Rediscovery of the Elements

The Strange Story of Stinkspat.

How Jim and Jenny Marshall rediscovered fluorine, the "stinky" element, and added it to their element collection.



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Figure 1. This sample of Stinkspat ("antozonite") was collected from Wölsendorf, Germany.

Fluorine is a common element in the earth's crust (ranking 13th in abundance) and yet because of its reactivity fluorine has never been observed in the native state in nature, but only as the fluoride.

Or has it?.... Since medieval days, fluorite (CaF_2, also known as fluorspar) has been mined and used as a flux for the smelting of iron and other metals. Fluorite is generally colorless, although it can take on hues of green blue, yellow, red, etc. An unusual form of dark, purplish fluorite known as "Stinkspat" (Figure 1) was known in the Middle Ages to render miners violently ill when dug up, because it spawned a noxious, acrid odor.[1] A well-known fluorite mine which has provided quantities of Stinkspat is Wölsendorf, Germany (N 49E 24.59, E 12E 11.24), in southeast Bavaria, 35 kilometers from the Czech border), from which the authors procured about a kilogram of Stinkspat for their collection and studies.

Earlier reports have suggested that the foul odor emanating from Stinkspat is due to elemental fluorine, which possibly may react with water vapor to produce HF, ozone, and finally hydrogen peroxide.[2,3] "Antozonite" was proposed as a name for this mineral variety of fluorite by Christian Friedrich Schönbein (1799–1868), the discoverer of ozone in 1839 (he was also the inventor of guncotton in 1845).[4] Henri Moissan (1852–1907), the Nobel laureate who first prepared elemental fluorine, thought he recognized the odor of F_2 from the pulverized mineral, thus lending credence that the foul odor was indeed elemental fluorine.[2] Recent mass spectral studies[5] have shown that samples of Stinkspat contain quantities of carbon tetrafluoride and sulfur hexafluoride. It was logical to hypothesize that these fluorine compounds were produced from the reaction of carbon and sulfur impurities with elemental fluorine somehow produced in the fluorite mineral. However, the presence of elemental fluorine could not be unequivocally established.

Kitchen chemistry. The authors wanted to investigate the possibility of elemental fluorine in Stinkspat, and turned to "kitchen chemistry" to gain evidence for its existence. (Figure 2) With our authentic samples of Stinkspat from Wölsendorf, we crushed small (1-gram) samples in a mortar. There was indeed an immediate nauseating stench, lasting only 2–5 seconds—which might be best described as a cross between a dead animal and chlorine.

At this point we thought it was important to ascertain the exact analysis of our samples. A



Figure 2. The authors often turned to "kitchen chemistry" in their home to investigate historical laboratory experiments. Here Jim is crushing a small bit of Stinkspat on Schönbein paper (see text).

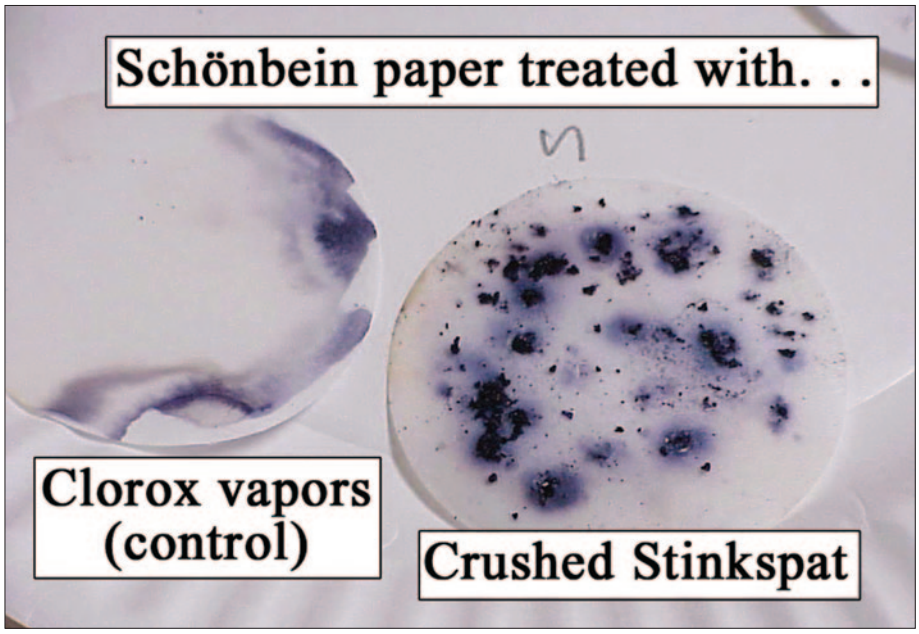


Figure 3. The pieces of Stinkspat, when crushed on Schönbein paper, give a splay of blue color of a iodine/starch produced when the released elemental fluorine reacts with the starch/potassium iodide combination of the test paper. The "control" demonstrates the appearance of another strong oxidizer (Clorox®) reacting with the Schönbein paper.

windowless EDX analysis gave the following data:[6]

F 47.18% wt
Mg 0.37
Al 1.38
Si 1.84
Ca 49.23
(No significant amounts of oxygen or chlorine)

If elemental fluorine were present, then it should prove positive for a strong oxidizer. We prepared "Schönbein paper" by soaking filter papers with a solution of potassium iodide and starch.[4] Schönbein paper was originally invented by the chemist for the testing of the presence of ozone; the ozone would react with potassium iodide (KI) to produce iodine which forms a blue complex with starch. When we crushed small pieces of Stinkspat on these wet pads, there was an immediate spray of blue surrounding the small specimen, proving there was indeed a strong oxidizer. Since EDX had shown there were no significant amounts of oxygen or chlorine, then the oxidizing agent must have been elemental fluorine, F_2. (Figure 3)

How would be elemental fluorine be produced in nature? An important observation by mineralogists has been that Stinkspat specimens are always seen in the presence of uranium (or thorium) minerals.[2] We studied our samples and observed indeed a low level of radioactivity. In our kitchen studies, it was noticed that this level of radioactivity varied considerably from sample to sample—just as there was a variation in the level of odor as well and blue "spray" on the Schönbein paper. A correlation among these three types of observations—odor, blue spray, and radioactivity—might have been interesting, but the elaborate experimental setup would have been difficult to establish quantitatively "in the kitchen."

Proof from NMR. It would be been very satisfying to be able to detect elemental fluorine in Stinkspat directly, and in fact an elegant experiment was subsequently performed by Kraus and coworkers in 2012.[7] In this research, "Occurrence of Difluorine F_2 in Nature—In situ Proof and Quantification of by NMR Spectroscopy," a solid-state magic-angle-spinning NMR study showed F_2 indeed occurs as "inclusions in antozonite." Quantitative ^{19}F NMR experiments on various specimens showed F_2 content of (0.012 ± 0.0015) $mmolg^{-1}$, that is (0.46 ± 0.06) mg of F_2 per gram in the samples. The authors completed the story as they discussed the production of these inclusions from radiation from neighboring inclusions of uranium minerals, noting that the dark purplish color of Stinkspat resulted from calcium clusters, similar to observations when pure CaF_2 crystals, which are colorless, are irradiated with beta-rays. As a final note, the authors describe that in a qualitative olfactory study of their laboratory, the odor of elemental fluorine is different from any of the other candidates which have been proposed in the literature for the odor of crushed Stinkspat; these candidates include O_3, Cl_2, HOF, HF, OF_2, and XeF_2.

The authors are grateful for the NMR evidence of Kraus et al., because it is now confirmed that our "Living Periodic Table"[8] is now complete—it now includes a specimen of "Stinkspat" which allows us to claim a sample of fluorine "in the elemental state."[9]

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