Rediscovery of the Elements

VISITING THE LAND OF THE CURIES.

Part 3. Fluorine: The Most Dangerous Element



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In the 2001 Spring issue of *The HEXAGON of Alpha Chi Sigma*, the first issue of the Rediscovery of the Elements series appeared, and since then 57 articles appeared to cover the entire project, culminating in the 2016 Summer issue, shortly after the unfortunate passing of Jenny in 2014. These articles can be found on the Rediscovery website:

www.chem.unt.edu/~jimm/REDISCOVERY

Many curious readers have queried, "Why did you take on this grand project? What was it like to actually be the first to revisit all of these sites of discovery of the elements?" In an attempt to answer these questions, a new series of articles has been written, starting in 2017. So far, 14 articles have appeared (these may be found at alphachisigmahexagon.com). Within this new series, a critically important site has been Paris, which was, among other things, the location of Lavoisier's revolutionary studies recognizing the true elements.

Part 1. Tous le monde est en grève! "Everyone is on strike" (Summer 2022)

Part 2. Inside the Museum (Fall 2023)

Jim and Jenny visit the Musée Henri Moissan in Paris. Émilie was waiting for us at the breakfast table with coffee and croissants. "Bon jour," Émilie said. "How was the Musée Curie yesterday?"

"Bon jour, Bon jour, it was wonderful, we were all alone and they paid special attention to us. We went on a 3-hour tour, all across the Latin quarter. "

"I am told the strike is over," said Émilie.

"Oh, thank the Lord," said Jenny as she sat down. She grabbed her cup of coffee that Émilie passed to her. She spooned from a blue ceramic sucrier and stirred. "I needed this! We had a long day."

"Where are you going today?" asked Émilie, as she passed my cup to me.

"To the Faculté de pharmacie, in the Latin Quarter. That's where a French scientist named Moissan discovered fluorine."

"La Faculté de Pharmacie? On the Avenue de l'Observatoire? Just south of le Jardin du Luxembourg? There's a statue of Vauquelin in front of the school."

"Ah, hah," said Jenny. "Vauquelin again. The French rival to Martin Klaproth of Germany." (See *HEXAGON* Spring 2022)

"I didn't know his statue was there," I said as I took a sip of coffee. "Did he work there?"



Figure 1. Clorox bleach in France is "Eau de Javel," named for the original site on the Seine where the chlorine bleach business was founded in the 1770s.



Figure 2. Jill Daneels, our guide for several visits we made in Paris, was well versed in the history of Paris.

"Not sure, said Françoise. "All I know is, he's holding a jar of something… . A scientist named Moissan worked there? Discovered fluorine?"

"Yes, the 'most dangerous element' according to some historians. Several chemists who tried to prepare it were poisoned by it. It's deadly. Worse than chlorine."

"What's chlorine?" asked Émilie. "Ah, yes, now I remember 'Eau de javel.'" (Figure 1).

I said, "Fluorine is in the same chemical family as chlorine. They're both members of the halogen family—fluorine, chlorine, bromine, and iodine. Fluorine is the top halogen in the Periodic Table. Fluorine is so reactive that a glass container can't hold it; it dissolves its container."

"So just what did Moissan keep it in?" asked Émilie.

"Fluorite, calcium fluoride bottles and tubes of CaF_2. Fluorine won't react with fluorite because fluorite is already 'reacted.'"

"What's fluorite?"

"A mineral used as a flux in the smelting of ores."

Francoise asked, "Is the Faculté de pharmacie expecting you?"

"Oh, yes, we have an appointment. In fact, they are bringing in a special Professor Emeritus to give us a personal tour."

"Does he speak English?"

"No, that's the difficulty. I know my French is weak. I found a tourist guide who can interpret—to be there just in case. Her name is Jill Daneels. She is British, but she caters to English-speaking tourists and sets up tours from the U.S. and Great Britain. A tourist agency in the U.S. found her for us."

"Well, good luck! We will see you tonight."

"Au revoir!"

"Au revoir!"

Meeting with our guide. Jill had suggested over the telephone that we meet at an outdoor café at the corner of Boulevard Saint-Michel and Rue Soufflot. "You can find me," she said. "I'll be wearing a blue scarf."

She was waiting for us at a table on the busy boulevard, indeed easy to spot (Figure 2). She reminded me of Shirley MacLaine, very neatly dressed in a blue outfit with a stylish aquamarine écharpe.

"Good morning," she said, "It's good to meet you." She shook hands with each of us.

"And good to know you. I have a feeling we will need you today!"

"Let's have a cup of coffee and chat a bit to make sure I know what you want," she suggested. "I never had an assignment quite like this."

"Fine with me," said Jenny, "I can always use more coffee."

We sat down and placed an order with the garçon. "This is quite an impressive view, don't you think?" asked Jill. Jill pointed north along the boulevard, where traffic was rolling smoothly by. "This is the Boulevard Michelin, called Boul Mich' (pronounced 'Bool Meech') by the Parisians. Straight down to the Seine, to the north. The other way, to the south, we find the Jardin du Luxembourg and the Faculté de pharmacie. Just to our east up Rue Soufflot is the impressive Panthéon, with its huge dome and Corinthian columns. Many historical French people are entombed there in its crypts. Including Pierre and Madam Curie. And since you're a scientist, perhaps you'd also like to see its Foucault's pendulum, if you have time later today."



Figure 3. After the metric system was invented in 1790, public areas defined the meter in several cities in Europe. This is the only site remaining in Paris.

"Wow," Jenny and I looked at each other. "Wonderful!"

Jill said, "So you're from Texas."

"Yes," said Jenny. She dug out a coin and gave it to Jill, "Here's a Texas commemorative quarter for a souvenir."

"I can tell from your twang that you're definitely from that part of the country."

"My daddy was a cowpuncher," said Jenny. "Also an oilman, and eventually a preacher and then a teacher."

"And so you and Jim ended up together, when?"

"One year ago."

Jill's eyebrows raised. "How lovely! Quite remarkable! I myself just met my friend Claude from Paris, a year ago. You didn't waste any time getting started on this project, did you? And just what is the nature of your research?"

"'Rediscovery of the Elements.' We started this summer visiting the sites where all the elements were discovered. So far we've been to Romania, Hungary, Germany, and now France. We hope to have maybe ten-fifteen elements finished this summer. And we'll be back to Europe as often as we can."

"And at the Faculté de pharmacie, what was discovered?"

"Fluorine. Chemically similar to chlorine. You know 'Eau de Javel?'"

"Of course," said Jill. "Made at Javel, an old fishing village downstream on the Seine River, since the 1700s. That site is presently occupied by an Citroën automobile factory. A chemist named Berthollet developed and commercialized chlorine bleach, just about the time Lavoisier was guillotined, in 1794."

"You know history well!" I said.

"Thank you, that's what I need for tourists interested in the historical aspects of Paris. And there is a lot of historical chemistry in Paris!"

Jill smiled, coyly, and her blue eyes wrinkled demurely. "Just between us Anglophiles," she said, "You made a good choice for a guide. The French are very good at being proud of their rich culture, but frequently lack factual details, just as any prideful citizen of any country. That's where I come in. I organize a lot of educational tours from America. … So, what are we going to do?"

"There will be an informal presentation graciously given by a professor emeritus, a Professeur Rivet. It will be a private meeting, an audience of just you, Jenny, and me. But he doesn't speak English, and I would be embarrassed by my lousy French."

"So I just listen."

"Yes. And interrupt if I have a question… and I will not hesitate to ask you if something is not clear."

"Well, that should be easy enough. Sounds like fun, too."

She put down her cup. "Well, shall we go?… Oh, incidentally, I want to show you something along the way."

A five-minute walk took us to the north end of Luxembourg Park. She took us inside an



Figure 4. La Faculté de pharmacie was founded in 1803. The Museé Henri Moissan is located on the first floor.

alcove of a building. "Look there," she said, pointing to a long horizontal groove with markings etched in the stone wall.

"What is it?" asked Jenny. "It looks like a ruler carved in the stone wall."

"It is! It's the only remaining public meter stick in Paris, left over from the early 1800s. Farmers from around the countryside could come in and take a measurement on a string. They would return to their village with this common unit of length measurement." (Figure 3)

"Paris is a museum of history!" I was impressed.

"Paris is history," said Jill, "every meter of it! Well, on to the Faculté," it's on the south end of the Luxembourg park. About a kilometer away."

Fifteen minutes later, we were there, la Faculté de pharmacie, an imposing white building towering over the Avenue de l'Observatoire (Figure 4). And sure enough, in front was a statue of sage in a long flowing philosophical robe (Figure 5).

"Look!" said Jenny. "There's the statue! Vauquelin! The name is on the pedestal. And there's the jar. …What does it say …'CHROME.'" She turned to me. That's chromium!"

At his feet was a scroll. "Can you read it?" Jill asked.

"Let's see…Easy enough…'Analysis of stones, mineral waters, organic compounds.' Yep, he did all that. Actually, he was mainly organic—that's why he was connected with the pharmaceutical school, which concentrated on medicines obtained from natural sources. Among other things, he discovered asparagine, the first amino acid ever isolated. Named it after asparagus, where he got it from."



Figure 5. In front of the Faculté is a statue of Louis Nicholas Vauquelin, who discovered chromium and beryllium. Vauquelin's main contributions were to biological chemistry (he discovered the first amino acid, asparagine).

"Let's go in," said Jill. Our appointment is for 10 a.m."

Inside, the receptionist led us past a long hallway 5 meters high with rich maroon velvet walls, exhibiting a gallery of perhaps 100 huge portraits. "These paintings are all the professors who had been a part of the Faculté," translated Jill, who was speaking with the receptionist.

"Are Vauquelin and Moissan among them?" I asked.

Jill relayed the question to the receptionist, who replied, "Oui, oui," and pointed out the portraits (Figures 6,7).

She took us into a large room with show cases of exhibits. "Voici le musée de Moissan," she explained. A sign above the door had a beautifully scripted welcome: "Bienvenue au Professeur James et Mme Marshall."

Jill said, "Well, the French jolly well know how to put up a good show, don't they?"

A kindly white-haired gentleman in a suit rose from a chair.

The receptionist said, "Je vous présente le Professor émerité Jacques Rivet." (Figure 8)

Jill graciously took charge and extended amenities were exchanged all around. Then we got down to business. Jenny asked, through Jill, if she could freely take photographs, and Professor Rivet enthusiastically approved. He moved from cabinet to cabinet, describing the contents of each and its historical significance. The language arrangement worked well—the good Professor talked slowly so that I understood fairly well—particularly since French



Figure 6. Henri Moissan's portrait in the gallery.



Figure 7. Louis Vauquelin's portrait in the gallery.

scientific terms are similar to English—and I whispered to Jenny the significance of each. If there was a question, I asked Jill to politely interrupt with a query, and the professor would patiently answer. This most interesting presentation took two hours.

One showcase had photographs of Moissan's youth; another of his military years; another of his academic years, where he progressed from pharmaceutical chemistry to inorganic chemistry. Next came several showcases full of his books. Another showcase included his furnaces he used in his attempts to make synthetic diamonds. And finally were the exhibits of the discovery of fluorine in 1886: his Nobel Prize citations; the electrolysis apparatus which he used to produce fluorine; then his tube which he used to study the optical properties of his gaseous element. Professor Rivet reminded us that "le fluor est l'élément le plus dangereux, c'est très toxique." Moissan's goal



Figure 8. Professor Jacques Rivet, Professor Emeritus, describes the contributions of Henri Moissan.



Figure 9. The electrolysis apparatus used by Moissan to prepare elemental fluorine.

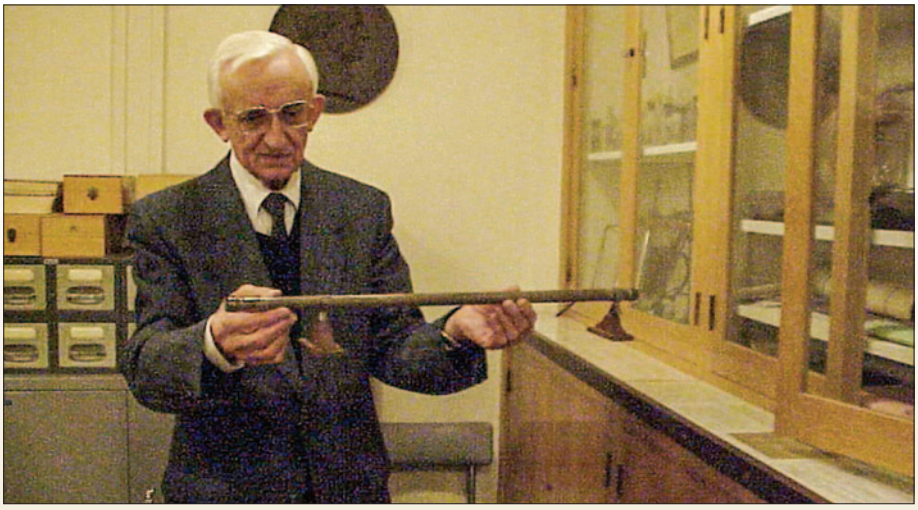


Figure 10. Moissan prepared a tube to study the optical properties of elemental fluorine, a yellow gas (compared with its family member green chlorine).

was to devise a means of electrolyzing hydrogen fluoride (itself a poisonous acid) safely and to contain the product (elemental fluorine, F_2) without exposing the experimenter to it. Moissan constructed a reaction vessel made of fluorite and used inert platinum electrodes (Figure 9). He cooled the reaction vessel to -23°C in a liquid methyl chloride bath to prevent chemical attack of the platinum electrodes. For the electrolyte reaction mixture, he could not use water (H_2O) because that would produce oxygen instead of fluorine. Instead, he used a solution of hydrogen fluoride/potassium fluoride (HF/KF), the KF serving as an ionic source to make the reaction solution electrically conductive.

As proof that he obtained elemental fluorine, Moissan devised a chemical test of using elemental silicon. When subjected to fluorine, a chip of silicon (unreactive in the atmosphere) immediately burst into flames. (see *HEXAGON* Fall 2016 for the authors' detection of elemental fluorine in their home laboratory)

And how to study the gas? Moissan constructed a tube of stainless steel (which reacts only slowly with elemental fluorine) with transparent fluorite caps. Viewing through the tube, it was shown that the color of fluorine is yellow—compared with the colors of others of the same chemical family: green, brown, and purple respectively for gaseous chlorine, liquid bromine, and solid iodine (Figure 10).

Finally, he said, "C'est tout" (that's all) and sat down. Jill knew what was appropriate to do next: "Merci, merci, c'est merveilleux!" She began applauding and Jenny and I took up the cue and joined in.

The good professor rested for a couple of minutes, and then stood up, "Et maintenant, mes amis, il est temps pour des rafraîchissements," as he stepped over to a side table and lifted a drape off the "refreshments."

"Oh, biscuits and punch!" said Jill. "How very lovely!"

Jenny looked puzzled, "Biscuits? Where is the gravy? And the punch bowl?"

Jill laughed," Brit for "cookies and juice."

Jenny sampled one of the biscuits. "Yum, they taste just like cookies that Grannie used to make."

Jill picked up the conversation with Professor Rivet, and Jenny and I, through her, chatted with the professor about more personal things, his family and his academic career. He was an emeritus of the school who specialized in alkaloids, but also was keenly interested in French chemical history. He mentioned that if we went upstairs, we would view beautiful stained glass windows depicting the history of chemistry in Paris. Also, there were statues of Moissan and Lavoisier.

There were a few more pleasantries, and then it was time to leave. We dusted off "biscuit crumbs" and gathered up our paraphernalia and shook hands all around, with effusive thanks for a wonderful day.

Out the museum door, Jenny said, "There are the stairs. Let's go up."

Sure enough, at the head of the stairs was a stately marble statue of Lavoisier, standing taller than life (Figure 11). Nearby was also a statue of Moissan (Figure 12). Behind the stairs was a stained glass window depicting Lavoisier in his laboratory—"Lavoisier dans son Laboratorire"— with several onlookers, all in their 18th-century costume and wigs, watching Lavoisier demonstrate one of his experiments with oxygen, heating a retort on a stove (Figure 13). "We keep bumping into Lavoisier,



Figure 11. Lavoisier's statue on the upper floor.



Figure 12. Moissan's statue on the upper floor.



Figure 13. Stained glass window depicting Lavoisier's preparation of oxygen. (The lower part was obscured by the staircase.)



Figure 14. Stained glass window showing activities in the botanical garden. The gardens of the Latin quarter, including the Jardin du Roi, were important in growing herbs from around the world, from which medicines could be extracted.

don't we? Said Jenny. "Looks just like Grannie's old wood stove, where she baked cookies—er, biscuits I mean," laughed Jenny.

Another window showed gentlemen overseeing workers hauling a wheelbarrow with a new imported herb to be planted in the Jardin des Plantes (Figure 14), and another showed the famous Swedish naturalist Linnaeus visiting the gardens.

Jill, who had picked up a pamphlet from the entrance desk, was reading to us: "Linnaeus was the one who devised 'binomial nomenclature' for the animal and plant kingdom. The botanical garden they are displaying is in the back. It was the source of the medicines they procured and studied."

Sure enough, outside was a large garden, measuring perhaps 50 meters on a side, choked with thickets of shrubs and other low-lying plants.

"Looks unkept," said Jenny. "Not like our farm in West Texas."

Jill read from the pamphlet, "Well, apparently in its day it was quite the thing. There are probably hundreds of species of plants in the garden. They gathered these, from all over the world, in a search for new medicines. Remember, Linnaeus, the 'father of modern taxonomy,' visited here."

Jenny was snooping through the vegetation. "No flowers. What an interesting garden, no flowers, just plants…Here's a sign by this bush. 'Belladonna.'"

"Yes," said Jill, "it lists Belladonna here in the pamphlet—famous with its long history of its use as an anesthetic, poison, and hallucinogen.

"This place is just full of scientific history," I said.

Jenny picked up, "The cutting edge of science in the 1700s, the French say. Didn't we say Paris was the center of science, culture, and fashion in those days? Let's go back in.

As we three passed through the gallery on the way out, Jill said, as she pointed to Moissan's portrait, "I didn't know he made synthetic diamonds, as Professor Rivet told us."

"He didn't," I said. "He reacted sand with charcoal and actually synthesized silicon carbide, which are almost as hard as diamonds. Today this substance is known by its mineral name, 'moissanite.'" Sometimes granules of moissanite are found in volcanoes. It's sometimes used as a gemstone in jewelry."

"But he got the Nobel Prize. The production of elemental fluorine must have been an incredibly significant achievement."

"It was. A historical chemist named Henry Roscoe in Manchester, England, called it 'one of the most difficult problems in modern chemistry.' But there was contention—and some historians today say Mendeleev should have received the Nobel Prize instead of losing out to Moissan."

"Mendeleev never received the Nobel Prize?"

"Never."

"I would have thought the Periodic Table would have been a more significant achievement. What excuse did they give for not giving it to him?"

"Among other things, he didn't predict the noble gases—helium, neon, argon, krypton, and xenon—but when discovered they fit into an expanded Periodic Table."

"So who should have gotten it?"

I thought for a moment, then "Maybe both of them—if that was possible."

By then we were at the door.

"Where to now," asked Jenny.

"Maybe we have time for the Panthéon?" asked Jill. "The Curies exhibits, and Foucault's pendulum."

"Wow," said Jenny. "How far?"

"Ten minutes walk. But first we take a quick side trip to the Observatory."

"Let's go!" Jenny said. ⬡