and then chairman in 1986. In 1993, the company moved again—to Trumball, Connecticut. The staff of Cameca Inc. grew from two persons in 1971 to 26 persons in 2006; this increase corresponded mainly to a strengthening of the after-sales service department required by the successes of the Camebax and the IMS 3F. A stock of spare parts was built up at Stamford to improve after-sales service.

From the end of the eighties, the solid establishment of JEOL in the United States hindered the sales of Cameca electron microprobes, and the U.S. market was first that of SIMS for semiconductor applications. In the twenty-first century, earth and space science research laboratories are very good customers of both the IMS 1280 and the NanoSIMS.

5.3.3. Japan

In Japan, Cameca needed to heed the excellence of companies such as Hitachi, JEOL, and Shimadzu in the field of scientific instrumentation. In fact, these companies enjoyed the national preference of their customers.

Nevertheless, Cameca succeeded in placing three SMI300s between 1970 and 1976 in Japan; that number represented 10% of overall production but only six Camebax instruments—one more than Algeria but less than India and the major markets, France, Western Europe, the U.S.S.R., and North America.

The situation changed radically in 1978 with the launching of the IMS 3F. At this time, the Japanese semiconductor industry was scoring points against the United States. A quarter of the produced IMS 3Fs were delivered to Japan. Cameca was then still a subsidiary of Thomson-CSF, the representative of which advised concluding an agreement with a big Japanese export-import firm, but finally the solution of creating a subsidiary, Cameca Japan, was decided on.

After succeeding in placing some twenty microprobes—Camebax or SX 50—Cameca gives up promoting its EPMA models in the early 1990s with the exception of shielded instruments for nuclear applications. JEOL and Shimadzu were in a price war that Cameca could not follow. It was also very difficult to ensure the same level of after-sales service.

5.3.4. Cameca Korea

Korea was a colony of Japan between 1910 and 1945, and given this painful past had few good feelings toward its powerful neighbor. From the moment that Korean industry established itself as a new force in more and more sectors, Korean decision-makers were open to any alternative to the Japanese monopoly. An IMS 4F was placed at Samsung in 1989, and this first order was followed by five SX50s between 1991 and 1994. During the same period, a single SX50 was placed in Japan. A French service engineer, Daniel Razon, settled in Seoul but was soon required to train Korean engineers for the maintenance and after-sales service. Thus, at the beginning Cameca Korea was an independent company and became a subsidiary in 2002 after the death of its chairman, D. H. Kim. PhDs were appointed as application engineers after the installation of shallow probe instruments at Samsung and an atom probe at POSTECH. Some years later, a subsidary was also created in Taiwan where many semiconductor plants would be SIMS and shallow probe customers.

6. TAKING WING (1987)

6.1. Sarfati Rule (1976–2001)

Sarfati had ruled Cameca for 25 years—more than both his predecessor ans his successor. Moreover, from 1985, when Cameca's expansion was in progress, he concentrated more power than Jacqmin, who was just an

executive of Thomson-CSF has ever had. Later, Sarfati's successor would be accountable to successive shareholders.

Sarfati did not share his power. Members of management were expected to fulfill a technical role. Only René Philippon, production manager until 1994, was allowed to stand up to him. At least fifteen people took orders directly from him. Sarfati claimed this kind of organization was, as he once called it at an annual general meeting, a "rake structure." I joined Cameca in 1989 as a project leader, and I must say that the Cameca atmosphere during Sarfati's time was not bad. As there could be only a single boss, no rivalry could arise among engineers. This situation generated camaraderie. When some tricky issue was arising that required a decision, we all prefered to search for a compromise among ouselves rather than submit to an arbitration by Sarfati. On the other hand, he kept an open mind about any new project that we proposed to him.

6.2. Projects Outside the Field of EPMA and SIMS

The history of Cameca can be read coarsely by following both threads of EPMA and SIMS. Nevertheless, it must be kept in mind that at least until 1985, these products coexisted with other minor products with shorter lifetimes and lower sales.

6.2.1. Infrared Spectrometry

In 1965–66, there was a "far-infrared" project. At this time, within the framework of his election campaign for the French Academy of Sciences, CSF CEO Maurice Ponte met Professor Lecomte, a pioneer in infrared spectrometry. This meeting resulted in Cameca undertaking a project of a far-infrared spectrometer under a patent of Armand Hadni, a student of Lecomte (Hadni, 1964). The spectrometer was marketed under the name of SI 36. This project, which seems to have involved only an engineer and a draftman, disappeared from the Cameca records after 1971.

6.2.2. Nuclear Magnetic Resonance

In 1968, Cameca's parent, CSF, was acquired by another French group, Thomson-Brandt. Cameca constituted a subsidiary of Thomson-CSF, which consisted of both the former CSF and the departments of Thomson involved in business activities similar to that of CSF (roughly, radars and radiodiffusion). Thomson-CSF then had more than 40,000 employees. A number of exotic scientific projects from the main business of Thomson-CSF were led toward Cameca: In 1973–77, it was a draft spectrometry nuclear magnetic resonance (NMR) project from a dissolved Thomson

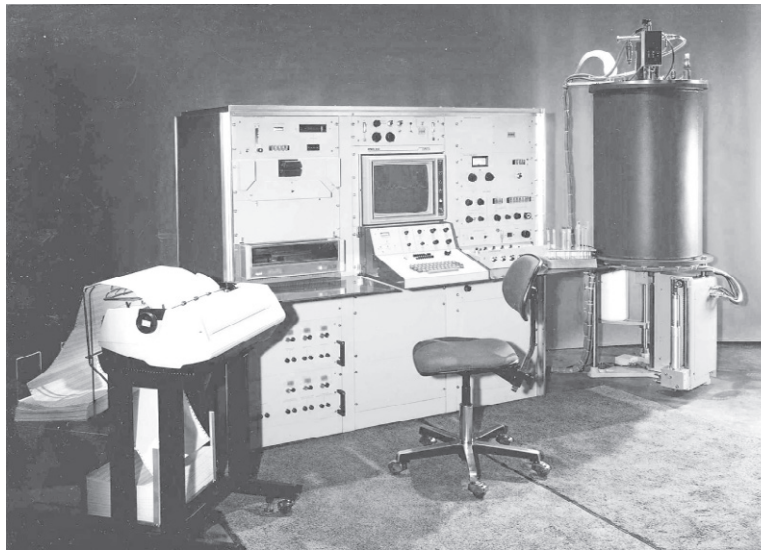


FIGURE 36 The NMR spectrometer RMN250 (1975).

unit, the Division Instrumentation Scientifique et Nucléaire (DISN). Several copies of the first model, RMN250 (Figure 36), were sold, but this project was stopped a few years after its introduction at Cameca by the lack of financial resources necessary to hope to compete succesfully with the German company Bruker.

6.2.3. Mass Spectrometry (1971–1985)

Before the merger between Thomson and CSF in 1968, CSF had developed in Saint-Égrève near Grenoble a business activity of mass spectrometry that was under the scientific direction of Jean Vastel, a co-worker of Grivet in the 1940s. This division proposed a range of instruments, including mass spectrometers for gas analysis, thermal ionization mass spectrometers (TIMS), and spark ionization mass spectrometers. Following the Thomson-CSF merger, Vastel was transferred to Chatou in the Paris area in the frame of the DISN. Finally, Vastel left Chatou in 1971 and joined Cameca, where he was involved in various activities—namely, the SMI300—as explained above. Finally, he was laid off by Sarfati in 1976.

In January 1974, twenty employees of the Mass Spectrometry Department of the DISN were transferred to Cameca, which offered several models of mass spectrometers up to 1985: the TSN 215P, a multicollector spectrometer dedicated to gas analysis for siderurgical applications, and the TSN 206S, a TIMS mass spectrometer designed by Jean-Jacques

Le Goux. This product line had been abandoned for a number of reasons: the market decline of the TSN 215P and the technical obsolescence of the TSN 206S. Le Goux eventually continued his carrer at Cameca as SIMS salesman (de Chambost, 2009, pp. 117–119).

In the early 1980s, Bernard Rasser (Figure 50) was appointed after his thesis to take charge of the project of a fully automated TIMS mass spectrometer named TMS5A. In fact, Cameca was not fully committed to facing competition with Finnigan and VG and the project was stopped in 1985. Rasser was then project leader of the SIMS product line, replacing Lepareur, who resigned for another job. As a major user of mass spectrometers of different types for his work in geochemistry, Claude Allègre was a consultant of Cameca from 1976. He pushed to abandon the Cameca TMS5A, which was not really competitive, to focus more on where Cameca offered an obvious competitive advantage: the IMS 3F.

6.2.4. Scanning Electron Microscopy

As already explained, Castaing had prejudices against scanning microscopy, which would have not been called "microscopy" in his opinion. In his defense, it must be said that the Everhart–Thornley secondary electron detector, which allowed SEM to really take off, was not developed before 1960. The launching of the Stereoscan from Cambridge Instruments was a tremendous success and SEM became very popular in the semiconductor laboratories. And in the CSF group (which merged with Thomson in 1968 and became Thomson-CSF), people were surprised that Cameca manufactured an exotic instrument, the MS46, which tackled a limited market of metallurgy while SEM seemed to be very promising.

In this situation, Cameca started a SEM project in 1967. Conty achieved the calculations for the electron column. He was also involved in the design of the secondary electron detector while Guernet designed the sample stage. The SEM was called "MEB07" (Figure 37), MEB standing for Microscope électronique à Balayage and 07 corresponding to 1970.

When the MEB07 was marketed, Cambridge Instrument was not the only player in the SEM field. The two Japanese companies, JEOL and Hitachi, and Philips flooded the world with several hundred instruments per year, achieving an economy of scale that Cameca could not afford. Only 41 instruments were eventually delivered between 1971 and 1973, which was not so bad for Cameca but trivial on the scale of the SEM market. Guernet had designed a goniometric stage with five motorized axes. After the first batch of 10 instruments, it was clear that it would be no longer be possible to sell others as long as they were simple SEMs. The MEB07 was then equipped with an X-ray spectrometer, an accessory of cathodoluminescence. The Camebax, launched in 1973, took advantage of

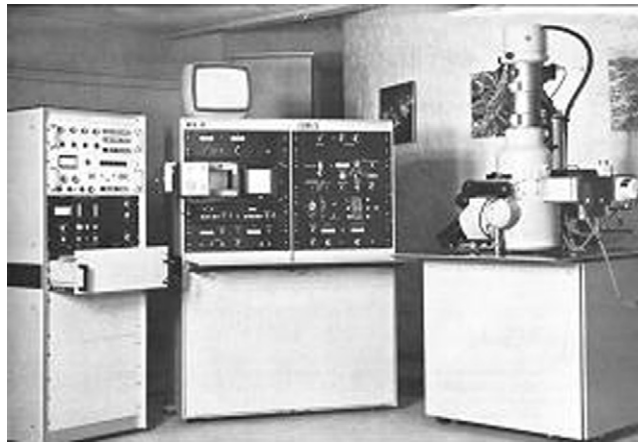


FIGURE 37 MEB07 (1971).

all the developments achieved for scanning microscopy. In the end, the MEB07 adventure would be more a step toward the Camebax than a real SEM project.

6.2.5. Microlithography

Eight kits consisting of an MEB07 column and the electronic hardware of a Camebax were delivered to the Thomson-CSF LCR (Laboratoire central de Recherches) between 1970 and 1980. They would be the base of the Masqueur électronique, later called the EPG102 (Cahen & Trotel, 1970), an e-beam vector scan lithography system designed by Jacques Trotel. These e-beam systems were the first in the world equipped with laser interferometry. The *Électrocomposeur* (Figure 38), another e-beam lithography system but of the raster scan type, based on the electronic hardware of the Camebax, was purposed for making masks of integrated circuits (Trotel, 1976). At the beginning, in 1975, it was equipped with the first lanthanum hexaboride (LaB6) electron gun developed at Cameca but was soon replaced by a conventional tungsten filament gun. This first LaB6 gun was based on the heating of an LaB6 rod by electrons accelerated from a spiral tungsten filament. It was not yet working reliably. Not until 2006 did Cameca eventually propose a reliable and efficient LaB6 gun for microprobes.

Around 1979–82, a French government plan substantially supported the development at the LCR (at Domaine de Corbeville, Orsay, 30 km from Paris) of an optical lithography machine and an e-beam one. Cameca, expected to be the manufacturer, was leading the project. The wafer stepper tackled a market far more important than that of the scientific

FIGURE 38 *Électrocomposeur* with its LaB6 gun in service in 1975 at the semiconductor factory of Saint-Égrève, near Grenoble.

instruments—the conventional business of Cameca. Cameca did not invest directly in these lithography instrument projects, employing up to 40 people at Corbeville. The overall development was funded by the Thomson-CSF group or the French government within the framework of the "Plan VLSI." Thomson eventually decided to stop production in 1982, using as a pretext the fact that the French government also supported another wafer stepper project. The extension of the factory in Courbevoie, initiated in 1981 to accommodate the new activity, was an opportunity for Cameca to develop a spacious assembly platform.

The e-beam lithography system called FEPG (Fast Electron Pattern Generator) (de Chambost et al., 1986), developed at that time at Corbeville, was based onto the principle of a rectangular variable shaped beam (see Figure 39). It did not include any standard subassembly of the Cameca electron probe except for the tungsten electron gun. Its targeted market was direct writing on wafers, a market far less important than wafer steppers, which could have been supported directly by Cameca.

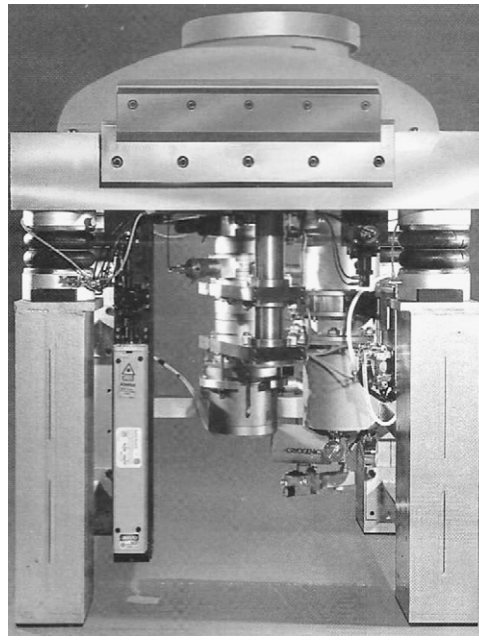


FIGURE 39 The FEPG (1981) electron column is inversed. At the first plane, one can see the interferometry laser, which controls the stage position with an accuracy of 10 nm.

FIGURE 40 SX50 (1986).

But the general strategy of Thomson in the early 1980s was refocusing rather than diversification. I was the project leader of the successor of the FEPG, developed by the LCR under the name of FEPG-HR (fast electron pattern generator–high resolution) (de Chambost et al., 1986), licensed to Cambridge Instrument in 1986 and violently critized later by (Sturrock, 2004).

In the early 1980s, the so-called SU new product line was an attempt to return to scanning microscopy with a model equipped with WDSs, but with some sacrifices in microanalysis that would have led to better performances in SEM. For the SU 30, the last lens is conic, while it is flat for the Camebax, which allows the sample holder to be tilted, a definitive requirement for SEM. Thus, the measured X-ray no longer passes through the pole pieces of the lens but through the aperture cone, taking the place of the Cassegrain objective, nonessential because the spectrometers are "inclined." Inclined WDSs are actually less sensitive to the location of the X-ray emission and therefore do not require a very precise optical microscope. The SU 30 was never clearly distanced from the basic model (then the SX50) and was dropped during the 1990s.

6.2.6. E-Beam Test

After its withdrawal from microlithography in 1983, Cameca still wanted to diversify into the semiconductor market that seemed particularly promising. At that time, the phone company was still a government monopoly, and the DAII (Department of Industrial and International Affairs) was the government agency dealing with telephony; the DAII had substantial funds and gave out juicy grants anywhere.

Electron beam testing is derived from the surface potential electron microscopy. An e-beam tester is coarsely an SEM where the detector measures the potential of the secondary electron emitting area. It produces a potential mapping of the sample surface (Ura & Fujioka, 1989).

This project, which never really had the slightest chance of commercial success, was fully funded by the French administration. Pierre Monsallut (Figure 68), a young junior engineer hired in late 1984 to develop the electronic harware, had mobilized many skills, particularly those of Rouberol and Tong. Cameca was never in the forefront of this field; the big players were first ABT, a company founded by defectors from Siemens, and from 1987 by Sentry, a subsidiary of Schlumberger, a large company with a dominant position in testing of integrated circuits. Sentry won the competition and gained most of the e-beam testing market. The plight of the SU tester also involved the evaluation of a field emission gun developed at the University of Reims, which had never been proven on a simple scanning microscope. It was not until late 1991 that Cameca abandoned the SU definitively (de Chambost, 2009, pp. 119–120).

6.3. Electron Microprobes after the Camebax

At the end of the 1970s, developments around the Camebax were ongoing. The "Microbeam," an automated Camebax, was launched in 1982. It was the first Cameca instrument that included microprocessors.

The SX50 was developed during the 1980s with the same technology as the Camebax Microbeam. It was targeted to access the accelerating voltages of 50 kV, which lent its name to the device. For this, the last magnetic lens had to be modified to avoid saturation. The study of the lens was made by Jacques Beauzamy with computer programs that Eric Munro had developed for electron beam microlithography (Munro, 1975).

Different parts of the SX50, launched in 1984, were controlled by 6809 and 68030 microprocessors, while the host computer was at first a PDP11 and later, in 1989, a SUN. A total of 169 SX50s were delivered between 1983 and 1993 and 130 SX100s between 1994 and 2008. In addition to the basic model, Cameca proposed the "SX Macro" equipped with a large sample stage. The down side of this large stage compatible with semiconductor wafers was that only inclined spectrometers could be implemented, which limited their number to three.

The SX100, the study of which started in 1987, had a new electronics system that used programmable logic devices known as *field-programmable gate arrays* (FPGAs), which can often replace an entire printed circuit board (PCB) by a single circuit. Marc Debaig was the coordinator of electronic development, and Monsallut more or less took over the responsibilities of Beauzamy, who had left Cameca. Until the end of the 1990s, the SX100 was controlled by a Unix workstation. James Phan was in charge of transferring all the programs toward a Windows workstation, which was proposed as "Peaksight" in 2001.

A shielded version of the SX100 was also available for radioactive samples; it is called the SXR (Figure 41). Six of them were delivered between 1983 and 1993 to research centers studying the aging of nuclear plants. (NOTE: The shielded MS46 had already been developed.) Each shielded SX had to be customized according to the specific needs of the customer's plant, which had its own protocol to circulate the hot samples.

Generally speaking, only a few resources were devoted to studies dealing with the improvement of the physical performance of the SX100, with the notable exception of the development in 2006 by Monsallut of an LaB6 electron gun that could replace the conventional tungsten filament gun. The first studies to develop a source LaB6 had been conducted in 1974.

6.4. Expansion Beyond Thomson-CSF

In 1981, the Thomson-CSF group was nationalized. The new chairman, Alain Gomez, decided to refocus the group on its main jobs—that is to

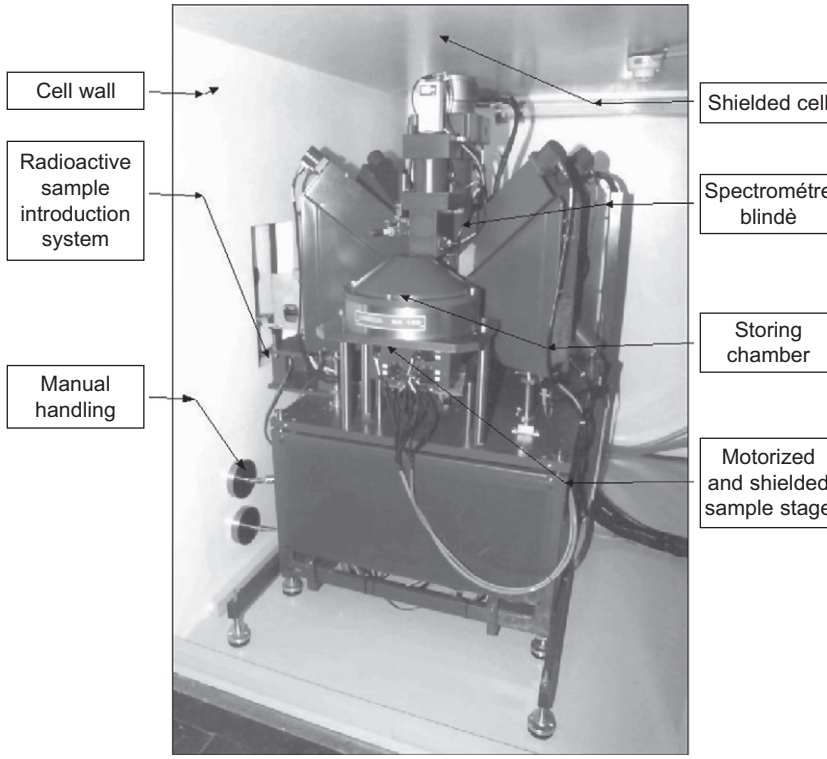


FIGURE 41 Shielded electron probe SXR dedicated for radioactive samples.

say, radar, aerospace, and navy information systems. Sarfati was given a mandate to find a buyer. He visited Cambridge Instruments but this contact did not result in any agreement. Finally, Sarfati set up a so-called leveraged management buyout (LMBO) where members of the Cameca staff became shareholders. In fact, at the begining of this move, Sarfati held 30% of the capital, other employees 30%, and banks 40%. The overall shareholders paid cash (10 million francs) and the company borrowed 35 million francs from the same banks that were shareholders, so Thomson-CSF received 45 million francs—that is, the equivalent of less than half of the turnover of Cameca. Since Sarfati was a direct employee of Thomson-CSF, he received 3 million francs that were used to pay for his shares. Cameca was independent of Thomson in 1987.

Since the 1980s were rather prosperous years for Cameca, the credit of 35 milion francs could be reimbursed without any problems over a few years. In 1996, the banks asked to withdraw. Other employee-shareholders withdrew as well. Another LMBO paid the outgoing shareholders nine times the 1987 price.

6.5. Liquidation of Riber (1989–1990)

The acquisition of Riber in 1989 represented a kind of apogee of the Sarfati era. The event took place at the time of my own arrival at Cameca. Doubtless subjective is the idea of glory that comes to mind to describe the period. What was not subjective is the workforce, which exceeded 250 workers, for the site at Courbevoie. Prestige expenditures with no direct commercial impact were then undertaken, which would never occur again in the history of Cameca.

When I say "glory," I remember a party given for staff in the lounges of the Meridien Hotel located at Porte Maillot, between the factory of Courbevoie and the Arc de Triomphe. This luxury was probably insignificant compared with that reported to me by senior members who had known the scopitone time when champagne flowed freely in the bars of Montmartre. Customers for these kinds of products were by no means followers of the Puritanism that more or less permeated the backgrounds of scientific instrumentation people. In the lounges of the Meridien Hotel, it was about creating a festive atmosphere likely to promote harmonious mixing between the Cameca people and those of Riber, which likely posed little problem for platform fitters, technicians, and engineers but could pose more among salesmen who had warred against each other on some deals.

Cameca had recovered for a symbolic franc the "scientific instrumentation" department of Riber, which was sustaining losses. The 65 people in the department settled down a bit everywhere as they could in the premises of Courbevoie. The Cameca catalog was enriched with the MIQ, a quadrupole SIMS, and the NanoScan, an Auger electron microscope. In fact, the NanoScan suffered some insurmountable handicaps compared with the competition; in particular, the energy analyzer was undoubtedly clever but its performance was less than a more conventional spherical hemisphere. As immediate steps, a squad from a computer service company was called in to achieve a software version of the same level as that of the competition. Until 1994 the NanoScan project leader Francois Horréard (Figure 50) strove to keep the project alive; Sarfati gave him the choice between dismissal and reassignment to the commercial support for Ion-TOF, which had recently made an agreement with Cameca.

As for the MIQ, it was removed from the catalog after one year. Let us first acknowledge that it was very difficult for a quadrupole to survive in this bastion of magnetic SIMS that was Cameca. Second, sooner or later the issue of modernizing the instrument arose. Was it valuable to disperse company efforts to develop a truly low-end instrument—that is to say, cheaper—with consequently lower profit margins in the highly speculative expectation of finding a new market? Cameca's answer had always been that when it was shown that a prospect is really poor—that is to say, the necessary funds could never be found for even the standard model, it

was always possible to finds a suitable solution, typically an old machine more or less refurbished.

The economic collapse of the U.S.S.R. presented the opportunity for a scheduled layoff program at Cameca and at the same time to liquidate most of the former Riber employees. Those who remained could easily upgrade in the traditional techniques and some would enjoy a great career at Cameca: Philippe Fercocq (Figure 65) was appointed production manager in 1998, and Horréard became NanoSIMS and atom probe product manager. Michel Outrequin focused passionately on the SX, supporting both sales and demonstrations. Philip Saliot succeeded Le Goux as SIMS salesman.

6.6. SIMS at Cameca after the IMS 3F

In 1986 the IMS 4F (Figure 42) followed the IMS 3F. From then on, changes to the basic model were grouped into models named IMS 4F, 5f, 6f. Some 110 IMS 4fs were delivered between 1986 and 1991.

In addition to the inevitable modernization of electronics, software, and workstations, the evolution of the so-called IMSxf consisted of a slow convergence toward what the instrument should have been if all the implemented concepts were integrated. The introduction of the normal incidence electron gun (NEG) deviated from this pattern. Developed by Slodzian on his SMI 300 for compensating the electric charges on insulating samples, it appeared to be a clearly superior solution to the previously used oblique incidence electron gun. A huge "retrofit" operation was initiated. Christian Le Pipec traveled the world to install it on already delivered instruments.

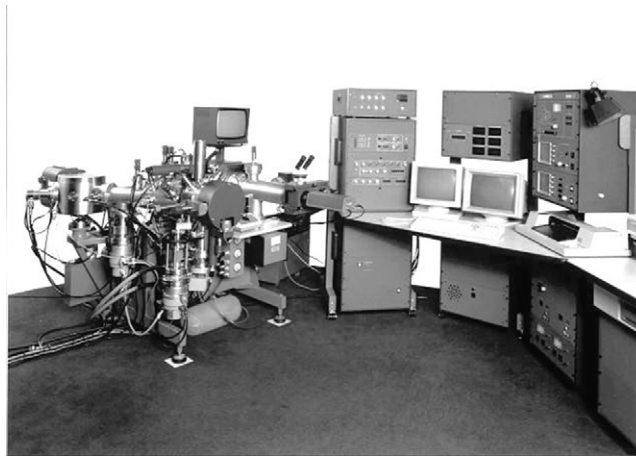


FIGURE 42 IMS 4F (1985). The monitor dedicated to the direct ionic image can be seen above the magnet.

The sintered cesium source manufactured by General Ionex was replaced by a microsource designed by the ONERA team who was developing what would be called the NanoSIMS. Again, Le Pipec adapted the new source to the IMS and improved it gradually from 1986 to 2008.

The IMS 4F was controlled by a Motorola 68030 microprocessor, which replaced the general purpose interface bus (GPIB) of the IMS 3F. The calculator was a PDP11 from 1986. The ionic image obtained with the microscope mode could be observed at the end of the instrument with a binocular microscope, but it could also be transferred onto a TV monitor. In addition to the NEG and the cesium microsource, another new accessory of the IMS 4F was the so-called dynamic transfer, which insured the capability of scanning an ion image. The "dynamic transfer" consists actually of an electrostatic deflector synchronized with the primary deflection plates located on the secondary axis to straighten the ion beam along the axis, which allowed achieving scanned images on a wide imaged field.

In 1985, Michel Lepareur was replaced by Bernard Rasser as the IMS project leader. Rasser was a physicist PhD while Lepareur's background was as an electrical engineer. His PhD thesis on ion sources and the design of the TMS5A made him the right man for his new job. At this time, the IMS product leader was Henri-Migeon, a chemistry PhD, assisted by Michel Schuhmacher (Figure 50) from 1987 for the application lab. Both Migeon and Schuhmacher, who has just finished a thesis on material science, had been users of Cameca SIMS instruments before joining Cameca.

Until 1987, the competition was not perceived as a serious threat: Cameca had a monopoly in the field of magnetic SIMS, beside which the quadrupole SIMS proposed by the German company Atomika looked like a poor relation. As for time-of flight (TOF)-SIMS, three players, including the start-up Ion-TOF created in Münster, Germany, by Professor Benninghoven and his student Ewald Niehus, and the Californian company PHI, had to share a market of a few units per year. However, Cameca was concerned by a slowdown in the market for semiconductors and was planning studies to diversify the applications toward geology, material sciences. and quantitative analysis (de Chambost, 2009, pp. 129–131).

The post-ionization is a sea serpent of SIMS: As a result of the primary ion striking, although the primary ions are chemically reactive, the bulk of the sample material is sputtered in the form of electrically neutral atoms, which would therefore be undetected. Achieving ionization of these neutral secondary atoms is highly desirable. Several joint projects, more or less supported by European subsidies, were undertaken for various kinds of post-ionization, namely with IMEC for resonant laser post-ionization (De Bisschop et al., 1990).

Implementing a liquid metal ion source (LMIS) for achieving very fine primary probes was also considered at this time. There was also a so-called COSTOF project that involved both primary probe scanning

and secondary ion TOF, which was targeted to compete with the low-cost quadrupole SIMS. Besides these exotic projects, there was continuous improvement of the secondary vacuum beyond the 10^{-10} torr range directed at reducing the detection limit of oxygen and hydrogen.

The IMS 3F was already present in the best laboratories in geochemistry, including the Gerald J. Wasserburg lab at Caltech (Navon et al., 1988), famous for analyzing the first lunar samples, but also the lab of his rival, Claude Allègre (Luck & Allègre, 1983), Paris-Jussieu, who in 1986 won the Crafoord Medal for iotope geology along with Wasserburg. But at this time, Wasserburg was furious that Cameca has served Caltech before Jussieu. Near Boston, a former student of Allègre, Nobu Shimizu, distinguished himself by publishing the first isotope ratios obtained by exploiting the high mass resolution of the IMS 3F (Shimizu, 1981). In CRPG Nancy, France, Pierre Albarède, another student of Allègre and a customer of Cameca for thermal mass spectrometers, also acquired an IMS 3F (Chaussidon et al., 1987). At Washington University in St. Louis, Ernst Zinner oversaw around his IMS 3F a series of PhD students (Zinner et al., 1983) who would be, for life, so many Cameca loyal supporters. For reinforcing this market of geology, Cameca included in its R&D program the improvement of the transmission and precision of the IMS 4F.

Claude Allègre, future Minister of National Education and Research, was a consultant to Cameca from 1975 until the mid-1990s. He encouraged Cameca to develop the IMS 3F and to withdraw from thermal mass spectrometry, but its availability for Cameca has been virtually nil since 1988 (de Chambost, 2009, p. 131).

7. PREDOMINANCE OF SIMS (1990–2000)

7.1. The IMS-5-6-7F (1990–2009)

All the SIMS development projects planned in 1987 gradually disintegrated as a result of two decisions made by Sarfati: The first was that of starting a project for a large-radius SIMS called the IMS 1270 and announced at the SIMS conference of 1989. The other decision was made in response to the threat of the British company Vacuum Generators (VG) that attacked Cameca in the magnetic SIMS field by proposing an entirely "computer controlled" model based onto a SUN workstation, much more modern than Cameca's PDP11, which was probably well suited to the real time tasks but already outmoded. The priority for improving the IMS 4F was placed on the computer control (i.e., the replacement of all the knobs by analog-to-digital [AD] converters). Note that since the very beginning of the IMS 3F equipped with the HP9815, analyses were processed automatically by the computer or later by the microprocessor, but until 1990,

all the ion optical devices had to be adjusted manually with potentiometers so that every time the analysis purpose required modification of the primary ion source, the secondary polarity, or the primary probe size, the operator had to re-tune the instrument. The IMS 4F with knobs replaced by AD converters was named the IMS 5f. A dedicated keyboard designed by Migeon and Marc Debaig was also developed for user-friendly tuning of the instrument: thumbwheels that could be assigned to every ion optics function. In 1992 and 1993, 18 IMS 5fs were delivered (de Chambost, 2009, pp. 132–133).

By 1985, CEA (the Drew Evans company), a big customer of IMS3Fs and IMS4Fs, had developed a Windows workstation and proposed licensing to Cameca, who turned down the offer. Thus Cameca and CEA had become partially competing, since many American customers of the semiconductor industry ordered an IMS 4F requiring it to be equipped with a CEA workstation. The Cameca electronics engineers had originally been tasked to make it technically impossible to connect the CEA workstation to the IMS 4F, but to counter VG, Sarfati decided to ally with Evans and asked his engineers to communicate to software developers of CEA the firmware that allowed a computer to control the electronic hardware.

Meanwhile, the Cameca software engineers were developing a SUN worstation under Unix, and only when the software was completed and tested in 1993 did Sarfati break the alliance with Evans and asks again his engineers to make the CEA-IMS connection impossible. Evans was no longer an ally, but in the short term, he could not be a competitor. VG, which had placed only two instruments, abandoned the magnetic SIMS, but the VG project was more or less transferred to another British company, Kratos, which developed another magnetic SIMS in cooperation with the University of Warwick and strong support of the government.

The IMS 6f (Figure 43) came out in 1994. While the IMS 4F was only a IMS 5F with the knobs replaced by converters, changes in the IMS 6f ran much deeper. The most obvious was the laminated magnet, which allowed faster switching than the IMS 4F. Moreover, the so-called Rogowski magnet shape also allowed proper processing of the heavy ions accelerated to 10 kV. The sample chamber was also updated with a new airlock transfer rod.

All the IMS hardware electronics were renovated under Debaig's supervision. The IMS5F's reputation for reliability was not very good. That of the IMS 6f was much better. About one hundred IMS 6fs were delivered between 1994 and 2003. Bernard Rasser was in charge of the physical evolution of the IMS 6f until that date. He developed accessories to allow better performance for depth profiles: first, an accel-decel system associated with the duoplasmatron to lower the impact energy up to 500-eV primary ions (Schuhmacher et al., 2000). In this case, the duoplasmatron plasma was polarized at 1100 V, the primary ions were accelerated

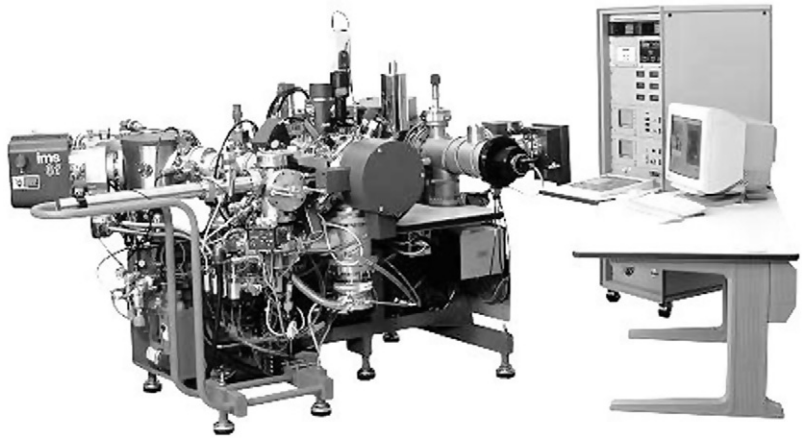


FIGURE 43 IMS 6f (1994). Compared with the IMS 4F, note the laminated magnet and the suppression of the monitor since all the IMS 6f images are displayed in a SUN workstation windows.

to several kilovolts, and then they were decelerated and traveled in the primary column at 1100 eV. The sample had to be biased at 600 V to obtain an impact energy of 500 eV. A post-acceleration system was then required at the detection stage because at 600 eV, the ion-to-electron yield of the first dynode is insufficient. The primary ion's low impact energy is needed to obtain good depth resolution. The sample rotating stage was another accessory designed to reduce roughness growth on metal samples during the depth profile analysis.

The IMS 7f (Figure 44), launched in 2004, was an old project that had been put on ice in 1996 to make way for some urgent improvements in the IMS 6f and the IMS Wf. The new generation of electronic boards developed for the successor of the IMS 6f (supposed to be named IMS 7f) was diverted to the IMS Wf while the IMS 6f kept the same electronic hardware until 2003.

In 2003, aside from the modernization of electronic components, the IMS 7f had no actual novelty with respect to the IMS 6f except an image definition of 1024 × 1024 pixels, instead of 256 × 256. Later some physical improvements were made regarding the measurement of the primary ion current by sampling mode, the secondary transmission with an additional hexapole, and the automation of all the mechanical stops and apertures that were not achieved with the IMS 6f. The commitment of major semiconductor manufacturers to the "Copy Exactly" principle, according to which an instrument installed in one plant must be absolutely identical to that delivered in another plant, also prolonged the life of the IMS 6f and delayed the marketing of the IMS 7f. From 2006, a PC running under

FIGURE 44 The IMS 7f (2003).

Windows replaced the SUN under Unix; 45 IMS 7fs were delivered from August 2004 to September 2009.

7.2. The Large-Radius SIMS: The IMS 1270–1280 (1992–2009)

I joined Cameca in 1989 and left the company in 2010; during this period, a large part of my time was devoted to the IMS 1270 and its successors, the IMS 1280 and IMS 1280-HR.

In 1987, Cameca was concerned about the cyclical nature of the semiconductor market and wanted to become more diversified in the field of geological applications. After a tour of U.S. geology labs, Migeon returned with the conviction that there was a small market for an instrument similar to the "Shrimp," developed in the 1970s in Canberra, Australia (Clement et al., 1977), in the wake of Liebl, but with an electrostatic sector and a magnet with a very large radius.

Since its invention by Aston in 1920, the mass spectrometer had been a powerful tool in geochemistry labs, well-suited for measuring the chemical or the isotopic abundances of geological material (Allègre et al., 1974). Whenever a sample cannot be assumed to be homogeneous, a localized analysis is relevant, and the ion microprobe was the right tool for the job. This was the case for uranium-lead analysis used for dating zircons; the lead/uranium ratio can determine the date of the last melting of the rock and this information is extremely interesting in developing a history of how a mountain has been formed, but the issue is the very low level of the detected ion signal, which is so low for two reasons. First, the abundance of lead is in the range of parts per million only. The second reason is that since almost all the elements in the Mendeleev periodic table can be found in micron amounts in a geological sample, that generates spurious peaks or "interferences" very close to the element being measured. In Figure 45, the ^{206}Pb peak is very close to hafnium-silicon (HfSi) interference. Both

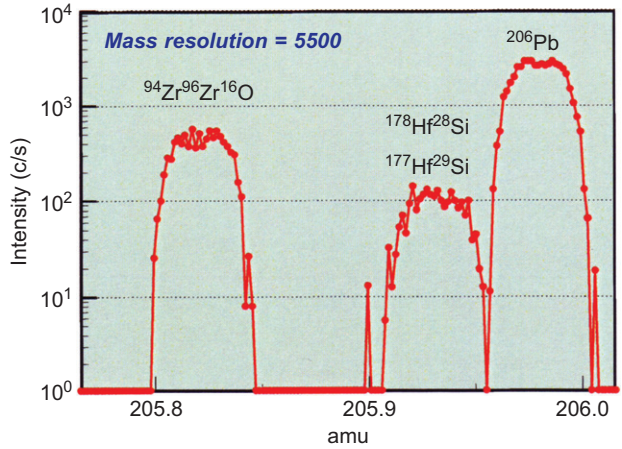


FIGURE 45 ^{206}Pb peak separation with an IMS 1270.

a very fine image of the entrance slit and a fairly close exit slit allow the ^{206}Pb peak to be separated from the HfSi peak. A high transmission of the spectrometer is required to keep the ^{206}Pb signal level high enough. Conversely, designing a physically large mass analyzer allows the instrument to be operated with wide slits and therefore pass more of the ion beam while maintaining a high mass resolution (Ireland, 1995).

In the first approach, the magnet radius must be large, but the different aberrations of the mass spectrometer also must be reduced dramatically. In order to meet this specification, the Australian team implemented the Matsuda design (Matsuda, 1974), ensuring cancellation of all the second-order aberrations.

The Shrimp laboratory in Canberra welcomed many foreign visitors who brought their zircons to be analyzed, and Cameca customers, familiar with the IMS 3F, believed that Cameca could manufacture a similar instrument. In 1989, the marketing people at Cameca found a codename, the IMS 1270, and produced a flyer revealing an artistic view of the future instrument. But in fact, the Cameca draftsmen had not drawn a single line and Rasser was completely engrossed by the miscellaneous improvements of the IMS 4F, then the cash cow of Cameca.

I joined Cameca in September 1989 and took charge of the IMS 1270 project. Sarfati fixed my roadmap: Complete the design and fabrication of the first instrument as quickly as possible; the cost did not matter any.

It was a chance for me to have a project for an actually existing market. My experience in electron beams was obviously an asset, but I also had the chance to be initiated by Rasser to the SIMS instrumentation, which was completely new for me. Bernard has already coded the ESA and magnet models as they were described by Enge (1967) and Wollnick (1967).

In principle, the IMS 1270 project was the highest priority for Cameca. Manpower resources were really unlimited for mechanics, but such was not exactly the case in electronics and regarding the software, there was a shortage of programmers; this shortage would remain an issue until 1993. Firmino Fernandes was already involved in the project. The earth and space laboratory of UCLA, headed by Mark Harrison, acquired the funding needed to purchase an instrument in the spring of 1990 and they placed an order in July. The lab had hired Kevin McKeegan, who was trained on the IMS 3F when he was a PhD student under Ernst Zinner at Washington University in St. Louis. Delivery was promised by 1991, a deadline impossible to meet. It was shipped at the end of 1992, which was not so bad. A multicollector was also scheduled for delivery one year after the IMS 1270 was delivered. UCLA eventually received its multicollector in 1997.

The codename of IMS 1270 stands for $1270 = 127 \times 10$,;127 mm was the supposed radius of the ion path within the IMS 4F magnet. In fact, the IMS 4F radius was not 127 mm but 117 mm, and the radius of the new instrument would be $117 \times 5 = 585$ mm, but the name of the IMS 1270, which sounded well, was not changed. In July 1990, when the order was passed, my calculations were far from completed, but I could give the main dimensions to the mechanical engineer, Daniel Colliaux, based on these radii of 585 mm. The big issue was reducing the second-order aberrations as much as possible while still retaining the capability of ion microscopy, absolutely mandatory from the point of view of the fans of Cameca.

A series of planar lenses, circular lenses, and hexapoles are inserted between the ESA and the magnet. The idea is to process separately the ion beam in, respectively, the radial and the transverse planes (de Chambost et al., 1991). When the machine was shipped at the end of 1992, the implementation of this concept did not work yet (de Chambost et al., 1993). I would understand the reason only with the help of a three-dimensional (3D) program of simulation, CPO3D, authored by Franck Read and Nick Bowring; I met them at a workshop in Delft in February 1994 (Read & Bowring, 1994).

Figure 46 shows that the double-focusing spectrometer of the IMS 1270 works coarsely in the radial plane with the same scheme as the IMS 4F. Its novelty consists of processing the beam separately in the transverse plane. By means of the correctly located hexapoles, it is possible to cancel the second-order aberrations X/AA and X/BB.

Transmission specifications had been expressed in counts per second per nanoamperes of primary ion current and parts per million of lead in zircons. Cameca had to demonstrate at least 5 cps/nA/ppm with the IMS 1270 (i.e., as much as the Shrimp was claiming). When Kevin McKeegan came to Cameca in November 1992 for the factory acceptance test, this

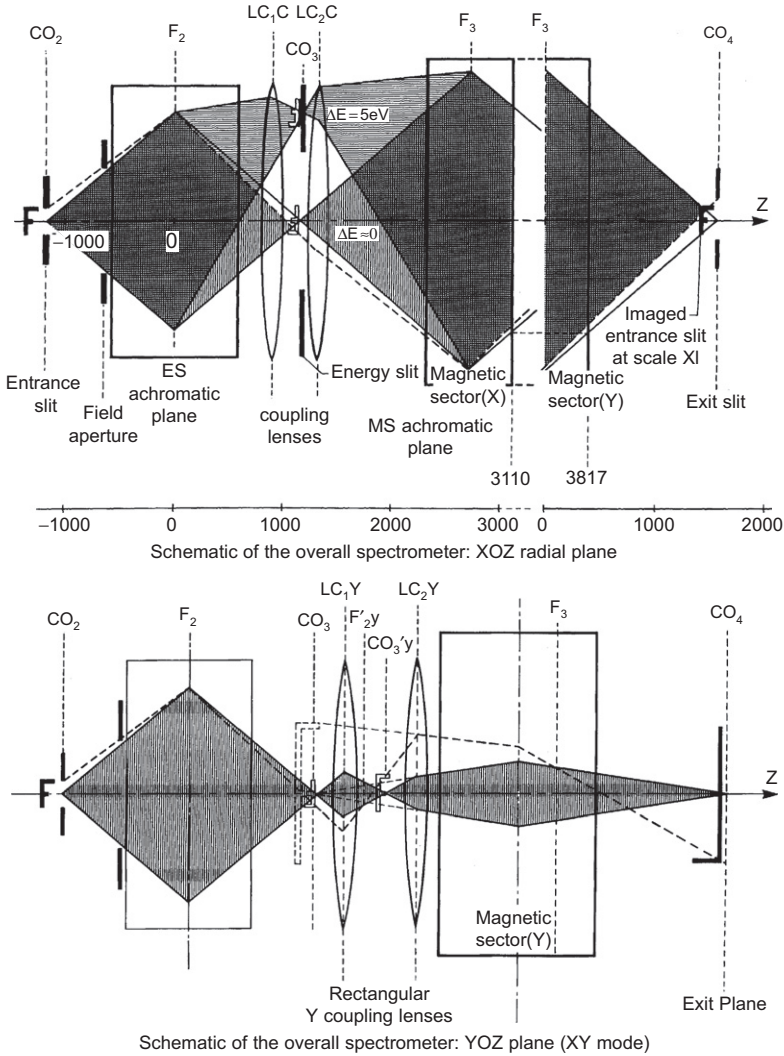


FIGURE 46 The IMS 1270 Spectrometer (a) is the radial plane and (b) the transverse plane.

performance was not easily met since the so-called XY mode involving a different ion optics sketch in the radial and the transverse planes did not work for reasons not yet understood. The night before Kevin's departure, with the strength of despair, I achieved more than 5 cps/nA/ppm. I had yet to find Kevin, who lived in the studio that Cameca kept in the building next door. He had gone to buy gifts for his family and was not back yet. I left a note on the door. When Kevin was back and read the note, he had

to call me from a public phone so I could open the main door at Cameca. At midnight, the 5 cps/nA/ppm were still there. Kevin called Mark Harrison, who dictated a testing protocol: to analyze another zircon and to confirm with oxygen flooding and without flooding. We left Cameca at two o'clock in the morning. The next day, Kevin could fly back home and testify he had seen the 5 cps/nA/ppm.

In 1994, the 3D simulation showed that the LC1Y lens, supposed to be active only in the transverse plane, also has an effect in the radial plane, making it impossible to achieve the energy focusing. With a small modification on this planar electrostatic lens, from 1995, the XY mode routinely provided a high transmission. Nevertheless, analytical data good enough to date zircons correctly are obtained as soon as the end of 1992 (Schuhmacher et al., 1993).

From 1993 to 1998, there would be many upgrades at the UCLA IMS1270: First, at the end of the installation, the PDP 11 was replaced by a SUN. In 1994, the magnet was machined in the Los Angeles area to enlarge the gap and therefore the field of view of the ionic image. In 1995, the LC1Y lens was modified. In 1996, a new software running under Labview was installed, and finally, the multicollector was mounted in 1997 (Figure 47).

In addition to the high transmission required for trace element applications such as zircon analysis, geochemists were demanding high reproducibility for the stable isotope analyses. Stable isotope studies are based on the physicochemical isotopic mass fractionation of the relatively light elements (H, C, O, and S) and are used as indicators of the mechanisms of mineral formation (Ireland, 1995, p. 82).

François Hillion, who had been appointed by Cameca to strengthen the ONERA team working on a joint project of a SIMS instrument based

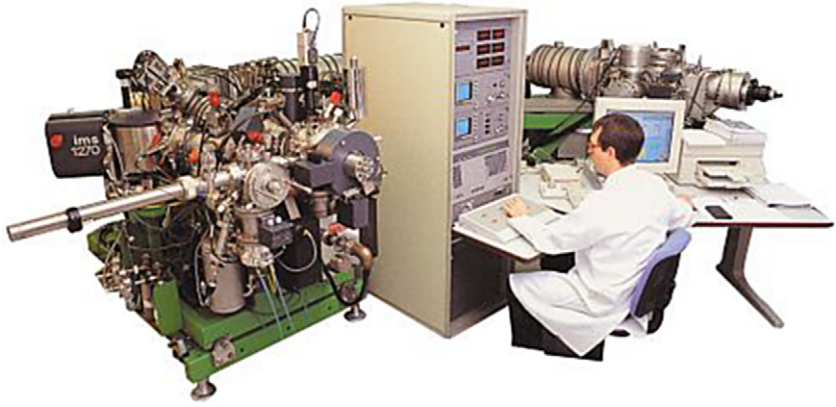


FIGURE 47 An IMS 1270 installed at Nancy CRPG.

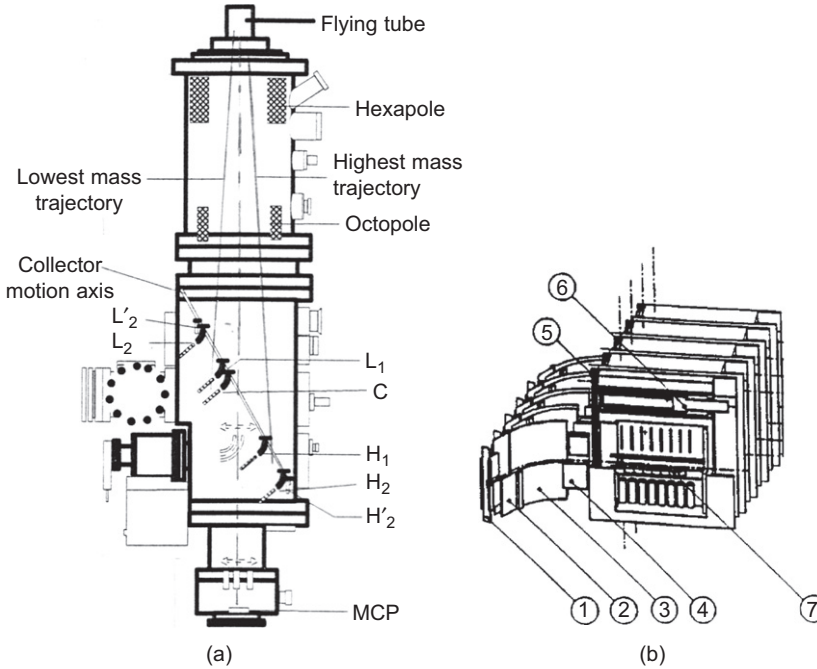


FIGURE 48 The IMS 1270 multicollector. Trolleys carrying a collector set move along a tilted mass focusing plane (a). In (b), the detector is an electron multiplier (7) mounted in a box (6). The overall collector consists also of an entrance slit (1), a deflector (2), and a curved electrostatic sector (3).

onto a Mattauch–Herzog spectrometer equipped with a multicollector, was asked to design the IMS 1270 multicollector. Every movable collector can be equipped either with a Faraday cup or a miniaturized electron multiplier developed especially by Hamamatsu (Figure 48). A very clever arrangement based on small electrostatic sectors made it possible to bring as close as 5.5 mm in the perpendicular plane two neighboring collectors with 13-mm thickness (Hillion & Colliaux, 1992). The IMS 1270 multicollector achieved simultaneous measurement with a $\pm 1/13$ maximum dynamic—that is, far more limited than the dynamic obtained with a Mattauch–Herzog magnet but well suited to isotopic measurements.

For the measurement with Faraday cups, there was an agreement with the German company Finnigan Mat to adapt to the IMS 1270 the thermostated electrometer chamber they developed for inductively coupled plasma mass spectroscopy (ICPMS) and thermal mass spectrometers. The required precision for each channel was 2×10^{-16} A. The same chamber would later be mounted on the NanoSIMS until 2005, and then Cameca would develop its own chamber.

When measuring stable isotope ratios in the Faraday mode, the targeted reproducibility was of a few 10^{-4} but such reproducibility was very difficult to obtain in real conditions whenever the analyzed grains were spread on the sample holder over an area as large as 16 mm × 16 mm. In 2002, Michel Schuhmacher, the IMS 1270 product manager, and Firmino Fernandes, in charge of developing the software under Labview, would spend days and nights in Edinburgh with John Craven (of the University of Edinburgh) working on the correct analysis "recipe" and meeting very difficult reproducibility specifications. Aided by the whisky copiously served by Craven, they finally succeeded and later the same reproducibility would be obtained routinely (Schuhmacher et al., 2003). Subsequently, Fernandes improved the magnetic field supply of the magnet by doubling the Hall effect control with an NMR control, which allowed chaining the analyses in the multicollection mode for tens of hours.

When the IMS 1270 project was launched in 1990, nobody at Cameca imagined that the main competitor would be the Shrimp. The Australian team was perceived as basically academic and therefore unable to offer proper customer service for installation and maintenance. The true competitor was considered the British company VG, which proposed a large-radius SIMS, the so-called ISOLAB, at the same time they proposed also another model to compete with the IMS 4F.

In fact, the VG balloon deflated rapidly, while the Australians succeeded in establishing a small industrial and commercial unit, ANUTECH (later Australian Scientific Instruments [ASI]), which over the years continued to win a number of affairs against Cameca, with an advantage whenever the customer was only interested in zircon analysis. The Shrimp, in addition to the instrument, offered both the expertise and an academic partnership with which Cameca had trouble competing.

The good results with the Edinburgh IMS 1270 led to complete modernization of the instrument, endowing it with electronics of the same generation as that of the IMS Wf or IMS 7f. The renovated instrument was named the IMS 1280 (Figure 49). The first client was the University of Wisconsin, which had recruited Noriko Kita, a former operator of the Japanese Tsukuba IMS 1270, to be responsible for the new IMS 1280. She would achieve dramatic results in terms of reproducibility (Kita et al., 2011).

In 2000, Albert Fahey, the owner of the IMS 1270 installed at the National Institute of Standards and Technology (NIST) in Washington, DC, demonstrated that his instrument was quite suitable to so-called nuclear forensics applications (i.e., dust samples from nuclear handling facilities in the search for non-declared nuclear activities). From 2003, five IMS 1280s were delivered to this unexpected market.

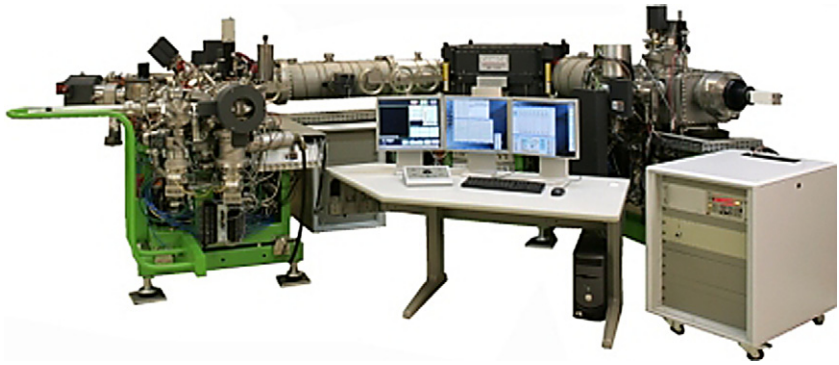


FIGURE 49 The IMS 1280 (2003).

FIGURE 50 Cameca personnel at Cape Carnaveral in 1998. This photograph was taken after a SIMS conference held in Orlando. From left to right: François Horréard, Max Sarfati, Michel Schuhmacher, Claude Conty, Georges Slodzian, Bernard Rasser, and Fabrice Le Duigou.

7.3. The Hesitations of 1994–1995

On September 23, 1994, Sarfati sent to a dozen people considered the leading core of the company a six-page memorandum dealing with some main strategic issues:

In 1994, Riber products had been given up for good and the diversification projects based on the SU were also stopped, but the SU was still

proposed in the Cameca catalog as an electron probe intermediary model between scanning microscopy and microanalysis; release of an updated version was expected in 1995. Cameca had therefore refocused on its two historical techniques, SIMS and EPMA, represented by two basic models, the IMS6f and SX50. In addition to this refocusing on core activities, there was a desire to extend as much as possible the field of SIMS. Thus, in addition to the IMS6f, Cameca offered a large-radius version, the IMS 1270. As for the NanoSIMS, the name of which had just been found, it was not yet offered in the catalog and was still confined to the ONERA laboratory. The IMS 1270 was the biggest project in the early 1990s. In 1994, the TOF SIMS attracted the interest of Sarfati since it was apparent that its market was taking off. Cameca had acquired a 25.1% stake of the German start-up founded by Alfred Benninghoven, professor at the University of Münster, and his former student, Ewald Niehus. Sarfati planned to assume full control of Ion-TOF but, of course, Benninghoven and Niehus were opposed to this plan. They had approached Cameca to benefit from its commercial network, but they fully intended to remain independent. The alliance between Cameca and Ion-TOF was finally beneficial to both sides as it allowed Ion-TOF to surpass its competitor, PHI, and Cameca to earn substantial commercial commissions, but as there was still complete trust between Courbevoie and Münster, both companies agree to "divorce" amicably in 2000.

In his memo, Sarfati noted that the R&D resources exceeded the needs of the program defined in the previous years, but he established the principle that R&D expenses should not be reduced. However, that did not prevent him from being irritated by the extension of what he called the "software cancer" that required ever-increasing resources. In the period from 1990 to 1996, the trend was still toward downsizing the mechanical engineering department. For projects such as the IMS 1270 and the shielded IMS 6f, thousands of hours of drawing were outsourced.

Sarfati made a rather pessimistic observation about the SX market: With the Japanese at the same technical level as Cameca, the cost savings achieved through advances in electronics and relocation would be absorbed by the reduction of the profit margin resulting from the competitive situation. All would be well, Sarfati noted, as long as SIMS allowed the company to survive, but if the SIMS was experiencing difficulties, how would the electron microprobe be kept alive? "What is to be done? Withdraw from EPMA? Unthinkable in our culture. . .," Sarfati concluded.

In fact, resources allocated to SX development had been reduced since 1990 with the dismissal of a number of people who were specifically assigned to the SX, particularly Boissel in 1990 and Tong a few years later. The idea of adapting a field effect source (FEG) was in mind—"Shall

we go?" Sarfati asked. In February 1995, contacts were made with Peter Sudraud, who had just left the University of Orsay and founded Orsay-Physics. But eventually, relations between Sarfati and Orsay-Physics became strained after a contract on a liquid cesium source for SIMS did not yield the expected results.

As for IMS, Cameca had just gotten rid of two British challengers, VG and Kratos, who wanted to participate in this lucrative niche market—the magnetic SIMS. They launched instruments very close to the IMS 4F or the IMS 5f. Fortunately for Cameca, they did not completely solve several minor problems that were precisely the skill of Cameca for 25 years. Both had not gone beyond the sale of a first instrument to a beta partner and they had to throw in the towel. The Kratos project, more or less the heir of the VG project, had received strong support from the British government through a collaboration with Mark Dowsett, professor at the University of Warwick. Dowsett was involved in all projects in competition with Cameca in the same way as Helmut Liebl had been 25 years earlier. In 1994, rumors were circulating that CEA (Drew Evans' company), was developing a magnetic SIMS with a radius of 30 cm—that is to say, intermediate between the IMS 6f and the IMS 1270. This project was not developed, but on the SIMS front, the threat came one year later from the quadrupole SIMS and from Mark Dowsett; the CEA instrument featured in-depth resolutions much better than the Cameca magnetic SIMS. One year later, this threat would be the starting point of the IMS Wf project.

The takeoff of the IMS 1270 rocket was successful enough to justify several orders, especially from Japan, but the success was not complete since Cameca had to share the market with the Australian Shrimp. They had just won an order from Stanford University, proposing the Shrimp-RG, a new model especially designed for very high mass resolution. This led Cameca to initiate studies to improve the transmission of the IMS 1270 at very high mass resolution (>20000). These studies were discontinued in 1995 when it was proved that progress on the Shrimp-RG project was seriously stuck and that geologists did not confirm their interest in applications requiring very high mass resolution mass. After the delivery of the first multicollector in 1996, the studies around the IMS 1270 paused for a few years.

8. STAR DUSTS AND FAB DUSTS (2000)

8.1. The NanoSIMS (2000–2009)

In 1980, an ion probe project based on the twin principles of the collinear objective lens and the Mattauch–Herzog magnet was started at ONERA

under the leadership of Slodzian. At that time, the name "NanoSIMS" had not yet been assigned. It would be given when Cameca was involved more deeply in the project, in the 1990s.

In the late 1950s, Castaing and Slodzian had realized that the technique they had developed as an ion microscope was perceived by others as a particular form of mass spectrometry. The ion microscope could be considered an ion analyzer that could be improved by using the mass spectrometry toolbox. In particular, the spectrometer proposed in 1934 by Mattauch and Herzog had quite interesting properties—namely, that of producing at the magnet exit plane a large part of the mass spectrum, much broader than with an IMSxF or an IMS 1270/1280. As far as the ion microscope capability could be given up, the Mattauch–Herzog spectrometer was better suited to the SIMS. Slodzian knew that even better since he had worked in the early 1970s for a project targeted to adapt to SIMS: the Mattauch–Herzog spectrometer manufactured by AEI for thermal mass spectrometers (Slodzian, 2008). The Mattauch–Herzog sketch shown in Figure 52 corresponds to the second prototype designed from 1990 and named NanoSIMS in 1994. The Mattauch–Herzog spectrometer, which also included an ESA for energy spread compensation, allowed simultaneous measurements of different masses within a range of 1 to 20.

The other basic idea of the project was to minimize the working distance of the primary column last lens. This reduced the aberrations of the lens and produced a finer primary spot. In a spot. In a SIMS instrument such as the IMS 3F, secondary immersion lens interfere with each other (Figure 51a), but nothing precludes the same set of electrodes from being both a primary last lens lens and a secondary extraction lens. (Liebl, 1974) developed this idea in 1974 without ever producing experimental results. The design of a coaxial lens (Figure 51b) was not really an issue, but the separation of both the primary and secondary beams, which must be achieved somewhere, was terribly difficult. The complexity of the problems to be resolved explains why the ONERA team took almost a decade before presenting scanned ion images demonstrating the validity of the principles of the project. Waiting ten years for results would not have been acceptable in a small company of 200 people who must necessarily prune the long-term projects in the lean periods when survival is the only objective.

In 1980, Castaing was at the head of ONERA and he heavily supported the project. A small team consisting of a talented engineer, Bernard Daigne, and a mathematician, Francois Girard, was put at the disposal of Slodzian, but Daigne was not fully available for the project. In 1987, Slodzian felt that the project was bogged down and he sought the help of Sarfati, who within the next twenty-four hours provided assistance in the form of an additional engineer. Thus, François Hillion (Figure 54) was recruited. For Cameca, it was a long-term investment that would

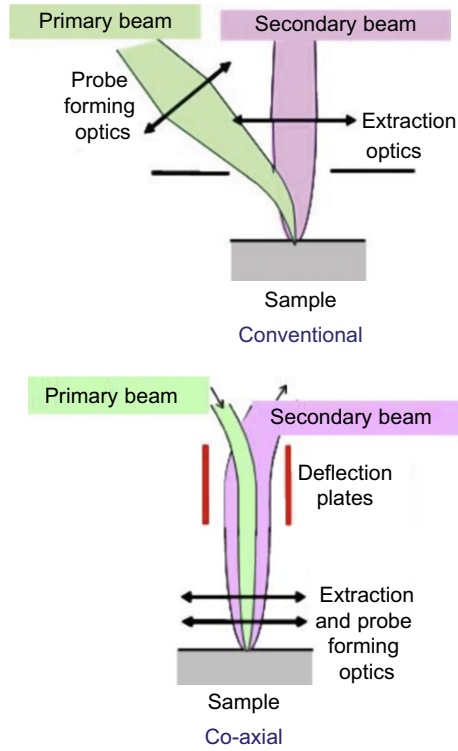


FIGURE 51 The NanoSIMS coaxial lens. (a) Sketch of the sample region with the primary last lens and the secondary extraction in the IMSxf case. (b) Sketch of the sample region with the coaxial lens in theNanoSIMS case.

not be fruitfult until the first order in 2000, but it actually was a particularly profitable investment because from that date, the catalog of Cameca was enriched with an instrument with no direct competitor in the world. In 1987, Slodzian was not yet engaged in any contractual relationship with ONERA. Gradually, Hillion became the key man for the NanoSIMS. In 2010, he was still the technical lead. Until 1996, Francois Girard was assigned full time to the project and achieved models of each part of the machine by developing his own codes in HP-BASIC. In January 1997, the new protopype in development by Hillion since 1990 finally left ONERA.

In 1989, a scanned ionic image was finally obtained with the first prototype (Figure 53) with a spatial resolution at least four times better than the IMS4F. The principles of this instrument had been published at the SIMS-VI conference in 1987 (Slodzian et al., 1987). With the codename MIB-IV, a new design was launched in 1990 within the framework of a partnership involving ONERA, Cameca, and ANVAR, a French government agency. All the principles considered in 1980 were retained, but all the parts except

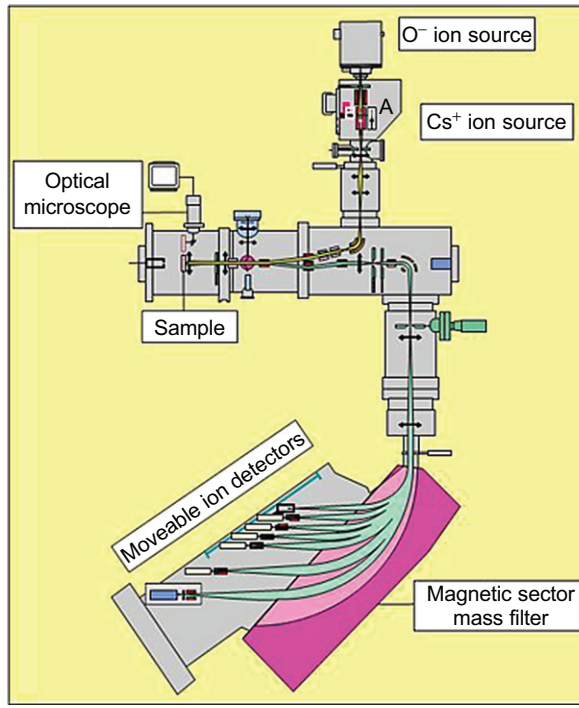


FIGURE 52 The NanoSIMS Mattauch–Herzog spectrometer.

the magnet were redesigned. In 1994, the first image (Figure 55) of the new prototype was obtained and the instrument was given NanoSIMS as its commercial name (Hillion et al., 1993, 1995).

At the end of 1996, the ONERA team was dispersed. The new prototype was moved to Cameca in 1998 and moved again in 1999 to Boston, at the Harvard Laboratory of Claude Lechêne, who expected to make the instrument attractive for biological applications.

The market targeted first by the NanoSIMS was cellular biology and isotope tracing, but early customers were actually not biologists but cosmochemists, as it turned out that the NanoSIMS (Figure 56) was perfectly suited to the analysis of submicron cosmic dust: The fine primary probe of the NanoSIMS could be directed exactly onto the grain. On the other hand, the multicollection concept allowed saving sample material that is rare. The first commercial instrument was delivered in 2000 to Washington University in St. Louis to the laboratory headed by Bob Walker in which Ernst Zinner had trained many students to use the IMS 3F for geological applications. François Horréard, who was charged by Sarfati to promote the TOF-SIMS around the world, was shifted to promoting

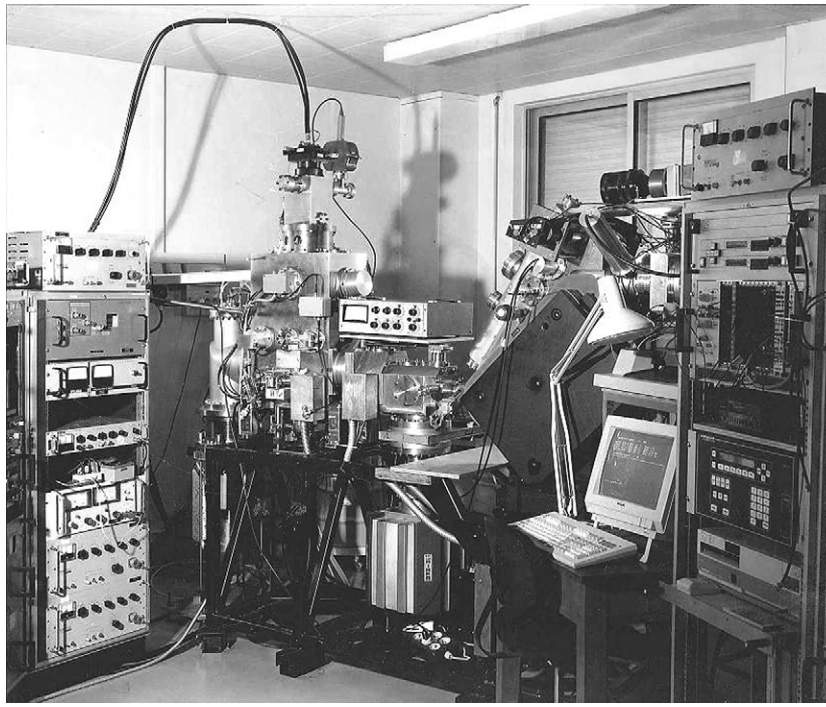


FIGURE 53 The ONERA prototype (1989).

FIGURE 54 François Hillion (1989).

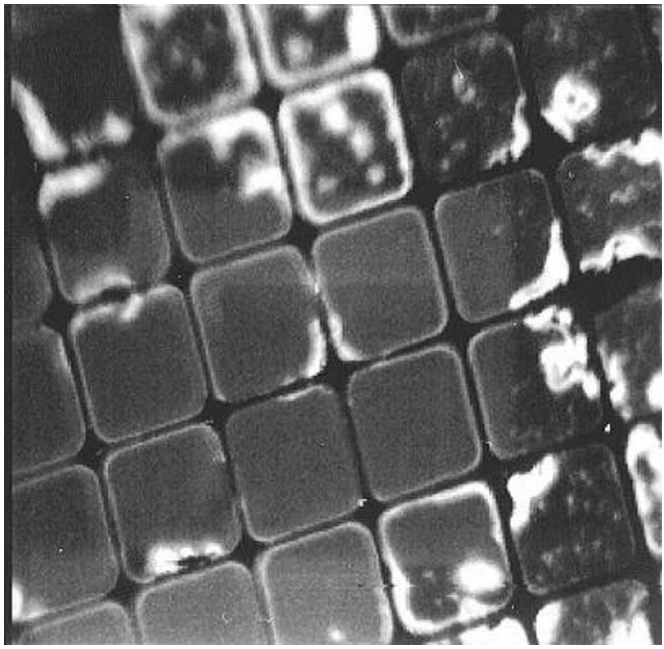


FIGURE 55 The first NanoSIMS image obtained at ONERA in March 1994. The grid step is of 10 μm.

(a) (b)

FIGURE 56 The NanoSIMS 50. (a) The overall instrument (1999). (b) A scanned ion image.

the NanoSIMS after the divorce with Ion-TOF. The drawing files had been transferred from ONERA and adapted to Cameca's production requirements.

During the years, Hillion would submit the instrument to a slow but inexorable trend: first, the adaptation of Cameca duoplasmatron, which could take the room of the cesium source by means of mechanical switching in order to have a negative primary ion source suitable for positive secondary ion analysis. Afterward, in 2005, a new version had an enlarged radius magnet, which was followed by the implementation of Faraday detectors with the same thermostated electrometer as for the IMS 1270. Finally, in 2009, the maximum current of the primary probe was increased (Saliot et al., 2010). Twenty-four NanoSIMS instruments were delivered worldwide between 1999 and 2009.

From 2007, following the installation of an instrument at the Max-Planck Institüt für Marine Mikrobiologie at Bremen in Germany (Musat et al., 2008), many NanoSIMS instruments were delivered for microbiology applications based on the images of the distribution and measurement of the accumulation of several molecules labeled with different stable isotopes (e.g., ^{15}N, ^{13}C, 2H, ^{18}O, ^{33}S, ^{74}Se).

8.2. IMS Wf and SC-Ultra (2000–2009)

From 1996 to 2001, I was personally very involved in the development of the IMS Wf. The "W" of IMS Wf stands for wafers: One of the major specifications of the IMS Wf was to directly run the semiconductor wafers.

Between 1970 and 1995, research and test labs associated with semiconductor manufacturing plants had made extensive use of the Cameca IMS to monitor implanted dopant profiles or contaminant traces in the active layer of the wafer all the way through the manufacturing process. However, it was not possible to introduce full wafers into the IMS; the diameter of the wafers had increased gradually from 50 mm in 1970 to 200 mm in the early 1990s and 300 mm later on. Therefore, it was necessary to break a test wafer in order to introduce a square piece of some 10 mm size into the IMS. This approach had several drawbacks: The broken test wafer was expensive, and it could be recycled if it was not broken. On the other hand, as breaking a wafer was forbidden in the clean room of the lab, the test wafer had to be transferred out of the clean room. And since the analysis result might lead to stopping all production, it was important to minimize the time between removal of a wafer for monitoring and obtaining the analysis results. Given these considerations, the belief arose in 1994–1995 that a simplified SIMS could be accepted in the clean room for go–no go testing. In this case, it was hoped that the SIMS market in semiconductor manufacturing would explode.

At the same time, it appeared that with the steady reduction in the size of circuits, the junction depth was no longer in the range of a few hundred nanometers but only a few dozens. These junctions very close to the surface were then called "shallow junctions" or "ultra-shallow junctions."

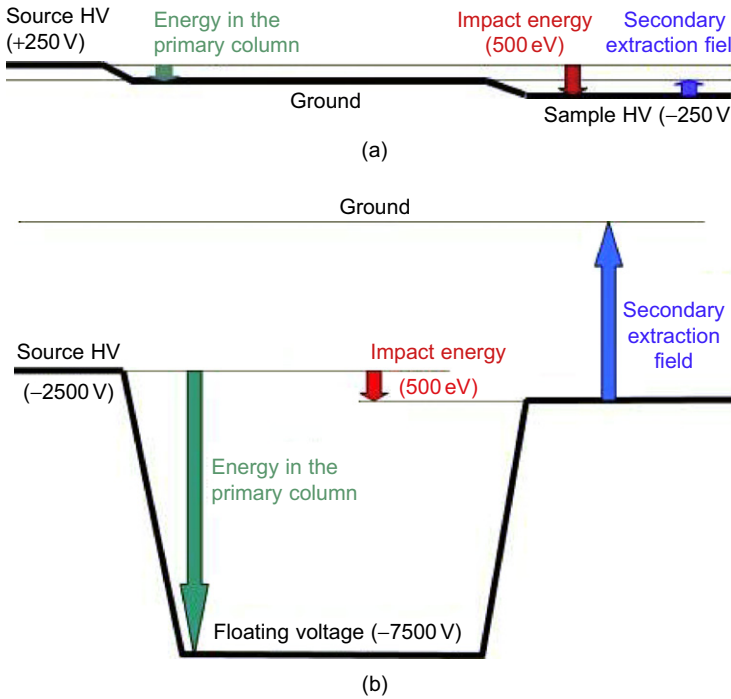


FIGURE 57 Conventional non-floating column and floating column. (a) Sketch of a non-floating primary column operated with positive primary ions and negative secondary ions giving a 500-eV impact energy. (b) Sketch of a floating column with the same requirements.

In order to measure profiles of shallow junctions with good accuracy, it was important for the instrument to have good in-depth resolution. And indeed, Mark Dowsett (University of Warwick, in England) had presented very good results obtained on a quadrupole SIMS in which the primary column is so-called floating (Figure 57), with a primary ion impact energy less than 500 eV.

Thus, the quadrupole SIMS, which was believed to be a low-end tool to such an extent that the Riber MIQ had been abandoned, turned out to be more efficient than the magnetic SIMS regarding depth resolution. The weakness of the quadrupole, the low acceleration energy that leads to low transmission, fit very well with low impact energies.

Figure 57 shows that an IMS 6f where the primary column is not floating, producing cesium (positive) primary ions with an impact energy of 500 eV to detect negative arsenic or phosphorus ions, should work with an accelerating primary voltage of 250 V and a secondary extraction voltage of 250 V. These voltage levels are so low that the performance of both

the primary column and the mass spectrometer are so degraded that this arrangement is beyond the scope of the practical use of the instrument.

Fortunately for the IMS 6f, applications such as boron in silicon involve positive primary ions and positive secondary ions. In this case, it was possible to improve a conventional non-floating instrument with the accessory "Accel-decel" mode, which allows a slight reduction in the duoplasmatron extraction voltage; 500 eV was the minimum impact energy obtained with the IMS 6f for boron in silicon.

At the end of 1995, Sarfati and Schuhmacher decided to develop a new magnetic SIMS instrument compatible with full wafers and equipped with a floating column. A little later the decision was made to add a system for measuring crater depth by laser interferometry. The IMS Wf project later called IMS Wf-SCUltra started in 1996. Between 1997 and 2002, this huge project, entirely supported by Cameca, encompassed all the ideas in the field of SIMS and engulfed more than half the Cameca R&D resources.

At first an alliance with Dowsett was considered. I visited him at Warwick in February 1996, but on the day of my visit he received the confirmation of an agreement providing the adjustment of his floating column for the Atomika quadrupole SIMS. He therefore could not cooperate with Cameca. I was rather relieved because it would have been far more difficult to adapt the Dowsett floating column to a magnetic SIMS. The past six years of work around the IMS 1270 had made me familiar with the SIMS ion optics. Moreover, since a workshop held at Delft in 1994, I had been in touch with the community of charged particle optics. In addition to Frank Read's program, well suited for dealing with all the 3D problems, there was close cooperation with Mikhaïl Yavor, a scientist at St. Petersburg Institute for Analytical Instrumentation (IAI) who had customized for Cameca his program ISIOS (Imperfect Static Ion Optical Systems) written with Sasha Berdnikov (Yavor & Berdnikov, 1995). The cooperation between Cameca and Yavor would go on after my departure from Cameca in 2009.

At the beginning of the project, the primary column axis had to be tilted 60° with respect to the secondary axis. It was more or less demonstrated to be the optimum angle for most applications involving cesium primary ions. As a matter of fact, the primary column must also be compatible with a full wafer. The variable rectangular spot then seemed to be the right solution to address all these constraints: Figure 58 shows the image of a square stencil formed onto another square stencil. An electrostatic deflection allowed moving the first square with respect to the second one.

In the past, I had designed a column based on this principle for an e-beam] (de Chambost et al., 1986b). In this last case, the so-called variable shaped spot principle, allows very fast switching of the spot dimensions. Fast switching of the spot size is not a requirement for SIMS instruments, but the ability to produce a square spot within the sample plane

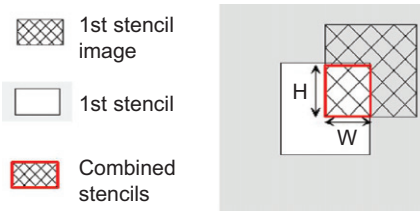


FIGURE 58 The IMS Wf variable rectangular spot.

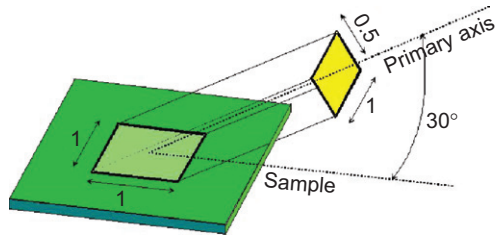


FIGURE 59 Projection of a rectangular spot as a square spot in the case of a 60° tilt angle.

by generating a rectangle with the pair of stencils is a great advantage for very tilted columns (Figure 59).

Another advantage of this column is that the beam aperture angle stop is not located close to the last lens plane but at the other end of the column, close to the ion source (Figure 60). An image of this stop is formed at the last lens plane. The size of this image can be varied by electrostatic lenses so that the sample analysis region, which in addition to the full wafer must contain both the secondary extraction lens and the primary last lens, need not also include a mechanical system of aperture switching.

In fact, at the first design, with my experience with the variable shaped beam for lithography, I was quite confident of the principle but I had not realized that the spherical aberration of the shaping lens was quite critical for proper imaging of the aperture stop within the last lens plane and that the spherical aberration was fairly more important with the electrostatic lenses than with the magnetic lenses used for electon beams. I was quite disappointed at the first tests in May 1999, which were unable to produce really square spots. The complete understanding of the phenomenon was possible after Yavor improved ISIOS to deal with the lens fifth-order aberrations: The third-order spherical aberration of the shaping lens results in a fifth-order aberration of the spot at the sample plane. Fortunately, it was possible to modify the design of the shaping lens.

The design efforts had concentrated mainly on the extraction region, which was considered the more critical. The issue was to prevent the

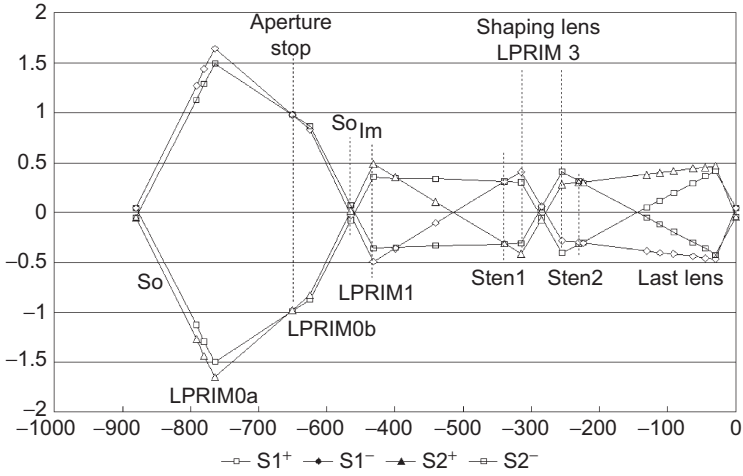


FIGURE 60 The IMS Wf primary column optical sketch. Two sources can be mounted simultaneously onto the 60° floating column. The cesium source is on-axis while the Duoplasmatron is at 90°. A spherical 90° ESA replaces the PBMF for switching the sources. The illumination doublet LPRIM0a-LPRIM0b represents either a real pair of on-axis lenses or the sperical ESA. The composite image of stencils is imaged in the sample plane at scale 1:8. The shaping lens LPRIM3 is a doublet, which allows making an image of the first stencil *(Sten1)* at the second stencil plane. The deflector at the center of the doublet is not represented. In this simplified sketch, the aperture stop is first reduced by the means of LPRIM1. The center of the shaping lens, and finally, the principal plane of the last lens are also conjugated with the aperture stop. In fact, another lens *(LPRIM2)* is also implemented and makes it possible to vary the size of the image of the aperture stop in the last lens plane.

extraction electric field at the sample plane from strongly disturbing the low-energy incident ions. A low extraction field reduces the perturbation onto the primary trajectories but increases the chromatic aberration of the immersion lens—or more exactly, the Recknagel aberration (Archard, 1956). Aberrations of the immersion lens led to degraded quality of the optical gating, key to depth profiling performance, the targeted application of the IMS Wf. The best compromise was to include in the immersion lens a shield electrode of the same voltage as the sample and as the last electrode of the primary last lens, an extraction electrode and a focusing electrode.

Around 1999–2000, while the first IMS Wfs were being mounted, data obtained with the first quadrupole SIMS equipped with a floating column demonstrated that the optimum angle for O_2^+ primary ions was certainly not 60° but probably less than 45°. The first two IMS Wfs were equipped with only a cesium source. The next two were also equipped with a duoplasmatron mounted on the same 60° column with a switching

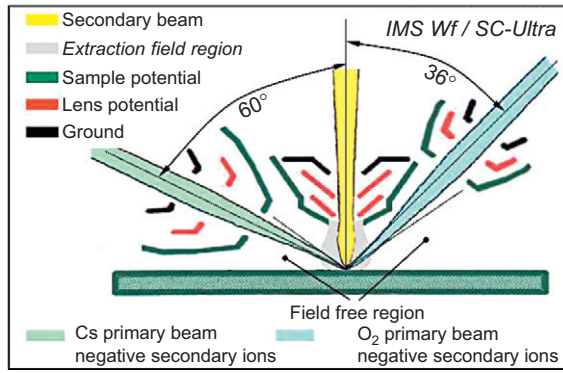


FIGURE 61 The IMS Wf immersion lens.

ESA, but all others would be equipped with both a 60° floating column providing Cs^+ ions and a 36° non-floating column providing O_2^+ ions. The design of an immersion lens compatible with both 60° and 36° turned out to be very tricky; this is not really displayed in Figure 61. The actual design was never disclosed and was still secret in 2010.

In 1997, 300-mm wafers were not yet processed in any semiconductor fabrication plant (fab). The standard was 8 inches (200 mm). In 1997, the decision was made to provide the IMS Wf with a sample stage compatible with 300-mm wafers after Intel announced the construction of its pilot fab D1C in Oregon for the development of 0.18-μm technology on 30-mm wafers. In 1997, the code name for the project was not yet IMS Wf, but CF (for *colonne flottante* [floating column]). Gradually, most of the Cameca R&D resources would rally around this project.

The first two IMS Wfs were ordered by the companies Lucent and Nortel, two major North American telecommunications companies involved in the manufacture of III-V lasers, which allow the transfer of huge flows of information in fiberoptic networks that Al Gore, vice president of the United States, popularized in 1993 under the name of "information highways" (Chapman & Rosenberg, 1995). Surprisingly, these first customers of the IMS Wf were not concerned by its performance in low impact energy nor by 300-mm itself. But the sample stage designed for 300-mm wafers allowed them to put several of their small III-V (typically, the indium Phosphide [InP]) 2- or 3-inch wafers.

Lucent and Nortel were also very interested in the depth measurement, since with multilayers it is not correct to make a single crater measurement after the analysis and to estimate the profile by assuming that the sputtering rate is constant. Pierre Monsallut was then appointed by Sarfati to find a solution to the crater depth measurement. He actually succeeded in integrating an interferometer system between the NEG and the sample.

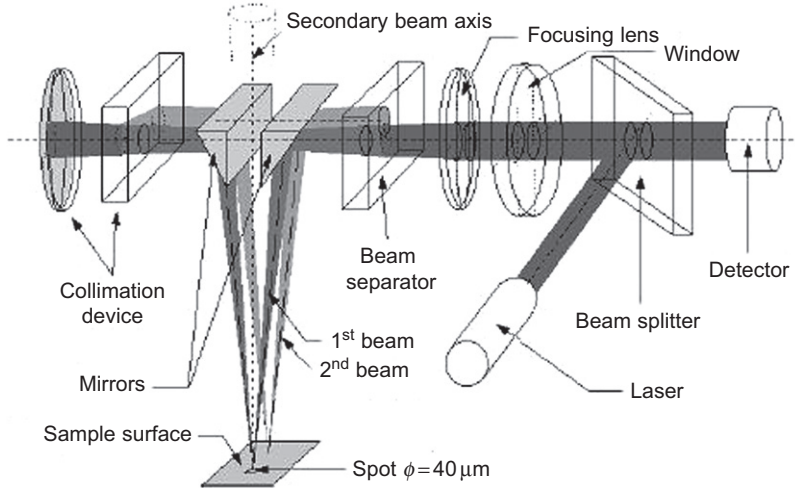


FIGURE 62 The crater depth measurement interferometer.

This interferometer, a Michelson type with a heterodyne laser, can measure in real time the crater depth corresponding to the layer being sputtered: As shown in Figure 62, a reference laser beam is reflected on the wafer surface while the measurement laser beam is reflected on the crater bottom. The phase shift between both beams gives the depth information (de Chambost et al., 2003). Such a system is quite well suited to applications involving III-V samples with multilayers of a few micrometers.

In 2001, a crisis occurred: the bursting of the "dot-com" bubble. Flourishing companies such as Nortel and Lucent were suddenly close to bankruptcy. There was actually overproduction of solid-state lasers. Nortel canceled the order for a second IMS Wf. From 2001, IMS Wf were produced for more conventional customers such as Samsung, Intel, or IBM motivated to experiment with the low impact energy. They were also happy to take advantage of the *in situ* depth measurement; but as a matter of fact, when the range of the measured profile depth is a few dozens of nanometers, the required precision of the depth measurement is less than 1 nm and Schuhmacher demonstrated that such precision cannot be obtained with non-homogeneous material because of secondary effects. A few years were needed to understand the phenomenon fully: The secondary effects are the same as those involved routinely in ellipsometry (Azzam & Bashara, 1987). The laser depth measurement must be abandoned for shallow profiles.

As Figure 63 shows, the IMS Wf looks like any instrument that can be found in a clean room: a box. The 300-mm wafer must be introduced in the airlock, which can contain two wafers, but the airlock is also compatible

FIGURE 63 The IMS Wf (2001).

with a cassette of wafers (a so-called FOUP [front-opening unified pod]) that can be mounted on the left-hand side. The C spectrometer has been tilted in a vertical plane to set the wafers horizontally. Rasser and the engineering department had to learn the rules and the skills of clean room technology, which were then unknown at Cameca: wafer handling, data transfer protocole, requirements for dusts and contamination.

The first results involving both positive primary ions (Cs^+) and positive secondary ions with an impact energy as low as 250 eV were demonstrated in 1999 and presented at the SIMS conference in Brussels in September (de Chambost et al., 1999). The combined advantage of a high mass resolution and a low impact energy was appreciated by the major semiconductor companies, but the SIMS would never be accepted in clean rooms as a controlled tool routinely used to test every wafer and for ellipsometry. Some customers asked that the 300-mm wafer holder be replaced by a 100 mm × 100-mm sample holder accepting an array of 25 different pieces of wafer.

The year 2000 was a bumper year for the semiconductor industry. To take advantage of the good economic situation, a batch of 20 instruments was launched but a reversal came sometime in 2001 before all the machines were ordered. No orders were placed in 2003 for these instruments slightly more expansive than the IMS 7f. The sales climate in 2004 was better, but there were rarely more than four orders per year.

Since 2006, Alex Merkulov has been in charge of developments to reduce the impact energy up to 100 eV and improve the depth resolution (Vandervorst et al., 2008) (Figure 64).

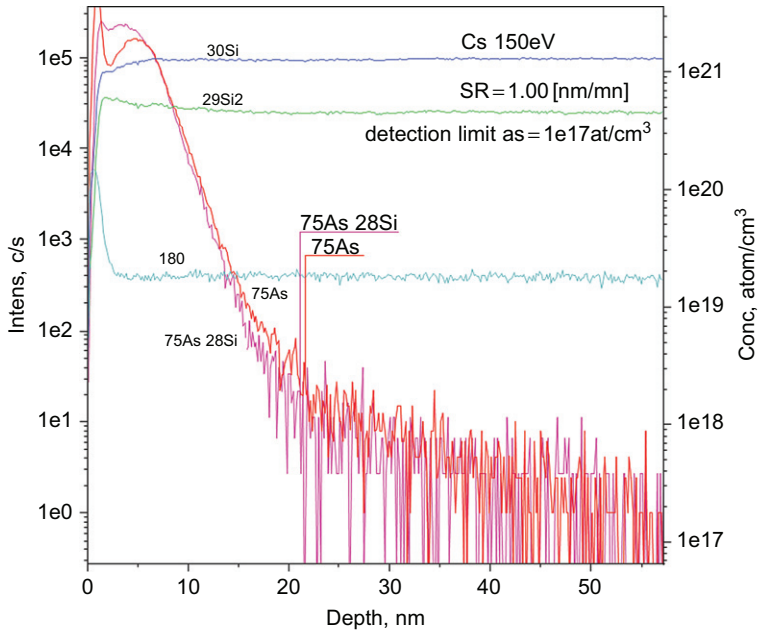


FIGURE 64 Arsenic depth profile at 150-eV impact energy.

8.3. Diversification of the SIMS Catalog (2000)

From 1968 to 1992, Cameca manufactured only one model of SIMS at a time. By the early twenty-first century, the situation completely changed: Cameca simultaneously offered a wide range of SIMS models. In addition to the basic model, the IMS 6f in 2000, customers could also choose more expensive models, specialized in a given application: the IMS 1270 for high transmission, the IMS Wf for low impact energies, the NanoSIMS for high lateral resolution, or the IMS 6f-R delivered to European nuclear plants.

This production arrangement did not simplify the work of the production and purchasing departments: How could they negotiate attractive prices with a subcontractor when it was not possible to guarantee a minimum volume for a given subset? The manufacturing costs tended to decline due to both the relocation in eastern European countries and the trend to compactness of the electronics, but the prices offered to customers did not fall because the SIMS continued to pay overhead and R&D of new products promised for the future.

In the field of magnetic SIMS, Cameca had no competitor except the Australian Shrimp, which could compete only with the IMS 1270 and from 2003 with the IMS 1280, but for many commercial cases, the Cameca SIMS

competed with the TOF-SIMS that appealed to academic labs because they covered a wider range of applications. The quadrupole SIMS was still attractive for the semiconductor industry because of its low prices and supposed simplicity of use.

In 2005, the opportunity arose to buy Atomika, which was taken by FEI but continued to take losses. This acquisition brought two quadrupole SIMS to the Cameca catalog: the SIMS 4550 and the SIMS 4600. This last, designed for full wafers, would never be sold. In 2006, Cameca also developed the IMS 7f-Geo targeted to measure isotope ratios.

Diversification concerned not only SIMS but EPMA as well. With the "shallow probe," EPMA could serve the semiconductor industry. Finally, as explained in the following text, in addition to the SIMS and EPMA, a third technique, the atom probe, was developed by Cameca at the beginning of the twenty-first century.

8.4. Cameca without Sarfati (2001–2009)

In 2001, Sarfati sold his shares of Cameca to Perfectis, a private equity fund linked to a large French insurance company, and was succeeded by Georges Antier (Figure 65), who was previously in charge of finance and the administration department. The transaction allowed Sarfati and other small shareholder-employees of Cameca to realize a gain of 1 to 50 relative to their initial bet in 1987.

George Antier did not exercise his option in the same way as Sarfati, who was both the owner and the manager and therefore accountable only to himself. Antier had to account to more or less nervous shareholders who had gained control of Cameca through a leveraged buyout and were constantly worried about losing or not earning enough money. The executive committee consisted of Georges Antier, Philippe Fercocq (in charge of the production department), Michel Schuhmacher (in charge of scientific marketing), Dominique Eriaud (who had the same position that Antier previously held), Regis Lefrançois (who took over from Jean-Jacques Legoux as sales director), Claude Guignes, (customer service manager) and myself, Emmanuel de Chambost (in charge of the R&D department. Bernard Rasser left the company in 2004 to join Orsay Physics.

8.5. The Shallow Probe (2001–2009)

The control of dopant implantation in semiconductors with precise depth profiling was a major application of SIMS, but one limitation of this technique is the measurement (within a few nanometers) near the surface in the area where the steady state involving the primary ion implantation,

FIGURE 65 A meeting in 2003 with new CEO Georges Antier. From left to right: José Belda, salesman in charge of the shallow probe project; Philippe Fercocq, production manager; Michel Schuhmacher, in charge of scientific marketing; and Georges Antier.

sample sputtering, and secondary ionization is not reached. This limitation is reduced with low impact energies, which is why the IMS Wf project was launched in 1996.

The trend was reversed for EPMA, Cameca's other technique. The closer the implantations are to the surface, the more easily they are measured. Before the 1990s, there were strong reasons to believe that EPMA was not suitable for implantation control: The most widely used dopant is boron, located a few hundred nanometers from the surface, a sufficient thickness to be opaque to boron's characteristic wavelength, 283 eV. If implanted layers are located close to the surface, those who have mastered the few equations that account for the electron penetration in solids and X-ray absorption could have known that the Castaing probe could be used to measure an implanted dose. It seems that it was not so simple, though, since EPMA would have to be renamed LEXES (Low-energy Electron-induced X-ray Emission Spectrometry) in two dissertation works achieved with an exotic experimental setup for realizing that ultimately it should be possible to make measurements of dose shallow implants with a simple Cameca SX.

In 1997 Pierre-Francois Staub (Figure 68), a young graduate, had just completed his doctorate under the direction of Christiane Bonnelle at

the Pierre and Marie Curie University, Paris. Staub developed IntriX, a model of the X-ray response to electron bombardment (Staub et al., 1998). Compared with existing models, his contribution was to calculate the corrections for light elements and low bombarding energies. IntriX was the name of this model of "($\Phi(\rho,z)$" type, well suited to deal with samples that are not homogeneous in depth, whereas the Monte Carlo method on which Jean Hénoch, for example, had worked extensively, were better suited for homogeneous samples.

Although the arrival of Staub roughly coincided with the departure of Hénoch, Staub was not appointed for perfecting his model but as product leader of the Castaing probe. Staub also helped Chrystel Hombourger, a new doctoral student of Bonnelle. Hombourger's thesis was supported by Cameca. Sarfati had insisted that Schuhmacher follow the progress of Hombourger's work so that applications relevant for Cameca were considered part of the thesis. Thus, Chrystel Hombourger came to Cameca at least twice to take stock of this work. In 1998, she made a presentation on the estimate of the implanted dose concerning samples of the so-called shallow implants provided by Schuhmacher.

Hombourger obtained her results on a prototype called IRIS (Hombourger, Jonnard, Bonnelle, & Staub, 2003), but it turned out that the Cameca standard SX100 could do the job as well. Meanwhile, Schumacher had written a specification of an instrument that could make WDS measurements of shallow implant doses.

The belief still persisted that what was possible for phosphorus and arsenic would never be possible for a light element such as boron. Actually, to obtain significant results on the shallow implant of boron, just a slight modification of the standard instrument, removing a stop, is needed to get a few microamps of primary current. This was achieved by a couple of Cameca engineers in June 1998 (Figure 66).

The results obtained with the SX made it much more concrete that it was possible that an instrument could perform dose measurements with an electron beam, one or more spectrometers WDSs. A project was launched with the code name of NDDM (standing for non-destructive dose measurement) (Hombourger et al., 2003).

It was briefly considered to make this an accessory NDDM for SIMS instruments, but the final configuration of the machine was fixed during a meeting on March 21, 2000, where it was decided to recycle the airlock and the 300-mm sample chamber of the IMS Wf and to design a new electron column to clearly differentiate the new instrument from the basic SX. The spectrometers are identical to those of the SX, but there are only three because of the 300-mm stage, which requires that the spectrometers be mounted inclined instead of vertically (Figure 67).

Some performances of the shallow probe were degraded compared with the SX—for example, the electronic spot size or the spectrometer

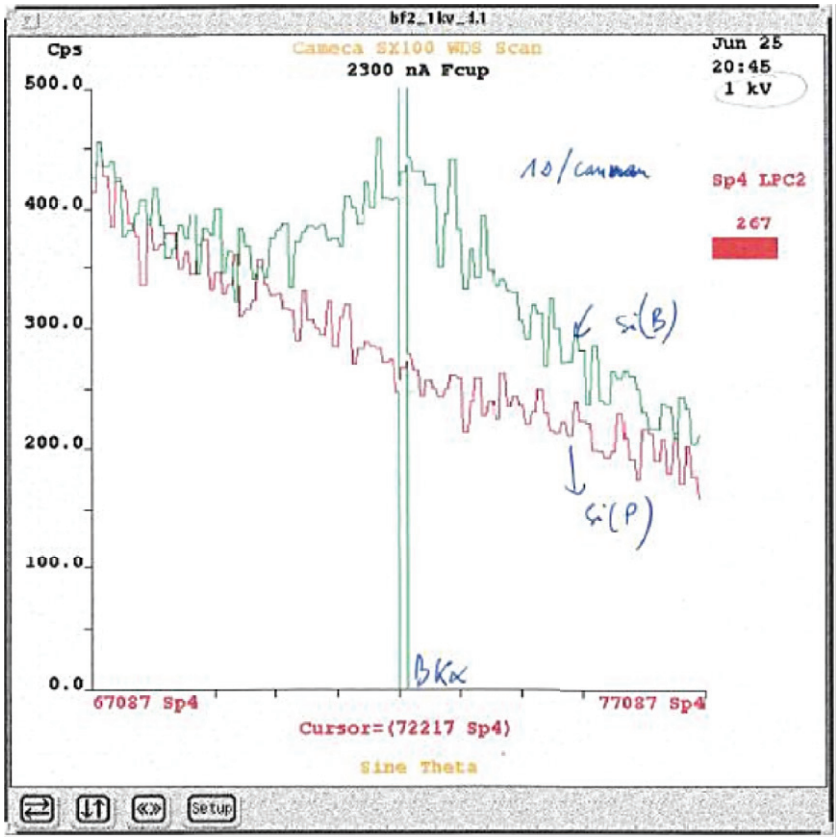
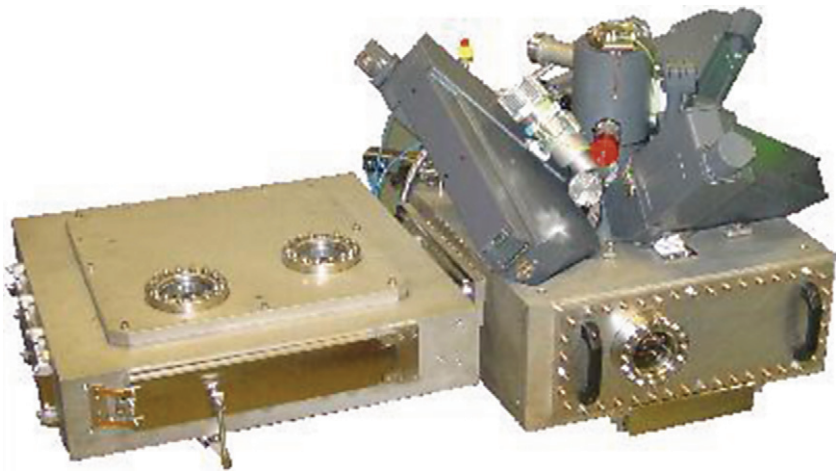


FIGURE 66 First measurement of a boron shallow implant with a SX100 (June 24–25, 1998).

resolution—but customers were increasingly demanding reproducibility much better than anything that had been obtained previously with the Castaing probes. It was observed that soft X-ray counting depends on weather conditions—the atmospheric pressure. To fix this issue, regulators were developed for the gas pressure of the proportional counter. Another customer concern was the number of dust particles larger than a tenth of a micron that could be deposited on the wafer after passing through the machine. This number must average less than one.

In 2000, Pierre Monsallut was appointed head of the shallow probe project. In 2002, a prototype was mounted in a platform after a schedule delay that was entirely reasonable. Good news came soon after the prototype was installed and produced its first data: Intel was interested in the shallow probe to control SiGe layers of the new generation of CMOS technology they called P1264, which corresponds to a linewidth of 65 nm.

(a)



(b)

FIGURE 67 The shallow probe (2002). (a) Outer view and (b) inner view.

In 2003, after the dot-com bubble burst and the IMS Wf business completely dried up, the shallow probe orders for Intel allowed Cameca to complete its annual budget without considering layoffs.

With the Intel shallow probes Cameca began to learn the craft of equipment supplier for clean rooms. Maintenance and service are completely different from what was proposed previously by Cameca within the framework of its standard maintenance contracts where the stipulated response time was never shorter than 48 hours. For semiconductor fab clean rooms, this period should be reduced to two hours. Therefore, so-called FSEs (field service engineers) had to be appointed locally, and they had to be trained to perform some simple maintenance tasks.

The shallow probe project for Intel was also an opportunity to rub shoulders with the tyranny of the customer and to learn the meaning of the verb "to escalate": If an issue was not fixed at the normal level, the supervisor of the rank "tool owner" would contact the supervisor of his usual interlocutor at Cameca, and finally Georges Antier, CEO of Cameca, might be awakened during the night because an instrument was inoperative in a plant somewhere in New Mexico. In addition, a production line in a fab might be entirely stopped because of a faulty shallow probe.

After the sale of seven instruments to the worldwide No. 1, a machine was sold to FWA (Full Wafer Analysis), a company founded by Drew Evans to provide services in LEXES analysis in the same manner as CEA, also founded by Evans 25 years earlier, for SIMS analysis. As shown in Figure 68, the shallow probe of FWA was the only one equipped with a small airlock for running small pieces of wafer instead of the full wafer.

At this point, it was hoped that the success of the shallow probe was assured. But throughout all of 2004, Cameca did not receive a single order for shallow probes. IBM had not even considered Cameca for a tender and preferred to accept the machine proposed by the competitor KLA-Tencor, a company at least twenty times larger and more specialized in testing for semiconductor fab and thus more credible than Cameca.

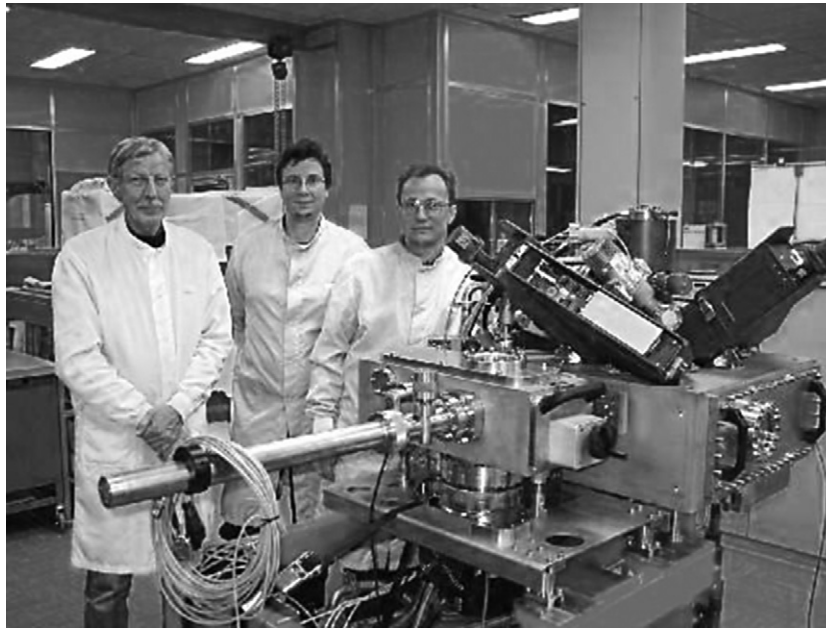


FIGURE 68 The FWA shallow probe at the Cameca platform (2003). From left to right: Jean Mascianica, Pierre Staub, and Pierre Monsallut.

On one hand, KLA had much more experience than Cameca in handling wafers under vacuum. On the other hand, Cameca had more experience with WDSs. The KLA instrument was equipped for fixed spectrometers, tuned for a given wavelength. Therefore, the device was mechanically set for a given application, which could be quite suitable if an application had emerged for which an instrument could be devoted 100% of the time, but a great variety of applications was still being sought—the implanted doses and nitrogen in oxynitrides, hafnium. Moreover, the solution to set the sample to high voltage to obtain a low impact energy was good and Cameca had patented it (de Chambost et al., 2002). After validation tests at two different customers in competition with KLA, Cameca won both contracts and KLA threw in the towel for this technique.

9. AMETEK AND THE ATOM PROBE (2007)

9.1. Ametek Acquires Cameca

In addition to launching the shallow probe, two events marked the history of Cameca during the first decade of the twenty-first century: its deeper involvement into the atom probe and the acquisition of the company by Ametek in 2007. These two events of a different nature are not completely independent, though, since the existence of expertise in the field of atom probe had greatly boosted the valuation of Cameca despite the turnover negligible in this market at the date of the acquisition.

Production of a third analysis technique, TAP (tomographic atom probe), was actually attempted at Cameca alongside EPMA and SIMS. Only after 2003 was this attempt, which began from 1995, carried out in a sustainable and relatively fixed way.

As reported earlier, after the reign of Sarfati, Cameca was acquired in 2001 by a French private equity investment company, Perfectis. The latter in turn sold the company in 2005 to another much better-known private equity firm, Carlyle. The acquisition was also made as a leveraged buyout. Incidentally, Carlyle had exerted much less pressure on the Cameca management than had Perfectis. Both private equity firms claimed at the time of their respective takeovers that they did not intend to permanently retain the companies they had bought and that their job consisted mostly of reselling the company at a profit some years later. Cameca employees believed then that the purchaser would likely be a "big player" in physical instrumentation or surface analysis (e.g., Thermo or FEI). The announcement of talks with the U.S. holding company Ametek was indeed a surprise, and no one at Cameca had heard of Ametek, which at that time controlled fifty companies the same size as Cameca, but especially in the area of electrical components for aerospace.

In the Ametek flowchart, Cameca is attached to the MAD (Material Analysis Division) division, which in 2007 included two other companies: EDAX and SPECTRO. EDAX is a U.S. company located in Pennsylvania that offers accessories for electron probes, including EDSs. SPECTRO is a German company based in Kleve that offers instruments of the same type as the Spectro-Lecteur (which Cameca had developed in the 1950s) and other instruments based on XRF (X-ray fluorescence) and ICPMS, all targeted mainly toward metallurgy applications.

Before the late 1990s, instrumental and analytical activities within the atom probe scientific community were not separated. For example, a student might be asked to develop for a thesis some new instrumentation, for which he or she would get a publishable result, often the observation of an atmosphere of Cottrell (i.e., dislocations pinned by carbon or nitrogen interstitials) in a metal alloy, but increasingly researchers wanted to use the most advanced instrumentation for their analytical work and not just the instrumentation developed in their lab. Thus, in Japan, Professor Hono equipped his lab with the multi-anode detector developed at Rouen in 1995. As a consequence of this rather old history, the situation was already competitive when Cameca started its cooperation with the University of Rouen.

Not until 2003 did evidence arise that the atom probe had its place in the labs involved in semiconductor R&D, with the hope that this market could be lucrative and that consequently Cameca should develop an instrument really designed by its own engineering department. This would be the LA-WATAP.

9.2. A Short History of the Atom Probe

At the origin of the atom probe as it was introduced at Cameca in the 1990s is the field ion microscope (FIM). The FIM was invented by the German Erwin Müller in Berlin in 1951. The FIM itself is a descendant of the field electron microscope (FEM) investigated before the war, also in Berlin, in a Siemens research laboratory (Ruska, 1980).

After the Second World War, Müller joined the Kaiser-Wilhelm-Institüt. One day he introduced a sample shaped in tip into a chamber filled with low-pressure hydrogen (about 10^{-3} Pascal). By biasing the tip, an electric field was produced at the surface of the tip; the hydrogen atoms were ionized and projected onto a screen where they formed the image of the tip at very high magnification. With this instrument images at the atomic scale were observed for the first time in the world. This technique thus allowed the observation of crystal defects at such a scale (Deconihout et al., 2004). In fact, the atoms were not observed in Berlin in 1951 but later at the University of Pennsylvania where Müller had accepted a position (Melmed, 2002).

The FIM invention was roughly contemporary with that of the microanalysis electron probe, but while the latter was ripe for widespread use among metallurgists and geologists a few years after the theory of Castaing, FIM would require several decades of improvement and maturation before becoming, as an atom probe, desirable for a wider maket than the small community of FIM and atom probe.

The FIM image displayed at the atomic scale does not provide chemical information about observed atoms. In 1967, Müller (always at the University of Pennsylvania) published a paper about an atom probe named APFIM (atom probe field ion microscopy). In this instrument, he removed the gas. The electric field at the surface of the tip was then used to evaporate the sample atoms. The evaporation was actually triggered by a voltage pulse, and a detector was placed one meter from the tip so that with a good oscilloscope it was possible to measure with a good oscilloscope the TOF between the pulse and the event recorded by the detector (Müller et al., 1968).

In addition to the FIM image, the 1967 APFIM could therefore determine the mass of the atom from the TOF. The APFIM already had all the basics of what is today called the 3D tomographic atom probe (TAP)—that is to say, that which allows reconstruction, atom per atom, of the sample volume as is displayed in the appendix in the figure with chromium and aluminum. The 1967 APFIM and all the following atom probes are TOF mass spectrometers (Kelly and Miller, 2007).

It would still take twenty years of improvements in detector electronics before both the TOF and the position of every evaporated atom could be measured together. These years would serve to establish the physical principles governing the evaporation of ions. In the 1970s, the colleagues of Müller—namely, Tsong and Panitz at the University of Pennsylvania—achieved most of the work. In 1980, Tsong published the first data obtained with a pulsed laser (Kellogg & Tsong, 1980), but only twenty-five years later the laser became an indispensable accessory to the atom probe.

In the late 1980s, it was time for new players to propose the first TAP that actually measured the atom position and mass, allowing reconstruction of volumes at the atomic scale: Alfred Cezero and his colleague Smith at the University of Oxford were undoubtedly the pioneers of the so-called 3D probe (Cerezo et al., 1988). At the University of Rouen, in France, Alain Bostel, a CNRS engineer working on Professor Menand's team, had just solved some problems of the multi-count detection issue in the framework of the doctoral work of Didier Blavette and realized he had the tools to do better than Cerezo (Bostel et al., 1989). The progress made in these laboratories on the position sensors was so advanced that many laboratories involved in atom probes preferred to purchase a copy of these detectors or even complete instruments rather than attempting to duplicate them. The time had come to market the atom probe. The Oxford scientists

created a start-up, Polaron, that would be redeemed and renamed Oxford Nanoscience. Those in Rouen contacted Cameca in 1995.

In 1998, Thomas Kelly, professor at the University of Wisconsin-Madison, also created IMAGO, a start-up devoted to manufacturing an atom probe instrument called LEAP (local electrode atom probe). His project was based on a so-called local electrode located at some tens of micrometers of the tip, according to an idea borrowed from Nishikawa (Nishikawa & Kimoto, 1994). Kelly succeeded in raising enough funds to maintain up to thirty people and invest heavily in FIB. Focused ion probes are an expensive but essential tool for shaping in tip the semiconductor samples concerning therefore the market with the greatest interest toward the atom probe. The FIB could etch any sample, while the electrolytic technique, used since the very origins of FIM, could be used only with metallic samples and required first samples in the form of wire.

At the University of Rouen, the introduction of the atom probe as a research topic occurred in the early 1970s. J. Gallot, who later became dean of the faculty at Rouen, had learned of the technique in England. A publication attests that work regarding FIM was carried out in Rouen from 1974 (Ménand & Gallot, 1974). Under Gallot, head of the LMI (Laboratoire de Microscopie Ionique), Jean-Marie Sarrau, presented a thesis in 1977 entitled "Development of a Probe Atom." An electronics engineer, Monique Bouët, also wrote a thesis dissertation, and then it was the turn of Alain Menand, future head of the lab, and of Didier Blavette, who would succeed Menand. Alain Bostel was assigned to design the instrumentation for each of these theses. Sarrau, Bouët, and Bostel were involved in 3D probe tomography, which was also the thesis topic of Bernard Deconihout in 1993 and led to a paper published in *Nature:* "An Atom Probe for Three-Dimensionnal Tomography." That is when the Rouen team got in touch with Cameca to market the instrumentation they had developed. In 2008, the Rouen GPM (Groupe de Physique des Matériaux) was a large lab of a hundred people headed by Didier Blavette and included a team of fifteen persons devoted to scientific instrumentation. The different models of atom probes provided by Cameca are detailed in the fourth appendix.

9.3. Introduction of the Atom Probe at Cameca

The atom probe was introduced at Cameca in 1995 with the delivery to NIMS, the laboratory of Professor Hono in Japan, of a multi-anode detector developed by the Rouen LMI. Other replicas of the Rouen atom probes were installed in academic labs around the world.

In this first generation of position-sensitive detectors (PSDs, Figure 69), the position detection was performed by an array of 10×10 discrete anodes. An ion extracted from the specimen was first converted into an electrical pulse. The electrical charge distribution on several anodes

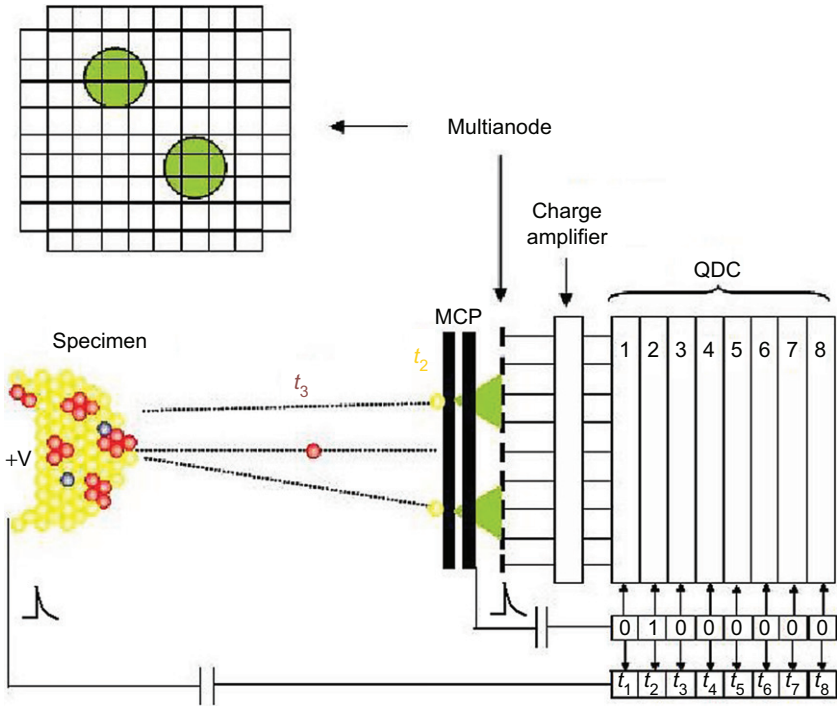


FIGURE 69 Atom prode multi-anode detector (1995). The overall detector area is $80 \times 80\ mm^2$.

can measure the position with accuracy much better than the elementary discrete anode.

Cameca's involvment was limited to marketing and installation until 2001. At that time, Cameca confirmed its intention to extend its skill to a third analysis technique by recruiting Ludovic Renaud, who had worked on a second-generation PSD (Figure 70) when he was a doctoral student at Rouen. This second generation of detectors, called OTAP (optical tomography atom probe), used a fast charge-coupled device (CCD) camera measuring the position. The accuracy of the TOF was improved: 0.5 ns compared with 2 ns with the multi-anode PSD.

Only in 2002 did Cameca decide to become more involved in the production and to assemble an EcoTAP (energy-compensated TAP) directly at Courbevoie. The EcoTAP includes a reflectron for energy compensation (Figure 71). In an atom probe, the position detector is one of the most critical components, because it must be accurate in both position and time. During the 1998–2004 period, Cameca benefited from the progress achieved in Rouen on position sensors.

The third generation of detectors would be the delay line detector (DLD), developed specifically for the atom probe by the German company

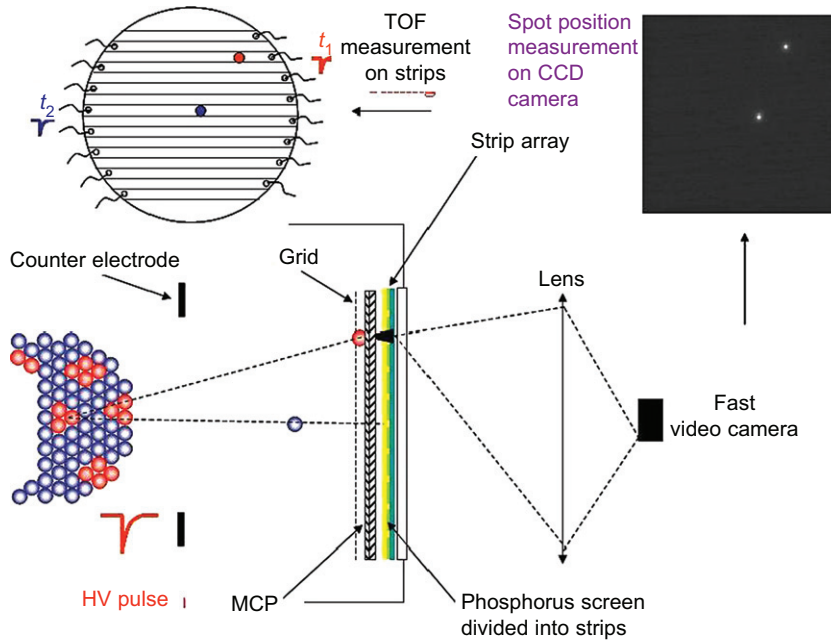


FIGURE 70 Optical tomographic atom probe (2001).

Roentdek, which specialized in sensors for particle accelerators (available since 2004) that provide better accuracies of TOF, but especially reduced to 1.2 ns the dead time that follows an ion detection (Figure 72).

In 2004, Cameca was even more firmly committed to the atom probe in developing a complete instrument in the engineering department. On the advice of Bernard Deconihout and his team, the distance between the tip and the sensor was shortened to 110 mm (this was the WATAP [wide-angle tomography atom probe]) (Figure 73). Always after the recommendations of the Rouen team, the instrument was equipped with a femtosecond laser emitting in the infrared range, which must replace the electrical pulse for insulating or semiconductor material. The first analytical results were obtained in Gennevilliers in late 2006. A machine was installed at Pohang University of Science and Technology (POSTECH) in Korea, and another one at Interuniversity Microelectronics Centre (IMEC) in Belgium.

9.4. Competition with IMAGO

Testing of the prototype roughly coincided with the move of the Cameca plant from Courbevoie to Gennevilliers, both located in the northwestern Paris area. At this time, in 2006, it was realized that the competitor (IMAGO) had a big lead over Cameca in semiconductor applications.

FIGURE 71 The EcoTAP (2002).

It was not only a matter of comparison between the two instruments; it was also the global know-how that allowed getting data from a raw sample—for example, a piece of wafer. The preparation of the tip is a very delicate operation that requires the availability of expensive equipment, the FIB (focused ion beam)—a focused gallium ion probe that allows, when it is properly programmed, etching the sample to give it the shape of a needle. The FIB is also used in TEMs to prepare samples shaped as a thin membrane.

The Rouen GPM was certainly one of the more skillful university teams in the field of atom probe, with the evidence arising that the academic competition in which the GPM was involved did not equate to the industrial competition, mortal, in which Cameca was involved. The efforts for the LA-WATAP were actually insufficient. Cameca needed to move up a gear: A dual-beam FIB was purchased for shaping of nonmetallic specimens. It was a huge investment for Cameca because a demonstration machine was tied up for the application lab. A complete team was formed within Cameca to develop applications as well as instrumentation.

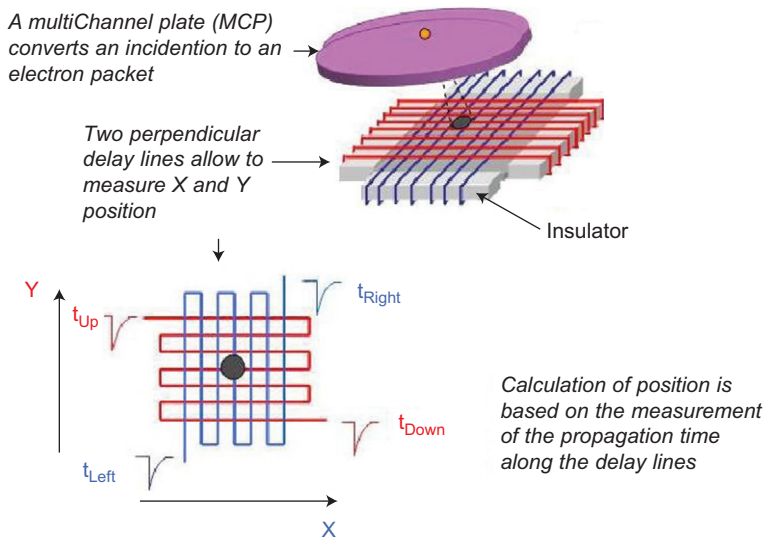


FIGURE 72 The DLD detector.

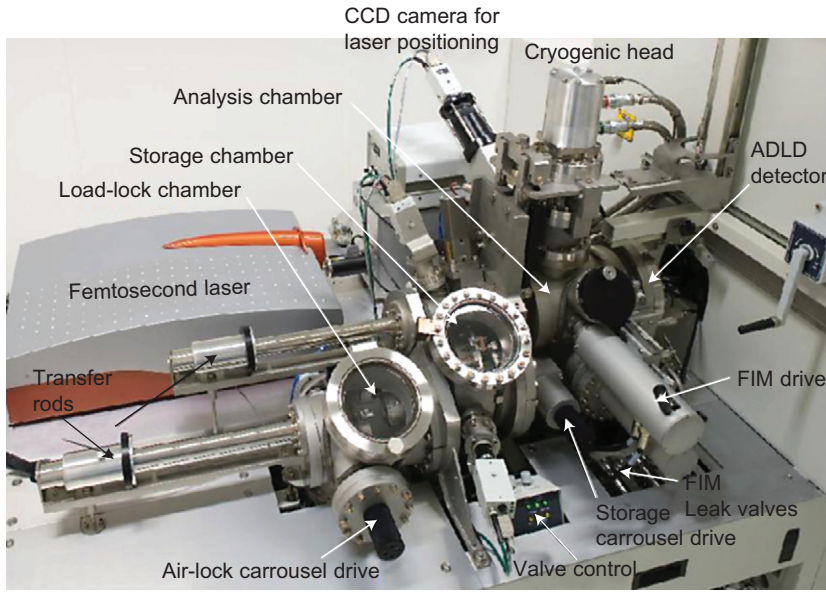


FIGURE 73 The LA-WATAP (2006).

Isabelle Martin, who had done her thesis in part at NIMS, under Hono, was hired to be responsible for the Cameca atom probe application lab. Béatrice Sallé was appointed to be responsible for intrumentation

developments. R&D efforts were expanded to develop a new model to stand out from the competition.

Imago scored more than Cameca considering the number of commercial cases won, but it was a long-distance race in which the leading competitor could collapse if it did not hold out. Imago was in the lead because its shareholders, venture capital firms, agreed that the first years might involve loss rather than profits. They pushed up the bidding in 2005 by acquiring the third player, Oxford NanoScience, but their financial equilibrium was never met; the company was on the verge of bankruptcy. The new owner of Cameca, Ametek, was approached, but the price offered by Ametek was considered insulting by Imago shareholders. Eventually, Imago formed a partnership with FEI, the leading provider of FIB. This alliance was formidable for Cameca. Fortunately, the 2008 global economiccrisis came at the right time: The commercial results achieved by Imago were insufficient for FEI to confirm its purchase option.

It soon appeared that a number of improvements to the LA-WATAP were imperative to withstand the competition with Imago. In particular, for many samples, the infrared is not the optimum wavelength. Pierre Monsallut, appointed as project leader of the LA-WATAP project, had to return to the shallow probe issues. Béatrice Sallé, completely involved in the atom probe project, adapted a frequency doubler to the laser and started the project codenamed FLEXTAP, which was based on the principle of so-called angle conversion to have both a wide angle of emission and a very long distance of flight.

The principle of angle conversion had been proposed by Alain Bostel in 2006. Mikhail Yavor was then asked to propose the design of an electrostatic lens that remains linear even for highly eccentric trajectories. Yavor's study resulted in a patent that is the base of the FLEXTAP (Bostel et al., 2007).

10. EPILOGUE

I started to gather some archives and to interview old members of Cameca in 2004 when the decision was made to relocate the plant where Cameca had been living over more than fifty years to the new plant of Gennevilliers. In September 2009, under French law, with 40 years of contributions, I became eligible to retire (Figure 74). Before leaving Cameca, I interviewed more systematically my colleagues and I published some months later a small book in french, "Histoire de Cameca (1954–2009)." I would like to warmly thank once more all those who helped me, especially Claude Conty, Jean-Jacques Legoux, Pierre Monsallut, and Jean-Michel Rouberol, who sent me written contributions. This paper is in part a summarized adaptation of the book.

FIGURE 74 At the retirement party, September 29 2009. Pictured in the foreground: Emmanuel de Chambost with Michel Schuhmacher, Pierre Staub, Bernard Rasser, and partially hidden François Hillion. In the background: Georges Antier, Michel Lepareur, and Jean-Michel Rouberol.

The history of Cameca did not stop with my departure. In late 2009, my colleagues Firmino Fernandes and Paula achieved spectacular results with an improved IMS 1280 model, the so-called IMS 1280-HR, to be delivered to the Nancy CRPG lab of Marc Chaussidon and Etienne Deloule and dedicated to K/Ca and Rb/Sr dating (Peres et al., 2010). A mass resolution at 10% of 35000 with a fair transmission was demonstrated.

In March 2010, Ametek announced its acquisition of Imago Scientific Instruments, and the war of atom probes was therefore ended. The thirty people at Imago based in Madison, Wisconsin, were included in the "Cameca business unit" of Ametek. For the first time in Cameca's history, all the R&D and manufacturing activities were no longer located in a single place in the Paris area. In february 2011, the FLEXTAP met its specifications and was delivered to a major US semiconductor company.

A new model of the Castaing probe including a field emission electron gun has been tested...

... Life goes on....

11. APPENDICES

These appendices give the nonspecialist a quick overview of the three analytical techniques that are the goodwill of Cameca in 2011.

11.1. EPMA

Figure 75 shows an EPMA probe also called the Castaing probe. This sketch corresponds to the instruments delivered by Cameca such as the SX100.

The sample (6) to be analyzed is struck by an electron beam the spot diameter of which is normally less than 1 μm. Part of the energy of the electrons penetrating the sample will contribute to the emission of X-rays. The principle of EPMA is to measure the X-ray spectrum (that is to say, the intensities corresponding to the wavelengths). As it is known that a given element (e.g., copper) emits well-defined wavelengths, the spectrum thus provides information on the sample composition at the beam impact location. The angular position of the spectrometer (4) selects a single wavelength. Mechanically rotating the spectrometer yields a characteristic spectrum of the sample. Up to five spectrometers can be mounted on the instrument.

Producing the electron beam requires an "electron gun" (1) that emits electrons. These electrons are accelerated by an electric field created between the source and the anode (2). The electron beam is focused using magnetic lenses (3). The last lens (5) is the more critical component since it

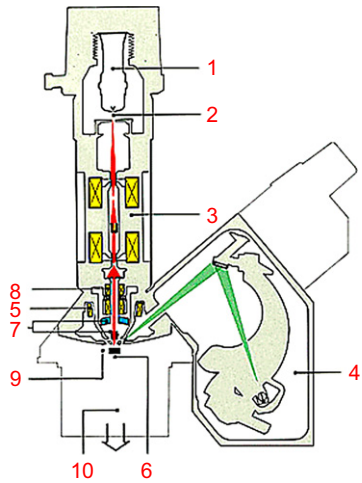


FIGURE 75 Schematics an EPMA Probe.

determines the sharpness of the electron spot and must incorporate deflection coils (8), a catadioptric mirror (7), and path for the X-ray beam of every spectrometer (4). The catadioptric mirror (7) makes it possible to include an optical microscope in the instrument.

A typical use of the instrument consists of setting every spectrometer to a position corresponding to an X-ray wavelength characteristic of a given element relevant for the sample to be analyzed and recording the respective X-ray intensities at different locations. Moving the sample stage makes it possible to achieve a mapping of the sample that displays the abundance of different chemical elements.

More detailed explanations on EPMA can be read in the litterature (Goldstein et al., 1994).

11.2. SIMS

As seen in Figure 76, a Cameca SIMS instrument such as the IMS 7f is equipped with primary ions sources, generally cesium or oxygen. A primary electromagnet is tuned for selecting the source used for the current analysis. The primary column suitably focuses the primary ion beam that is used to bombard the sample to be analyzed.

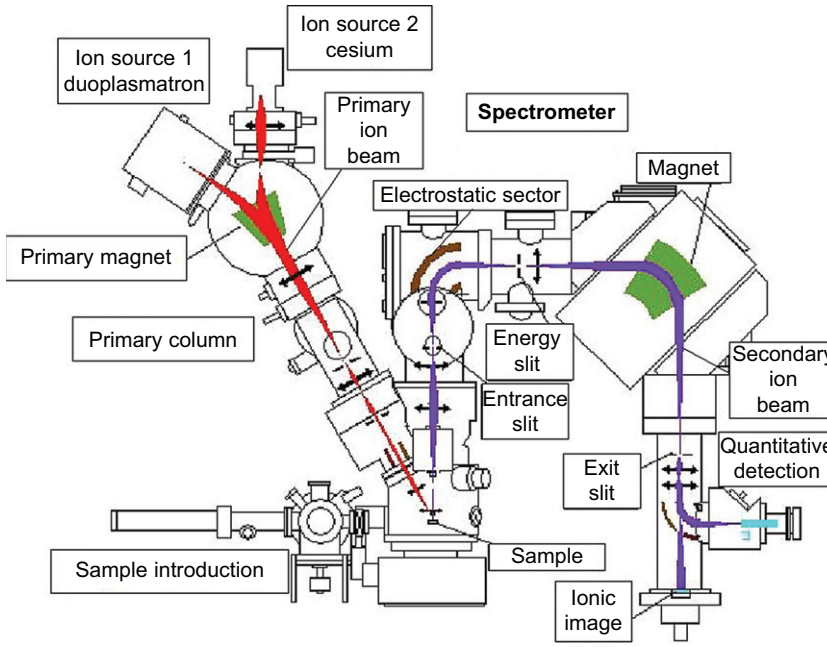


FIGURE 76 Cameca IMS 7f sketch.

The primary ions sputter the sample surface. Some of the sputtered atoms are accelerated toward a mass spectrometer, which filters the mass of the ions to be measured. The spectrometer, of the double-focusing type, consists of an electrostatic sector and an electromagnet. The magnet is purposed to create mass dispersion, which means that upstream from the magnet the secondary ions of any masses are processed in the same way, while downstream from the magnet, a single mass is on axis so that a single mass passes through the exit slit.

The secondary ions are very energy dispersed. And because the magnet produces dispersion in both mass and energy, the electrostatic sector is purposed to compensate exactly the magnet energy dispersion. Both the magnet and the electrostatic sector are shaped so they have stigmatic properties, like lenses; this allows an entrance slit image to be focused at the exit slit plane. The entrance slit width must be reduced whenever a high mass resolution is required. A high mass resolution may be required because several molecular ions may have their respective masses very close. For instance, the atomic weight of the phosphorus ion, $^{31}P^-$, is close to that of $^{30}SiH^-$. Downstream from the exit slit, an ionic image of the sample, filtered in mass, can be converted into a photon image and recorded by a camera. For quantitative analytical purposes, the secondary ion beam may be directed toward an electron multiplier that can count the ions, one per one, or a Faraday cup that measures the ion current.

More detailed explanations on SIMS can be read in the litterature (Benninghoven et al., 1987).

11.3. Comparison between SIMS and EPMA

Finally, both techniques—EPMA and SIMS—may be used to answer the same question: "What is the composition of a given sample?" There are differences between both techniques that distinguish the field applications of each one.

- Unlike EPMA, which is a nondestructive technique, SIMS is destructive. This is not only a drawback: Sputtering the sample with primary ions allows access to sample layers gradually deeper, which makes it possible to measure depth profiles. This makes the SIMS technique popular in the semiconductor industry.
- An advantage of EPMA is that it gives quantitative results—that is to say, it is possible to measure with good precision, for instance, that the concentration of nickel in the sample at the point of analysis is 2%, whereas SIMS gives only qualitative results ("a little," "very much"). That explains why EPMA is much more popular than SIMS in metallurgy.

- EPMA, which is a chemical analysis, cannot distinguish two isotopes of the same species, but SIMS, which achieves a mass measurement, can give a precise isotope ratio.

11.4. Atom Probe, FIM

The atom probe does not use a primary beam to probe the sample, contrary to EPMA (electrons) or SIMS (ions). Samples must first be prepared as a needle, whose point radius of curvature is about 50 nms. This can be achieved by advanced methods such as electropolishing for metallic material or focused beam methods (FIB) in the case of semiconductor materials.

An atom probe analysis consists of placing such a needle in an ultra-high vacuum chamber. After introduction into the vacuum system, the sample is handled such that the needle's tip is aimed toward an ion detector. A pulsed high-voltage source is generated and applied to the specimen. The application of the pulsed voltage results in ejection of an ionized atom from the sample surface at a known time. The delay between application of the pulse and detection of the ion is a TOF, which can be concerted in a mass/charge ratio.

Figure 77 displays the sketch of the WA-TAP designed at Cameca at the turn of 2005. The ejected atom i is accelerated toward a position-sensitive detector (PSD). The (Xi, Yi) position of the impact on the detector provides information on the original position of the atoms removed from the surface of the tip. The TOF between the electrical impulse and the

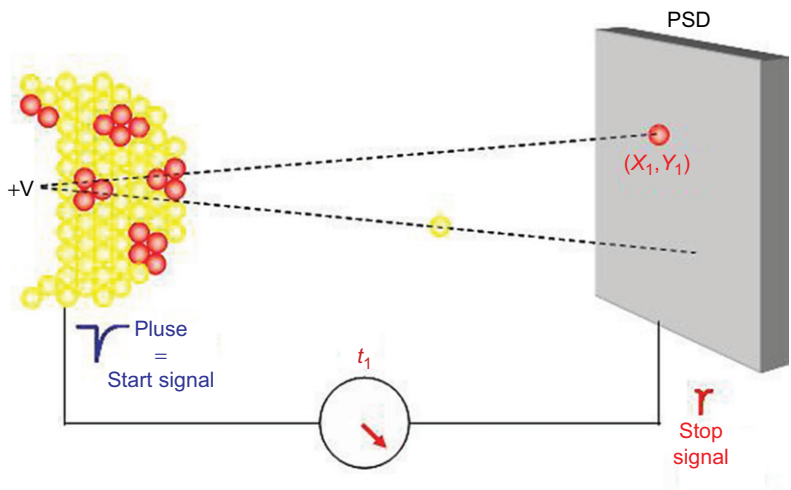


FIGURE 77 Sketch of the WATAP atom probe.

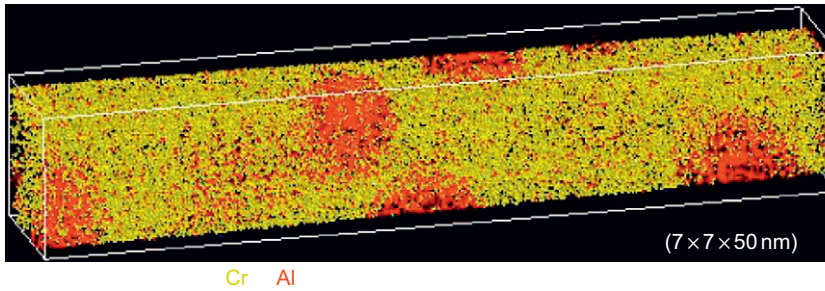


FIGURE 78 Aluminum-enriched particle nickel-base superalloy (Blavette et al., 1993).

impact on the detector provides information on the mass of the ejected atom.

In the case of an insulator or semiconductor specimen, it is worthwhile to initiate the atom evaporation, not with an electrical pulse but with a femtosecond laser.

Knowing the position and the species of each ejected atom, it is posible to reconstruct at the atomic scale the volume of the sample before analysis (Figure 78). This obviously requires a good physical model and relatively simple computer processing.

The atom probe is derived from the field ion microscope (FIM). A FIM image can still be obtained with a basic atom probe chamber provided a gas at low pressure has been introduced in the tip chamber and that a suitable imaging device, typically an assembly of a multi-channel plate, a phosphorus screen, and a camera, is inserted at some distance from the tip.

The photograph in Figure 79 is a FIM image taken in the twenty-first century but not too different from that observed by Mueller's students in the late 1960s. It accounts for the changes in local curvature radius. Atoms (bright spots) can be seen, which correspond to steps between two crystal planes.

A question arises: Why can an image at the atomic scale be obtained so easily without the need for a special anti-vibration system?" It is well known that with a conventional optical microscope, observing an image at high magnification requires a perfectly stable support of the sample and that it is impossible to see microscopic details if the sample holder is subjected to vibration greater than 10 μm, for example. In FIM, from the moment a tip with a radius of curvature of 50 nm is achieved and presented at 100 mm from a phosphorescent screen, a simple conic projection onto the screen shows a disk of 20 mm imaging the disk of 10 nm at the tip end. Two atom images are therefore separated on the screen by half a millimeter, which is visible to the naked eye, and if the tip is subjected to a

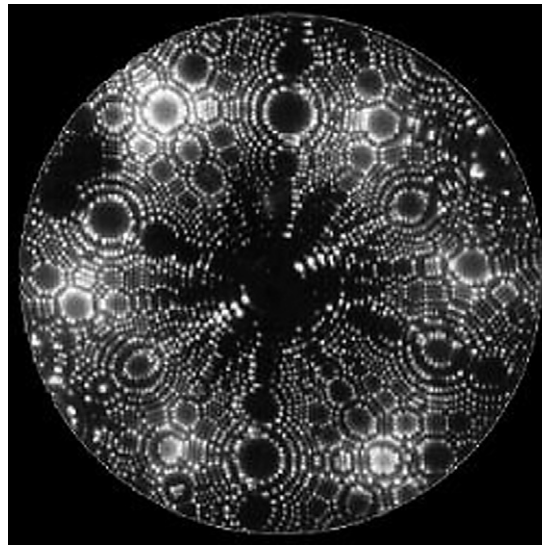


FIGURE 79 FIM image.

vibration of 10 μm, this vibration is not magnified; it is simply translated and remains far smaller than the image of an interatomic distance.

More detailed explanations of the atom probe can be read in the litterature (Miller, 2000).

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