

Rediscovery of the Elements

Oliver Sacks, The Periodic Table, and Stinkspat



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One day during the autumn of 2000, I received a telephone call from Dr. Oliver Sacks. "I just read about your element collection in the *Journal of Chemical Education*," he said, "the one about your 'Living Periodic Table.' I'd like to see it."¹ This was a pleasant surprise; this was the well-known Oliver Sacks, the neurologist from New York City who had published articles of scientific interest in the *New Yorker*,² as well as several books on neurology and anthropology, such as *The Man Who Mistook His Wife for a Hat* and *Awakenings*. This latter contribution inspired a play, and then a movie starring Robert De Niro and Robin Williams.

I was curious why a neurologist would want to see an element collection. "Who told you about that?" I asked.

"Roald Hoffmann—I presume you know about him?"

The Nobel Laureate from Cornell! "Golly, I knew he was well-read—but I didn't know he read the 'minor' literature by lesser-knowns, too!"

"Well, I'm writing a book about my boyhood experiences in chemistry, and I'd like to 'relive' some of my memories by seeing the elements again."



Figure 1. Oliver Sacks in front of the element collection. His favorite element was bromine. The Blue Willow cup in the foreground contains hot tea and melted gallium!

Being flattered by Oliver's kind comments, I gladly agreed to his Sacks' visit, and arrangements were made for him to travel to Texas a few weeks later.

I picked him up at the DFW airport, recognizing him from his beard, as he suggested. In turn, I had told him my general description, but he had said that it would be easier if I found him instead. (I did not learn until years later³ that he suffered from prosopagnosia, or inability to recognize faces).

I drove him to Denton, 35 miles north, and we settled in our living room and he quickly gravitated to the element collection, a three-cabinet 6x9-foot display spread across the living room. He spent a full afternoon playing with one element after the other (Figure 1). Like a schoolboy with a new Gilbert chemistry set, he pulled specimens from the shelves, one by one, fondling each lovingly, telling stories about each one.

"You have a big sample of tungsten! Number 74. This is heavy!" In his palm he bounced a hefty slab of tungsten, as heavy as gold (we did not know at the time that his book about his boyhood chemistry experiences would be called *Uncle Tungsten*). Then he picked up what appeared to be a small dull-gray sprinkler head, sealed in a 4-oz. vial. "And this is beryllium. Number 4." He juggled it with his fingertips. "Light as a feather!"

He asked Jenny to make a cup of hot tea, into which he dropped the gallium. "Look at it melt!" He sipped carefully, then asked for an ice cube to freeze the gallium back to a shiny blob, dried it off with a towel, and returned it to the shelf.

"You have a bar of bismuth!" he cried. "Do you have a string?" He suspended the 3-inch bar to our ceiling lamp, and then tested it with our iron-boron-neodymium magnet. "See," he exclaimed. "It is diamagnetic!" Indeed, the bar

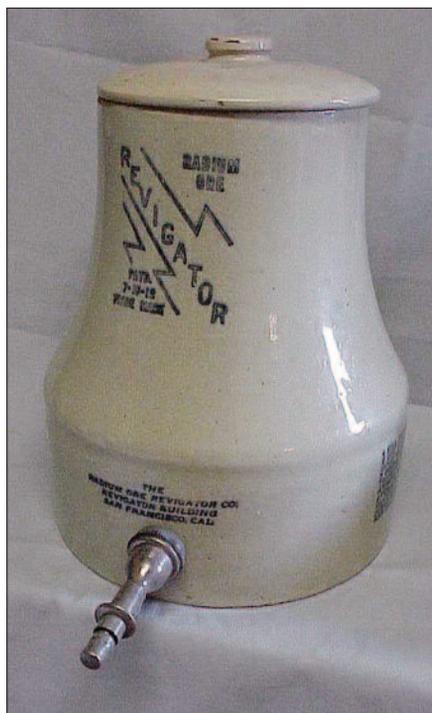


Figure 2. The “Revigator” is a crock pot lined with radium ore, in which water was stored and then drained into a cup to be taken “liberally, six times a day, to improve one’s health,” according to literature of the 1920s.⁴⁶ We had purchased our revigator from a Health Quack museum in Kansas, but kept it in the garage, not in the house.

was repelled and rotated away from the magnet.

“And yes, you have gadolinium. Let us try a magnet on it...” First, dunked the metallic button in hot water^{4h} and showed it was no longer ferromagnetic. “See, it’s above the Fermi temperature... now let’s drop it into a cup of ice cubes.” The button snapped back up to the magnet; it was now below the Fermi temperature of 16° C.

“Ah, you have a diamond,” as he pressed the pea-sized octahedral crystal to his lips. “It’s cold!... as it should be—a great thermal conductor.”

“I have another thermal conductor to show you,” I said, “here’s a slab of beryllia (BeO). It has been used as a thermal sink in police mobile radios. I obtained it from Motorola when I worked there.”

“It’s *really* cold!” he exclaimed. “I’ve never felt this before!”

“Now you’d better wash your hands,” I said, “beryllium is poisonous!”

We spent the whole afternoon going through each element. He held each lovingly, like a precious gem, chattering away and issuing facts about each. Very quickly I learned that afternoon that he had extensive knowledge of

the elements, far beyond the ordinary experience of most chemists. He knew, for example, that radon (Figure 2) was *not* discovered by H. C. Dorn (as proclaimed in all of the scientific literature),⁵ but instead by Ernest Rutherford and Frederick Soddy, as Jenny and I had found^{4e5} from our “Rediscovery” travels. He knew that phosphoro di bologna (barium sulfate), a thermally fluorescent stone, obtained by us from a muddy slope in the Apennine Mountains of Italy,^{4a} was not actually the active luminescent principle; instead, it was the reduced barium sulfide.

Finally, as sunset approached, it was time for supper. While consuming soup and a sandwich, he was curious, “You appear to have all of the elements, as well as samples of the ore from which each element was obtained. You mean, from the *exact* mine for each element?”

“Yes, for example, the Riddarhyttan copper mine in Sweden for cobalt; Himmelfürst silver mine in Germany for germanium; Pierrefitte lead mine in France for gallium; Facebánya gold mine in Romania for tellurium; Tangen feldspar and quartz mine in Norway for hafnium; Bisberg iron mine in Sweden for tungsten; and so on and so on.”

“And you have a sample of each element not only in its combined state (how it was discovered), but also in its elemental state?”

“Well, through uranium (atomic number 92), yes. But regrettably there are exceptions. We don’t have the radioactive elements appearing in minute quantities—astatine, francium, protactinium, actinium. For those a lump of pitchblende will have to suffice—a specimen of pitchblende, for example, is estimated to have a few atoms of francium. And there is one more exception of a more common element—fluorine. We have samples of each gas in glass bulbs, but not fluorine—it reacts with glass. We only have a sample of fluorite, calcium fluoride, although it is from the original mine where Scheele found it. (Figure 3) But—as we toured mineral shows across the U.S. and Europe and spoke with several German collectors, we learned that elemental fluorine *might* be present as inclusions in a special form of fluorite—it’s called “Stinkspat.” If that is true, then a specimen of Stinkspat would be the final addition to our collection. We hope to do that, during a future trip to Germany.”

“Well,” said Oliver. “Today was indeed pleasant... time to return to New York.” Oliver’s secretary (Kate Edgar) had reserved a motel for Oliver in Denton and arranged a limousine to take him back to DFW the next morning.

It was during the next year that “9-11” (September 11, 2001) occurred, the disaster where the twin towers were destroyed by terrorists. We were very worried; we hadn’t heard

from Oliver in the meantime. But we received in the mail, a draft of Oliver’s book, *Uncle Tungsten—Memories of a Chemical Boyhood*, just before it appeared in print—with a note thanking us for his “very lovely afternoon indeed” that he spent with us.

Stinkspat. We had learned from German mineralogists that the prime source of Stinkspat was Wölsendorf in Bavaria, Germany. Stinkspat was a dark-violet form of fluorite which, when pulverized, exuded a nauseating gas which sometimes forced the miners to leave and recuperate by resting at home for a day. The mineralogists *thought* that the noxious gas was elemental fluorine itself, in the form of microscopic inclusion that could be released by crushing. The fluorite would have been a perfect container for the highly reactive fluorine, since CaF₂ does not react with F₂. (Henri Moissan (1852–1907), the Nobel laureate who discovered elemental fluorine,^{4d} used fluorite caps at each end of a steel tube to contain the fluorine gas during his optical studies of the gas^{4d}). Stinkspat always contains uranium (sometimes thorium). It was conjectured that the irradiation from uranium somehow produced elemental fluorine from CaF₂, as well as a dark form of the mineral itself.⁶

The “scientific name” for Stinkspat was “antozonite,” an informal label that was never recognized officially,⁷ but which has been used extensively in the scientific and layman literature. The name “antozonite” was given in 1862 by Christian Friedrich Schönbein (1799–1868).⁸



Figure 3. A historically important specimen of fluorite (CaF₂) from the Garpenberg mine, the source of Scheele’s fluorite.^{4d} Carl Wilhelm Scheele (1742–1786) is considered to be the discoverer of fluorine in 1771, but could only isolate it in compound form, HF (hydrogen fluoride). Henri Moissan finally isolated the violently reactive element in 1886.^{3d}



Figure 4. Wölsendorf mine. The area, about 1 km east of the village of Wölsendorf, Germany, is pitted with many mine shafts that furnished first silver, and then deposits of fluor spar (fluorite), used in the fluxing and smelting of metal ores. This is the the Heinrich Kocher Stollen mine (N49° 24.59 E12° 11.24), reconstructed and maintained for historical interest by the local citizens.^{4d} The main source of Stinkspat was the Marienschacht, 500 meters south (N49° 24.29 E12° 11.19), one of many mines pitting the area—now appearing as large holes in the ground, filled in. The Marienschacht was developed in 1896, and decommissioned in 1979. A total of 1,000,000 metric tons of fluor spar was removed from the Wölsendorf area. A street Marienschachtweg (“Marienschacht street”) leads eastward from the village to the mine area.

(Schönbein was the discoverer of ozone in 1839 and gun cotton in 1845).⁹

Four years after Oliver’s visit to Denton, we were able to visit Wölsendorf, in the southeast part of Germany close to the Czech border (Figure 4), and we returned with two pounds of this dark mineral (Figure 5).

Kitchen chemistry of Stinkspat. It was time for us to study the Stinkspat samples (Figure 6) in an attempt to gain evidence that they contained elemental fluorine. A preliminary step was to obtain an EDX analysis in order to make sure there were not other interfering oxidants such as chlorine. This analysis showed the presence of calcium, fluorine, and lesser amounts of uranium with traces of silicon, magnesium, and aluminum. Our kitchen had been used previously for chemical experiments¹⁰—we had studied Sniadecki’s “vestium” and showed it could not be ruthenium^{4f,11a} and we had repeated Collet-Descotils’ studies with vanadinite and showed his experiments (“proving” vanadium was actually chromium) were sloppy and incorrect.^{4b,11b} (These “kitchen experiments” have been a modest copy of the model provided by Agnes Pockels (1862–1935), whose home-made studies with soaps in her kitchen in Braunschweig, Germany, eventually gained the attention of Lord Rayleigh and to eventual publication of her “Surface Tension” in *Nature*.¹²

Our first experiment was to smash a Stinkspat sample with a hammer. Pew!! The immediate stench made us ill; our best description of the odor was a cross between rotten road kill and Clorox. To proceed with the chemical tests, we prepared Schönbein paper⁹ by soaking blotter paper with a solution of potassium iodide and starch—this paper, when treated with an oxidizing agent, turns blue. The



Figure 5. Stinkspat, or antozonite (left), and classical fluorite (right). The Stinkspat was collected from the same source (Wölsendorf) as the Kraus NMR specimen.⁶ The fluorite specimen was collected from Denton County, Illinois. Stinkspat is dark, opaque whereas classical fluorite is transparent or translucent, of variable hues of clear, pink, green, and blue.

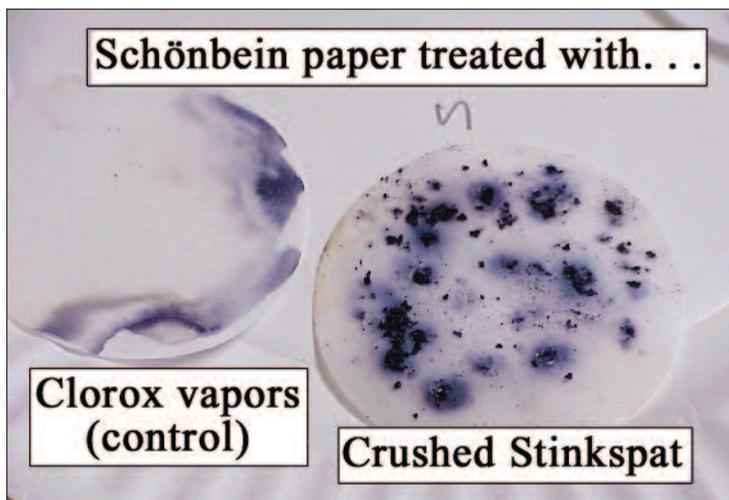
final step was crushing pieces of Stinkspat on wet Schönbein paper. The result is shown in Figure 7: proof that indeed a strong oxidizer is present in the Stinkspat.

The exact nature of the oxidizer. Moissan, who certainly knew what fluorine smelled like, thought he recognized the odor of F₂ from the pulverized antozonite^{13a}—but this sensory observation was not definitive. Other possible malodorous oxidative fluorine compounds might exist (such as sulfonyl fluorides or fluorine dioxide,⁹) and there existed the possibility that fluorine might be generated from the electrical discharge when antozonite is crushed.⁶ Other suggestions in the literature included the possibility that even if fluorine *did* exist in the antozonite, when the mineral was crushed, the fluorine might rapidly react with water vapor to produce HF, then ozone, and finally hydrogen peroxide,⁶ hence, the effusion from antozonite

might be a mixture of oxidizers.¹³ Recent mass spectral studies¹⁴ showed that samples of antozonite contain quantities of carbon tetrafluoride and sulfur hexafluoride,¹⁴ the amount of which correlated with the amount of radioactivity present; but this experimental procedure was not able to confirm the evolution of F₂ or other corrosive gases whose molecules would not survive the instrumental environment.

Final proof of native elemental fluorine. The authors noted that when the Stinkspat was crushed, there was an *immediate* production of the nauseating odor and blue spray on the Schönbein paper. The authors concluded that the evidence was quite convincing that there was elemental fluorine present in the mineral. But it would be nice to get *direct* proof!

Such proof was not long in coming—from an NMR laboratory in Germany.⁶ Florian Kraus and coauthors investigated antozonite (“fetid



LEFT: Figure 6. The author pursuing “kitchen chemistry” in the home, smashing Stinkspat on Schönbein paper.

ABOVE: Figure 7. Photos of crushed Stinkspat on Schönbein paper. As the crystals were smashed, a blue stain squirted out immediately, proving an oxidant was present in the mineral. To show the blue color was due to developed iodine-starch complex and not to another type of unusual stain, it was then reacted with thiosulfate, whereupon the color disappeared.

fluorite”) from Wölsendorf using ^{19}F magic-angle-spinning solid-state NMR. In their elegant study, an isolated single peak of ^{19}F at 425 ppm was shown to be elemental F_2 , apart from the main ^{19}F peak of CaF_2 at -108.8 ppm. Thus, “unambiguous, in situ evidence” was obtained that “elemental F_2 exists in nature.”⁶ In this same study, the authors showed that the dark color of antozonite was caused by the existence of calcium clusters formed by the radioactive uranium: pure synthetic CaF_2 was observed to give such clusters upon irradiation with β -rays.⁶

Our “Living Periodic Table”¹ was now complete—it included a specimen of “Stinkspat” which allowed us to claim a sample of fluorine “in the native state.”

Final tribute to Oliver Sacks. Since the visit of Oliver to our home in Denton, we kept in communication with him; in a *HEXAGON* article a photograph is included of Oliver laying a wreath on the grave of Carl Wilhelm Scheele (1742–1786) in Köping, Sweden^{4c}—Oliver visited Köping and its Scheele museum after receiving travel instructions from us, as we had been preparing our “Rediscovery” DVD. During his 70th birthday in 2003, we could not accept his gracious invitation to his birthday party in New York City as we were in Europe, but we could celebrate “in absentia” (Figure 8). During this correspondence with him in 2003, upon his request, we sent to him a sample of hafnium, in anticipation of his 72nd birthday two years later.

It was with extreme sadness as we learned of Oliver’s illness and his eventual passing on

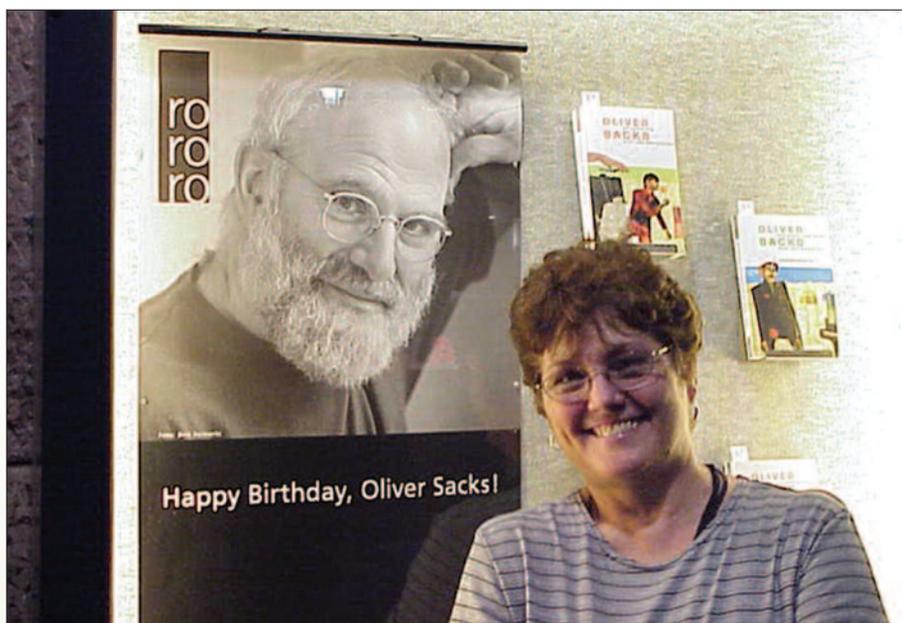


Figure 8. This promotion in a Freiburg im Breisgau, Germany, bookstore was prominently displayed during Oliver Sacks’ birthday in 2003. His translated book “Onkel Wolfram—Erinnerungen” (“Uncle Tungsten—Memories”) was on sale inside the bookstore. Coincidentally, Oliver Sacks’ middle name was “Wolf.”

August 30, 2015. No one appreciated the simplistic beauty of the Periodic Table more than he. In his final (posthumous) publication, *Gratitude*,¹⁵ he included an essay “My Periodic Table.”^{15b} On his round table of knickknacks, he assembled samples of elements with atomic numbers corresponding to his latter years. Next to lead (82, the age he reached) is a sample of beautiful iridescent crystals “terraced like a

Hopi village” (i.e., hopper crystals of bismuth, atomic number 83). “I do not think I will see my 83rd birthday,” he said, “but I feel there is something hopeful, encouraging, about having ‘83’ around.” Utterly curious and optimistic to the very end, as he expressed in another essay,^{15a} “My Own Life,” “... my predominant feeling is one of gratitude... I have been a sentient being, a thinking animal, on this beautiful planet, and

that in itself has been an enormous privilege and adventure.”

We will miss you, Oliver Sacks. And our top shelf of our Living Periodic Table, we have dedicated the specimen of Stinkspat, with its caged native fluorine, to you. ☹

References.

1. J. L. Marshall, *J. Chem. Ed.*, **2000**, 77(8), 979–983; 77(9), 1119
2. <http://www.newyorker.com/books/double-take/oliver-sacks-in-the-new-yorker> (August 30, 2015)
3. O. Sacks, *On the Move*, **2015**, Knoff, 121.
4. (a) J. L. Marshall and V. R. Marshall, *The Hexagon of Alpha Chi Sigma*, (a) **2002**, 93(2), 24–26; (b) **2004**, 95(2), 24–28; (c) **2005**, 96(1), 8–13; (d) **2006**, 97(3), 42–46; (e) **2008**, 99(4), 68–71; (f) **2009**, 100(2), 20–23, 31; (g) **2010**, 101(2), 22–26; (h) **2015**, 106(3), 40–45.
5. J. L. Marshall and V. R. Marshall, *Bull. Hist. Chem.*, **2003**, 28(2), 76–83.
6. J. Schmedt auf der Günne, M. Mangstl, and F. Kraus, *Angew. Chem. Int. Ed.*, **2012**, 51, 1–4.
7. P. Bayliss, *Glossary of Obsolete Mineral Names*, **2000**, The Mineralogical Record, 11.
8. Tenth Supplement to Dana’s Mineralogy, 1862. *Amer. J. Science*, **1862**, 84, 211. Later “antozonite” was considered to be an “obsolete”: see ref 5.
9. M. Rubin, *Bull. Hist. Chem.*, **2001**, 26(1), 40–56.
10. G. B. Kauffman, J. L. Marshall, and V. R. Marshall, *Chem. Educator*, **2014**, 19, 106–115;
11. J. L. Marshall and V. R. Marshall, 248th National ACS Meeting (San Francisco), invited papers to History Division Symposium on “Found and Lost: Incredible Tales of Spurious, Erroneous and Rehabilitated Elements,” August 11, 2014; (a) “The Legend of Vestium,” (b) “Undiscovery of Erythronium.”
12. https://en.wikipedia.org/wiki/Agnes_Pockels. Pockels did her research at Hagenstraße 34 in Braunschweig, now named Steinbrecherstraße 34 (N 52° 16.11 E 10° 32.29). Her published article was A. Pockels, “Surface Tension,” *Nature*, **1891**, 43, 437–439.
13. (a) F. Henrich, *Z. angew. Chemie*, **1920**, 33, 20–22; (b) H. Strunz, *Naturwissenschaftlicher Verein*, **1962**, Regensburg, Germany, 35–39.
14. J. Harnisch and A. Eisenhauer, *Geophys. Res. Letters*, **1998**, 25(13), 2401–2404.
15. O. Sacks, *Gratitude*, **2015**, Knoff, (a) 13–20; (b) 21–30.

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