



Occurrence of Difluorine F₂ in Nature—In Situ Proof and Quantification by NMR Spectroscopy**

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Elemental fluorine, F₂, is the most reactive chemical element. Great experimental skill and special equipment are necessary to handle it safely. It reacts with any element or compound, except for the lighter noble gases He and Ne, and highly oxidized fluorides such as CaF₂ and UF₆. For this reason, elemental fluorine has been claimed not to occur in nature, where it is found only in the form of minerals like fluorapatite, cryolite, and fluorite, as taught in basic chemistry classes and stated by textbooks.^[1–3] However, a very controversial debate on the “natural existence” of F₂ started already 200 years ago, in 1816, and has not been resolved since. Here we present the first direct evidence from in situ NMR spectroscopy that elemental difluorine indeed occurs in nature in the form of a gas included in some varieties of the mineral fluorite (CaF₂). With the help of ¹⁹F magic-angle-spinning solid-state NMR spectroscopy we were able to identify and quantify the content of F₂ within “antozonite” and thus rule out a number of other explanations previously given for the peculiar smell of these minerals when they are crushed.

Fluorite (lat. fluere: to flow) has been used since the early medieval ages as a fluxing agent for iron-based metals and was first mentioned in 1530 by Agricola.^[4] As early as in 1670, Schwanhard from Nuremberg used mixtures of fluorite and

sulfuric acid to produce frosted glass for decoration purposes and in 1771 Scheele conducted thorough studies on the hydrofluoric acid responsible for the etching process.^[5,6] Ampere recognized in 1810 that hydrofluoric acid contains hydrogen atoms and another element he suggested calling “phthore”, greek for destruction.^[7] In the many attempts to isolate “phthore”, it was found to react with practically everything thus preventing its isolation. Davy also made several attempts to prepare “phthore” and proposed the name “fluorine (Fl)” in 1811.^[7,8] So, fluorine’s name was coined long before its actual synthesis. Around 1860, hydrofluoric acid of technical grade became commercially available in various concentrations for etching purposes. Finally in 1886 Henry Moissan succeeded in the preparation of elemental fluorine and received the Nobel Prize in 1906 for his discoveries.^[9,10] For a detailed summary on the discovery of fluorine please refer to the literature.^[11] Industrial production of F₂ by electrolysis started around 1940 thanks to the importance of fluorine in uranium enrichment. In 1986, one hundred years after Moissan’s discovery, Christie succeeded in the chemical synthesis of fluorine.^[12] Unfortunately many school and university textbooks still refer to the chemical synthesis as an impossible task.

Naturally occurring fluorite is rarely found in colorless form. It can show various colors, spanning from yellow, orange, and red to green, blue, and even violet. The reasons for the different colors have been well investigated and are discussed in the literature.^[13–15] In Wölsendorf (Upper Palatinate, Bavaria, Germany), a brittle, dark violet or even black variety of fluorite is found, which is called “fetid fluorite”, “stinkspar”, and “antozonite”, owing to the unpleasant odor detected when the mineral is crushed.^[14,16] However, this discovery is not unique, and this mineral has been found in other locations worldwide, for example, in France,^[17–19] Spain,^[20] Hungary,^[21] England,^[22] USA,^[23,24] and Canada.^[25–28] At all these locations radioactive minerals of uranium or sometimes thorium are in coexistence with the “antozonite”. The color of the “antozonite” is explained by clusters of elemental calcium,^[15] which have also been observed in irradiation experiments on artificial CaF₂ and naturally colorless CaF₂. Regarding the species responsible for the peculiar smell, many speculations, chemical analyses, and mass spectroscopic studies claimed ozone, “antozone”, compounds of phosphorus, arsenic, sulfur, and selenium, fluorinated hydrocarbons, iodine, chlorine, hypochlorous acid, and finally, of course, fluorine to be responsible (see Figure 1 and the Supporting Information for details).

Some researchers have argued that fluorine is formed from the electrical discharge generated when “antozonite” is crushed and that it is not occluded in the mineral.^[29,30]

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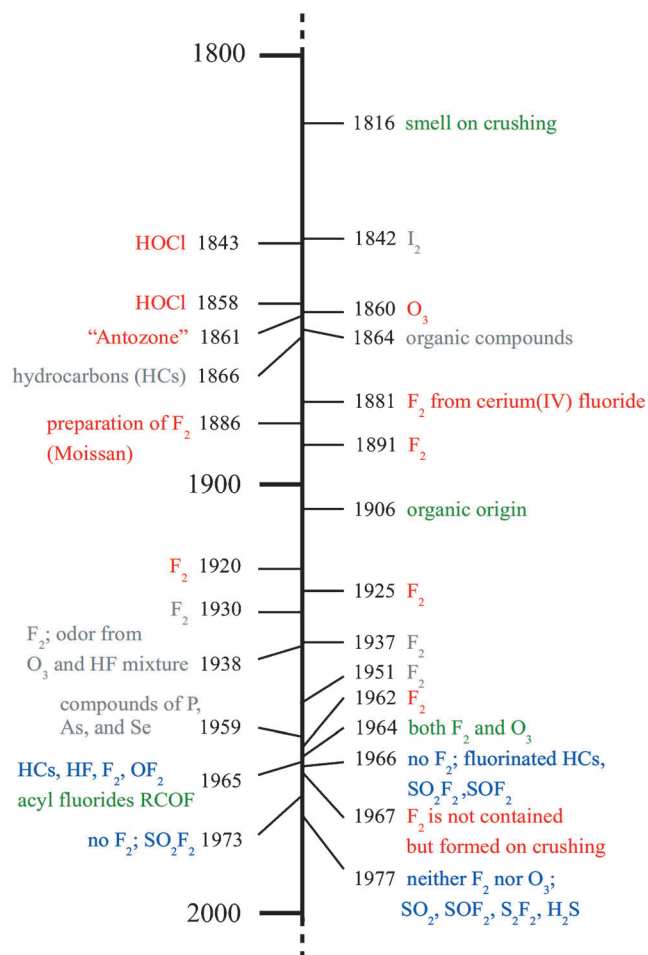


Figure 1. Timeline of literature on the reasons for the peculiar smell of the freshly crushed CaF_2 mineral “antozonite”; the color coding refers to the method used for the investigation (red: chemical evidence, blue: mass spectrometry, green: olfactory identification, gray: unknown method). Up to now no in situ method has proven the inclusion of F_2 or any other of the listed compounds in “antozonite”.

Attempts to quantify the strong oxidant included in “antozonite” were undertaken by several authors.^[26,31] Their chemical analyses gave amounts between 0.2 to 0.47 mg of the strong oxidant per gram of “antozonite”. Since the authors could not identify the actual oxidizing species, they considered the content to be “antozone” (O^+), oxygen, or fluorine. However, it was evident^[26,31] that a stronger oxidant than oxygen or hydrogen peroxide must be present, with singlet oxygen, ozone, oxidizing fluorides like OF_2 , and F_2 itself as candidates. All these findings were heavily debated, confirmed, and disapproved (see the Supporting Information). In summary, none of the analytical methods were capable of proving in situ that F_2 is present in “antozonite”. Instead, compilations and reviews of compounds putatively responsible for the smell of “antozonite” were frequently published,^[15,18] the first in 1914.^[32] The discussion also extended beyond the purely scientific community and became of broader, public interest.^[33–35]

Chemically pure, synthetic fluorite, a colorless compound, is used extensively for the manufacture of optical components of high-power lasers and outer-space telescopes because of its chemical inertness, wide band gap, and other physical proper-

ties. However, since CaF_2 may suffer from radiation damage, several investigations using γ , β , and laser irradiation were undertaken to clarify the formation of defects in the crystal lattice. From these experiments it became evident that the blue/violet color of irradiated CaF_2 is caused by Ca clusters. Also, the formation of gas bubbles within CaF_2 during electron-beam irradiation was observed,^[36–38] the occluded gas was identified as elemental fluorine, F_2 .^[37,38] Taking into account the known mechanisms for the formation of elemental F_2 upon irradiation of naturally colorless or artificial CaF_2 ,^[37,38] it becomes evident that the occurrence of “antozonite”, its color, its smell and its morphology, can be related to natural inclusions of uranium, sometimes also thorium, and their respective decay products. Henrich seems to be the first to assume that the color as well as the smell of crushed “antozonite” might be related to the occurrence of the radioactive minerals.^[32] Our samples of “antozonite” contain uranium and its daughter nuclides in an amount of approximately $2.93 \times 10^{-1} \text{ Bq g}^{-1}$, which corresponds to 2.36×10^{-5} grams of uranium per gram of sample; this was determined by γ spectroscopy on the daughter nuclides of ^{235}U and ^{238}U . As the fluorite from Wölsendorf is roughly $2\text{--}3 \times 10^8$ years old,^[39] and the half-life of ^{238}U is 4.468×10^9 years,^[40] the β -radiation-emitting daughter nuclides ^{234}Th , $^{234\text{m}}\text{Pa}$, ^{214}Pb , ^{214}Bi , ^{210}Pb , and ^{210}Bi account for extended irradiation of the fluorite and hence the formation of F_2 .

Our “antozonite” samples were obtained from the mine “Grube Maria” at Wölsendorf.^[14] X-ray powder diffractometry showed pure, highly crystalline CaF_2 to be present. We compared the smell of crushed “antozonite” directly with authentic F_2 gas and unambiguously confirmed that the odor of the mineral corresponds to F_2 . The smell of F_2 is decisively different from that of O_3 , Cl_2 , HOF , HF , OF_2 , and XeF_2 , which were also smelled in direct comparison. F_2 is detectable by humans in minute amounts; its odor threshold is reported to be 0.035–0.2 ppm.^[41] Because olfactory testing may be biased, we also employed other analytical methods. We used ^{19}F solid-state magic-angle-spinning (MAS) NMR spectroscopy to obtain highly resolved spectra from various “antozonite” specimens; an example is shown in Figure 2. The assignment of the observed peaks in the spectrum is straightforward by comparison to literature values^[42] (Table S1 in the Supporting Information). The peak (including spinning sidebands) at -109 ppm is assigned to F^- ions in CaF_2 and the peak at 425 ppm to difluorine F_2 . Pure gaseous and liquid F_2 are reported to have isotropic chemical shift values of 419 and 422 ppm, respectively.^[43] The small deviation is a consequence of sample susceptibility and pressure. Because of the short $\text{F}\text{--}\text{F}$ distance in F_2 the homonuclear magnetic dipole–dipole coupling constant in F_2 molecules is of the order of -80 kHz, which would cause a significant number of spinning sidebands under the given experimental conditions for a static F_2 molecule. The absence of spinning sidebands gives evidence of fast rotational motion as in a fluid which is able to average out the homonuclear dipolar interaction. In agreement with our interpretations we observe fast T_1 relaxation for the F_2 peak at 425 ppm ($T_1 = 27$ ms) and slow relaxation for the F^- peak at -109 ppm ($T_1 = 64$ s). The ^{19}F NMR spectrum (Figure 2, gray spectrum) shows that inclusions of other

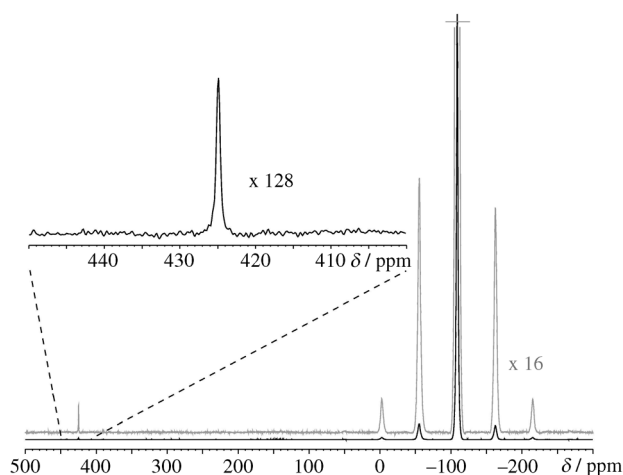


Figure 2. Quantitative ^{19}F MAS NMR spectrum of “antozonite”, obtained by direct excitation. The peak at 425 ppm is assigned to F_2 , the peak (and its spinning sidebands) at -108.8 ppm to F^- in CaF_2 ; no other peaks were observed in an extended range from -1100 to $+20\,000$ ppm.

oxidative fluorine compounds previously discussed (Table S1) are not detectable down to the noise level of the NMR experiment.

Because of the dark color of the natural mineral, it was necessary to make sure, by quantitative ^{19}F MAS NMR spectroscopy, that the spectrum is representative for the bulk sample. By measuring the sample against an internal reference compound (BaF_2) we ascertained that paramagnetic atoms do not mask (by relaxational processes or through large paramagnetic shifts, see the Supporting Information) any significant part of the spectrum of the mineral. The observed amount of (25.1 ± 0.8) mmol of total fluorine (F) per gram of “antozonite”, which was determined by a back-extrapolated spin-echo technique and corrected for offset effects and relaxation,^[44] agrees with the expected value for pure CaF_2 (25.6 mmol g^{-1}) within the error limits. Quantitative ^{19}F NMR experiments on various specimens resulted so far in a maximum F_2 content of $(0.012 \pm 0.0015) \text{ mmol g}^{-1}$, that is $(0.46 \pm 0.06) \text{ mg}$ of F_2 per gram of the “antozonite” samples.

In conclusion, ^{19}F solid-state NMR spectroscopy on the CaF_2 mineral “antozonite” from Wölsendorf has provided unambiguous in situ evidence that elemental F_2 occurs in nature. The presence of elemental F_2 as an occlusion in “antozonite” is likely to be a result of natural radioactivity and the dark color a consequence of elemental calcium clusters similar to those which have been observed upon irradiation of pure synthetic CaF_2 with β -rays.

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- [1] C. E. Housecroft, E. L. Constable, *Chemistry*, Pearson Education Limited, England, **2010**.
- [2] A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch Der Anorganischen Chemie*, Walter De Gruyter, Berlin, **2007**.

- [3] D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, F. A. Armstrong, *Inorganic Chemistry*, Oxford University Press, Oxford, **2006**.
- [4] G. Agricola, *Bermannuns, Sive De Re Metallica*, Basel, **1530**.
- [5] J. von Sandrart, *L'Academia Todesca della Architectura, Scultura & Pittura oder Teutsche Academie der Bau- Bild- und Mahlerey-Künste*, <http://ta.sandrart.net/568>, Nürnberg, **1675**.
- [6] C. W. Scheele, *Der Königlich Schwedischen Akademie der Wissenschaften neue Abhandlungen aus der Naturlehre, Haushaltungskunst und Mechanik* **1771**, 33, 122–139.
- [7] H. Davy, *Philos. Trans. R. Soc. London* **1813**, 103, 263–279.
- [8] J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, Leipzig, **1833**.
- [9] H. Moissan, *C. R. Hebd. Seances Acad. Sci.* **1886**, 102, 1543–1544.
- [10] H. Moissan, *C. R. Hebd. Seances Acad. Sci.* **1886**, 103, 202–205.
- [11] M. E. Weeks, *J. Chem. Educ.* **1933**, 9, 1915–1939.
- [12] K. O. Christe, *Inorg. Chem.* **1986**, 25, 3721–3722.
- [13] H. Bill, G. Calas, *Phys. Chem. Miner.* **1978**, 3, 117–131.
- [14] H. G. Dill, B. Weber, *Neues Jahrb. Mineral. Abh.* **2010**, 187, 113–132.
- [15] R. S. W. Braithwaite, W. T. Flowers, R. N. Haszeldine, M. Russell, *Min. Mag.* **1973**, 39, 401–411.
- [16] H. G. Dill, B. Weber, *Ore Geol. Rev.* **2010**, 37, 65–86.
- [17] H. Moissan, *Le Fluor et ses Composés*, Paris, **1900**.
- [18] R. Vochten, E. Esmans, W. Vermeersch, *Chem. Geol.* **1977**, 20, 253–263.
- [19] J. Garnier, *C. R. Hebd. Seances Acad. Sci.* **1901**, 132, 95–96.
- [20] A. Arribas, *Estud. Geol.* **1964**, 20, 149–169.
- [21] P. Assadi, M. Chaigneau, *C. R. Hebd. Seances Acad. Sci.* **1962**, 255, 2798–2800.
- [22] P. Asadi, *Phys. Status Solidi* **1967**, 20, K71–72.
- [23] R. A. Christman, M. R. Brock, R. C. Pearson, Q. D. Singewald, *U. S. Geol. Surv. Bull.* **1959**, 1072-H.
- [24] E. W. Heinrich, R. J. Anderson, *Am. Mineral.* **1965**, 50, 1914–1920.
- [25] H. V. Ellsworth, *Econ. Geol. Rep. Geol. Surv. Can.* **1932**, 11.
- [26] F. L. Sine, *Univ. Toronto Stud. Geol. Ser.* **1925**, 20, 22–24.
- [27] S. Iimori, *Rikagaku Kenkyusho Iho* **1932**, 11, 1237–1243.
- [28] H. S. Spence, R. K. Carnochan, *Trans. Can. Inst. Min. Metall. Min. Soc. N. S.* **1930**, 33, 43–48.
- [29] P. Asadi, *Phys. Status Solidi* **1967**, 20, K59–61.
- [30] P. Assadi, Dissertation, Paris, **1967**.
- [31] C. F. Schönbein, *J. Prakt. Chem. (Leipzig)* **1861**, 83, 86–106.
- [32] F. Henrich, *Sitzungsber. Phys.-Med. Soz. Erlangen* **1914**, 46, 1–14.
- [33] H. A. Gilg, *Extra-Lapis English* **2006**, 9, 114–116.
- [34] H. G. Dill, M. Füßl, B. Weber, *Oberpfälzer Heimat* **2008**, 53, 213–225.
- [35] B. Weber, *Aufschluss* **2010**, 107–118.
- [36] E. Johnson, L. T. Chadderton, *Radiat. Eff.* **1983**, 79, 183–233.
- [37] R. Zanetti, A. J. Bleloch, M. P. Grimshaw, G. A. C. Jones, *Philos. Mag. Lett.* **1994**, 69, 285–290.
- [38] R. Bennewitz, D. Smith, M. Reichling, *Phys. Rev. B* **1999**, 59, 8237–8246.
- [39] H. G. Dill, B. T. Hansen, B. Weber, *Ore Geol. Rev.* **2011**, 40, 132–148.
- [40] J. Magill, G. Pfennig, J. Galy, *Karlsruher Nuklidkarte*, Habersbeck, Lage/Lippe, **2006**.
- [41] *Gesundheitsschädliche Arbeitsstoffe, Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten* (Ed.: D. Henschler), Verlag Chemie, Weinheim, **1986**.
- [42] K. MacKenzie, M. E. Smith, *Multinuclear Solid-state NMR of Inorganic Materials*, Pergamon, Oxford, **2002**.
- [43] J. W. Nebgen, W. B. Rose, F. I. Metz, *J. Mol. Spectrosc.* **1966**, 20, 72–74.
- [44] Y. S. Avadhut, D. Schneider, J. Schmedt auf der Gönne, *J. Magn. Reson.* **2009**, 201, 1–6.