

## A diverse ecosystem response to volcanic aerosols

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### Abstract

Unexpectedly high aluminium concentrations beside fluoride and essential elements are released from metal salts adsorbed to volcanic ash. Through simulation of the mixing of pristine volcanic ash leachate with fresh water and seawater using PHREEQC, we found an increased potential toxicity in fresh waters through the combination of high aluminium and fluoride concentrations. Owing to the mixing of acid ash leachate with fresh water, aluminofluoride complexes ( $\text{AlF}_x^{+3-x}$ ) persist in aqueous systems with low turnover rates, and could be toxic to both plants and animals. In contrast, due to the well-buffered and relatively high pH in seawater, the speciation of the ash leachate/seawater mixture shows that complexes of fluoride and aluminium (i.e.  $\text{AlF}_x^{+3-x}$ ) will not dominate in a well-mixed marine system; instead,  $\text{Al}(\text{OH})_x^{+3-x}$  species will occur at greatest concentration. Consequently, compared with fresh water environments, the mixing of ash leachate with seawater indicates reduced toxic effects due to decreased formation of  $\text{AlF}_x^{+3-x}$  complexes and the low solubility of Al-hydroxides. In addition, the deposition of volcanic aerosols may enhance biological activity in the marine environment by providing micronutrients as some oceanic phytoplankton species tolerates extreme concentrations of fluoride (F).

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### 1. Introduction

Volcanic gases are removed from the atmosphere by chemical reactions, wet and dry deposition, and by adsorption onto volcanic ash (tephra). Volatiles scavenged by tephra reach the ground more rapidly than they would by dry deposition, because of the faster deposition velocities of the tephra (Witham et al., 2005). Pristine and “dry”, newly erupted tephra is highly reactive and it is thus of great importance that the tephra becomes sampled in volcanic areas with a cold and/or a dry

climate to perform successful studies. When it comes in contact with surface waters, acid and metal salts adsorbed onto the tephra surfaces dissolve within an hour, releasing acids and metals to the environment (Frogner et al., 2001). Thus, volcanic eruptions cause acidification and contamination of soils and surface water, which has a serious impact on vegetation, animals and people.

During the 1783–84 eruption of Laki, Iceland, 50% of the livestock in Iceland perished, many probably as a result of fluorine poisoning (Thorarinsson, 1969; Grattan and Charman, 1994; Steingrimssson and Kunz, 1998). Several recent eruptions have had high quantities of fluorine adsorbed on the tephra, including: Hekla, Iceland in 1970, 1991, and 2000 (Thorarinsson and

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Sigvaldason, 1972; Gudmundsson et al., 1992; Frogner et al., 2001), Lonquimay, Chile in 1989–1990 (Araya et al., 1990, 1993) and Ruapehu, New Zealand in, 1995–1996 (Cronin et al., 2003; Shanks, 1997). Many animals were affected by the tephra and even perished, due primarily to fluorosis. For example, several thousand sheep were lost following the 1995 eruption of Ruapehu, New Zealand (Shanks, 1997). Despite these negative effects, it has also been shown that volcanic ash has a fertilizing effect and may enhance the sequestration of atmospheric carbon dioxide by the oceans (Frogner et al., 2001).

The F content of volcanic ash is determined by magma type, which influences the composition of magmatic gases that will condense and adsorb to tephra. In general, S, Cl and F concentrations are similar in andesites and rhyolites, but the S concentrations in basalts are about 10 times higher than the Cl and F concentrations (Giggenbach, 1996; Oppenheimer, 2003). The F concentrations of Icelandic tholeiites and alkaline basalts are similar to the concentrations in the same rock types from other areas of the world (Sigvaldason and Oskarsson, 1986). There is a conspicuous co-variation between the F concentration and K concentration in all volcanic rocks in Iceland; the highest F values are in silica and potassium rich rocks. The F concentration ranges from less than 15 ppm in picrite to 1981 ppm in rhyolite (Sigvaldason and Oskarsson, 1986; Stecher, 1998). Most of these measurements were done on lava flows that had been degassed during their eruption and solidification. Thordarson et al. (1996) and Thordarson and Self (1996) measured the degree of degassing of the 1783–84 quartz-normative tholeiitic Laki, Iceland eruption, and the quartz-normative tholeiitic Roza eruption ( $\approx 14.7$ ), Columbia River Basalt (USA). The average F concentration of the crystalline Laki lava was 315 ppm, but the F concentration in glass inclusions in phenocrysts was 665 ppm. Thus, about 52% of the original F in the magma was degassed during the eruption and lava solidification, taking into account degassing of the tephra. More than half of that degassing took place at the vents. The average F concentration of the crystalline Roza lava was 830 ppm, but the F concentration in glass inclusions in phenocrysts was 1310 ppm. About 37% of the original F in the magma was degassed during the eruption and lava solidification.

The last four eruptions of Hekla (1970, 1980, 1991 and 2000) have produced lavas of constant composition; Fe-rich basaltic andesites (often called icelandites) with  $\text{SiO}_2$  close to 55% (e.g. Baldridge et al., 1973; Gudmundsson et al., 1992; Frogner et al., 2001). The F concentration of the crystalline lava flows of the Hekla

1970 eruption ranged from 1029 to 1267 ppm (Sigvaldason and Oskarsson, 1986).

The objective of this study was to study the potential toxicity of pristine volcanic ash leachate as it mixes with fresh water and seawater, in terms of aluminium and fluoride species. For this purpose the leachate from the Hekla 2000 eruption in Iceland (Frogner et al., 2001) was used. Mixing simulations were performed by the PHREEQC computer code (Parkhurst and Appelo, 1999).

## 2. Fluorine and aluminium in the environment

Fluorine is an essential element for human and animal growth. Humans are primarily exposed to F via drinking water. Fluorine deficiency is linked to the incidence of dental caries, such that fluoride is added to toothpastes and mouthwashes in order to mitigate dental health problems. However, excessive doses of F are linked to dental fluorosis and, in extreme cases, skeletal fluorosis and perhaps even cancer (Edmunds and Smedley, 2005). In the natural environment, F occurs as the fluoride ( $\text{F}^-$ ). Because of its anionic properties, it can substitute for hydroxyl anions ( $\text{OH}^-$ ) in phyllosilicates and amphiboles. Therefore, in addition to fluorite ( $\text{CaF}_2$ ) and fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$ ], a major geological source of F in aqueous systems is biotite and amphiboles in granites.

The upper limit on fluoride concentrations in natural waters is primarily controlled by fluorite solubility (Edmunds and Smedley, 2005). However,  $\text{F}^-$  is generally not very mobile in terrestrial environments, as it readily adsorbs to soil minerals. However, complexation with dissolved aluminium and ferric iron increases its mobility (Wenzel and Blum, 1992) and thus its bioavailability.

Fluorine is not an essential element for plant growth, but plants may accumulate F when F is readily available, such as at high soil acidity and at high F loadings (from, e.g. fertilizers, HF deposition). In addition to harming the plants, livestock ingesting these plants may be afflicted by chronic fluorosis (Loganathan et al., 2001; Mackowiak et al., 2003). An example of this is the Laki eruption on Iceland in 1783, which caused damage to crops and trees throughout western Europe and Britain and resulted in the death of a huge quantity of grazing animals in Iceland (Thorarinnsson, 1969; Grattan and Charman, 1994; Grattan and Gilbertson, 1994; Steingrímsson and Kunz, 1998; Grattan and Pyatt, 1999; Thordarson and Self, 2003). Such catastrophic events indicate that acidification and an increase in fluoride are significant contributors to ecosystem decline and death in regions that are exposed to volcanic ash aerosols.

Fluorine is not the only element in volcanic ash that can produce significant environmental impacts. Aluminium is also readily released in experiments done on pristine tephra (Frogner et al., 2001) and builds strong inorganic complexes with fluoride. Studies have shown (e.g. Gensemer and Playle, 1999; Palmer and Driscoll, 2002) that acid deposition and the resulting aluminium toxicity may be a major mechanism behind the decline of terrestrial and aquatic ecosystems. Aluminium is associated with bone diseases (e.g. osteomalacia) and neurological diseases (Klein, 1998). Compared with fluoride, most Al compounds are poorly absorbed through the lungs, skin and gastrointestinal tract of animals. There is, however, evidence of increased uptake of Al in the presence of fluorine by the uncharged inorganic Al-complex  $\text{AlF}_3$  in animals (Klein, 1995, 1998; Varner et al., 1998; Kausz et al., 1999; van der Voet et al., 1999; Strunicka and Patocka, 1999). In acid solutions ( $\text{pH} < 5.5$ ), fluoride becomes phyto-available through complexation as soluble aluminium-fluoride compounds (Stevens et al., 1997). It is clear that the influence of Al on bone formation leading to osteomalacia is affected by the formation of complexes with fluorine (Gomez-Alonso et al., 1999).

The above discussion explains the need to investigate the combined Al–F toxicity following volcanic eruptions, which is directly related to the predominance of specific Al–F species in solution. This paper illuminates the importance of the combined Al–F toxicity in fresh water systems as a pathway for symptoms of illness similar to the fluorosis disease following volcanic eruptions. On the other hand, volcanic ash contains phosphate and trace elements, and we propose that volcanic ash may have an opposite and fertilizing effect on some plankton species important for the sequestration of  $\text{CO}_2$  in marine ecosystems.

### 3. Method

This study is based on volcanic ash that was collected in situ during the Hekla 2000 eruption in Iceland. The sub-zero air temperature and low humidity at the time of the eruption (Lacasse et al., 2004) helped in preserving adsorbed soluble salts on the ash grains, which would have otherwise been completely or partly leached from the ash in a warmer and more humid climate. That is most likely the reason why our fluoride salts were better preserved than in ash leachate studies performed on volcanic ash from other volcanic regions with basically the same type of magma composition (e.g. Witham et al., 2005). The ash of this study is thus unique. Furthermore, tephra, partly derived from hydrothermal systems, such

as the one from Ruapehu, New Zealand (Cronin et al., 2003) may continue to leach F for some time after deposition presumably as it is retained in less soluble compounds than the one formed on “dry” magmatic tephra such as the one of this study.

After collection, the ash was handled extremely carefully in that it was kept deeply frozen and then freeze-dried to preserve the highly soluble salts adsorbed to the ash grains. Finally, controlled plug-flow-through leaching experiments were performed for the first time on pristine volcanic ash (see Frogner et al., 2001).

In order to investigate the impact of ash deposition on aluminium and fluoride speciation in fresh water and seawater systems, the geochemical model PHREEQC2 (Parkhurst and Appelo, 1999) was used. Since accurate and consistent thermodynamic constants for the Al–F system are required, the reviewed and internally consistent stability constants from Nordstrom et al. (1990) were used, and the more extensive MINTEQA2 database (Allison et al., 1991) was coupled to the simulations for the speciation of additional elements. For the simulations, Hekla ash leachate was mixed with increasingly greater proportions of fresh water and seawater (see Table 1 for compositions). The ash leachate composition was obtained at the initial release of major and trace elements in deionised water in flow-through experiments of pristine volcanic ash described in detail in the experimental work by Frogner et al. (2001). Fresh water was chosen with the same composition as the River Laxá i Kjos (data from Stefansson and Gislason, 2001), a river draining basaltic rocks in the southwestern Iceland. The alkalinity of River Laxá is mostly represented by the DIC in Table 1 (416  $\mu\text{mol}/\text{kg}$ ). It is similar to the average DIC of African and South American rivers, but only half of the world average river DIC concentration, dominated by rivers draining limestones (Meybeck, 1979) Thus the Laxá river is a good representative of rivers draining crystalline rocks but not rivers draining sedimentary rocks. The seawater composition was taken from Nordstrom et al. (1979). The mixed solutions were equilibrated with atmospheric oxygen and carbon dioxide ( $\text{PO}_2 = 0.21 \text{ atm}$ ,  $\text{PCO}_2 = 10^{-3.5} \text{ atm}$ ), since it is assumed that near-surface waters are well-mixed by wave action. Supersaturated Al and Fe hydroxides and calcite were allowed to precipitate ( $\log K_{\text{sp}}$  values of 10.38, 4.891, and  $-8.475$  were used for amorphous Al  $(\text{OH})_3$ , ferrihydrite and calcite, respectively; from Allison et al. (1991). Furthermore, fluorite ( $\text{CaF}_2$ ,  $\log K_{\text{sp}} = -10.96$ ) was allowed to precipitate from solution when supersaturated, since studies have shown that fluoride concentrations in fresh water systems are controlled by fluorite solubility. It should

Table 1  
Composition of Hekla ash leachate, river water and seawater used in the model

	Units	Hekla ash leachate	River water <i>Laxá i Kjos</i>	Seawater
Temp	°C	5	5	5
pH	–	3.4	7.43	8.22
pe	–	4	4	8.451
Al	μM	2700	0.25	0.0000385 <sup>a</sup>
Ca	mM	1.17	0.13	10.29
Fe	mM	1.92	0.001	0.0000036
K	mM	0.64	0.0068	10.21
Mg	mM	1.12	0.094	53.13
Mn(2)	μM	92	n.a.	0.0036
Na	mM	4.87	0.306	468.36
Si	mM	2.60	0.204	0.045
Sr	μM	1.4	n.a.	n.a.
Cl <sup>-</sup>	mM	4.35	0.319	545.88
F <sup>-</sup>	μM	23410	1.9	63.2 <sup>b</sup>
NO <sub>3</sub> <sup>-</sup>	μM	2.7	3.46	4.7
NH <sub>4</sub> <sup>+</sup>	μM	n.a.	1.38	1.67
PO <sub>4</sub> <sup>3-</sup>	μM	89	0.08	n.a.
SO <sub>4</sub> <sup>2-</sup>	μM	130	22	28232
TIC <sup>c</sup>	μM	n.d.	416	2322

Data from leaching experiments in deionised water described by Frogner et al., 2001 and river water data from Stefansson and Gislason (2001) used in geochemical modelling. Seawater data from Nordstrom et al. (1979). n.a. = not analysed; n.d. = not detected.

<sup>a</sup> Measures (1995).

<sup>b</sup> Riley and Skirrow (1965).

<sup>c</sup> Total inorganic carbon.

be noted that the lower range of simulated dilution ratios (up to 1; dilution ratio = log river water volume/leachate volume) have a pH that is slightly lower than the original

ash leachate (pH 3.4, Table 1), since PHREEQC has adjusted the solution pH for charge balance after fluorite precipitation and gas equilibration.

For these simulations, Al complexation with natural organic matter (e.g. humic substances) was not considered because of the lack of consistent thermodynamic data for these reactions, and because of the large number of assumptions that would be required. Furthermore, the fluoride concentration in the ash leachate should greatly exceed the concentration of organic ligands in most fresh water and marine systems (i.e. <1 mM; Gislason and Oelkers, 2003), such that fluoride would be the dominating ligand at low dilution ratios. Sensitivity analyses, using EDTA as a model organic ligand, suggest that EDTA concentrations as high as 1 mM would not noticeably affect the Al–F speciation at low dilution ratios. In order to determine if the formation of polymeric Al<sub>13</sub> species was significant for these simulations, the modelling was also performed using the Lawrence Livermore National Laboratory database provided with PHREEQC2. The results of these simulations (not shown) indicate that monomeric Al compounds dominate in the modelled solutions.

#### 4. Results

Volcanic ash from the 2000 Hekla eruption produces an acidic leachate (pH 3.4) with high fluoride and aluminium concentration (23 and 2.7 mM, respectively) when exposed to deionized water (Table 1).

The geochemical modelling of the mixing of ash leachate with river water from Iceland indicates that

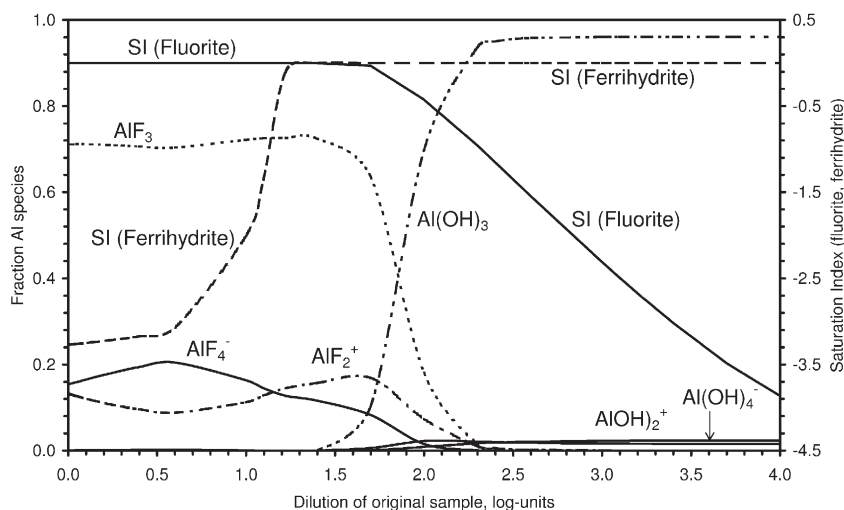


Fig. 1. Al speciation and saturation indices (SI) of fluorite and ferrihydrite, as a function of ash leachate dilution with river water. SI=0 indicates saturation with respect to a specific mineral, SI>0 indicates supersaturation, and SI<0 indicates undersaturation.

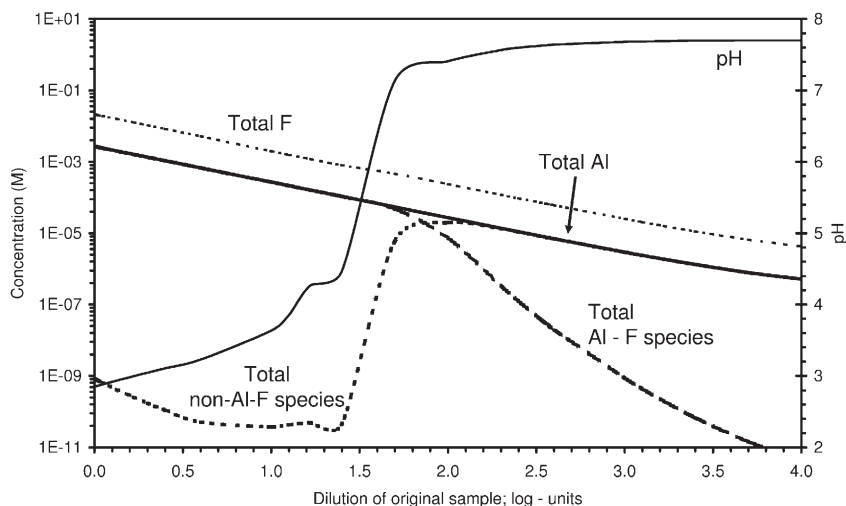


Fig. 2. Al and F concentration and pH in solution as a function of dilution. Speciation of Al is shown in Fig. 1.

$\text{AlF}_x^{+3-x}$  complexes dominate in solution at high concentrations of F (Figs. 1 and 2) and low pH. At low dilution ratios (<1.5) it is found that fluorite precipitates from solution so that the F concentration will become limited by fluorite solubility. However, this is not apparent in Fig. 2 since the degree of fluorite precipitation is low compared to the total F concentrations. At greater levels of dilution, F concentration has decreased below fluorite solubility. As pH increases and F concentration decreases with dilution (dilution ratio > 2.5),  $\text{Al}(\text{OH})_x^{+3-x}$  species exceed fluoride species in concentration. In addition, ferrihydrite precipitates (saturation index (SI)=0 at dilution ratio > 1.4), but this has very little effect on solution pH and Al speciation. At a dilution

ratio of ca. 3.5 (i.e. diluted 3160 times; Fig. 2), the geochemical modelling shows that the total Al concentration has decreased to less than 1  $\mu\text{M}$ . The surface water contamination therefore decreases with time as the ash leachate is diluted, resulting in a higher pH, lower Al and F concentrations, and thereby lower levels of Al-complexed fluoride (Fig. 2).

The geochemical modelling of the mixing of ash leachate with seawater yields results that are qualitatively similar to the fresh water mixing solutions. The  $\text{AlF}_x^{+3-x}$  complexes dominate in solution at high concentrations of F and low pH (Figs. 3 and 5). As pH increases and F concentration decreases with dilution (dilution ratio > 1),  $\text{Al}(\text{OH})_x^{+3-x}$  species exceed fluoride

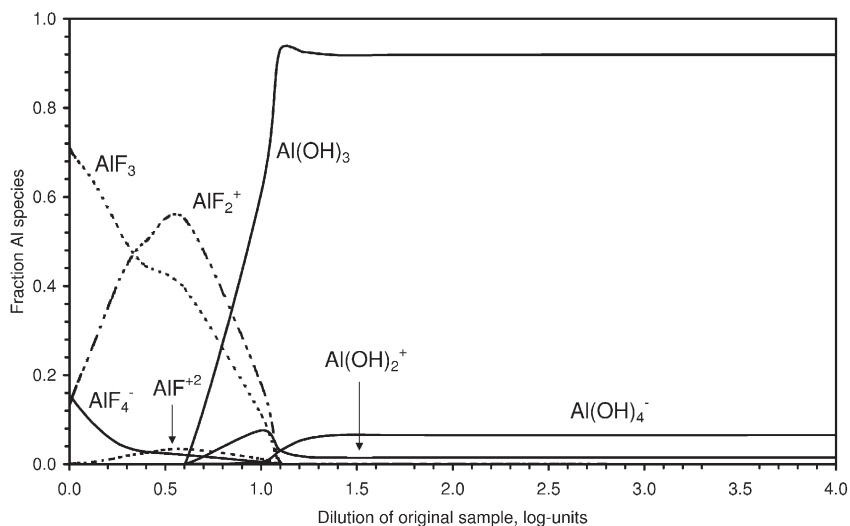


Fig. 3. Al speciation as a function of ash leachate dilution with seawater.

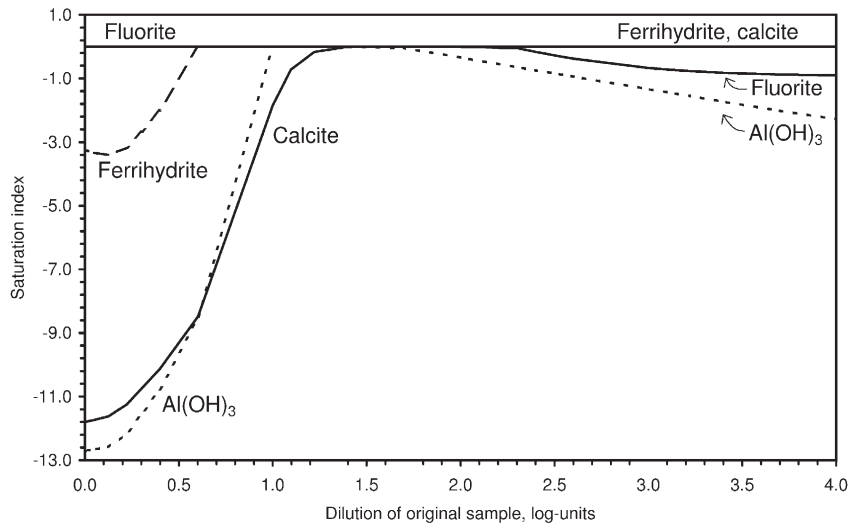


Fig. 4. Saturation indices (SI) for precipitating solid phases, as a function of ash leachate dilution with seawater.

species in concentration. The greatest difference between these two scenarios is the more rapid decrease in  $\text{AlF}_x^{+3-x}$  complex concentration with dilution in seawater compared to fresh water. Amorphous  $\text{Al}(\text{OH})_3$  briefly reaches saturation and precipitates as the pH increases (Fig. 4). In contrast with leachate mixing with fresh water, calcite reaches saturation after a dilution ratio of ca. 1.4 with seawater (Fig. 4). At greater levels of dilution, calcite solubility controls the Ca concentration in these simulations. Calcite precipitation will somewhat depress the pH of the aqueous system as protons are dissociated from bicarbonate.

## 5. Discussion

### 5.1. Implications for freshwater systems

The geochemical modelling of ash leachate mixed with the fresh water in this study shows that  $\text{AlF}_x^{+3-x}$  complexes dominate Al speciation in solution at low levels of dilution (Figs. 1 and 2). Thus, all terrestrial areas reached by ash falls will be contaminated to some extent, as potentially toxic levels of aluminofluoride complexes,  $\text{AlF}_x^{+3-x}$ , will persist in poorly mixed, weakly buffered aqueous systems. Although aluminium

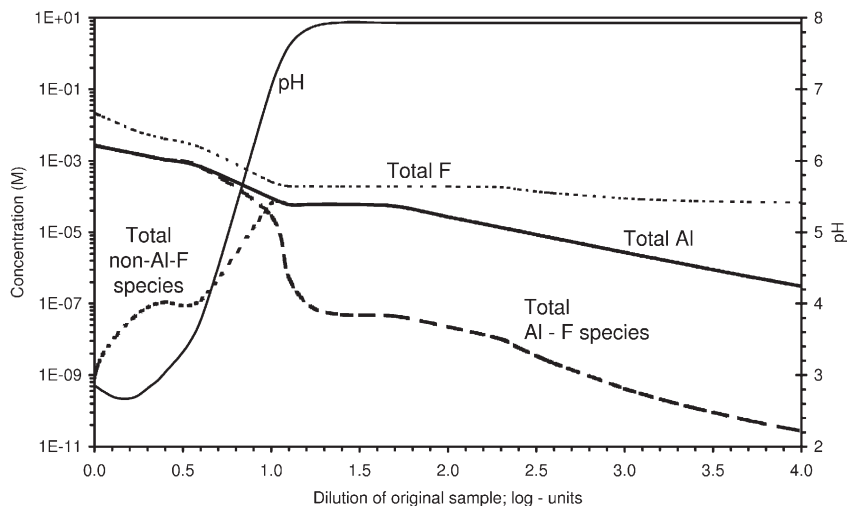


Fig. 5. Al and F concentration and pH in solution as a function of dilution with seawater. Speciation of Al is shown in Fig. 3.

would be expected to bind strongly with multidentate ligands such as humic acids in these systems (Tipping et al., 2002), the initial fluoride concentrations in this study (i.e. 23.4 mM) are much higher than the expected concentrations of such ligands. It is clear, however, that as the dilution ratio in the simulations increases, and the total F concentration decreases as the result of dilution, then the significance of natural organic matter as a complexing agent increases. However, at these high dilution ratios, fluoride is no longer an important ligand.

In fresh water systems that are impacted by the deposition of Icelandic ash, Al–F complexation may increase Al and F solubility which would otherwise be limited by the precipitation of Al hydroxides and adsorption to organic and mineral surfaces. The predominance of an uncharged  $\text{AlF}_3^0$  species (see Fig. 1) suggests a greatly enhanced mobility compared with low F conditions that may otherwise prevail. The interplay between acids, F, and Al in the ash leachate may yield enhanced fluoride toxicity and an increased uptake of both fluoride and aluminium by plants and grazing animals. It should be noted, however, that these results cannot be directly extrapolated to soil environments where water–mineral interactions can greatly contribute to acid neutralisation and the binding of Al and F to mineral and organic matter surfaces. For soils, it is not possible to consider the behaviour of Al–F complexes without also considering soil surfaces.

### 5.2. Implications for marine environments

The geochemical modelling of the mixing of ash leachate with seawater shows that  $\text{AlF}_x^{3-x}$  complexes dominate in solution at high concentrations of F and low pH (Figs. 3 and 5). As pH increases and F concentration decreases with dilution (logarithm of the dilution ratio > 1.0),  $\text{Al(OH)}_x^{3-x}$  species exceed  $\text{AlF}_x^{3-x}$  complexes. Because of the higher pH buffering capacity of seawater, hydroxo-aluminium complexes are more important at low levels of dilution than in fresh water systems.

Despite the potential negative impacts of volcanic eruptions, as has been discussed up to this point, ash deposition in marine environments can have positive effects as well. When volcanic ash comes in contact with seawater, both macronutrients (e.g.  $\text{PO}_4$ ) and trace metals (e.g. Fe, Mn and Si; see Table 1) are released and become available for biological production (Frogner et al., 2001). In parts of the equatorial and in the southern Pacific Ocean, iron is thought to be rate limiting for the growth of biota. Addition of iron in nanomolar concentrations is sometimes enough to trigger phytoplank-

ton blooms (Martin et al., 1994; Boyd et al., 2000). Iron input to the ocean by volcanic ash may be important to support algal biomass (Frogner et al., 2001). The silica release, an essential nutrient for the growth of diatoms, would also enhance volcanic ash fertilization of the oceans. Iron seeding experiments in the polar southern ocean showed that it was mostly diatom growth that was affected (Boyd et al., 2000). This observation is of special interest when considering the mixing of ash leachate with sea water because some diatom species when exposed to fluoride seem to be tolerant to the increased fluoride concentrations that would be the result of ash falls (Oliveira et al., 1978; Antia and Klut, 1981).

The 2000 Hekla eruption produced an acidic leachate with high fluoride and aluminium concentrations along with essential nutrients (Table 1). Surface fresh water fluoride concentrations tend to range from 0.0005 to 0.026 mM, whereas typical marine concentrations range from 0.063 to 0.079 mM (WHO, 2002). Higher concentrations are found in areas of geothermal or volcanic activity. Behaviour experiments on adult Pacific salmon in soft-water rivers indicate that an increase in the fluoride concentrations to 0.026 mM can adversely affect migration of salmon (Wilkinson et al., 1990). When 12 phytoplankton species were exposed to fluoride in 2.6–10.5 mM concentrations (Oliveira et al., 1978) no effects on growth were observed on 9 of 12 species tested. In contrast, marine dinoflagellates like *Amphidinium carteri* were inhibited up to 25% at 7.9 mM and were unable to grow in nutrient enriched seawater containing 10.5 mM fluoride (Antia and Klut, 1981). Different plankton species may react differently to an ash fall where some autotrophic species, e.g. diatoms, will benefit from released nutrients and herbivorous species, e.g. dinoflagellates, may be growth-inhibited by exposure to fluoride.

Aluminium usually enters natural waters from the weathering of aluminium-containing rocks and minerals, which has declined as a source in response to decreased acid deposition in the past 30 years (Palmer and Driscoll, 2002). This study shows that volcanic ash aerosols can be an additional important source of Al (Table 1) in addition to the release of Al from minerals in soils caused by the acid deposition during volcanic eruptions. In fresh waters acidified by acid rain, Al toxicity has led to fish-kills (Flaten et al., 1996). Studies have shown that Al concentrations as low as 2  $\mu\text{M}$  may have adverse effects on salmon and trout populations (Wilkinson et al., 1990; Gensemer and Playle, 1999). Al toxicity is usually reported as related to the concentrations of  $\text{Al}^{3+}$  at pH lower than 5. At higher pH, aluminium is deposited directly onto fish gills leading to respiratory failure. A plausible mechanism for the respiratory effects of Al is

the precipitation or polymerization of Al when acidic, Al-rich water passes into the gill microenvironment which is more basic due to ammonia released at the gills (Teien et al., 2004). Compared to lakes and streams, marine waters contain much lower aluminium concentrations (less than 0.04  $\mu\text{M}$ ) and, as illustrated in Figs. 2 and 5, the proton buffering capacity of seawater is greater than fresh water. Consequently, when ash falls over a well-mixed marine environment, aluminium will form primarily  $\text{Al}(\text{OH})_x^{+3-x}$  species and aluminium will not persist in large concentrations in the surface water because of low solubility of Al-hydroxides at near neutral pH. Therefore aluminium will not likely reach toxic levels following an ash-fall in the marine environment. However, non-aqueous forms of Al could still co-precipitate nutrients thus inhibiting the growth of algae.

## 6. Conclusions

Volcanic ash from the 2000 Hekla eruption produces an acidic leachate with high fluoride and aluminium concentration along with essential elements when exposed to deionized water.

Through simulation of the mixing of pristine volcanic ash leachate with fresh water and seawater, we propose that volcanic aerosols may act as fertilisers in the marine environment, but may produce toxic effects in fresh water systems. The toxic effect in fresh waters is increased by the combination of high aluminium (Al) and fluoride (F) concentrations of the ash leachate. Owing to the mixing of acid ash leachate with fresh water, aluminofluoride complexes ( $\text{AlF}_x^{+3-x}$ ) persist in aqueous systems with low turnover rates and could be toxic to both plants and animals. The combination of high Al and F concentrations may thus contribute to symptoms of illness related to Al toxicity and fluorosis in terrestrial ecosystems. In contrast, due to the well-buffered and relatively high pH in seawater, the speciation of the ash leachate/seawater mixture shows that complexes of fluoride and aluminium will not dominate in a well-mixed marine system. Hydroxo-aluminium complexes are more important at low levels of dilution than in fresh water systems. Consequently, when ash is falling over the marine environment, aluminium will form primarily  $\text{Al}(\text{OH})_x^{+3-x}$  species and aluminium will not persist at large concentrations in the surface water because of low solubility of Al-hydroxides at near neutral pH.

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