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# Advances in Pursuit of Fluorine in the Interstellar Medium and Beyond: Relevance to its Terrestrial Chemistry

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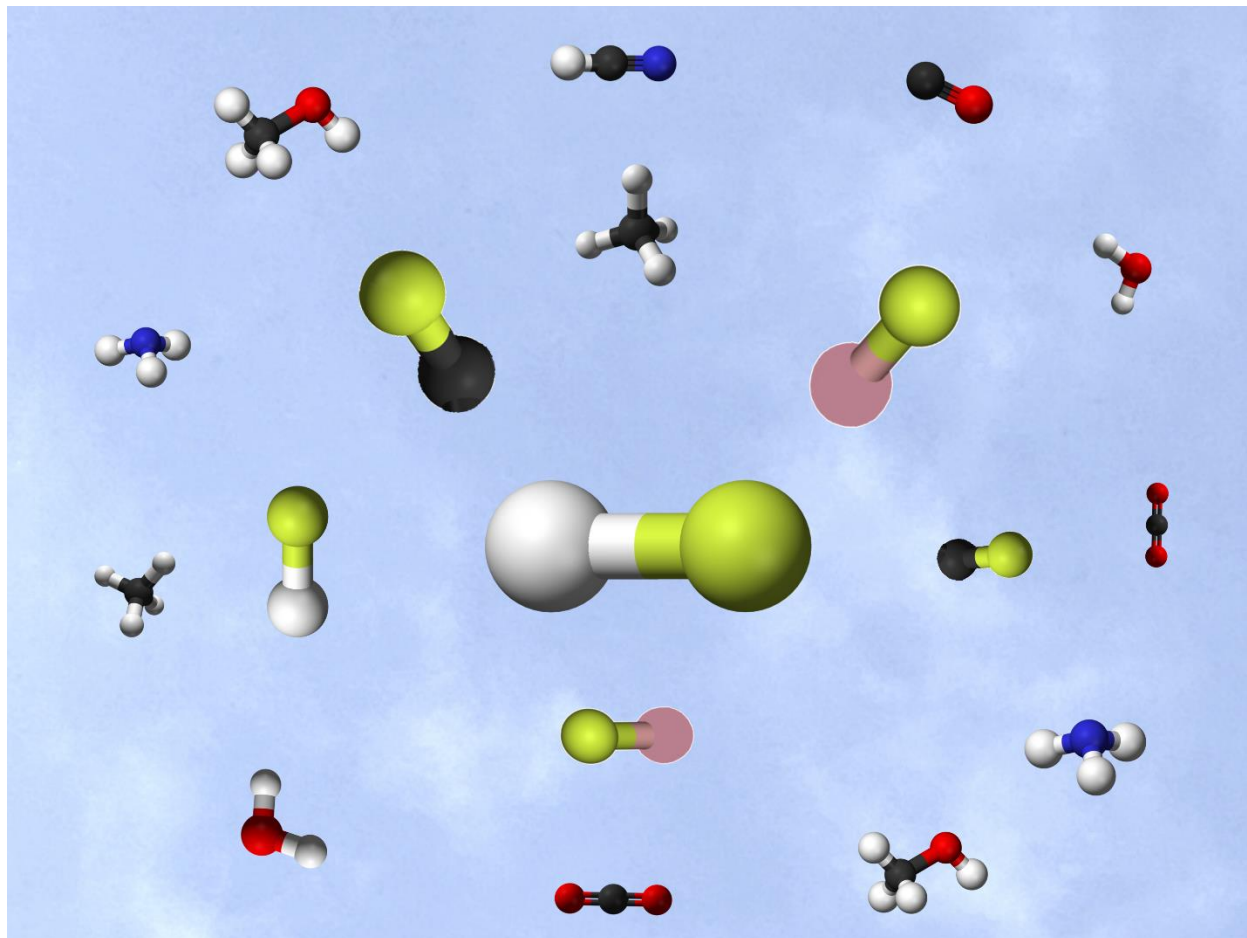
**ABSTRACT:** Fluorine plays a significant role in the geochemical world, despite its low abundance. The presence of fluorine and fluorinated moieties in chemical compounds results in significant changes in their physicochemical and biological properties. Therefore, the study of the origin and abundance of fluorine not only here on Earth but in any region outside of Earth- in other planets, stars and star-forming galaxies, circumstellar, interstellar media (ISM), and the protoplanetary regions, is vital and can contribute significantly to our knowledge on its relevance to its terrestrial origin, abundance, and its chemistry. With an introduction on the formation, presence, and significance of fluorine and its compounds under terrestrial context, the present review attempts to consolidate the literature on the search for fluorine, fluorides and fluorinated ions in the extraterrestrial region, its abundance as well as their implications in both terrestrial and extraterrestrial fluorine chemistry. Revealed through a continued search over many decades, its formation and significant abundance in asymptotic giant branch (AGB) stars and Wolf-Rayet stars, in neutrino spallation during supernovae (type II), or even in far distant star-forming galaxy indicate the possible ubiquity of fluorine in the vast stellar and diffuse interstellar medium. Because of the growing influence of fluorine in the terrestrial world, studying the fluorine effect in extraterrestrial atmosphere is quite intriguing.

**KEYWORDS:** *interstellar medium, volcanic magma, cosmic fluorine, stellar evolution, nucleosynthesis, supernova*

## Highlights

- Intriguing studies on the search for extraterrestrial fluorine is covered in this review.
- Similar to the root source of all materials on Earth, fluorine also has a cosmic origin.
- Survival of fluorine nucleus after its nucleosynthesis is difficult due to further reactions.
- Fluorine is formed in Type II supernovae, asymptotic giant branch (AGB) and Wolf-Rayet stars.
- Fluorine has been detected in a far distant high- $z$  galaxy and Martian soil.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Fluorine is the most electronegative and reactive member of the periodic table of elements with unique chemical characteristics and behavior [1]. In abundance, it has the 13th place (0.059wt%) ahead of carbon (0.02wt%, 17th) and chlorine (0.017%, 19th) in the Earth's crust, but the 24th place in the solar system [2]. Among halogens, it is the most abundant one in the form of fluoride minerals. Though its relative abundance is low, it has a profound role in geomorphology, especially in the transportation of metal ores and minerals, thus in the composition of hydrothermal fluids as well as magmas and their nature and behavior [3]. Due to high reactivity and low terrene stability, accessibility of halogens, especially fluorine in elemental form, is extremely scarce. However, incorporation of F and fluorinated functional moieties into organic molecules, forming a strong C-F bond (485 kJ/mol) [4], leads to significant changes in their properties. The past few decades have seen a high volume of applications of fluorinated chemicals in our daily life- household plastics with high chemical inertness and temperature resistance (e.g., Teflon), refrigerants, anesthetics, effective therapeutics in pharmaceuticals, and agrochemicals [5,6].

Among the earthly identified fluoride minerals (Table 1) [7], the three industrially predominant fluoride minerals are fluorite ( $\text{CaF}_2$ , fluorspar), fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) and cryolite ( $\text{Na}_3\text{AlF}_6$ ). Fluorite is the most common and major commercial source of fluorine [8]. The first preparation of hydrofluoric acid was made by Marggraf in 1764 while heating fluorite with sulfuric acid in glass and found the glass highly corroded by the product [5,9]. Scheele was the one who first studied the glass etching properties of hydrofluoric acid and prepared it in an almost anhydrous form. HF is the most versatile compound of fluorine and one of the most useful superacids (in its anhydrous form), especially in the petroleum industry [10-15]. In 1809,

French scientist André-Marie Ampère suggested that the constituents of fluoric acid are hydrogen and a new element analogous to chlorine [16]. Sir Humphry Davy discovered this new element in 1813, giving it the name fluorine, suggested by Ampère in his correspondence with Davy [17,18]. As per Ampère’s original suggestion in 1810, Henry Moissan (Nobel Prize, 1906) isolated elemental fluorine in 1886 by the electrolysis of potassium hydrogen difluoride ( $\text{KHF}_2$ ) dissolved in liquid hydrogen fluoride ( $\text{HF}$ ) [19-21]. A few articles discussing the history and significance of F and other natural halogens are cited here [5,21-23].

**Table 1.** Earthly Identified Fluorine-containing Minerals

Entry	Name	Chemical Formula	F Content
a	Fluorite	$\text{CaF}_2$	48.9%
b	Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	3.8%
c	Cryolite	$\text{Na}_3\text{AlF}_6$	54.3%
d	Sellaite	$\text{MgF}_2$	61%
e	Topaz	$(\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$	11%
f	Villiaumite	$\text{NaF}$	45.25%

Centuries-old quest and search for the accessible natural source of elemental  $\text{F}_2$  bloomed in 2012 when Kraus and coworkers [24] gave direct evidence for the occurrence of elemental fluorine in nature in the form of gas. They found it in some varieties of the mineral fluorite ( $\text{CaF}_2$ ) known as “antozonite,” a radioactive fluorite variety with multiple inclusions of  $\text{F}_2$  gas. This stinky rock delivered  $\text{F}_2$  gas when broken and crushed. It was successfully identified and quantified the content of  $\text{F}_2$  with the help of  $^{19}\text{F}$  MAS (magic-angle-spinning) solid-state NMR spectroscopy.

In telluric perspective, the presence of fluorine in a molecule results in significant changes in its chemical and biological properties. In fluoropharmaceuticals, it increases the metabolic stability and varies the lipophilicity considerably, often improving their therapeutic efficacy. Therefore, there is an increased activity in the synthesis and pharmacokinetic/pharmacodynamic study of organofluorine compounds in recent years (25). ]

Many papers have been published summarizing the studies to find the presence and abundance of fluorine and fluorinated matter in the interstellar medium and stellar surfaces [26-36]. The continued studies have shown its stellar formation, conversion to fluorides, and influence on various astrochemical events. Recently, Franco et al. [37] reported the detection of fluorine in significant abundance in a far distant high- $z$  (redshift) galaxy of about 12 billion light years away, the first time ever in such a distant star-forming galaxy. They found HF in the gravitationally lensed massive young galaxy NGP-190387 at redshift  $z = 4.420$  at 211.6–230.0 GHz with the Atacama Large Millimeter/Submillimeter Array (ALMA) in partnership with European Southern Observatory (ESO). They noticed the HF absorption at this redshift with a signal-to-noise ratio of 8 and column density ratio  $N_{\text{HF}}/N_{\text{H}_2}$  as high as  $2 \times 10^{-9}$ , indicating a rapid ramp-up phase of chemical enrichment. A recent theoretical study by Palmer and Fortenberry suggested HOO $\cdot$  as a plausible fluorine-containing candidate for atmospheric and astronomical detection [38]. The presence of fluorine and hydroperoxyl radical (HO $_2$ ) in those environments may result in fluorinated molecules such as HOO $\cdot$ F on dust grains of protoplanetary disks in the planet-forming regions of  $\rho$  Ophiuchi cloud complex and the Earth's atmosphere. In recent years, two book chapters, one in 2017 by Jönsson and Ryde summarizing the studies on possible sources and cosmic origin of fluorine [39] and the other in 2019, by Tressaud, giving a more detailed account of the "genesis and cosmos-chemistry of fluorine" [40]



have been published. Here, in this brief review, we give a summary of the reports on the formation, abundance, and the astrochemistry of fluorine in the interstellar/circumstellar media, protoplanetary and galactic regions.

## **2. TERRESTRIAL FLUORINE IN MINERALS AND VOLCANIC MAGMA**

Terrestrial, as well as the extraterrestrial presence of fluorine and fluoride minerals, always poses the question of its source and genesis. All halogens, including fluorine, are suggested to have initially arrived at the planetary surface through geothermal processes [41] and from much higher energetic activities such as volcanic eruptions. Although fluorides are more abundant in Earth's crust, perhaps due to the low solubility of the fluorides in water, it is quite rare in the oceans (only ~1.3 ppm), while chlorides are much more common (~19,000 ppm) [42-44]. Among more than 4300 organohalogens of biogenic origin [41,45,46], only about 100, including the C-F bond forming enzyme fluorinase, contain C-F bonds. In addition, it has been generally proposed that a main source of most of the elements, their molecules, including their minerals, is of extraterrestrial origin, being transported as part of many extraterrestrial events and sources including supernovae, comets, meteorites, asteroids, etc. [47-52]. The latest report suggests that the Earth's water might have originated from hydrogen delivered by enstatite chondrite (EC) meteorites [53].

An important scenario discussed is the feasibility of fluorine-rich planetary environments as possible habitats for life [42]. The evolution of a probable scenario is presumable on a planet (on an exoplanet or even on terrestrial planets including Earth), when all its oxygen is used up by oxidation reactions, and fluorine gets into action. This is a scenario when fluorine released by fluorine-rich volcanic magma would play a similar role in the planetary atmosphere as oxygen does on Earth, leading to the evolution of animal-like organisms [54]. Results from innovative

work in synthetic and xenobiology [55], and studies related to the proteome-wide introduction of fluorine [56], shed light on such remote possibilities.

An understanding of halogen geochemistry at active volcanoes and the abundance of halogens in volcanic magma, atmospheric (both tropospheric and stratospheric) processing of volcanic halogens, and their consequential impacts is crucial while we deal with the halogenated minerals and gems. The data on halogen concentration in Earth's primitive mantle [57-61] show the presence of F in 18-25 ppm [59,60] and Cl in 1.4- 35 ppm concentration [60,61]. Knowledge of magmatic abundances of F and Cl is generally sufficient [62] to interpret volcanic processes in some tectonic environments though not in all cases. Studies have shown that fluorine has a noticeable effect on the viscosities of geological and diopside melts. The presence of a small amount of F (4-6 wt%) reduced the viscosity of albite melt significantly though the change is small for diopside melts [63]. But the effect of F in reducing melt viscosity is the most profound in low-temperature, silica-rich rhyolitic melts. Studies on fluoride concentration and its connection to geology and seasonal hydrology have also revealed the impact of fluorine-rich granite intrusion on the extent and distribution of fluoride in specific areas [64].

The studies on the formation of various fluorine-containing mineral deposits exposed the effect of fluorine on the nature and structural features as well as the origin of these deposits [2,63-65]. Examples of these minerals include fluorite and topaz in carbonatite and granite intrusive rocks, volcanic rocks and magmas in various geological regions [65-69]. Topaz of magmatic origin (in rhyolites and topazites) is greatly fluorine-enriched and topaz of hydrothermal origin may be more hydroxyl-enriched [70,71]. Studies by Jago and Gittins [65] showed that fluorine helps the carbonatite magmas to remain in the liquid state at geologically relevant temperatures and pressures. Results show that just 8 wt% fluorine can achieve an effect

similar to that incurred by large amounts of water (as much as 95%). Studies on the crystallization of primary pyrochlore in carbonatite magmas also revealed the role of fluorine in the crystallization process [72] and the effect of variation in fluorine activity in the case of pyrochlore, enriched in rare earth elements (REEs) and high field strength elements (HFSEs) [73].

Among other terrestrial planets, in Venus's atmosphere, the presence of fluorine was detected as HF gas in trace amounts (~5 ppb by volume above and below the clouds) [74,75]. Studies suggest that there is an equilibrium between HF gas in the atmosphere and surface rocks [76,77]. It was also shown that the mineral deposits in Martian Gale Crater [78] contain calcium fluoride (*vide infra*).

### **3. MAJOR CHALLENGES FACING THE DETECTION OF COSMIC FLUORINE**

The accurate discovery of the cosmic origin of highly reactive elements such as fluorine is difficult because the conditions required to form their nucleus are often harmful and detrimental to their survival. The fluorine nucleus does not survive under the nuclear processes occurring in stellar interiors [32-37] (mainly reactions with hydrogen and helium -  $^{19}\text{F}(p, \alpha)^{16}\text{O}$  and  $^{19}\text{F}(\alpha, p)^{22}\text{Ne}$ ). Therefore, if its swift transfer to a safe region, where it can survive before its annihilation is possible, its identification becomes feasible. The measured fluorine abundances can set tight constraints on models of stellar evolution and also on the chemical evolution of certain stellar populations due to the sensitivity to the physical conditions of the production site. Due to high volatility and reactivity of fluorine, the measurement of fluorine abundance in solar photosphere and similar atmosphere is difficult. Its abundance is derived from sunspot spectra [79,80]. The new solar fluorine abundance determined by Maiorca et al. from sunspot data analysis showed a value of  $A(\text{F})_{\odot} = 4.40 \pm 0.25$  [81], close to the meteoritic value estimated by

Lodders et al. [82]. The atomic or ionized fluorine does not show any distinctive spectral lines that help to determine its stellar presence. There are very few observations of F outside the solar system. Therefore, the presence of fluorine has to be determined by observing spectral features associated with the vibration-rotation transition of hydrogen fluoride (HF) molecule by tracing infrared HF molecular spectral lines. But, the terrestrial atmosphere is opaque to the wavelength regions of HF spectral lines, making these lines invisible to terrestrial observatories and failing to accurately show the signs of stellar formation and abundance of fluorine.

However, in 1981, Snow & York [83], using the Copernicus satellite, detected interstellar monatomic fluorine  $F_I$  transition at 95.4 nm toward the line of sight of  $\delta$ -Scorpii. Later, Liu reported [84] the observations of definitive fluorine abundance outside the solar system in a planetary nebula (NGC 4361) via  $F_{IV}$  line at  $\lambda$  406 nm. Further studies revealed the presence of extensive column densities of very stable ion  $CF^+$  in the Orion Bar region of the Trapezium cluster of stars [85] and aluminum fluoride in the carbon-rich circumstellar shell of IRC +10216 [86]. In 2018, Kamiński et al. [87] reported that they observed millimeter-wave rotational lines of emission of radioactive aluminum monofluoride isotopologue  $^{26}AlF$  towards CK Vul, which is deemed as a stellar merger remnant. The emission showed high content of the radioactive isotope  $^{26}Al$ . These fluorinated species naturally intrigue our search for more fluorides of other elements, including fluorinated cations and anions in the galaxies and the interstellar medium.

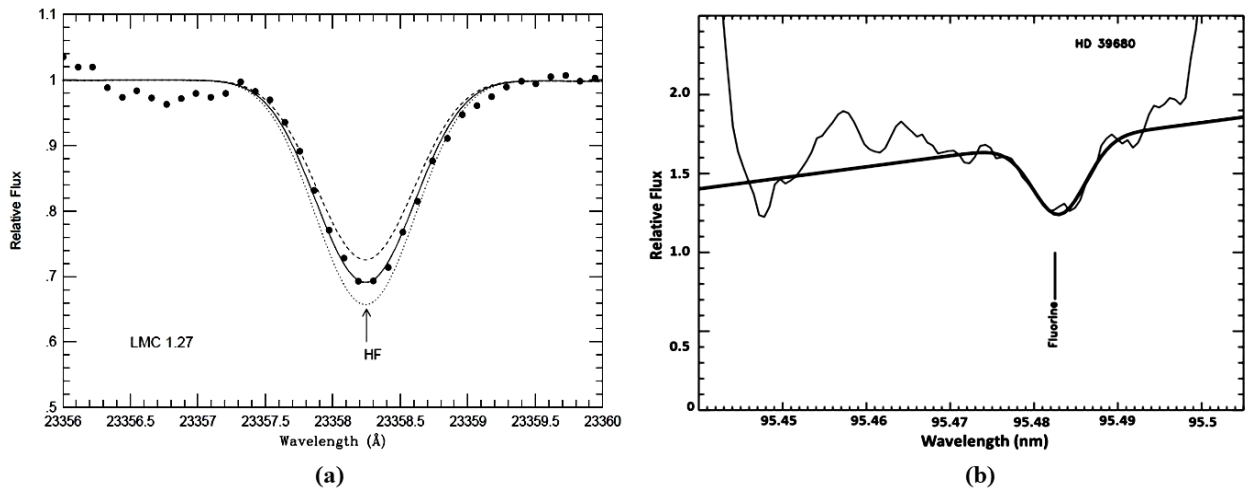
#### **4. INTERSTELLAR HYDROGEN FLUORIDE AND ESTIMATION OF FLUORINE ABUNDANCE**

In 1997, Neufeld et al. [88] reported the observation of hydrogen fluoride (HF) gas in a giant gas cloud in Sagittarius B2 (southern part of the Sagittarius constellation) near the center of the Milky Way galaxy, about 20,000 light-years from Earth. The concentration of HF there is

$10^{10}$  times lower than that of hydrogen. At the very low temperatures ( $\sim 50$  K) of the interstellar medium, HF is probably present in solid nongaseous form adhered to the minerals in cosmic dust grains. Using the Long Wavelength Spectrometer aboard the *Infrared Space Observatory* (launched by European Space Agency), Neufeld and coworkers [88] were able to observe an absorption line at  $121.6973\ \mu\text{m}$  in the far-infrared region ( $25\text{--}350\ \mu\text{m}$ ), characteristic of the  $J\ 2\text{--}1$  rotational transition of H–F. This was the first time the presence of a new interstellar molecule (HF) had been demonstrated by IR spectrometry, although the presence of over 100 molecular entities in the interstellar medium had been reported by that time. In the interstellar and circumstellar media, the presence of over 270 molecular species has been reported by 2022 [89]. Recently, Yang et al. [90] proposed that quantum tunneling effect is an important source of HF in interstellar clouds. Although monatomic fluorine [91] has been observed in the interstellar medium and even “F<sup>+</sup>” [92] in planetary nebulae as well as in stars, including our Sun, due to extremely high reactivity, fluorine is often identified as HF molecules by its chemical reaction with molecular hydrogen, the main constituent of the interstellar gas [93].

HF recognized via vibrational-rotational lines in the infrared is limited to the coolest giant stars [26]. The characteristic spectral lines of HF indicative of stellar fluorine abundances are the vibrational-rotational absorption lines around  $2.3\ \mu\text{m}$ . Using a model suggested by Kobayashi et al. [36], Jönsson and coworkers searched for pure rotational lines of the HF molecule around  $12\ \mu\text{m}$  using a mid-IR high-resolution spectrometer [39,94,95]. They also analyzed the near-infrared spectra, covering  $2.3\ \mu\text{m}$  lines using an FT spectrometer. These transitions located in the near-IR K band are the most accessible lines. The most used spectral line for tracing stellar HF in the study of nucleosynthesis and galactic evolution of  $^{19}\text{F}$  is the HF (1-0) R9 line at  $\lambda\ 2.3358\ \mu\text{m}$  ( $2335.8\ \text{nm}$ ) [26,29, 39,96,97].

In addition to abundances derived from stellar HF lines, Federman et al. [98] confirmed the detection of interstellar F<sub>I</sub> lines (at 95.4 nm in the far-UV region) along two lines of sight into the Cepheus OB2 stellar association using the *Far Ultraviolet Spectroscopic Explorer* (FUSE). Later, Snow et al. [91] found results for a star HD 39680 similar to those observed in the interstellar spectra of  $\delta$ -Scorpii [83] (Figure 1). The observation of HF is limited to its location in relatively cool stars because HF molecules are prone to dissociation in stars of rather moderate temperatures ( $\sim 6000$  K). For example, absorption lines of HF are detected only in the cooler, magnetically induced sunspots, not in the “normal,” undisturbed atmosphere of the Sun. High volatility and reactivity of fluorine and susceptibility of HF to dissociation under such conditions make the measurement of fluorine abundance difficult. This means that for the measurement of fluorine abundance in stars, one has to (a) consider stars that are relatively cooler than the hot Sun-like stars, (b) focus on the observation of molecular spectral lines, not spectral lines of atomic or ionized forms, that are often used, and (c) conduct the observations in the near-infrared (IR) region instead of the generally used visible wavelength region.



**Figure 1.** Observed (dotted line) and synthetic (solid and dashed lines) spectra in the region of HF lines for the stars (a) LMC 1.27 (The synthetic lines were calculated for the logarithmic fluorine abundance  $A(F) = 3.83, 3.93$ , and  $4.03$  for LMC 1.27 (b) The 95.4 nm F I line in the far

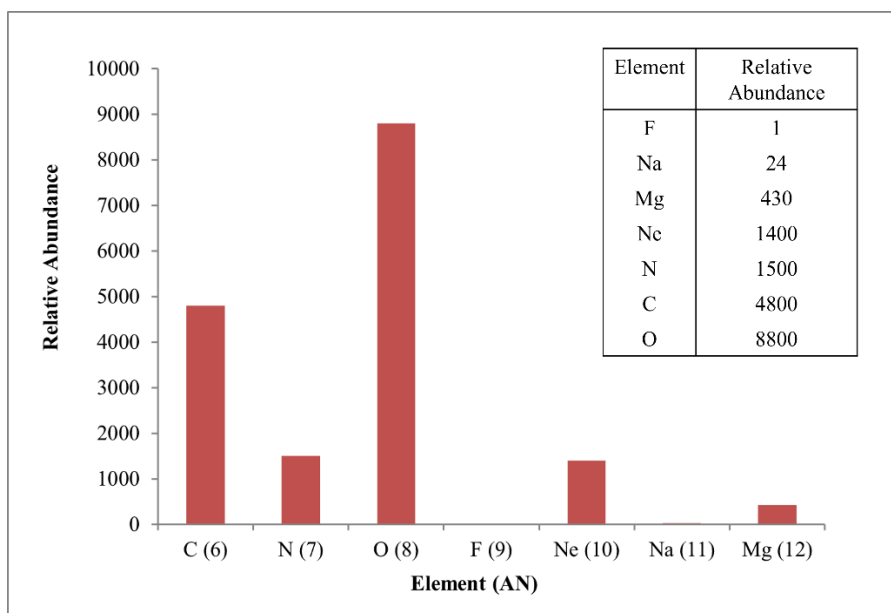
UV region for the star HD 39680 (with a single Gaussian after dividing out the H<sub>2</sub>, *see ref. 29,91*). *Reproduced by permission of AAS.*

## 5. ORIGIN OF FLUORINE IN THE EXTRATERRESTRIAL REGIONS

As it is now widely known, only the three very lightest elements, hydrogen, helium, and lithium, were formed in the Big Bang when our universe was created. All other elements were produced at various stages of nuclear evolution by stars of several types. Though the main sites of origin of most elements and isotopes in the periodic table have been revealed over the years, there are still a number of elements, including fluorine, whose cosmic origin is still elusive to a great extent. Besides being intriguing in its own right, any knowledge and data regarding the origin of the elements and their molecules observed in the universe can be used to answer a plethora of astronomically interesting questions. Knowledge of the nature and size of stars, in which particular key elements are formed, is necessary to shed light on the origin and formation of galaxies and their components. The galaxy formation is considered one of the areas of most intense research in astronomy today. From the abundance of different key elements in stars in various parts of our own galaxy, the Milky Way, we can have a good understanding of the formation and evolution of the different galactic subparts and our whole galaxy. Similar to other key elements, fluorine also might have a prominent role in the proper understanding of the creation and evolution of the Bulge, the innermost parts of our galaxy [99]. This leads us to the inevitable and more basic question of how fluorine is formed in the universe. As the astronomical values of fluorine abundance have always been uncertain, one has to depend on terrestrial and meteoritic values. The solar abundance of fluorine with respect to hydrogen is only  $3 \times 10^{-8}$ . The amount of fluorine in the universe is about 400 ppb, estimated to be the 24th most common element in the universe, much lower than what is expected for a light element.

Relative abundances of six common elements relative to that of fluorine in the order of increase in atomic number are given in Figure 2 [100,101].

In 1934, Ida and Walter Noddack reported the value of fluorine abundance in meteorites as 30 ppm [102]. Later in 1956, Suess and Urey estimated the abundance of fluorine (in primitive solar nonvolatile material) as 200 ppm relative to silicon [103]. The fluorine content of some chondritic meteorites was later reported by Fischer [104]. In a subsequent study involving 21 meteorites, Allen and Clark calculated that the fluorine content in a non-magnetic fraction of various meteorites varies from 14-45 ppm, and in a separate metal fraction, the value varies from 17-295 ppm [105].



**Figure 2.** Relative abundance of six common elements in the universe with fluorine abundance as unity.



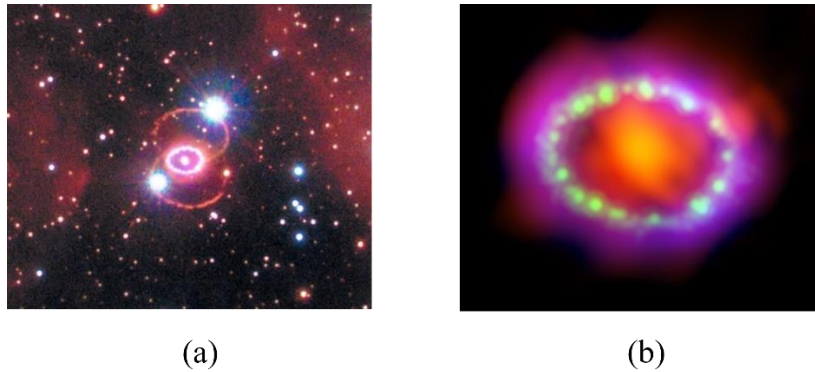
Reed and Jovanoic [106] reported that the fluorine contents of a number of lunar samples collected during Apollo 14 and 15 missions range from less than one ppm for anorthosite rock fragments to 165 ppm in soil and breccias. In recent years, studies of different samples with advanced analytical techniques such as secondary ion mass spectrometry (SIMS) showed more accurate data. SIMS analysis of three Apollo 14 apatite samples showed 2.48-2.9 wt% of fluorine [107]. Analysis of the volatile contents of three samples of lunar volcanic glasses (very low, low and high Ti glasses) in Moon's interior showed 4-40 ppm of fluorine content. [108]. Renda et al. presented a model for the chemical evolution of fluorine in the Milky Way using a semi-analytic multizone chemical evolution model and gave a brief account of the major fluorine formation sites [109]. Recently, Womack et al sought to find out the dominant contributors in the Milky Way stars to the galactic fluorine by comparing chemical evolution models to observations of fluorine abundances [35]. They summarized that the three possible processes for the nucleosynthesis of  $^{19}\text{F}$  much discussed in the cosmic origin of fluorine are (1) from  $^{20}\text{Ne}$  by the v-process through a neutrino capture process during Type II supernovae [31,110]; (2) through both helium burning and combined hydrogen-helium burning followed by a subsequent mass loss in the asymptotic giant branch (AGB) stars [111-113]; (3) and by internal helium burning in Wolf-Rayet stars followed by rapid ejection of fluorine in stellar swirl winds [114,115].

## **6. THREE POSSIBLE PROCESSES FOR NUCLEOSYNTHESIS OF $^{19}\text{F}$**

### *6.1. $^{19}\text{F}$ Nucleosynthesis by neutrino spallation during type II supernovae*

In 1980, observations using Copernicus satellite indicated the presence of fluorine in the line of sight toward  $\delta$ -Scorpii [83]. In 1987, Ian Shelton at the Las Campanas Observatory (LCO, Chile) reported the detection of a neutrino burst from supernova 1987A (Figure 3), a type

II supernova in the Large Magellanic Cloud (LMC, a dwarf galaxy satellite of the Milky Way). His studies [116-119] suggested a flux of neutrinos generated by the core-collapse of a massive star. Supernovae, the largest explosions that take place in space, radiate more energy than the Sun can do in its entire lifespan. About 163,000 light-years away, LMC is the abode of a firestorm of star birth, where Supernova 1987A resides. Supernovae are also the primary source of heavy elements in the universe and can briefly outshine entire galaxies. The observations provided evidence for the involvement of neutrinos in the synthesis of fluorine during supernova explosions of supergiant stars. Fluorine has even been detected in the Omega Centauri cluster, where very little iron is present (5–10% compared to the Sun's value).



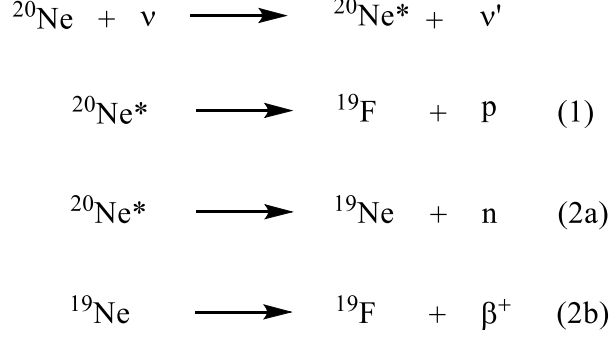
**Figure 3.** (a) Supernova 1987A located in the Large Magellanic Cloud, a satellite galaxy of the Milky Way; (b) Multi-wavelength image of supernova 1987A in 2017- Combination of images from the Atacama Large Millimeter/submillimeter Array (ALMA) telescope, NASA's Hubble Space Telescope, and NASA's Chandra X-ray Observatory. *Credit:ALMA (ESO/NAOJ/NRAO/A Angelich. Visible light image: the NASA/ESA Hubble Space Telescope. X-Ray image: The NASA Chandra X-Ray Observatory- <http://eso.org/public/images/esp1401a/>.*

According to Woosley and Haxton [31,110], fluoride could be created and stabilized by supernovae in stellar explosions that eject fluorine into space quickly enough to prevent its

annihilation. The highly energetic and exotic neutrinos spewed out during the explosion would pass through all but the iron core and inner silicon shell of the collapsing star with little interaction due to their weak coupling to matter. According to the models favored at the time, the total number of  $\mu^-$  and  $\tau^-$ -neutrinos and antineutrinos produced during the core-collapse in massive stars to supernovae was estimated to be  $\sim 5 \times 10^{58}$ . Woosley et al. [120] suggested that the source of most of the fluorine in the universe would come from these supernovae neutrinos and proposed a satisfactory mechanism for the nucleosynthesis of  $^{19}\text{F}$ . The core-collapse supernovae, also referred to as type II supernovae, are the explosions ending the lives of massive stars. They show that the solar abundance of fluorine constrains the temperature of  $\mu^-$  and  $\tau^-$ -neutrinos to values close to those expected from the standard model (8-10 MeV). Their analysis focused on the reactions of these neutrinos with parent nuclei that have much higher solar (and presumably galactic) abundances than their daughter nuclei, possessing one less proton or neutron [31,110,120]. They inferred that as daughter nuclei, the stable isotope of fluorine  $^{19}\text{F}$  is the suitable example, the only one which has a solar abundance of 1/3100 relative to the parent nuclei,  $^{20}\text{Ne}$ . Their detailed analysis suggested that the entire observed abundance of  $^{19}\text{F}$  could be accounted for in the same site where  $^{20}\text{Ne}$  is synthesized, with a relative efficiency of only 0.03%.

For example, before a massive star such as Antares turns into a supernova, a large pile of  $^{20}\text{Ne}$  (nuclei with ten protons and ten neutrons) is produced. Some of the neutrinos from the neutrinos stockpile ( $\sim 10^{58}$ ) formed in supernova explosion while passing through the  $^{20}\text{Ne}$  layers form the highly excited and energetic  $^{20}\text{Ne}^*$ , which by subsequent decay processes leads to the formation of  $^{19}\text{F}$ . The main decay pathways of the excited states of  $^{20}\text{Ne}$  involve the proton

channel (Eq. 1) and neutron channel (Eq. 2a), with subsequent  $\beta^+$  decay of  $^{19}\text{Ne}$  to  $^{19}\text{F}$  (Eq. 2b) as shown below.



**Scheme 1.** Nucleosynthetic Pathways leading to  $^{19}\text{F}$  from  $^{20}\text{Ne}^*$ .

Although both pathways lead to  $^{19}\text{F}$ , the  $^{19}\text{Ne}$  to  $^{19}\text{F}$  pathway is limited because many events destroy  $^{19}\text{Ne}$  almost entirely. Hence, the branching ratio between neutrons and protons is crucial. The yields calculated by Woosley and Haxton [31,110] for the production of  $^{19}\text{F}$  by proton and neutron pathways are 0.66 and 0.30, respectively, for the neutrino spectrum with  $T \approx 10$  MeV. Considering both major destruction pathways before and after the shock passage (Scheme 2, Eq. 1 & 2), at the temperature values of  $\mu$ - and  $\tau$ -neutrinos, expected from the standard model (8-10 MeV),  $^{19}\text{F}$  is produced in adequate proportions with respect to neon. Therefore, if supernovae type II are the production site of  $^{20}\text{Ne}$  [121], the formation of fluorine ( $^{19}\text{F}$ ) in our galaxy could be attributed to the processes discussed in Scheme 1 despite the uncertainty in the  $^{19}\text{F}/^{20}\text{Ne}$  ratio of abundance [31,120]. However, it is worth noting that such a hypothesis remains still speculative as the detection of  $^{19}\text{F}$  during supernova explosions is not yet achieved, and later, Sieverding et al. confirmed that the  $\nu$ -process could not be the primary origin of  $^{19}\text{F}$  [122].



**Scheme 2.** Major pathways leading to  $^{19}\text{F}$  destruction.

## 6.2. $^{19}\text{F}$ Nucleosynthesis by helium/hydrogen-helium burning in Asymptotic Giant Branch (AGB) stars

The next source of fluorine discussed over the last three decades involve low and intermediate-mass asymptotic-giant-branch (AGB) stars [111,112]. As  $^{19}\text{F}$  is quickly destroyed by proton capture at stellar temperatures [26,11] as already discussed, the high probability of being evaded by normal stellar evolution, as well as the difficulty in its detection by representative atomic fluorine spectral lines, led to further attempts to solve this problem. Also, if fluorine is produced by neutrino-induced emission from  $^{20}\text{Ne}$  during the type II supernova explosion, as proposed by Woosley et al. [31], the fluorine abundance should be connected to the abundance of other elements, such as oxygen. It indicates that the fluorine-to-oxygen ratio would be the same as the solar system value. This underscores the fact that the slowly evolving low and intermediate-mass AGB stars would be a probable source of fluorine [123].

In 1992, Jorissen, Smith, and Lambert reported observational evidence for the production of highly reactive and elusive fluorine in dozens of red-giant stars during their thermal pulsing (TP) phase occurring at the He-shell burning site [26]. While studying the elements in giant stars, they detected infrared signals of hydrogen fluoride, which was, in fact, prior confirmation of Jorissen's theory [26,124,125]. Till their discovery, the presence of fluorine element has been reported in the Sun, the envelope of red supergiant carbon star Betelgeuse, planet Venus, and in a

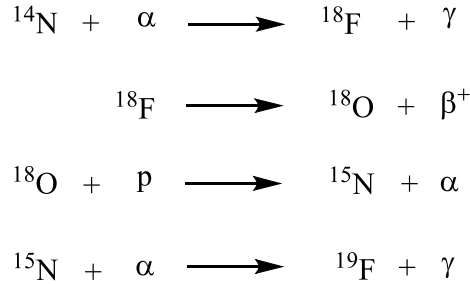
couple of nebulae [126]. However, within a short time, the observation of fluorine in more than 65 giant stars was reported. The fluorine abundance in most K and M-type stars is of the order of that found in the Sun. More studies on a number of carbon stars showed that they have fluorine abundances up to 65 times more than the Sun, indicating the possibility of fluorine synthesis in the stars by themselves as predicted by Jorissen [111] and as appropriately reiterated later by Mathews [113].

Though the production of fluorine by low and intermediate AGB stars ( $M \leq 7 M_{\odot}$ , [127] surface C/O ratio  $> 1$ ) has been experimentally shown multiple times in various observations, the very first detection of fluorine in red-giant stars by Jorissen et al. [26] is the most noted one. In this scenario, fluorine is synthesized by nuclear reactions starting from  $^{14}\text{N}$ , including  $\alpha$  particle, neutron, and proton captures. They obtained fluorine abundances on the surfaces of various red giant stars from the infrared rotation-vibration lines of HF molecules providing strong evidence that fluorine is produced in the deep interiors of red giant stars during episodic flashes of thermonuclear burning. Their discovery showing the overabundance of fluorine at the surfaces of C (Carbon-rich AGB stars) and S stars (AGB stars rich in s-process elements, with less carbon than C stars but more than M stars) highlighted the possibility that these stars are the net producers of  $^{19}\text{F}$  [31,111,112,128,129].

Later, Abia et al. [96,123,130], in their studies on fluorine abundance in three Galactic AGB carbon stars (TX Psc, AQ Sgr, and R Sc1), found that the values derived for these stars are systematically lower by  $\sim 0.8$  dex (i.e.,  $10^{0.8}$ ) [131] on average with respect to the value estimated by Jorissen et al. [26], the difference may be due to the possible blending with C-bearing molecules (CN and  $\text{C}_2$  molecules), which was not properly accounted during their study. The

new values of F abundances are in better agreement with the predicted values of full network stellar models of low-mass ( $< 3 M_{\odot}$ ) AGB stars.

The two major fusion reactions that power asymptotic giant branch stars are (a) hydrogen  $\rightarrow$  helium occurring in the outer shell via the CNO cycle (which converts carbon and oxygen to nitrogen) and (b) helium  $\rightarrow$  carbon by helium ignition in a shell deeper inside the star resulting in ‘helium-shell flash’ due to extremely high temperature and carbon is pulled up to the star’s surface by the convection in the star’s outer envelope. Through this process, a giant star is transformed into a carbon star.  $^{14}\text{N}$  produced from the hydrogen-burning CNO cycle mixed with the helium ash can be transformed into  $^{19}\text{F}$  in subsequent steps by the helium-shell flash (Scheme 3). In that same drag, fluorine is lifted up faster to the star’s cooler upper levels before being destroyed by the fluorine-fleecing helium nuclei. Thus, during the star’s death, fluorine enriched atmosphere is flushed into space through a beautiful planetary nebula (PNe).



**Scheme 3.** Nucleosynthetic pathway for  $^{19}\text{F}$  in AGB stars.

Though the production of fluorine by Asymptotic Giant Branch stars (red giant stars) has been pointed out in many reports, in the galactic chemical evolution of fluorine, whether any other process could be a dominant source and produces a significant amount of fluorine is still under debate. Through a series of investigations on stellar populations of different ages, there

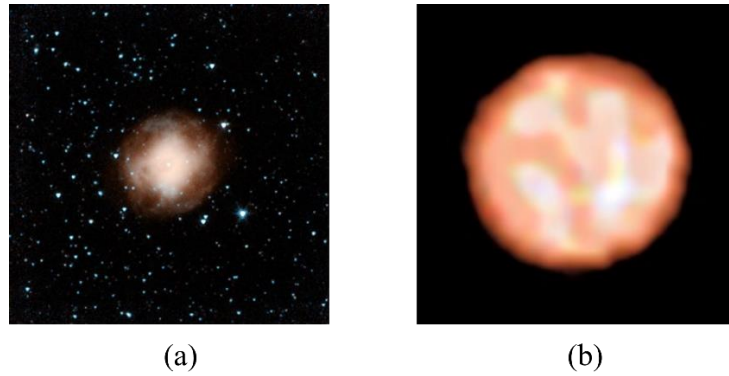
were attempts to assess the relative contribution of the different production channels. However, recording the stellar spectra of relevant objects still remains a real challenge. These stars are dying stars in the last stages of stellar evolution with an approximate lifetime of a few thousand to 1 billion years as red giants. The Sun will have a similar fate, eventually turning into a red giant star, expanding and engulfing the inner planets successively, possibly even Earth, in due time.

Abia et al. in 2019 [132] reported their high-resolution IR observations in a sample of eleven AGB carbon stars: five SC-type (AGB stars with more carbon than S stars, with an almost equal abundance of carbon and oxygen) and six normal N-type stars, including a new extragalactic AGB carbon star (in the Sagittarius dwarf spheroidal galaxy) from a study to measure  $^{19}\text{F}$  and s-element contents. For comparison, two metal-poor CH/Ba stars were also studied. They found comparable F enrichments for SC- and N-type stars with metallicity close to the solar value ( $z_{\odot} = 0.0134$ ). In the full range of metallicity studied, the F overabundances are moderate, suggesting that AGB stars are not the main contributors of F in the solar neighborhood, in agreement with recent chemical evolution models [27,34,35].

The evolution of AGB stars in binary systems plays a crucial role in understanding the formation of asymmetries in planetary nebulae (PNe, Figure 4a). To identify the factors that cause the observed asymmetries in the environment of the evolved AGB star  $\pi^1$  Gruis (Figure 4b) on large and small scales, Mayer et al. [133] conducted studies using a Photodetector Array Camera and Spectrometer (PACS) on board the Herschel Space Observatory. Some of these AGB stars possess an asymmetric circumstellar envelope (CSE). The morphology of the envelope is often dependent on its interaction with a stellar companion in its proximity. In 2017, using the Very Large Telescope (VLT) in the European Southern Observatory, the surface of  $\pi^1$



Gruis and its periodic transformation were studied in detail [134]. The helium in the core is eventually exhausted, shutting down the fusion process. The star shrinks again with the ignition of successive helium shells beyond and the expansion of the star's outer layers. The star becomes a "white dwarf," extremely dense and compact, with its core collapsing in itself. The outer layers of the dense star burst into huge clouds of gas and dust known as the planetary nebula, the signature event in stellar demise.



**Figure 4.** (a) Infrared picture of PNe NGC 4361 (Nasa's Spitzer Telescope on July 18, 2009). (b) Surface of the AGB star  $\pi^1$  Gruis. *Credit: NASA.*

Liu reported the first reliable measurement of the fluorine abundance for a planetary nebula [84]. For the planetary nebula NGC 4361 in the Corvus constellation (Figure 4a), having stars with 1-2  $M_{\odot}$ , they found an F/H abundance ratio of  $4.5 \times 10^{-8}$  from the  $[F_{IV}]$  spectral line at  $\lambda 4060$ . The  $[F/O]$  and  $C/O$  abundance ratios derived for NGC 4361 are in reasonable agreement with the correlation found between these two quantities among red giant and AGB stars, with the predicted values from theoretical models of fluorine production in thermally pulsing AGB stars. Zhang and Liu determined fluorine abundances from the  $[F_{II}]$   $\lambda 4789$  and  $[F_{IV}]$   $\lambda 4060$  nebular emission lines for a sample of NGC 4361 [92]. They also found the  $[F_{II}]$   $\lambda 4789$  line in the spectrum of a low-excitation PNe, IC 418, and the  $[F_{IV}]$   $\lambda 4060$  line in the spectrum of a high-

excitation PNe, NGC 7027. Their results showed that fluorine is generally overabundant in PNe, providing new evidence for fluorine synthesis in asymptotic giant branch (AGB) stars.

### 6.3. $^{19}\text{F}$ Nucleosynthesis in bright and massive Wolf-Rayet stars

The third possible source for the cosmic origin of fluorine is the Wolf-Rayet stars [31,114,115]. The latest observation of fluorine presence in the far distant high- $z$  galaxy [37] showed that the sources for the observed fluorine abundance are Wolf-Rayet stars. It provides an understanding of the processes behind the ramp-up phase of chemical enrichment in a young and massive high- $z$  galaxy. The blue giant Wolf-Rayet stars are very hot, massive ( $M > 20 M_{\odot}$ ) and bright stars at their end stage. Many brightest and most massive stars in our Milky Way galaxy are Wolf-Rayet stars. They are supernova progenitors, finally ending their lives as type II supernova. They blast out their outer shells as massive stellar wind particles in space experiencing a large successive mass loss. Therefore, except in Wolf-Rayet galaxies, only a few of these stars per galaxy are found. The youngest wind-nebula M1-67 was observed around Wolf-Rayet star 124 in our Milky Way galaxy located in the Sagittarius constellation 10,000-15,000 light years away [135-137]. Figure 5a shows the magnificent image of the M1-67 wind nebula around WR 124, made of the ejected material from the star taken by the Hubble Space Telescope [124,138]. WR 124 is one of the hottest Wolf-Rayet stars known, with an estimated mass of  $\sim 20 M_{\odot}$ .

Another Wolf-Rayet star cluster is found in R136 (Figure 5b), the central concentration of stars in the large NGC 270 stellar cluster lying at the center of Tarantula Nebula of the Large Magellanic Cloud (LMC) [139]. Wolf-Rayet star R136 a1 in the R136 cluster is also one of the hottest stars (53,000 K) with the highest mass ( $315 M_{\odot}$ ) and luminosity (8.7 million  $L_{\odot}$ ) of

any known star so far [140-142]. It is currently in the hydrogen-to-helium fusion process, predominantly by the CNO cycle, due to the high temperatures at the core.



**Figure 5.** (a) WR 124 in the M1-67 wind-nebula in the Sagittarius constellation, (b) A near-infrared image of the R136 star concentration of the Tarantula Nebula in the Large Magellanic Cloud, obtained at high resolution with the Multi-conjugate Adaptive optics Demonstrator (MAD) at ESO's Very Large Telescope (*Credit. NASA & ESO*).

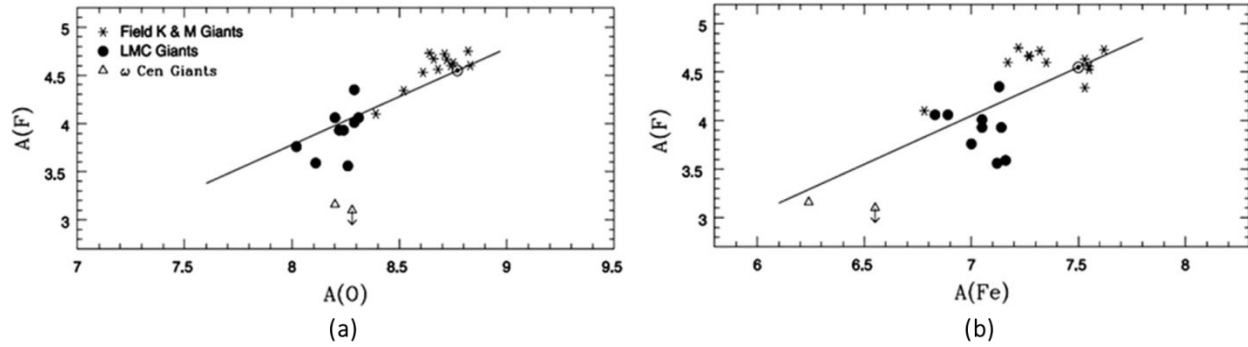
Based on the suggestion by Goriely et al. [143], Meynet and Arnold [114] studied the  $^{19}\text{F}$  synthesis of secondary nature in the burning of He-shell hydrostatically and found that the production is relatively modest in stars of mass  $\leq 20 M_{\odot}$ . But in the case of the more massive stars (also considered as Wolf-Rayet stars), a significant amount of fluorine, synthesized in the core during the beginning of their He-burning phase, is expelled through intense stellar winds. They proposed that in Wolf-Rayet stars, the  $^{19}\text{F}$  is formed from the  $^{14}\text{N}$  left over by the previous CNO-burning core, following a nucleosynthetic pathway similar to the one occurring in the case of AGB stars (Scheme 3). It is blasted out in the interstellar medium while the star enters its WC phase (Wolf-Rayet stars of carbon sequence) [113,114]. While they shed their outer envelopes, any fluorine produced in the later hot CNO cycles might be saved from destruction by radiatively driven stellar wind [115], as mentioned earlier in the case of AGB stars. This implies that extensive mass loss in these massive stars can contribute to higher fluorine production signifying

Wolf-Rayet stars as a prominent fluorine source because the produced fluorine is ejected in the lost mass before its destruction. The  $^{19}\text{F}$  synthesis in the hot CNO cycle invokes its dependence on metallicity (abundance of elements other than hydrogen and helium). Their calculated yields were based on detailed stellar evolutionary sequences for a series of initial masses ranging from 25 to 120  $M_{\odot}$  and metallicities  $Z_{\odot} = 0.008, 0.02, \text{ and } 0.04$ . Meynet and Arnould [115] pointed out that the mass loss is metallicity dependent, predicting a strong dependence of fluorine yields in Wolf-Rayet stars on metallicity. Recently, Guerço et al. reported  $^{19}\text{F}$  abundance and  $^{16}\text{O}/^{17}\text{O}$  isotopic ratio in a sample of six young red giants in the Galactic center, five of which belong to a nuclear star cluster orbiting a gigantic black hole [144].

As metallicity is one of the underlying criteria determining the formation of Wolf-Rayet stars, Wolf-Rayet theory predicts that the nucleosynthesis of fluorine in the galaxy occurred after it attained critical metallicity. Poor metallicity suggests a poor chance of observing fluorine in Wolf-Rayet stars. An O-type star (bright white-blue giant star, surface temperature 30000-50000 K) becomes a Wolf-Rayet star by blowing off its atmosphere. Underscoring their prediction [115], studies by Cunha et al. [29] showed a decrease in the F/O abundance ratio as the oxygen abundance decreases, as well as the low production of fluorine at low metallicities from WR stars by stellar wind blow.

As mentioned earlier, the source of HF observation might be fluorine itself. Cunha et al. [29] obtained fluorine abundances for nine stars in the Large Magellanic Cloud and two stars in the globular cluster  $\omega$ -Centauri (Figure 6). All have lower metallicities than the K and M giants studied by Jorissen et al. [26]. Figure 6 gives a comparison of fluorine abundance with oxygen (a) and iron abundances (b). The solid line depicts the corresponding solar F/O and F/Fe abundance ratios. All these LMC red giants as well as K and M giants have F/O abundance ratios

scattering around the solar line (solid black line). The field K and M giant abundances are very close to solar abundance. They have F/Fe abundance ratio, showing values more scattered (almost twice as large) than those about the F/O line. It is noteworthy that the two Omega Centauri giants in the globular cluster have values ( $\Delta$ ) significantly lower than solar F/O abundance. Omega Centauri giants have iron abundances of just 5 and 10 percent of solar abundance, indicating a significant age [29,111]. By comparing the fluorine abundances with those of oxygen and iron, it was concluded that fluorine originates chiefly in high-mass stars—either when these stars explode and shoot neutrinos through their neon, or via nuclear reactions in Wolf-Rayet stars or both.



**Figure 6.** (a) Logarithmic Abundance of fluorine  $A(F)$  as a function of oxygen  $A(O)$  and (b) iron  $A(Fe)$  in the field K & M giants in the Milky Way (star symbol), LMC (black dots), and  $\omega$  Centauri (triangles). The circled black dots correspond to the abundance of fluorine in the Sun. The solid line denotes solar F/O and F/Fe abundance ratios (*see work by Cunha et al., ref. 29*). *Reproduced by permission of AAS.*

Considering all the three suggested sources—Supernovae type II neutrinos, AGB stars, and Wolf-Rayet stars, one can hope that further studies involving a model-independent investigation of the cosmic origin of fluorine can give a greater insight into the sources of galactic evolution of fluorine and fluorine abundance in the interstellar medium.

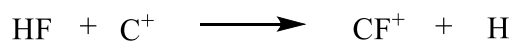
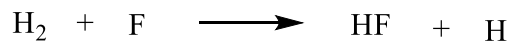
## 7. FLUOROCARBON IONS IN CIRCUMSTELLAR AND INTERSTELLAR MEDIA

Beyond Earth in the interstellar or circumstellar media in our galaxy, more than 270 different molecular species ranging in size from two atoms (e.g., methylidyne) to 70 atoms (e.g., rugbyballene, C<sub>70</sub>) have been spotted and identified till 2022 [89]. Among these molecular species, hydrocarbons (those containing carbon and hydrogen) represent the major group of derivatives. More than 95% of these species involve just six elements – hydrogen, carbon, nitrogen, oxygen, silicon, and sulfur – all of which have moderately high abundances ( $\geq 10^{-5}$  relative to hydrogen in the Sun). Attempts in recent years to find the presence of organic molecules and ions outside of terrestrial atmosphere include extensive studies on the nature and composition of the upper atmosphere of Titan (Saturn's moon) using the Cassini spacecraft with its onboard instruments, the Ion Neutral Mass Spectrometer (INMS) and the Cassini Plasma Spectrometer (CAPS). These studies revealed significant and extensive spectroscopic data confirming the presence of a wide variety of carbocations. Ali et al. [145] analyzed and interpreted the spectral data and found that they are similar to those studied by Olah et al. [11] under condensed-state terrestrial conditions in superacid media. Ali suggested that the transformation of extraterrestrial methane to its ions is based on CH<sub>5</sub><sup>+</sup> and Olah's related nonclassical carbonium ion chemistry. In this context, the search for fluorocarbon ions is also very intriguing.

The chemistry of fluorine-bearing molecules in the interstellar medium is mainly derived from hydrogen fluoride, the dominant reservoir of gas-phase F nuclei, formed from the exothermic reaction of F atoms with H<sub>2</sub> [146]. As shown by Neufeld et al. in their theoretical investigation [146], at the characteristic thermal conditions and chemical composition in molecular clouds, reactions of HF with C<sup>+</sup> and Si<sup>+</sup> are the most thermochemically feasible ions,

leading to the stable molecular ions  $\text{CF}^+$  (isoelectronic with CO) and  $\text{SiF}^+$  (isoelectronic with SiO) with enthalpies of formation -748 kJ/mol and -608 kJ/mol, respectively [146]. HF is abundant in the close vicinity of UV-irradiated cloud surfaces where  $\text{C}^+$  is dominant in a reservoir of carbon in the gas phase. Therefore, the reaction of HF with  $\text{C}^+$  can lead to potentially measurable column densities of the very stable  $\text{CF}^+$  ion. Intrigued by this and the theoretical models that predicted  $\text{CF}^+$  abundances in UV-irradiated molecular regions where  $\text{C}^+$  is present (though in meager amounts), they searched for the fluoromethyldynium ion ( $\text{CF}^+$ ) using the IRAM 30 m and APEX 12 m telescopes [85]. They were able to observe its corresponding rotational transitions  $J = 1-0$  at 102.6 GHz,  $J = 2-1$  at 205.2 GHz, and  $J = 3-2$  at 307.7 GHz toward the Orion Bar region, southeast of the Trapezium cluster of stars. The results indicate the presence of  $\text{CF}^+$  column densities  $\geq 10^{12} \text{ cm}^{-2}$  over a region of size  $>1'$  matching their theoretical prediction [85,146]. The formation and the annihilation of  $\text{CF}^+$  ions occur by the reaction sequences as predicted theoretically in Scheme 4. In 2015, Fechtenbaum et al. reported the first detection of  $\text{CF}^+$  towards a young and massive protostar CygX-N63 of the Cygnus X region by identifying its  $J = 1-0$  (102.6 GHz) rotational lines [147]. These results support the theories of interstellar fluorine chemistry, which imply the extensive presence of HF, its detection, and its application as an effective tracer for molecular materials in interstellar gas clouds. Benjamin et al. successfully applied non-LTE excitation models that reveal population inversion in physical conditions typical of photodissociation regions in the interstellar medium (ISM) to fit the previously observed  $\text{CF}^+$  emission lines. These models aid in using  $\text{CF}^+$  as a probe to study molecular clouds in strong stellar radiation fields in the ISM [148].

A. Formation of CF<sup>+</sup>



B. Annihilation of CF<sup>+</sup>



**Scheme 4.** Formation and annihilation pathways for fluoromethyldynium ion (CF<sup>+</sup>).

## 8. METAL FLUORIDES IN CIRCUMSTELLAR MEDIA, INTERSTELLAR MEDIA, AND MARTIAN SOIL

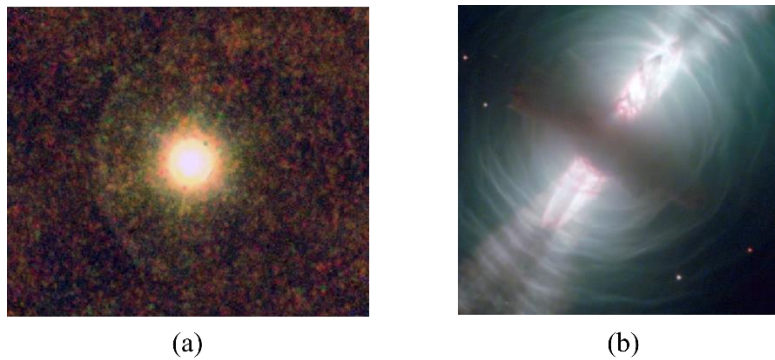
### 8. 1. Observation of aluminum fluoride

Studies around the carbon star IRC +10216 (Figure 8, also known as CW Leonis) showed the presence of metal halide in its carbon-rich circumstellar shell [149]. In 1987, Cernicharo and Guelin [150] reported the observation of many metallic halides towards IRC +10216. They detected NaCl, KCl, AlCl, and tentatively AlF from their observations during spectral survey using 30 mm telescope at IRAM (Institute for Radio Astronomy in the Millimeter Range, France). As the cosmic abundance of fluorine is lower than that of chlorine by a factor of 5, the conclusion regarding the presence of AlF was unclear. However, later studies by Ziurys et al. [151] showed three new rotational transitions of aluminum monofluoride in IRC +10216 at 0.8 and 1.2 mm with  $J = 10-9$ ,  $J = 8-7$ , and  $J = 7-6$  lines at 230, 263, and 329 GHz, respectively using the Caltech Submillimeter Observatory (CSO). Comparing with the earlier results, they could confirm the presence of aluminum fluoride in the carbon-rich circumstellar shell of IRC +10216. The CSO and the IRAM data analysis shows the presence of aluminum monofluoride chiefly in the inner envelope of IRC +10216 with a column density of  $(0.3-1.1) \times 10^{15} \text{cm}^{-2}$  indicating a fractional abundance of  $\sim 10^{-9}$  relative to H<sub>2</sub>. Aluminum monofluoride (AlF) is



suggested to be one of the leading carriers of fluorine in the gas phase in the outflow of evolved gases. Saberi et al. have reported the detection of AlF line emission towards M-type AGB stars for the first time recently [152]. However, results from the search for the other metal fluoride species  $\text{CaF}_2$  and  $\text{MgF}_2$  were not yet positive.

The presence of AlF in IRC +10216 also indicates that large quantities of fluorine must be present in the inner stellar envelope and point towards the production of fluorine primarily in helium shell flashes (as shown by HF spectroscopy of RGB stars) rather than in explosive nucleosynthesis. Highberger et al. [153] reported the detection of AlF, MgNC, and NaCN in the protoplanetary nebula (PPN) CRL 2688, also known as the Egg Nebula. The data from the rotational temperature analysis of the Egg Nebula suggested that the presence of AlF was constricted to its inner envelope. Unlike observed for IRC +10216, the abundance of AlF in Egg Nebula is less than the  $^{19}\text{F}$  solar abundance. These observations are indicative of an AGB wind and production of  $^{19}\text{F}$  in thermal pulses in the AGB phase. Guélin et al. reported the detection of a line at 234433 MHz in the circumstellar envelope IRC +10216, tentatively identified as  $J = 7-6$  transition of radioactive  $^{26}\text{AlF}$ , and they could derive a  $^{26}\text{Al}/^{27}\text{Al}$  isotopic ratio of 0.04 [154,155].

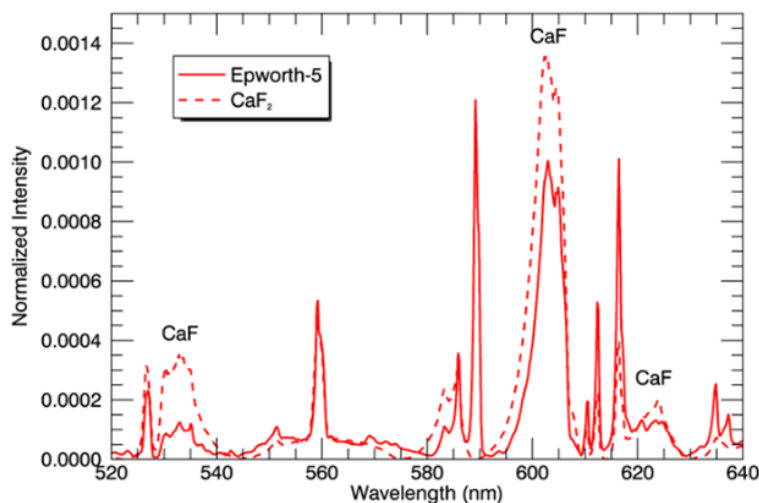


**Figure 7.** (a) Color-composite image of CW Leonis (IRC +10216), obtained with the SPIRE and PACS instruments on the ESA Herschel Space Observatory (*Credit: ESA/PACS/SPIRE/MESS Consortia*); (b) Image of the protoplanetary nebula CRL 2688 (Egg Nebula) obtained by

Hubble's Wide Field Camera 3 from exposures in visible and infrared light (*Credit: ESA/Hubble & NASA*).

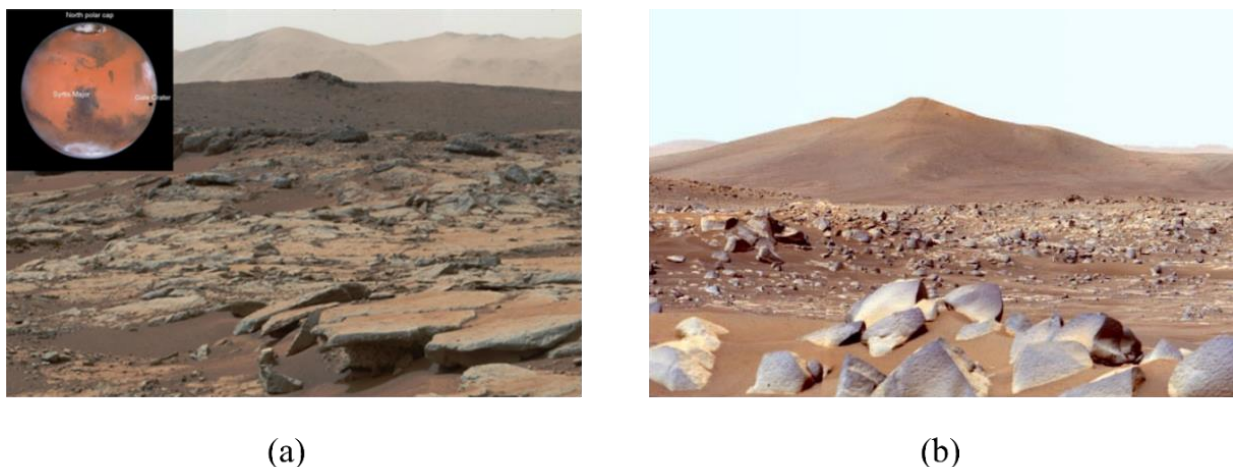
## *8. 2. Observation of calcium fluoride on Mars*

As earlier mentioned, in the data reported by Allen Clark on 21 meteorites, the presence of an average fluorine level of 20-90 ppm has been found (vide infra) [105]. The data shows an inverse relationship between the fluorine concentration in the magnetic phase and the metal content in the meteorite. They suggested that in ordinary chondrites, fluoride is present as part of either aluminum-based plagioclase or calcium-based mineral apatite [156]. Fluoride was also found in lunar glass samples that were brought back to Earth during various Apollo expeditions [157,158]. Studies on Martian meteorite samples also showed the presence of fluorine in low concentration. As the exploration of Martian soil advanced in the past two decades, in 2015, Forni et al. [78], using the data obtained from the Chemical Camera Instrument onboard Mars Science Laboratory Rover Curiosity [159], identified the presence of two fluorine-bearing mineral deposits on Mars. They analyzed the emission spectrum obtained by Laser-Induced Breakdown Spectroscopy (LIBS) using the Epworth-5 soil sample and identified Ca-F molecular-band emissions that appear when recombination occurs in the cooling plasma [78]. These emission lines enable much more sensitive detection of fluorine and halogens with respect to the usual atomic emissions. Two principal F-based types of minerals have been identified. The first one has high aluminum and low carbon content with aluminosilicate as the fluorine bearing phase. The second set has samples with high calcium contents, most likely  $\text{CaF}_2$  as fluorapatites and/or fluorites. The possibility of the presence of not only  $\text{CaF}_2$  but other fluoride minerals in their hydrated form also over a long period in the past is worth examining.



**Figure 8.** Comparison of the emission spectra of the Epworth-5 soil sample (solid line) and pure  $\text{CaF}_2$  (dashed line) obtained under Martian conditions (*copy provided by O. Forni, see ref. 78*).

By comparing the emission spectrum of the Epworth-5 soil sample from the Gale Crater (bold line) obtained by Laser-Induced Breakdown Spectroscopy (LIBS) and that of the pure fluorite (Figure 8, dashed lines), a preliminary estimate of the fluorine content was calculated as ~10wt% [68]. Further studies [160] in the search for the original source of fluorine in Martian soil, whether it is a part of evolved magma from the Martian crust, a secondary mineral transformation process in the Gale Crater, or biological activity under the Martian atmosphere could shed light on its geological past and the evolutionary processes [40,161].



**Figure 9.** (a) Sedimentary deposits in the Glenelg area of Gale Crater (image from Mastcam instrument on the NASA Mars Science Laboratory (MSL) onboard the rover Curiosity, Mars inset); (b) “Santacruz” hill and sediments in the Jezero Crater (image from Mastcam-Z imager on Mars Perseverance rover). *Credit: NASA/JPL-Caltech/ASU/MSS.*

Following the studies of the samples of sediments in delta deposits of Gale Crater, analysis of sediments from Jezero Crater is also in progress to detect the presence of minerals and organics (Figure 9). Recently, the results from studies using the SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals) instrument in Perseverance Rover, which landed in Jezero Crater, confirmed the presence of carbon-containing molecules in rocks and dust in the crater [162,163]. Future explorations can bring forth more information on the history and structural details of various organics and minerals, including fluorides in Martian soil.

## 9. CONCLUSION

In conclusion, search over many decades for fluorine outside the Earth and its atmosphere has revealed its formation and abundance in atomic, molecular, and ionic forms ( $F$ ,  $F^+$ ,  $HF$ ,  $CF^+$ ,  $AlF$ ,  $CaF_2$ , etc.) in one or more sites of the interstellar medium, planetary surfaces, stars, and their carbon envelopes. Due to high reactivity, monatomic  $F$  and  $F^+$  were identified as  $HF$ . However, it must be noted that although several nucleosynthetic pathway possibilities are

proposed for the origin of fluorine, the processes still need to be better understood. Further studies and observations are required in order to comprehend the chemical evolution of fluorine, especially in the solar neighborhood [164]. Astrophysical studies have shown the presence of more than 270 molecular species in the extraterrestrial region [89], and a few of them were directly observed by onboard instruments of spacecrafts such as the Cassini–Huygens spacecraft from the surface of Titan (the moon of Saturn) and the Philae lander that landed on comet 67P/Churyumov-Gerasimenko [165-168]. Therefore, it is evident that as our knowledge of extraterrestrial chemistry and chemical entities increases, continued search for fluorides, fluorinated ions, and fluoroorganics in the extraterrestrial expanse will shed light on various astrochemical transformations and their possible role, if any, in the origin and chemistry of planets and even possibly terrestrial life. Although no fluorine-rich planetary environment is so far known, any clue suggesting the possibility of the presence of fluorine-containing monomers or building blocks observed along with fluoride minerals in planets such as Mars can promote further studies in search for chemistry that may support life in such environments. For example, the presence of fluorocarbon entities such as fluoromethyldynium ion ( $\text{CF}^+$ ) in the interstellar medium in the Orion Bar region [147] throws light on the possibility of forming the fluoroorganic monomers as building blocks of organized polymeric structures in fluorine-rich planetary environments. As the search continues, we hope to find evidence pointing to the presence of more fluorine-containing molecules or ions, including organics.

In summary, as the presence and activity of HF, fluoride minerals, and fluorocarbon ions are already known on stellar, interstellar, or planetary surfaces, future explorations can reveal the possibility of the formation and stability of many organofluorine molecules such as fluorinated methanol, which are unstable under normal terrestrial conditions. This can also provide valuable

information on the subsequent transformation of these simple fluorinated species to higher fluorinated hydrocarbon derivatives, fluoropolymers, etc. Also, the formation of fluorinated derivatives of more complex molecules such as sugars, nucleic acid bases, amino acids, polypeptides and proteins can be envisaged, and its implication on terrestrial chemistry can be explored.

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