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Detection of terrestrial fluorine by proton induced gamma emission (PIGE): A rapid quantification for Antarctic meteorites

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Abstract–The enrichment of fluorine on the surface of Antarctic meteorites is investigated by applying the nuclear reactions $^{19}F(p, \alpha\gamma)^{16}O$ or $^{19}F(p, p'\gamma)^{19}F$ with the proton induced gamma emission (PIGE) technique, a class of nuclear reaction analysis (NRA). Results for the Antarctic meteorites ALHA77294, TIL 82409, LEW 86015, ALHA77003, and ALH 83108 are presented. Possible sources of terrestrial F are: volcanic exhalation, tephra layers (volcanic glass), continental soil dust, or sea spray. Material from blue-ice dust-band samples also shows concentrations of F that are significantly higher than the bulk concentrations of meteorites. Finally, a quick investigation for Antarctic meteorites by external PIGE is proposed, leading to a F-contamination index that supplements the qualitative ABC-weathering index.

INTRODUCTION

During the 1980s terrestrial weathering was found to produce effects on Antarctic meteorites other than the obvious oxidation of meteoritic iron: chemical alteration of trace elements by leaching effects or by terrestrial contamination (e.g., Biwas et al. 1981; Dreibus and Wänke 1983; Dreibus et al. 1986; Heumann et al. 1987) and formation of evaporates within short time spans (e.g., Gooding 1986; Velbel et al. 1991; Jull et al. 1988). In the 1990s, these observations were further confirmed by Langenauer and Krähenbühl (1993a, b), demonstrating that all halogens are enriched on the surface of Antarctic H5 and H6 chondrites. The degree of such a contamination can be used as a tool for evaluating the limits of exposure on the ice surface. Fluorine proved to be especially helpful because only a small percentage of it can be leached by melt water.

A number of quantitative methods were suggested to supplement the qualitative ABC-weathering index. Miyamoto (1991) tried infrared diffuse reflectance spectroscopy, while Shinonaga et al. (1994) and Burns et al. (1995) examined Mössbauer spectroscopy. These techniques are sensitive to processes that form rust and evaporates. All these methods depend on the pulverizing of sample material. Thus, an analytical method for the non-destructive and rapid examination of terrestrial contaminants is an appealing supplement to the above-mentioned techniques.

Measurement of the enrichment of fluorine by proton induced gamma emission (PIGE) is advantageous due to its rapid and non-destructive analysis capabilities. Moreover, fluorine is well-suited to characterize inorganic contamination due to its low concentration in meteorites and the low leach ability of fluoride ions in silicates that lead to continuous accumulation. The possibility of using an external proton beam offers a non-destructive measurement of whole rocks.

We have already published the results of fluorine measurements obtained by PIGE (e.g., Noll et al. 1998). Besides presenting new data, the goal of this paper is to suggest PIGE analysis of F as a possible routine determination for obtaining a quantitative contamination index. Furthermore, a discussion about the possible sources of terrestrial F is added.

EXPERIMENTAL METHOD

Descriptions of the method and the experimental set-up of the accelerator facilities used in Zurich (Switzerland) and Dresden-Rossendorf (Germany) are given in Noll et al. (1998). A short synopsis of the PIGE technique follows. PIGE analysis is non-destructive and works by detection of γ-rays from nuclear reactions that are induced by a high energy proton beam (Coote 1992). To analyze fluorine concentrations, two nuclear reactions must be evaluated: $^{19}F(p, \alpha\gamma)^{16}O$ using a proton energy of 2.7 MeV on the

tandem accelerator of ETH Zurich and $^{19}F(p, p'\gamma)^{19}F$ with 3.4 MeV protons on the tandetron accelerator of FZ Dresden-Rossendorf. Both nuclear reactions give reliable results, but the gamma signals of $^{19}F(p, p'\gamma)^{19}F$ are easier to evaluate. The γ-rays of interest are proportional to the F concentration in a sample layer depth of approximately 50 μm. A focused proton beam is rastered across the target to detect the distribution of fluorine. The typical areas of investigation were 4 mm^2 for $^{19}F(p, p'\gamma)^{19}F$ and 4 to 10 mm^2 for $^{19}F(p, \alpha\gamma)^{16}O$. Detection limits values (3σ) of the measured or calculated γ-background were 3–4 μg/g F for $^{19}F(p, p'\gamma)^{19}F$ and 4–5 μg/g F for the $^{19}F(p, \alpha\gamma)^{16}O$ reaction. Depending on the observed content, measuring the surface concentrations of F for a given meteorite takes 10 to 20 min.

SAMPLES

The Antarctic meteorites that were studied are listed in Table 1a. The 3 H chondrites were chosen for their wide range of weathering degrees. The fusion crust of split 29 from ALH 83108 allowed for the investigation of 2 surfaces of an Antarctic meteorite that were exposed to the Antarctic environment differently. Two samples stemming from dust bands in the blue ice areas of the Antarctic Lewis Cliff region (Koeberl et al. 1988) were also studied. Because such dust bands are common features of all Antarctic blue ice regions, material of this kind is a possible contamination source for meteorites on the blue ice surface.

Table 1a. Samples investigated for this paper. Antarctic meteorites.

Meteorite	Split Parent	Class	Terrestrial age in 10^3 years[a]	Weathering index
ALHA77294	62/–	H5	10 ± 1	A
TIL 82409	5/0	H5	–[b]	B
LEW 86015	11/5	H6	–[b]	C
ALHA77003	107/7	C3O	110 ± 70	A
ALH 83108	29/0	C3O	–[b]	A

[a]Nishiizumi et al. (1989).
[b]No data available.

Table 1b. Samples investigated for this paper. Material of dust bands in blue ice areas in the Antarctic Lewis Cliff region.[a]

Sample	Average particle diameter	Sort of material	Presumed geological source
17–02	10 μm (max. 40)	tephra (volcanic ash)	Antarctic Volcano: The Pleiades
86–5	400–600 μm	scraped-up rock debris	Beacon Supergroup (Local sandstone)

[a]Sampled and described by Koeberl et al. [1988].

RESULTS AND DISCUSSION

Internal and Surface Concentration of F

Table 2 shows the average F contents for the contaminated surface layer, the inner bulk material, and, as a result of these values, the absolute enrichment of terrestrial fluorine found in the surface layer. The bulk concentrations of F found by PIGE (Table 2) fit well with published data of H and C3O chondrites (e.g., Dreibus et al. 1979; Langenauer and Krähenbühl 1993b). The error limits of the results obtained by PIGE are up to twice as large as with the previous method, leading to less precise values at low concentrations of F.

The concentrations on the meteoritic surface, given in Table 2, show a clear enrichment of fluorine due to terrestrial contamination. A comparison of the new results with data obtained by PIGE reveals that the surface concentrations for ALHA77294, LEW 86015, and TIL 82409, are approximately 5 times higher than with the previous method (Langenauer and Krähenbühl 1993a, b). This difference is reasonable and expected because of the different layer thicknesses; the analyzed layer with PIGE has a depth of about 50 μm instead of 500 μm for the earlier method, indicating that about the half of the terrestrial F is located in the first 50 μm of the surface. Thus, the concentration profiles of F enrichment decrease rather steeply in Antarctic meteorites (Noll et al. 1998). Accordingly, the depths beyond which no enrichment of terrestrial F could be detected in the meteorites studied here are rather shallow: less than 1.2 mm for ALHA77294, LEW 86015, and TIL 82409, under 1.0 mm for ALH 83108, and only 0.2 mm for ALHA77003.

A meteorite could possibly be contaminated from one preferable direction (e.g., the prevalent direction of wind). Some discussion of the problem has taken place previously (Krähenbühl et al. 1998). The final answer will be obtained when some heavy Antarctic meteorites that cannot be moved by the catabatic wind are measured on all sides of their surfaces. The split 29/0 of ALH 83108 has a fusion-crust that is divided by a right angle in 2 even areas, which are marked by means of footnotes as ALH 83108[a] and ALH 83108[b]. These 2 areas show a difference in their average F enrichment of more than 100%. This finding supports the observation that different sides of Antarctic meteorites can collect quite diverse amounts of contaminants depending, on their exposure. Therefore, conclusions drawn from the F enrichment of a single split may have restricted validity for the whole stone.

Distribution of F on the Surface

A sufficiently large area (of some mm^2) must be analyzed to obtain a realistic average value of the F-enrichment of an Antarctic meteorite. Analyzing terrestrial F distribution with a higher spatial resolution shows an irregular surface

Table 2. Average F content of the investigated meteorites in 10^{-6} g/g.

Meteorite	Surface content (50 μm layer)	Bulk content (volume)	F-enrichment of surface layer
Examined by nuclear reaction $^{19}F(p, \alpha\gamma)^{16}O$.			
ALHA77294	118 ± 6	10 ± 2.3	108 ± 6.4
TIL 82409	333 ± 14	12 ± 2	321 ± 14.1
LEW 86015	491 ± 19	14 ± 2	477 ± 19.1
ALHA77003	92 ± 5	21 ± 2.3	71 ± 5.5
ALH 83108[a]	232 ± 10	17 ± 2.2	215 ± 10
Examined by nuclear reaction $^{19}F(p, p'\gamma)^{19}F$.			
ALHA77294	98 ± 18	18 ± 3	80 ± 18.2
TIL 82409	316 ± 18	n.d.	n.d.
LEW 86015	n.d.	n.d.	n.d.
ALHA77003	90 ± 5	19 ± 2	71 ± 5.4
ALH 83108[a]	259 ± 16	–	245 ± 16.1
ALH 83108[b]	103 ± 7	14 ± 2	89 ± 7.3

[a]Refers to a differently exposed surface of Split 29 of ALH 83108. See text for a detailed explanation.

[b]Refers to a differently exposed surface of Split 29 of ALH 83108. See text for a detailed explanation.

distribution. We investigated the range of these irregularities for TIL 82409, ALH 83108, and ALHA77003 using the $^{19}F(p, p'\gamma)^{19}F$ reaction and a beam diameter of 0.1 mm. We found averages for the surface concentrations of 316 ± 18 μg/g, 103 ± 7 μg/g, and 90 ± 7 μg/g, respectively, with ranges of 46–883 μg/g, 7–436 μg/g, and 18–119 μg/g. Whether this irregularity of the F-enrichment should be interpreted as the result of particulate contaminants (aerosols or silicic dust) or of uneven weathering is not yet clear. X-rays were detected simultaneously with the usual γ-signals in these determinations, leading to a simultaneous PIGE-PIXE-measurement (PIXE: proton induced X-ray emission). The aim of the PIXE measurement was to observe whether concentrations of any heavier elements than F were correlated with the fluorine signal. No such correlation could be found, partly because PIXE detection limits were too low for several elements of interest (about 200 ppm for Cl and S).

Quantification of the F-enrichment and Exposure Duration on the Antarctic Ice

For F-enrichment quantification (Table 2), we used the surface enrichment minus the volume concentrations ($C_{surface} - C_{internal}$) in concentration units.

Since an enrichment of terrestrial fluorine on the surface of Antarctic meteorites only occurs when the stone is resting on the surface of the ice, we can evaluate the duration of this exposure by comparing the degree of fluorine enrichment (e.g., Langenauer and Krähenbühl 1993a, b). In this evaluation, a meteorite with a young terrestrial age is used as a reference standard assuming a constant flux of F leading to the observed contamination. The assessment is based on the values of F-enrichment obtained by $^{19}F(p, \alpha\gamma)^{16}O$. For ALHA77294, the reference meteorite sample, a surface exposure age of 3100 yr, which was evaluated by Langenauer and Krähenbühl (1993b), is accepted. The exposure durations for the meteorites described in this paper are given in Table 3. The exposure duration of TIL 82409 and LEW 86015 have a higher uncertainty because evaluating exposure times by comparison with the contamination level of another meteorite from a different blue ice field is not normally ideal.

Fluorine Content of Samples from Blue Ice Dust Bands

Clearly visible dust bands (or "dirt layers") are a common feature of Antarctic blue ice fields. Such layers in ice can be produced by: a) by volcanic ash, also called "tephra;" b) eroded material from subglacial bedrock; and c) continental soil dust. The most significant dirt layers found in the Antarctic blue ice proved to be volcanic tephra layers (Kyle et al. 1982). Their thickness varies from a few cm to 15 cm, and, where they are cropping out, the ice forms narrow shallow troughs due to the increased albedo of the layer. In several meteorite-rich blue ice fields (e.g., Yamato Mountains, Allan Hills, Lewis Cliff), an array of prominent dirt layers was identified as tephra (Koeberl 1989; Nishio 1985, 1984). The alkaline tephra from the Allan Hills and Lewis Cliff ice fields must come from the volcanic regions of the Western Ross region or Mary Byrd Land. The now inactive "Pleiades" volcanoes are the most likely source for the tephra layer 17–02 on Lewis Cliff (Koeberl et al. 1988).

Tephra layers in blue ice fields steadily release ash particles during ice ablation, which are blown across the blue ice field by katabatic winds. This way, meteorites downwind may be in contact with a small but constant flux of fine-grained tephra, which is often rich in fluorine (Coote et al. 1997). Therefore, tephra might be a source for the contamination of Antarctic meteorites with terrestrial fluorine. Thus, we measured the fluorine concentration of a tephra layer (17–02) from the Lewis Cliff ice field (Koeberl et al. 1988). From the same location, dust band material (86–5) consisting of glacially ground local sandstone was also analyzed. Large fragments, 400 to 600 μm, of this material could be examined directly by a beam spot of 100 μm in diameter. Tephra sample 17–02 (particle diameter of 10–40 μm) was analyzed in the "thick target" configuration of an agglomeration.

The analyzed fluorine content of tephra 17–02, with 1200 μg/g, is approximately 100 times larger than the F concentration in H chondrites (Table 4). The real fluorine content of 17–02 must have been even higher because the sample was isolated in Antarctica by melting the ice. Thus, the tephra lost its water-soluble fraction of F. For a tephra sample of similar particle size (40 μm), Óskarsson (1980) found a water leachable F-portion of 1500 μg/g. Consequently, tephra similar to 17–02 has a high potential for

Table 3. Maximum exposure duration on the Antarctic ice compared with terrestrial age and weathering index.

Meteorite	Exposure time in 10^3 yr[a]	Terrestrial age in 10^3 yr[b]	Weathering index
ALHA77294	3.1[c]	10 ± 1	A
TIL 82409	9.2	–[d]	B
LEW 86015	13.7	–[d]	C
ALHA77003	2.0	110 ± 70	A
ALH 83108	6.2	–[d]	A

[a]Evaluated relative to ALHA77294.
[b]Nishiizumi et al. 1989.
[c]Value equal to the value evaluated by Langenauer and Krähenbühl (1993).
[d]No data available.

contaminating Antarctic meteorites with fluorine. Also, material similar to that of 86–5, which is composed of local sandstone, could contaminate meteorites with fluorine, because its average content of F (314 μg/g) is larger than the usual meteoritic concentrations.

OTHER SOURCES FOR CONTAMINATING ANTARCTIC METEORITES WITH FLUORINE

Sea Salt Aerosols

Langenauer and Krähenbühl (1993b) found that, on Antarctic meteorites, the weight ratio of enrichment between chlorine and fluorine is about 40 and is fairly similar for all investigated locations. In addition, relative to the enrichment of iodine, the enrichment of Cl and F was found to decrease with increasing distance from the open sea. Therefore, terrestrial F and Cl on Antarctic meteorites were concluded to have come from the same main source (i.e., sea salt aerosols). However, De Angelis and Legrand (1994) demonstrated that primary sea spray emissions represent only a negligible contribution to the total F influx in Greenland. An analogous conclusion is also valid for Antarctica.

Gaseous Volcanic Exhalations

Besides tephra, gaseous emission of HF from the active Antarctic volcano Mt. Erebus on Ross Island, which is steadily degassing large amounts of volcanic fumes with an unusual high content of HF (Kyle et al. 1990; Zreda-Gostynska et al. 1993; Table 5), could be a potential F contributor. The Cl/F weight ratio of volcanic gasses usually lies between 2–75 with an average ratio of 15. This is of the same order of magnitude as the ratio of 40 found on Antarctic meteorites. Because of this similar Cl/F ratio, one could speculate that the terrestrial enrichment of chlorine on Antarctic meteorites could come from volcanic exhalation as well, corresponding to a suggestion of Buchwald and Clarke (1989). But, this proposal is not convincing because the overwhelming portion of atmospheric chlorine in Antarctica comes from sea spray (Legrand and Delmas 1988). Furthermore, the analyzed Cl/F weight ratio of 2.3 in the gaseous exhalations of Mt. Erebus is significantly smaller than the Antarctic meteorites ratio of 40. Consequently, the Cl/F enrichment ratio of 40 measured on Antarctic meteorites is better explained by the mixing of volcanic sources (Cl and F) with marine sources (almost entirely Cl). The observation of Langenauer and Krähenbühl (1993b) that the enrichment of both Cl and F decreases with increasing distance to the open sea is not sufficient proof for a common marine source. An alternative explanation is given by the simple fact that the distances between the investigated blue ice fields, the open sea, and also Mt. Erebus are quite similar. Thus, making identical measurements of Yamato meteorites would be interesting. Since the Yamato ice field is as close to the sea as the Allan Hills region, but more distant from the next potential volcanoes, a different Cl/F ratio would be expected.

Table 4. Fluorine content (in 10^{-6}g/g) of samples from dust-bands of the Antarctic Lewis cliff blue ice area, examined by nuclear reaction $^{19}F(p, p'\gamma)^{19}F$.

Sample number	Material	Average F content	F content measured on various single particles of the sample
17–02	Tephra	1200 ± 68	Particle size is to small for single detection
86–5	Scraped-up rock debris	314 ± 23	389 ± 27, 360 ± 25, 350 ± 24, 327 ± 23, 281 ± 20, 174 ± 12

Table 5. Emissions of SO_2, HCl, and HF of Mount Erebus, Antarctica, per year in Gg (10^9g).[a]

	Year	SO^2	HCI	HF
According to Rose et al. (1985)	1983	84	1.8–49[b]	.25–25[b]
According to Radke (1982)	1980	40	.86–23[b]	.12–12[b]
According to Kyle et al. (1990)	1983	84	~440[c]	~180[c]
According to Zreda-Gostynska et al. (1993)	1991	26	~13.3[d]	~6[d]

[a]The activity and the composition of the lava lake of Mount Erebus is variable. Therefore, these values are meant to be the annual average for the year of measurement. The data of Rose et al. (1985) and Kyle et al. (1990) belong to 1983; this year, before the explosive activities of September 1984, is suggested to represent the rather steady exhalation period between 1976–1984.
[b]Estimations inferred by help of the measured emission of SO_2 and according to the usually range of ratios between SO_2 and HCl or HF given by Symonds et al. (1988). For Mt. Erebus, as a volcano with alkaline magma, the estimates at the upper limit are more likely.
[c]Estimation from the measured emission of SO_2 by Rose et al. (1985) and ratios between SO_2 and HCl or HF measured by Kyle (1986) in the plume of Mt. Erebus.
[d]Results of direct measurements of Cl and F in the volcanic plume of Mt. Erebus.

Continental Soil Dust

Continental soil dust could also be a F contributor to Antarctic meteorites, but its effect is difficult to estimate. Fluorine contamination from continental soil dust could have been more significant earlier because the ablated ice of blue ice fields is quite old (Koeberl 1989), and the input of continental dust was much higher during ice ages (De Angelis et al. 1992; Petit et al. 1981). Thus, even if the current input of continental dust is low, the higher dust content of old blue ice, liberated by ablation, may also contaminate meteorites. The concentrations of all contaminants discussed are controlled by atmospheric transportation.

All conceivable sources of F on meteorites are shown schematically in Fig 1. The idea that volcanic ash could contaminate Antarctic meteorites was already suggested by Koeberl and Cassidy (1991), who proposed tephra as a likely source for Se enrichments.

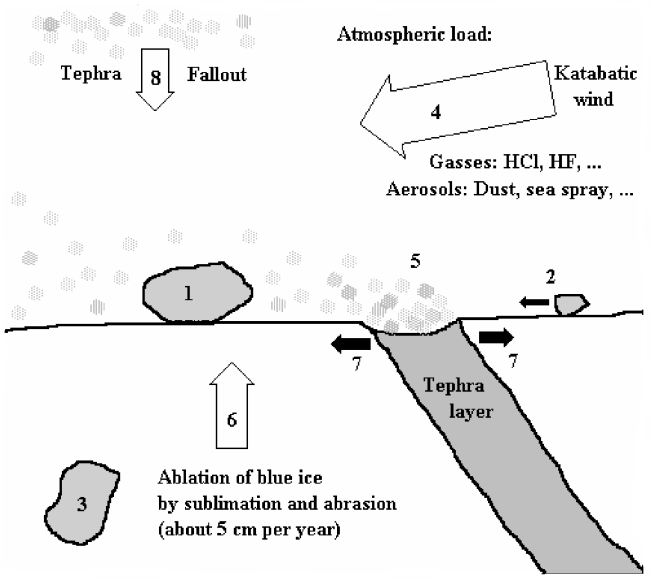

Fig. 1. Pathways for terrestrial contamination of Antarctic meteorites on blue ice ablation zones depicted schematically by: a heavy meteorite immovable by wind (1); a small meteorite driven by wind (2); a meteorite enclosed by and flowing with the ice, not encountering any material flow (3); a strong katabatic wind that transports the atmospheric load and impurities of the sublimed ice to the meteorites and away from the ablation zone (4); and a trough of an emerging tephra layer produced by the layer's higher albedo (5), which may trap smaller wind driven meteorites for some time. From there, tephra is steadily released by sublimation of its enveloping ice. Owing to ablation by sublimation, the impurities of the old blue ice are constantly released and may also influence meteorites. Strong enrichment of such material on the ice surface is prevented by the abrasive ablation (6). Tephra layers might alter their position in one or other direction and can so meet heavier meteorites (7). Direct tephra fallout would only influence meteorites already emerged because loose volcanic ash would be removed by wind from the blue ice field very swiftly (8).

POSSIBLE USE OF EXTERNAL PIGE IN FUTURE CONTAMINATION STUDIES

The degree of fluorine enrichment in Antarctic meteorites provides a quantitative measure for terrestrial contamination and could supplement the qualitative ABC-weathering index. Normally, all ion beam analysis techniques, such as PIGE or PIXE, are performed in a vacuum. However, for investigations of large or delicate objects, e.g., precious historic paintings, an external ion beam analysis was developed. Here, the beam is led through a very thin foil out of the vacuum system into a chamber of normal pressure (Doyle et al. 1991; Mandò 1994). Such a procedure could be used to obtain F-enrichment indices of pristine Antarctic meteorites. To examine the averaged F-enrichment, measurements of a meteorite's crust would be performed with a beam spot of a few mm^2. The F-enrichment could be expressed by the absolute F-excess in the analyzed 50 μm thick surface layer. The bulk concentration of F is fairly uniform for identical classes of meteorites and must not be analyzed for every stone. For measurement, the nuclear reaction of choice is $^{19}F(p, p'\gamma)^{19}F$ because $^{19}F(p, \alpha\gamma)^{16}O$ requires laborious background correction in the lower ppm-range (Noll 1998; Grambole et al. 2000).

CONCLUSIONS

- The PIGE technique allows the determination of terrestrial enrichment of F on Antarctic meteorites and on their bulk concentration of F. This simple, rapid, and non-destructive analysis would enable us to obtain an "F-enrichment index" for a large number of Antarctic meteorites.
- The measured surfaces from Antarctic meteorites show significant differences in their enrichment of fluorine, which are not sufficiently reflected by the qualitative ABC-weathering index.
- Terrestrial fluorine on Antarctic meteorites remains close on the surface. The deepest enrichment studied in this work was less than 1.2 mm deep. A comparison with previous analyses show that approximately 50% of the terrestrial F, detected in a 0.5 mm thick top layer, occurs in the uppermost 50 μm of the surface.
- A tephra sample (volcanic ash) from the Antarctic Lewis Cliff region showed soluble-free fluorine contents of 1200 μg/g. Thus, tephra particles from dust bands have a high potential to be an important source for contaminating Antarctic meteorites with F. Besides tephra, volcanic gasses from Mount Rebus (Ross Island), with their large concentrations of HF, are proposed to be a substantial fluorine contributor for the Antarctic meteorite case.

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