

Accepted Manuscript

<http://dx.doi.org/10.1002/chem.201603402>

V.R. Celinski, M. Ditter, F. Kraus, F. Fujara, and J. Schmedt auf der Günne. Trace determination, pressure and density estimation of difluorine F₂ caused by irradiation damage in minerals and synthetic fluorides. *Chem. - Eur. J.*, 22:1--7, 2016.

Trace determination and pressure estimation of fluorine F₂ caused by irradiation damage in minerals and synthetic fluorides

Vinicius R. Celinski^[a], Michael Ditter^[b], Florian Kraus^[c], Franz Fujara^[b], and Jörn Schmedt auf der Günne^{*[a]}

Abstract: Irradiated alkali and earth alkali halides can form metal colloids and halogen molecules, which stay trapped inside the crystal. In this paper we provide ¹⁹F NMR evidence of trapped F₂ fluids in heavy ion bombarded synthesized LiF crystals as well as in a variety of the mineral Villiaumite (NaF). This is the 2nd mineral in which F₂ is unambiguously detected in nature. The trace quantification of the latter is in the order of magnitude of 10⁻⁶ mol/g. Pressures and densities of the F₂ fluids are estimated based on the theory of nuclear spin relaxation in dilute gases.

Introduction

Many insulators are ionic crystalline materials. It is known for a long time now, that defects in such materials can be generated by ionizing photon or particle irradiation.¹⁻³ The radiation may stem from a natural environment (e.g. cosmic radiation or radioactive atoms in rocks) or from a more or less controlled one as in a nuclear facility along with its radioactive waste, a fusion reactor, a particle accelerator or a laser. For instance, a CaF₂ crystal can be used as an optical window that is subjected to high-energy radiation of a laser⁴ or as a scintillator.⁵ A salt dome for the disposal of radioactive waste will inevitably be exposed to nuclear radiation and is intended to be safe for disposed containers for thousands of years. Recently, Villiaumite (NaF) was found to be the dominant fluoride species in zircaloy cladding waste, which results in large amounts from removing zircaloy cladding from nuclear fuel rods.⁶

Alkali halides feature a large band gap, making them not only electrical insulators, but also transparent to light over a wide frequency range.⁷ In this respect LiF stands out for being one of the best materials for transmission of vacuum UV light. For these reasons it is merchandised in the form of mirrors, optical windows and lenses for various purposes. Furthermore, it finds use in thermoluminescent dosimeters⁸ and has a potential use as a thermal neutron detector in both fusion and fission nuclear reactors.^{5,9} As far as heavy ion induced defects are concerned LiF is one of the best studied ionic crystals.¹⁰

The formation of halogen bubbles and metallic colloids are well known as a result of irradiation of alkali halides.^{11,12} In neutron-irradiated LiF these cavities were assumed to contain molecular F₂, which was evidenced by ¹⁹F NMR.^{13,14} After swift ion irradiation swelling has been reported as a reaction to an increased volume, among other crystals, also in LiF.¹⁵ The formation of micron-sized F₂ bubbles has already been observed in CaF₂ by atomic force microscopy, where a pressure of the F₂ fluid was estimated to be around 50 MPa.¹⁶ The occurrence and quantification of F₂ in the natural mineral "Antozonite", a variant of fluorite, suggested its occlusions to originate due to natural radioactivity.¹⁷ Recently, attention was drawn to the stability of polyfluoride anions and the existence of F₅⁻ in a neon matrix.^{18,19}

In the present work we intend to provide evidence of the trapped F₂ fluid and quantify its amount in a further natural mineral as well as in heavy-ion-bombarded synthetic fluorides. Is it possible to estimate pressure and density of the fluid inside the formed cavities as was done in the case of trapped H₂ in irradiated LiH?^{20,21} Do the molecules feature the expected isotropic motion as in a fluid state in spite of the supposed small size of the cavities?

Results and Discussion

¹⁹F NMR quantification

The ¹⁹F NMR spectra of the studied crystals are shown in Fig. 1. The amounts of F₂ fluid inside the cavities of the samples was determined by quantitative ¹⁹F NMR experiments and is gathered in table 1. The trace determination of F₂ in the mineral Villiaumite by ¹⁹F NMR is the second direct evidence of elemental fluorine in nature. We speculate that its formation must also derive from the effects of radiation arising from nearby radioactive minerals, as in the case of the mineral "Antozonite", where elemental fluorine in nature was detected for the first time.¹⁷

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- [a] Dr., V. R., Celinski, and Prof. Dr., J., Schmedt auf der Günne
Department für Chemie und Biologie
Universität Siegen
Adolf-Reichwein-Straße 2, 57080 Siegen (Germany)
E-mail: schmedt_auf_der_guenne@chemie.uni-siegen.de
- [b] Dr., M., Ditter, and Prof. Dr., F., Fujara
Fachbereich Physik
Technische Universität Darmstadt
Hochschulstraße 6, 64289 Darmstadt (Germany)
- [b] Prof. Dr., F., Kraus
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Straße 4, 35032 Marburg (Germany)

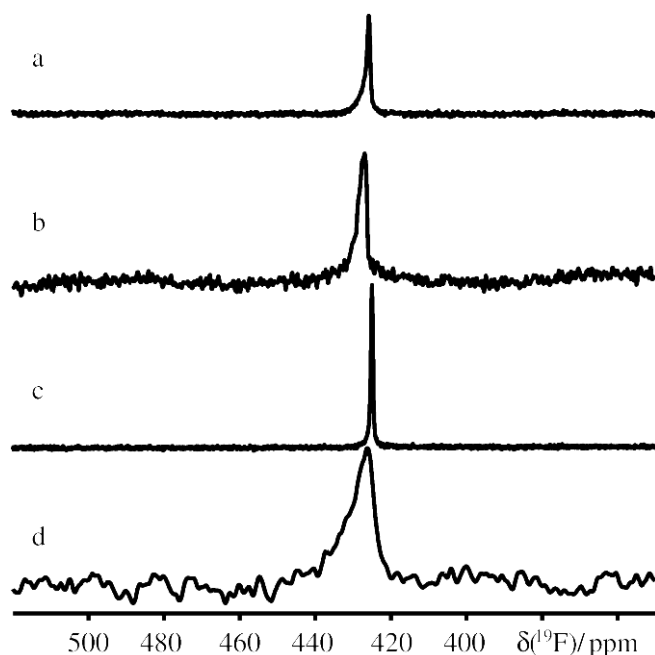


Figure 1. ^{19}F NMR spectra of a) LiF irradiated with Pb ions, b) LiF irradiated with Xe ions, c) "Antozonite" (CaF_2) and d) Villiaumite (NaF). All spectra, except for c (static), were acquired at a sample spinning speed of 10 kHz. Spectra a and b were gained by single pulse and c and d by spin-echo experiments.

Maximum fluid density in crystals damaged by irradiation

We aim at determining the upper limit for the density of an F_2 fluid in a cavity formed after irradiation. For that we assume that there is F_2 diffusion neither into nor out of the cavities after irradiation damage has occurred. In this manner we determine a maximum F_2 fluid density $\rho_{\text{F}_2, \text{max}, \text{crystal}}$ can be formed in a crystal containing stoichiometric amounts of fluoride (e.g. NaF) after being damaged by irradiation:

$$\rho_{\text{F}_2, \text{max}, \text{crystal}} = \frac{Z_{\text{fluoride}}}{2(V_{\text{UC}} - V_{\text{M}})N_{\text{A}}} \quad (1)$$

where Z_{fluoride} is equal to the number of fluoride ions per unit cell, V_{UC} the unit cell volume, V_{M} the volume of the formed material after irradiation other than the F_2 fluid (e.g. solid Na) and N_{A} the Avogadro constant. The maximum fluid densities $\rho_{\text{F}_2, \text{max}, \text{crystal}}$ of newly formed F_2 after irradiation damage of the studied crystals were calculated according to equation 1 and can be found in table 1. We deliberately set $v_{\text{M}} = 0$, corresponding to a scenario where the extra formed material diffuses away from the bubble towards the crystal surface.

Table 1. Amount n and mass m of F_2 per unit mass of sample, T_1 relaxation time, densities ρ and pressures p of F_2 in fluorides.

	Villiaumite (NaF)	Antozonite LiF (CaF_2)	LiF (3×10^{11} Xe/cm^2)	LiF (2×10^{12} Pb/cm^2)	F_2 (0.1-0.2 MPa) ^[b]
$n(\text{F}_2)/m(\text{total})/$ (mmol g^{-1})	$0.0008 \pm$ 0.0001	$0.012 \pm$ 0.002 ^[a]	$0.045 \pm$ 0.005	$0.017 \pm$ 0.002	26.316
$m(\text{F}_2)/m(\text{total})/$ (mg g^{-1})	$0.03 \pm$ 0.01	$0.46 \pm$ 0.1 ^[a]	$1.7 \pm$ 0.2	$0.6 \pm$ 0.1	1000.0
$T_{1, \text{exp}}(^{19}\text{F})/$ ms	$15 \pm$ 1.4	12.3 ^[a]	$14.1 \pm$ 1.3	$8.2 \pm$ 0.8	0.045
ρ_{calc} ^[c] / (mol cm^{-3})	0.014-0.028	0.011-0.023	0.013-0.026	0.008-0.015	-
$\rho_{\text{F}_2, \text{max}, \text{crystal}}$ ^[d] / (mol cm^{-3})	0.030	0.041	0.051	0.051	-
p ^[e] /(MPa)	33.8-67.6	27.7-55.4	31.8-63.5	18.5-36.9	0.1-0.2

[a] data from literature.¹⁷ [b] Ampoule filled with F_2 gas at a pressure $p = 1$ -2 atmospheres.³¹ [c] density ρ_{calc} calculated with equation (4); ranges are caused by the calibration error.⁵ [d] maximum density $\rho_{\text{F}_2, \text{max}, \text{crystal}}$ calculated with equation 1 with $v_{\text{M}} = 0$. [e] pressure p calculated according to the equation of state of F_2 .³²

F_2 fluid density and pressure inside the cavities by ^{19}F NMR

Based on the assumption that longitudinal relaxation of the ^{19}F NMR signal in F_2 molecules occurs mainly through the spin-rotation mechanism, there is a link between $T_1(^{19}\text{F})$ values and pressure (equations 2 and 3). In this case the ratio (T_1 / ρ) shows a temperature dependence:³³⁻³⁵

$$(T_1 / \rho) = \frac{3\hbar^2 \bar{v} \sigma_{\text{eff}}}{4C^2 kT} \quad (2)$$

Here \hbar is the reduced Planck constant, \bar{v} the mean relative velocity of the molecules, σ_{eff} the cross section for the transfer of angular momentum during a collision, C the spin rotation constant with an experimental value of $157 \times 2\pi$ kHz³⁶ that shows good agreement with the theoretical value³⁷, I the molecular moment of inertia with an experimental value of 3.17×10^{-46} kg m²³⁸, k the Boltzmann constant and T the temperature of the gas.

We denote that the longitudinal relaxation under the spin-rotation mechanism is field independent.³⁹ Under these circumstances the value of $k_{\text{lit}} = (T_1/\rho)T^{3/2}$ is constant so that we define k_{lit} :³³⁻³⁵

$$k_{\text{lit}} = (T_1/\rho)T^{3/2} \quad (3)$$

Values for F_2 have been reported in literature $((T_1/\rho)_{\text{lit}})$, where T_1 is the experimentally determined longitudinal relaxation time constant for ^{19}F and ρ the density of the F_2 gas.⁴⁰ There, the density ρ is calculated from the known pressure p with the help of second virial coefficients.⁴¹ Based on those values we can calculate the density ρ_{calc} of the F_2 molecules inside the cavities of the crystals under investigation, as in equation 4:

$$\rho_{\text{calc}} = \frac{T_{1, \text{exp}} T^{3/2}}{k_{\text{lit}}} \quad (4)$$

The values of ρ_{calc} can be converted to pressure values p as shown in 2 according to the F_2 equation of state.³² These values

are of the same order of magnitude as the pressure value of F_2 bubbles in an irradiated CaF_2 crystal that was determined to be around 50 MPa.¹⁶ Furthermore, the calculated maximum fluid densities inside a crystal after irradiation (equation 1) indicate a similar range, where such pressure values can be found. We note here that higher calculated maximum fluid densities would be achieved in a scenario where part of the extra formed material stays in the bulk ($v_M > 0$). Thus, we conclude that F_2 bubbles are present inside the studied samples, where F_2 is in a supercritical state at room temperature, its critical pressure being 5.2 MPa and its critical temperature 144.4 K.³²

At such high pressures the viscosity of supercritical F_2 might get close to that of liquid F_2 just below its critical temperature.⁴² The longitudinal relaxation time of liquid F_2 at different temperatures has been determined to be around 70-100 ms.⁴³ In the regime of dense gases the assumption about collisions is not valid anymore and the density of the gas needs to be multiplied by a correction term.^{39,44} Even though this new density term shows a similar temperature dependence as in the case of dilute gases, strictly speaking equation 3 does not hold any longer. However, it still seems to be a fair approximation to estimate the order of magnitude of F_2 fluid pressure inside the crystals, since there exists no data on relaxation rates of F_2 at such high pressures. For instance, the prediction of (T_1/ρ) of hydrogen gas at around 300 MPa is underestimated by a factor of 2 as compared to experimental data.⁴⁴ An underestimation of (T_1/ρ) translates into higher densities and therefore even higher pressures. According to the concept in section 0 this would be possible if part (or all) of the formed material other than F_2 (in our cases either metallic lithium, sodium or calcium) would stay inside the bulk.

Transverse relaxation and linewidth

Spins that relax under the spin-rotation mechanism feature a T_1 that is not dependent on the field.³⁹ We tested that for the F_2 signal in "Antozonite" and determined the same value within experimental error. Moreover, it is also expected that $T_1 = T_2$. We determined T_2 values with a spin-echo²² ($T_2 = (9.6 \pm 0.2)$ ms) as well as with the Carr-Purcell-Meiboom-Gill (CPMG)²³ pulse sequence ($T_2 = (8.7 \pm 0.2)$ ms), both being similar to each other but smaller than T_1 .

At higher signal to noise ratios one can see weak spinning side bands (Fig. 2), which are typical for the MAS spectra of solids and depend on the anisotropy of interactions. The lineshape of the F_2 signal in "Antozonite" can be deconvoluted by two peaks that feature a similar T_1 and practically the same chemical shift. The broadening of the linewidth of the narrow signal (around 250 Hz) can be explained by its spin-spin relaxation time T_2 . The smaller and broader peak, however, features a linewidth around three times broader than the narrow peak, indicating the influence of another interaction.

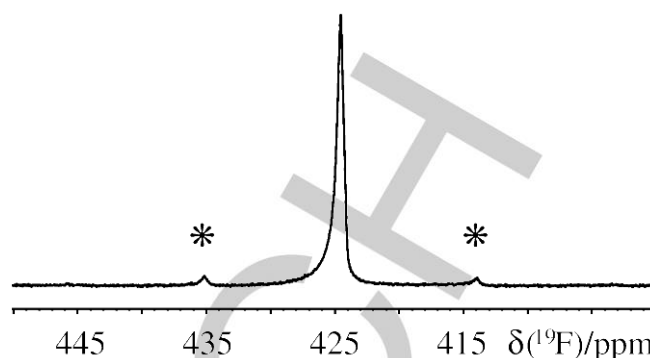


Figure 2. ^{19}F MAS NMR spectrum of "Antozonite" (CaF_2) featuring side bands, which are typical for the MAS spectra of solids. Acquired at a sample spinning speed of 5 kHz.

The dipole-dipole interaction between the two fluorine atoms in F_2 is around -36.4 kHz, if one assumes a distance of 1.43 Å. If F_2 would be static, this would lead to many side bands under the current experimental conditions (sample spinning frequency $\nu_r = 10$ kHz). On the other hand, fast molecular tumbling, as in a fluid, is able to completely average out this interaction. The presence of weak side bands is an indication that the truth might lie somewhere in between. We therefore hypothesized a residual dipole-dipole interaction. If this is the case, one might be able to excite double-quantum coherences.

Double-quantum excitation and size of the bubbles

The normalized²⁷ double-quantum build up curve of the F_2 NMR signal in "Antozonite" is shown in Fig. 3. As discussed above, the successful excitation of double-quantum coherence is evidence of a residual dipole-dipole coupling. The normalized intensity is expected to reach a plateau at the value of 0.5 for a 2-spin system with increasing excitation time $\tau_{DQ,exc.}$. However, the experiment levels out at a value slightly higher than 0.1. We conclude that only part of the F_2 molecules features an anisotropic motion and contributes to the excitation of double-quantum coherence (actually $2n+2$ quantum orders). The remaining ones do not contribute to the latter due to isotropic molecular tumbling, but still contribute to the reference signal through coherence transfer pathways of the order $4n$, with $n \in N$. The amplitude of the 2-spin simulation was scaled down in order to fit the experimental data. From that fit we extracted the value of (350 ± 150) Hz for the residual dipole-dipole coupling.

The self-diffusion coefficients of liquid F_2 at different temperatures have been determined.^{43,45,46} Linear extrapolation to room temperature gives a value of the order of 3×10^{-8} m²/s. We therefore expect the F_2 fluid to have many encounters with the walls during an NMR experiment at room temperature, if the cavity is in the sub-micrometer range.

Based on the findings above, we propose a rough model where F_2 molecules are confined in tiny cavities. As a consequence of the non-fully isotropic motional tumbling in some of these cavities the intermolecular dipole-dipole interaction is not entirely averaged out. However, the measurement gives evidence of different kinds of cavities. The majority of the cavities allows for isotropic motion which leads to a complete suppression of the

dipole-dipole interaction of the F_2 molecules therein. From the normalized double-quantum build up curve (Fig. 3) we estimate that 1 out of 5 molecules is subjected to a hindered motion.

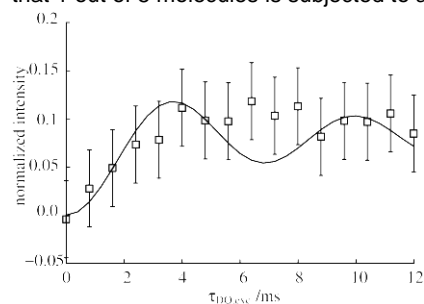


Figure 3. Experimental normalized²⁷ double-quantum build up curve of the F_2 signal in "Antozonite" (squares) as a function of the excitation time and a 2-spin simulation (line) with a dipole-dipole coupling of 350 Hz; sample spinning frequency of 10 kHz; error bars were estimated from experimental data.

Conclusions

In this contribution we have successfully detected the ^{19}F NMR signal of F_2 fluid in the natural mineral Villiaumite (NaF) as well as in heavy-ion-irradiated synthetic LiF crystals. This is in accordance with previous findings where the formation of F_2 bubbles has been identified after irradiation. We were able to quantify not only the amount of F_2 in the synthetic crystals, but also determine a trace of F_2 ($\sim 10^{-6}$ mol/g) in Villiaumite. The presence of polyfluoride anions was not indicated by extra unassignable NMR peaks.

The pressure of F_2 inside the cavities was estimated based on the theory of nuclear spin relaxation of dilute gases. Since the determined pressures are of the order of magnitude of 100 MPa we conclude that F_2 is in a supercritical state at room temperature, featuring corresponding high densities. The maximum fluid density expected in irradiation-damaged crystals is of the same order as the estimation of F_2 densities.

We observed weak side bands during MAS NMR experiments and were able to excite double-quantum coherences thereby extracting a value for the residual dipole-dipole coupling. Polarization transfer between the molecules and lattice fluoride ions could not be observed. From that we conclude that part of the trapped molecules feature an anisotropic motion.

We believe that our contribution helps to understand the mechanism of defect formation in irradiated crystals. The size and aspect ratio of cavities could possibly influence the properties of the crystals. Moreover, one might address the question of how much of the formed material other than F_2 diffuses towards the surface and how much of it is interstitial. This could be important for radioactive waste disposal in salt domes, where a chemical reaction of the containers with a possible continuously formed halogen gas is not desired. Furthermore, it might also be significant for lenses that cannot be easily maintained and are exposed to irradiation, as for example on satellites.

Experimental Section

One of the LiF single crystals was irradiated with Pb ions at the UNILAC linear accelerator of the GSI Helmholtz Center in Darmstadt, Germany. The energy of Pb ions was 1.78 GeV with a fluence of 2×10^{12} ions cm^{-2} . The other LiF single crystal was irradiated with Xe ions at the SIS synchrotron of the Darmstadt Center also in Darmstadt, Germany. The energy of Xe ions was 22.1 GeV with an ion fluence of 3×10^{11} ions cm^{-2} . The mineral Villiaumite (NaF) stems from the Kola Peninsula in Russia and features a red color. The mineral "Antozonite" (CaF_2) comes from Wölsendorf in Germany and features a black color.

Quantification, T_1 saturation recovery and T_1 inverse recovery NMR experiments were conducted at a magnetic field of 4.7 T on a Bruker Avance II-200 spectrometer equipped with a home-built 4 mm MAS probe working at the 1H frequency of 200.0 MHz. Spectra in Fig. 1 were acquired at a sample spinning speed of 10 kHz, except for the spectrum of "Antozonite". Spectra *a* and *b* in Fig. 1 were gained with a single pulse excitation experiment, while spectra *c* and *d* were gained with a spin-echo experiment. T_1 saturation recovery, spin-echo²², CPMG²³, single pulse excitation and double-quantum NMR experiments on "Antozonite" were conducted at a magnetic field of 11.7 T on a Bruker Avance III-500 spectrometer equipped with a commercial 4 mm MAS probe working at the 1H frequency of 500.13 MHz. We used a transient-corrected double-quantum experiment^{24,25} at a sample spinning frequency of 10 kHz, accumulating 128 transients/FID and the POST C-element²⁶ with equal excitation and reconversion times that added up to 1.6 ms. The phase cycles were chosen as to satisfy a normalization approach described elsewhere.²⁷ The single excitation experiment (Fig. 2) accumulated 1950 transients at a sample spinning frequency of 5 kHz with a repetition delay of 0.1 s. For all experiments the 1H resonance of 1% tetramethylsilane in $CDCl_3$ served as an external secondary reference for the ^{19}F resonance of neat CCl_3F using the δ values for ^{19}F as reported by the IUPAC.²⁸ The SIMPSON package (version 3.1.2) was used for simulations.²⁹

We determined the amount of F_2 in the crystals by performing quantitative ^{19}F NMR experiments for the F_2 signal as well as for the signal originating from fluoride ions (1). Subsequently, the peak areas divided by the number of scans was used for the quantification.

Table 2. Acquisition parameters for the ^{19}F -quantification by solid state NMR.

Head 1 ^[a]	Villiaumite (NaF)	LiF (3×10^{11} Xe/cm ²)	LiF (2×10^{12} Pb/cm ²)
Repetition delay (F_2) / s	0.1	0.1	0.1
Repetition delay (F^-) / s	8192	300	224
Number of scans (F_2)	2081008	8192	4359
Number of scans (F^-)	1	1	1

The very aggressive nature of F_2 leads to a chemical reaction with almost every container material. Moreover, even small amounts of water on the wall of a container will react with F_2 to form HF, and several oxygen containing species. If the container is a typical laboratory glass, HF will eventually react with it to form SiF_4 and again water, that can start the cycle once more until F_2 is completely consumed. A polymer container (e.g. FEP,

PFA or PTFE) on the other hand enables the diffusion of F₂ through its walls. From our experience, a sufficiently large number of repetitions of a ¹⁹F NMR single pulse excitation experiment can even provide evidence of trapped F₂ in the polymer wall (not shown).³⁰ We used the value for the longitudinal relaxation time T₁ of F₂ in accordance with literature: T₁(F₂; 293 K; 100–200 kPa) = 45 μs.³¹

Acknowledgements

We thank Mineralogical State Collection Munich (SNSB) and Dr. Rupert Hochleitner for the mineral Villiaumite, Dr. Thomas Bräuniger and Professor Wolfgang Schnick for spectrometer time and Christian Minke for technical NMR support. Funding from Deutsche Forschungsgemeinschaft (FU 308/12-1) is gratefully acknowledged.

Keywords: NMR, relaxation, radiation damage, double-quantum, Fluorine

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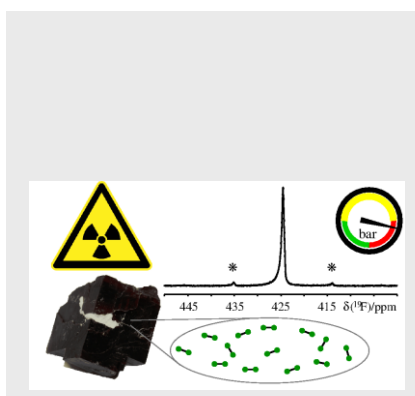
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Layout 1:

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A trace quantification of elemental F₂ is provided in the mineral Villaumite NaF. This is the 2nd mineral in which F₂ is unambiguously detected in nature.



*Vinicius R. Celinski, Michael Ditter, Florian Kraus, Franz Fujara, and Jörn Schmedt auf der Günne**

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Trace determination and pressure estimation of fluorine F₂ caused by irradiation damage in minerals and synthetic fluorides