NORDIC VOLCANOLOGICAL INSTITUTE 79 04
UNIVERSITY OF ICELAND

# THE CHEMISTRY OF ICELANDIC LAVA INCRUSTATIONS AND THE LATEST STAGES OF MAGMA DEGASSING

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## CONTENT

## ABSTRACT

Incrustation mineral assembalges from cooling lavas are formed by fractional condensation of volatile halides. Sulfate assemblages are of a secondary origin formed during oxidation of the degassing volatiles. The trace metal chemistry of the incrustations is controlled by the F/Cl ratio of the transporting gas phase rather than element abundances in the degassing silicate melt. The F/Cl ratio of the gas phase, inferred from incrustation mineral equilibria, indicate a regional difference in the halogene content of Icelandic magmas. The rift zone volcanism (tholeiites) is distinguished by low halogene content and very low F/Cl ratios, while the off rift volcanism (alkaline rocks) is associated with high halogen content and high F/Cl ratios.

## INTRODUCTION

This report deals with the chemistry and morphology of 77 incrustation samples collected from the surface of five Icelandic lavas. The lavas were produced in the following eruptions: Askja 1961 (4 samples), Surtsey 1963-67 (9 samples), Hekla 1970 (50 samples), Heimaey 1973 (11 samples) and Leirhnjúkur 1975-77 (3 samples). The locations of the volcanoes within the volcanic zones of Iceland (Jakobsson, 1972; Imsland, 1978) is shown in Fig. 1. The Askja and Leirhnjúkur eruptions produced tholeiitic basalts in fissure eruptions within the caldera structures of silicic volcanic centers on the active NE-rift zone (Thorarinsson & Sigvaldason, 1962; Björnsson et al., 1976). The other volcanoes are on the SE-volcanic zone known to produce magmas with alkaline affinities in non-rifting volcano-tectonical environment. The Surtsey eruption (Steinthorsson, 1966) produced mildly alkaline basalt, the Heimaey eruption (Thorarinsson et al., 1973) produced hawaiite and the Hekla eruption (Sigvaldason, 1974) produced icelandite.

A detailed knowledge of the composition and formation of volcanic incrustations is a useful background to the study of water soluble particulates and aerosols produced in volcanic eruptive clouds. Further, the chemistry of incrustations gives qualitative information on the composition of the gas phase evolved in the respective eruptions. The present study is based on phase analysis and chemical analysis of the incrustations formed during cooling and solidification of the lavas. The mineral assemblages of the incrustations from the different lavas are compared and their chemistry discussed with emphasis on their mode of formation and compositional differences in the gas phase giving rise to them.

The term "volcanic incrustations" refers to solids condensing from a magmatic gas phase and the solid reaction products of magmatic gas and its surroundings. The reactive gases $SO_2$, HCl, HF and $NH_3$, along with the alkali metals, calcium, aluminium and silica of the cosangueneous silicate melt, are the major source of incrustations.

No clear distinction can be made between volcanic incrustations and fumarole incrustations in volcanic areas since the two differ in respect to environment of formation rather than origin of the major anions. Lacroix (1907) outlined a classification of incrustations formed in fumarole activity following the 1906 Vesuvius eruption. This classification was based on the observed thermal zonation of incrustation mineral assemblages with alkali chlorides and sulfates dominating at temperatures above 650°C and salammoniac below 300°C. Stoiber & Rose (1974) suggested a generalized zoning pattern of volcanic fumarole incrustations, based on temperature and oxygen fugacity during their formation. Among the wealth of minerals cited in their comprehensive work, a large number of hydrated, mixed chlorides and sulfates of the alkalis, alkaline earths, aluminium and iron seems to result from reactions of acid condensates with the wall-rock of the fumaroles. These authors favour "cation input from the wall-rock" as the major process of incrustation formation with exception of the simple high temperature halite and thenardite assemblages, calling for a separation of the cations by distillation of gaseous molecules, most likely to be active at magmatic temperatures. Incrustations from cooling Hawaiian lavas were described by Naughton et al. (1974), and the chemistry of Hawaiian incrustations and condensates was discussed by Naughton (1976). These authors consider the condensation of gaseous halide molecules as the principal source of incrustations and point out the importance of conversion of halides to sulfates upon oxidation of the magmatic gas.

The type of incrustations under study (lava incrustations might be a more specific term) appear at the openings of cracks forming a conduit from the lava surface to the still molten interior of the lava. The sampling sites can be looked upon as the upper end of a stationary column of the degassed volatiles, since the gas release is slow during the late degassing of a lava. The temperature and oxygen fugacities prevailing in this environment are indicated on Fig. 2. Although greatly simplified, the figure illustrates well that the initial oxygen fugacity of the evolved gas phase is most likely near the FMQ mineral buffer. During cooling of the escaping gases the oxygen fugacity is most likely controlled by the major components of the gas phase. This is illustrated by the $CO_2/CO$ and $H_2O/H_2$ buffers of the Surtsey volcanic gases shown in Fig. 2 (Sigvaldason & Elísson, 1968; Steinthorsson, 1972). As the solidification front migrates into the lava, volatiles more soluble in the melt than the solid phases are enriched in the molten region. During the slow rise and cooling of the gases, condensation of metal halides distilled form the melt sets on (Naughton, 1976). The condensation of water in a supersaturated gas phase (Owe Berg & George, 1968) might serve as a model for the above mentioned condensation. Proceeding as a chain reaction producing aerosols of few microns in diameter the condensation in itself is a nonequilibrium process in contrast to equilibrium condensation on a wall. This mode of formation of incrustation compounds conforms well to Naughton´s (1969) observation that aerosols in a volcanic fume were maximum 4 micron in diameter. Condensates of volcanic fumes are acid solutions or deliquescent acid mixtures of the common incrustation cations (Stoiber & Rose, 1970; Naughton, 1976). This indicates as stated by Oana (1962), that incrustation minerals are formed by fractional condensation of the volcanic fume leaving excess acids in the gas phase. The deposition of spontaneously formed aerosols along with possible equilibrium condensation on the wallrock renders incrustation mineral assemblages in general unfeasible for equilibrium calculations. A prolonged fractional condensation as idealized in Fig. 2, however, makes the chemistry of incrustations a sensitive indicator of condensible trace compounds involved in the latest stages of magma degassing.

In the present study trace elements of the incrustation minerals were analysed in order to evaluate their mode of transport. This might at the same time serve as a small contribution to the study of magmatic ore deposits revealing the importance of the F/Cl ratio of the medium transporting volatile metal halides (Zies, 1929; Krauskopf, 1959; Naboko, 1959). The incrustations give limited information on the less reactive major compounds of the volcanic fume, the discussion in this text will therefore primarily be concerning the halogen and sulfur chemistry of the samples starting with a brief morphological description of their solid phases.

## THE CRYSTALLINE PHASES OF THE INCRUSTATIONS, THEIR OCCURRENCE AND MORPHOLOGY

The multitude of forms and colours displayed by incrustation minerals in the field, reflects their differing environments of formation, level of impurities and trace element substitution. In the following the occurrence and morphological features of each phase will be mentioned briefly. Only fourteen chemical compounds were observed in the samples, occurring in the sixteen phases listed in Table 1.

SULFUR is an essential incrustation mineral occurring at all sampling locations, commonly condensed as dendritic needles of the monocline form. Orthorhombic pseudomorps of the monocline form are common. Sulfur is also found as a thin coating on lava surfaces, probably melted by increased temperature at the site of deposition.

SALAMMONIAC is the most common low temperature incrustation mineral occurring at all sampling locations except Surtsey, where only high temperature incrustations were collected. Three morphological types are observed.

(a) A mass of white to yellow granular crystallites (0.1-0.5 mm) occurring admixed with halite at Hekla, Heimaey and Leirhnjúkur. Somewhat coarser, white granular form occurs admixed with cryptohalite at Hekla and Heimaey.

(b) Clear to yellow sweeps of fibrous crystals pointing away from the base they condens on.

(c) Clear euhedral crystals, few mm in diameter, embedded in impure salammoniac of the fibrous type. This form is believed to be resublimates of the impure fibres.

Salammoniac always show excellent XRD-patterns, even the most coloured species. Under the microscope the yellow colouring is shown to arise from traces of sulfur and a brownish to opaque phase, probably iron (III) chloride and iron oxides.

AMMONIUM IRON (III) CHLORIDE occurs as tiny purple crystals associated with dark yellow salammoniac in one sample from Askja (Sigvaldason, 1964).

SYLVITE occurs admixed with halite as white hard crusts on the wallrock.

HALITE is among the most common incrustation minerals occurring at all sampling localities except Surtsey, appearing as very fine-grained white to yellow incrustation or small dust-like fragments on the wallrock.

GALEITE occurs in one sample from Surtsey forming fibrous sweeps of dendritic clear needles growing, supposedly from a gas phase, on the surface of thenardite incrustation.

CALCIUM ALUMINIUM FLUORIDE and ALUMINIUM HYDROXIDE FLUORIDE HEXAHYDRATE are found together and admixed with amorphous silica as hard, white coating on the wallrock, in one sample from Hekla. XRD-studies indicate distorted crystal structures.

MASCAGNITE occurs in few smaples from Hekla as a trace mineral. When analysed by XRD few weeks after the eruption 1970 only one sample contained this mineral, but when reexamined the summer 1977, few samples of salammoniac admixed with sulfur showed traces of mascagnite. The mineral is thus considered to be of a secondary origin, a reaction product of salammonaic, sulfur and water vapour at room temperature.

ALUMINIUM SULFATE is found mixed with thenardite and amorphous silica in one sample from Hekla. The incrustation is poorly crystallized, extremely fine-grained, hard white coating on the wallrock, but showing small vesicles in its thickest section.

THENARDITE and META-THENARDITE are the most common high temperature incrustation minerals found at all sampling localities except Heimaey. Thenardite occurs as three morphological types:

(a) In admixture with aphthitalite as a hard coating on the wallrock, white but occasionally showing bluish tint.

(b) Hard crusts of the pure mineral well crystallized but extremely fine-grained, frequently showing pink to reddish colours on the surface and bluish tint at the base.

(c) Dust-like fragments of pure thenardite or meta-thenardite, adhering to the wallrock.

APHTHITALITE is found admixed with thenardite in samples from Surtsey, forming hard dense crusts on the wallrock. The mineral is poorly crystallized, always showing bluish tint. Internal vesicles elongated from the interior to the surface of the incrustations are always present.

CRYPTOHALITE occurs only in samples from Hekla and Heimaey, frequently admixed with salammoniac. The mineral, when occurring alone, forms clear to white granular aggregates, but frequently fibrous crusts, when found with excess of salammoniac.

The morphology of the incrustations seems to be more depending on their environment of formation than habits of their crystalline phases. Few general remarks can be made:

(1) The mixed sulfates are, when studied by X-ray diffraction techniques, observed to be poorly crystallized. Colouring, probably due to exsolution phenomena, is always observed.

(2) Thenardite, although occasionally showing morphology similar to that of the mixed sulfates, commonly forms well crystallized dust on the wallrock, best exemplified by meta-thenardite.

(3) Halite is found as hard crusts, alone or admixed with sylvite, or aggregate of small particulates on the wallrock.

(4) The ammonium salts form well crystallized incrustations of fibrous or granular habit, probably condensed from a gas phase (sublimates).

(5) Sulfur is in most cases a secondary sublimate on the surface of other incrustations.

## CHEMISTRY AND FORMATION OF THE INCRUSTATION MINERALS

Chemical analysis of major and trace elements (Appendix I) were performed on few samples selected as a compromise between a sufficient amount of material and a simple phase composition, believed to represent homogeneous mineral assembalges. Each incrustation sample consists of only few minerals or even a single mineral. In this chapter the chemistry of such simple assemblages will be discussed with emphasis on their mode of formation. The compositional restrictions of the incrustations and their regional distribution will be reserved to a later section.

## Halides

Table II lists chemical analysis of halides. The sampling locations and phase compositions derived from XRD data and major element analysis are reported in the footnotes of the table.

Sample no. 1 is a complex fluoride from Hekla (Fig. 1). The compound $CaAlF_5$ appears to be a reaction product of $CaF_2$ and $AlF_3$ but data on its stability are lacking. The composition points towards a fluoride assemblage in a reaction relation to ammonia favouring the hydroxide. The presence of ammonia in the gas phase is indicated by salammoniac condensing at lower temperature zones at the same location. The trace metal composition of the fluoride is characterized by the metals known to form volatile fluorides and oxides (Mg, Sr, Y, Ti, Zr, Mo, Nb and Si). Metals forming volatile chlorides (Fe, Cu, Zn) are subordinate in the composition. The amounts of chlorine and bromine are low, indicating that the alkalis are fixed as fluorides.

Sample no. 2 from Hekla is a salammoniac with minor amount of halite, collected at about 300°C. Here Ca, Mg, Ti and Mo are an order of magnitude lower than in the fluoride (sample no. 1), but Fe and Cu are present at a comparable level. The concentration of Zn is also characteristic for most salammoniac samples from the same location.

Sample no. 3 and 4 from Hekla are salammoniac with minor cryptohalite collected at about 200°C. The increased bromine and low alkaline earths indicate still more fractionation of the gas that gave rise to samples no. 1 and 2.

The halides from Hekla (No. 1-4, Table II) indicate a gas phase rich in HF. The condensation of the halides is dominated by fluorides at high temperatures, but at lower temperatures the condensation of chlorides and bromides increases. The ammonium salts (salammoniac and cryptohalite) dominate the incrustations at the lowest temperatures below 200°C.

Sample no. 5 and 6 are salammoniac from Leirhnjúkur (Fig. 1). Sample no. 5 is rich in fluorine (associated with traces of Mg and Ti) and low in bromine as compared to sample no. 6. The fluorine is, however, much lower than in sample no. 2 and silica is absent.

Sample no. 7 from Heimaey (Fig. 1) is a mixture of halite and sylvite. The Fe content is very low but Zn is present in fairly high amount. The presence of Rb is explained by the similar chemistry of K and Rb.

The samples no. 8 and 9 from Heimaey are salammoniac and cryptohalite respectively. Here bromine and Fe reside in the chloride but Ti clearly favours the fluoride as noted above. Sample no. 10 from Askja is a salammoniac with a low fluoride concentration as compared to samples no. 5 and 6 from Leirhnjúkur.

The chemistry of the halides in general reflects the chemical fractionation of the escaping gas phase during incrustation formation. This results in zonation of minerals in the gas conduit. The volatile fluorides and silica are condensed before the volatile chlorides. The trace metals of the incrustations therefore indicate the dominating halogen at a sampling location. The volatile metal halides are probably removed from the gas phase prior to formation of the ammonium salts.

Cryptohalite and salammoniac are both formed as gaseous molecules. The formation of cryptohalite is favoured by low temperatures, since the HF/$SiF_4$ ratio of the gas phase decreases rapidly below 200°C (Rosenberg, 1973). The reaction of $SiF_4$ with excess of HF leads to the formation of cryptohalite in the gas phase idealized by the reaction

$$SiF_{4(g)}+2HF_{(g)}+2NH_{3(g)} \longrightarrow (NH_4)_2SiF_{6(g)}.$$

At Hekla and Heimaey halite occurs with salammoniac below its sublimation temperature (338°C) but cryptohalite and salammoniac condense together at temperatures between 100-200°C.

## Sulfates

Analysis of sulfates are listed in Table III. Sampling locations and proportions of the solid phases derived form XRD data and major element analysis are listed in the footnotes of the table.

Samples no. 1-3 from Surtsey are aphthitalite/thenardite, collected at 580°C. The galeite found at the same location is probably formed at temperatures well below 500°C in the system $Na_2SO_4$-NaF-NaCl (Pabst et al., 1963). The major element composition of the samples is reported in footnote as a mixture of the compounds $K_3Na(SO_4)_2$ and $Na_2SO_4$. Among the trace and minor elements only rubidium and lithium reflect directly the major element chemistry of the samples. The very high amount of the metals forming volatile chlorides at magmatic temperatures (Krauskopf, 1959) in spite of the extremely low concentrations of the halogens points towards a secondary origin of the sulfate anion.

The samples seem to be originally deposited as halite/sylvite and chlorides of the minor and trace metals. After deposition of the halide and oxidation of the gas phase, conversion to sulfate proceeds by the reaction

$$2MCl_{(c)}+SO_{3(g)}+H_2O_{(g)} \rightarrow M_2SO_{4(c)}+2HCl_{(g)}.$$

The aphthitalite is crystallized in the $K_2SO_4$-$Na_2SO_4$ solid solution system, in the case of Surtsey with excess thenardite. Exsolution colours, know to appear in aphthitalites below 427°C (Dana, 1951), indicate their extensive transition metal substitution. This could explain their distorted X-ray diffraction patterns.

The morphology of the samples, characterized by vesicles reflecting internal gas release during formation supports the assumption of a secondary origin. During the convertion of chlorides to sulfates HCl is released. Gaseous transfer of cations from the wallrock is probably active to some extent at reducing conditions (Stoiber & Rose, 1974). Metal chlorides instable compared to the respective oxides with increasing temperature are formed at intermediate temperatures. This can be illustrated by the reversible reaction

$$Fe_3O_{4(c)}+8HCl_{(g)} \rightleftarrows FeCl_{2(g)}+FeCl_{3(g)}+4H_2O.$$

A similar course of events for metals forming stable sulfides at magmatic temperatures is:

$$ZnS_{(c)}+2HCl_{(g)} \rightarrow ZnCl_{2(g)}+H_2S_{(g)}.$$

Condensation and deposition of volatile metal halides in a gas conduit (Fig. 2) of steep thermal gradient leads inevitably to an incrustation containing a number of the available metals.

Sample no. 4 is from Hekla. The phase composition is aluminium sulfate and thenardite, admixed with amorphous silica, closely resembling the cation composition of sample no. 1, Table II, from the same location.

The transition metals forming volatile chlorides associated with thenardite are mentioned earlier for the Surtsey samples, but the group Ti and Zr, Nb and Mo are here considered to be derived by similar course of events in HF-rich environment.

The gaseous molecule, $AlF_3$ with sublimation temperature of 760°C, is a feasible initial compound for the sample along with halite. Idealized formation of the sample starting with the fluoride then becomes

$$2AlF_{3(c)} + 3SO_{3(g)} + 3H_2O_{(g)} \longrightarrow Al_2(SO_4)_{3(c)} + 6HF_{(g)} \quad \text{and}$$

$$2NaCl_{(c)} + SO_{3(g)} + H_2O_{(g)} \longrightarrow Na_2SO_{4(c)} + 2HCl_{(g)}.$$

The amorphous silica is assumed to be derived from the gaseous SiO molecule (Naughton et al., 1974).

Samples no. 5 and 6 are thenardites with low transition metals abundancies. The thenardite from Hekla (no. 5) is noted for its high fluorine and magnesium content in contrast to sample no. 6 from Askja. The formation of this group of sulfates is well described by the action of sulfuric acid on aerosol particulates suspended in the gas phase or clustered to the wallrock. The meta-thenardite collected at Leirhnjúkur might exemplify an early stage of this morphological type.

The chemistry and morphology of the sulfates in general indicate their secondary origin. The trace metals further indicate different F/Cl ratios at the various sampling locations.

## COMPOSITIONAL RESTRICTIONS OF INCRUSTATION ASSEMBLAGES AND THEIR REGIONAL DISTRIBUTION

### Phase assemblages

The simple phase assemblage found among Icelandic lava incrustations are listed in Table IV. The groups from the different lavas are listed in order of decreasing temperature of formation for the halides - then the sulfates are listed and finally sulfur, which occurs at all locations. The order of condensation is: fluorides, chlorides, salammoniac, cryptohalite, sulfur. The sulfates generally resemble some halide in their cation composition (halite/sylvite vs. aphthitalite, halite vs. thenardite, Al-sulfate vs. Al-fluoride, salammoniac vs. mascagnite). The galeite ($Na_2SO_4 \cdot Na(F,Cl)$) from Surtsey (assemblage 1) is a remarkable intermediate stage of the transition from halide to sulfate assemblage. The halogenated sulfate forms in a gas phase in the system $Na_2SO$-NaF-NaCl-gas (Pabst et al., 1963). Further the galeite occurs on the surface of a thenardite incrustation. The intermediate formation of the galeite is here interpretated as the end stage of the halide/sulfate conversion.

In assemblage no. 5 from Hekla a small amount of mascagnite $(NH_4)_2SO_4$ is believed to illustrate the breakdown of the salammoniac in oxidizing environment in the presence of native sulfur. Cryptohalite supposedly converts to opaline silica, HF, $N_2$ and $H_2O$ in this environment.

The assemblages from Hekla and Leirhnjúkur are believed to represent all varities of incrustations formed during cooling of these lavas, and the collection from Heimaey contains all the reduced varities formed at that location. At Heimaey only the incrustations believed to be unaffected by atmospheric air were collected. Although halite is not found in the collection from Askja the presence of thenardite suggests that halite was the primary incrustation phase.

With the exception of the galeite mentioned above the assemblages from Surtsey are completely oxidized. The galeite indicate a previous halite/villaumite (NaF) assemblage and the aphthitalite indicates halite/sylvite assemblage. It is therefore concluded that if unoxidized low temperature incrustations had been sampled at Surtsey they would have consisted of salammoniac and cryptohalite. The incrustation assemblages from the geologically closely related Heimaey and Surtsey volcanoes are then formed along almost similar paths, but differ markedly in respect to oxidation.

The content of Table IV shows that incrustation formation at the different locations give rise to a parallel succession of assemblages outlined in Fig. 3. This zoning of the incrustations reflects a fractionation of the evolving gas phase during cooling. An interesting hypothesis deduced from Table IV is that the absence of fluorides from the Askja and Leirhnjúkur assemblages indicate a significant difference in the volatile composition of their consagueneous magmas as compared to Surtsey, Hekla and Heimaey. If correct this difference bears on important genetic differences of these magmas, since the absence of fluoride incrustations is confined to volcanoes on the NE rift zone of Iceland (Fig. 1), but the others are on the non-rifting SE volcanic zone. A different halogen composition of the two magma suites might serve as an indication of different mineral control of the volatiles at depth or a lack of such control.

In the following some compositional restrictions of the gas phase giving rise to high temperature halides will be discussed qualitatively. The questions to be answered are primarily:

(1) Do high temperature incrustations condense from an unfractionated magmatic gas?

(2) If not, what processes can modify the gas compositions from different volcanoes to form almost similar incrustation assemblages?

(3) Is the absence of fluorides among incrustation minerals a proof of a vanishingly low activity of HF in the magmatic gas phase?

(4) What genetic differences are displayed by different halogen ratios?

## Compositional restrictions during incrustation formation

For degassing of volatile solutes from a liquid the sum of their partial pressures has to exceed the confining pressure of the chemical system. During ascent to the surface the degassing of a magma is initiated at an unknown depth. A rapid pressure drop favours spontaneous degassing (nonequilibrium degassing). Spontaneous degassing might be controlled by the diffusion rate of the solutes in the liquid. At this stage the different diffusion behaviour of volatiles dissolved in a magma inevitably results in compositional fractionation of the degassing species. At surface conditions the latest stages of degassing can be modelled as an equilibrium process, where the liquid remains in equilibrium with its degassing products at about 1 atm.

The degassing species can be grouped into three different categories, each resembling a specified reaction relation to the magma.

(1) Gases in no reaction relation to the magma.

(2) Gases in a reaction relation to minerals of the magma.

(3) Gases in a reaction relation to dissolved species of the magma.

Gases of the first group enter the gas phase first formed (fixed gases). The second group, assumed to be controlled by solid state reactions, is exemplified by $O_2$ and $S_2$ and the reactions (Gerlach & Nordlie, 1975):

$$3Fe_2SiO_{4(c)}+O_{2(g)} \longrightarrow 2Fe_3O_{4(c)}+3SiO_{2(glass)};\ \text{(FMQ-buffer)}$$

$$6FeS_{(c)}+4O_{2(g)} \longrightarrow 2Fe_3O_{4(c)}+3S_{2(g)}.$$

The idealized situation is that of a constant partial pressure of $O_2$ and $S_2$ at a given temperature. Further the reaction products of sulfur and oxygen are fixed by the reactions:

$$O_2+ 1/2\ S_2 \longrightarrow SO_2 \quad \text{and} \quad SO_2+ 1/2\ O_2 \longrightarrow SO_3.$$

The carbon gases, although probably belonging to the first group at low pressures, are also in a reaction relation to the FMQ-buffer: $CO+ 1/2\ O_2 \longrightarrow CO_2$. The mineral control of $S_2$ and $O_2$ persists down to the solidus temperatures of the magma. The evolution of $S_2$ during the entire range of degassing supports the validity of this statement.

The gases in a reaction relation to the dissolved species of the magma are probably best exemplified by hydrogen. The $pH_2$ is related to $pO_2$ by the reaction $H_2+ 1/2\ O_2 \longrightarrow H_2O$. The water is, on the other hand, dissociated in the silicate melt (Burnham & Jahns, 1962). During the spontaneous initial degassing the removal of hydrogen is much faster than the removal of $O_2$ due to the higher diffusion rate of the former. A complete removal of hydrogen by diffusion during ascent of magma seems, however, unrealistic, since the diffusion rate of $OH^-$ controls its formation. Two possible mechanisms of "drying" of magma by hydrogen diffusion are evident:

(a) Hydrogen release from the magma depends on the rate of a solid state reaction (FMQ) or

(b) that the magma becomes momentarily oxidized as a result of hydrogen removal but restores its $pO_2$ buffer position as hydrogen diminishes in amount.

The net effect is in both cases "drying" of the magma.

The halogen acids are also volatiles in a reaction relation to the liquid. Assuming dissociation of HF and HCl and a solution behaviour of the halogens somewhat similar to the OH , hydrogen release tends to retard their vaporization as the halogen acids. It is therefore concluded that degassing of HCl and HF decreases rapidly as hydrogen diffuses from the liquid.

The above qualitative evaluation of the early degassing shows that hydrogen, the carbon gases and steam are removed from the melt, but the halogens are held back in the liquid relative to other volatiles. At the same time sulfur and oxygen persist at their buffered level in the melt.

The low $SO_3$ partial pressure in equilibrium with $FeS_{(c)}$ and $Fe_3O_{4(c)}$ rule out the primary formation of sulfates from the gas phase. In contrast the distillation of metal halides from the liquid is favoured in water deficient environment. Idealized reaction describing halite and fluorite in equilibrium with a silicate melt were studied by Mueller (1970).

(1) $2NaCl_{(c)}+AlSiO_{5(c)}+SiO_{2(c)}+H_2O_{(g)} \longrightarrow 2NaAlSi_3O_{8(c)}+2HCl_{(g)}$

(2) $CaF_{2(c)}+SiO_{2(c)}+H_2O_{(g)} \longrightarrow CaSiO_{3(c)}+2HF_{(g)}$

the equilibrium expressions are:

$$K_1 = \frac{(pHCl)^2}{pH_2O} \qquad \text{and} \qquad K_2 = \frac{(pHF)^2}{pH_2O}$$

At 1200°C the values of $K_1$ and $K_2$ are $10^{-0.219}$ and $10^{-1.94}$ respectively. The $HCl/H_2O$ ratio assigned to a primary magmatic gas (Sigvaldason & Elísson, 1968) is clearly too low to permit formation of the halides.

It is further evident, that at a constant $pH_2O$ the HF/HCl ratio is of the order 0.1. If the incrustation minerals control the degassing in the temperature interval between the solidus and liquidus temperatures of a lava, the halogen release form the magma is a fractionation process leaving the degassed rocks with slightly higher HF/HCl ratio than the original magma. The absence of fluorides at the lowest temperatures of incrustation formation can be taken as an indication of vanishingly low activities of HF in the gas phase. The fact that NaCl is a liquid and a gaseous molecule at magmatic temperatures and forms aerosol droplets during the late degassing of a lava, however, speaks against the above idealized equilibrium conditions. A generalization of that situation points towards a liquid and a gas of the incrustation compounds in equilibrium with the melt and the degassed volatiles. A supporting evidence for this mode of formation is the intimate mixture of compounds of different vapour pressures observed or inferred in incrustations. Examples are the compounds NaCl-NaF-KCl-$AlF_2$-CaF.

This very complex situation requires a knowledge on the activities of the incrustation compounds in aerosol droplets. Although such values could be estimated, the element ratios observed in primary incrustation phases are too scattered to permit a meaningful interpretation.

The compositional restrictions during incrustation formation can be summarized in the following:

(1) The incrustations do not form in unfractionated magmatic gas.

(2) Hydrogen release by diffusion ("drying") from the otherwise buffered magma favours the distillation of metal halides.

(3) The absence of fluorides among incrustation minerals, at the lowest temperature, indicate very low HF activities in the gas phase.

## Notes on regional distribution and genesis

The fluorine rich incrustation assemblages from the volcanoes on the SE-zone (Fig. 1) stimulated a research on the halogen ratios of Icelandic rocks in general (Sigvaldason & Óskarsson, in prep.). It became evident that the F/Cl ratio of the alkaline basaltic rocks from the SE-zone and the SNZ (Fig. 1) are 2-6, while the tholeiitic rocks from the active rift zones hafe F/Cl ratios below 1, but the majority of evolved tholeiitic basalts have F/Cl about 2. Further the abundances of the halogens increase with alkalinity of the rocks (Sigvaldason & Óskarsson, 1976). The F/Cl ratios of the Icelandic basalts is outlined in Fig. 4. The F/Cl ratios of the alkaline basalts is remarkably high as compared to the tholeiites. An explanation to this is given in a recent review on the petrology of Iceland (Óskarsson, Sigvaldason & Steinthorsson, 1979), where the halogen ratios of the tholeiitic and alkaline rock suites are assigned to their different source regions. While the primitive tholeiites are assumed to reflect the halogen ratio of the oceanic mantle the alkaline rocks are believed to be formed by remelting of a chemically fractionated amphibole bearing crust. The halogen ratios of the alkaline rock suite, produced on the SE-zone (Fig. 1), therefore reflect the breakdown of a fluorine rich phase during magma genesis.

At a depth great enough to stabilize amphiboles and micas in magmas of compositions compatible with these minerals, the halogens and hydroxyl obey a mineral control as outlined above for volatiles of the second group. The breakdown of such minerals during pressure release might indeed initiate the formation of a gas phase and eventually be the main reason for explosive volcanism. In this case the halogen acids might well be degassed to a large extent during the spontaneous stage.

The evolved tholeiites show variable halogen ratios in between the crustal derived alkaline magmas and the primitive olivine tholeiites. This pattern is believed to reflect equilibration of the mantle derived olivine tholeiite with amphibole bearing crust resulting in uptake of volatiles into the magma.

## SUMMARY

The lava incrustations collected from five Icelandic volcanoes are formed as halides destilled form the silicate melt. Diffusion of hydrogen from the silicate melt during an early spontaneous degassing stage results in lowering of the $pH_2O$. This favours the distillation of halides rather than the halogen acids. The F/Cl ratio of the gas phase controls the metal chemistry of the incrustation. In a Cl rich system the alkali metals dominate and the most abundant trace metals are Fe, Cu and Zn. In a F rich system the major cations are Ca, Al, Na and Si, while Ti, Mg, Mo and Sr are abundant trace metals.

It is not clear whether the incrustations form as equilibrium products of the evolved gas phase or spontaneously condensed aerosols. The morphology of the samples favour the latter alternative in many ways.

Sulfates among the incrustations are formed by conversion of halides to sulfates as a result of oxidation of $S_2$, continually given off by the solidifying lava. The major and trace metal chemistry of the sulfates, however, indicate the previous halogene proportions.

At lower temperatures the ammonium salts dominate the incrustation assemblages. The regional distribution of incrustation assemblages is an utterly sensitive index of petrogenetic differences, since the condensed products of the latest stages of magma degassing reveal different volatile chemistry.

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## TEXT TO FIGURES

Fig. 1. The volcanoes Leirhnjúkur and Askja are shown in the NE rift zone of Iceland (NEZ) and Hekla, Heimaey and Surtsey are marked on the SE volcanic zone (SEZ). The western flank of the biforced Icelandic rift system (WRZ) is a direct continuation of the Reykjanes ridge. The eastern flank is joined to the Kolbeinsey ridge by the Tjörnes fracture zone. The rift zone volcanism produces tholeiitic rocks exclusively. The SEZ and SNS volcanic zones produce mildly alkaline rocks in nonrifting tectonic environment.

Fig. 2. The figure shows the idealized environment of incrustation formation on a cooling lava. To the left a section through a cooling lava flow is shown in relation to the FMQ and HM oxygen buffers (right). The melting point of halite is indicated as a typical temperature for the deposition of halides. The sublimation temperature of salammoniac is marked as a typical temperature for the formation of low temperature assemblages. As the front of solidification migrates into the lava, the dissolved gases become enriched in the molten region. When these gases reach saturation in the liquid they are degassed in equilibrium with the liquid. During rise to the surface the incrustations form by fractionational condensation.

Fig. 3. The figure shows a fractionation scheme for the incrustations as inferred from the observed assemblages. The chlorine rich environment is shown in the lower left and the fluorine rich environment in the lower right. The compounds are ordered in an arbitrary temperature scale as shown by an arrow to the left. The trace metals typical for the two divisions are listed below the scheme. On the top of the schemes the respective oxidized assemblages are listed.

Fig. 4. The figure shows the halogen ratios for basaltic rocks in Iceland. The fields for primitive olivine tholeiites ($MgO > 9.5$, $K_2O < 0.05$) is shown in the lower left in comparison with the fields for evolved tholeiites and the alkaline basalts.

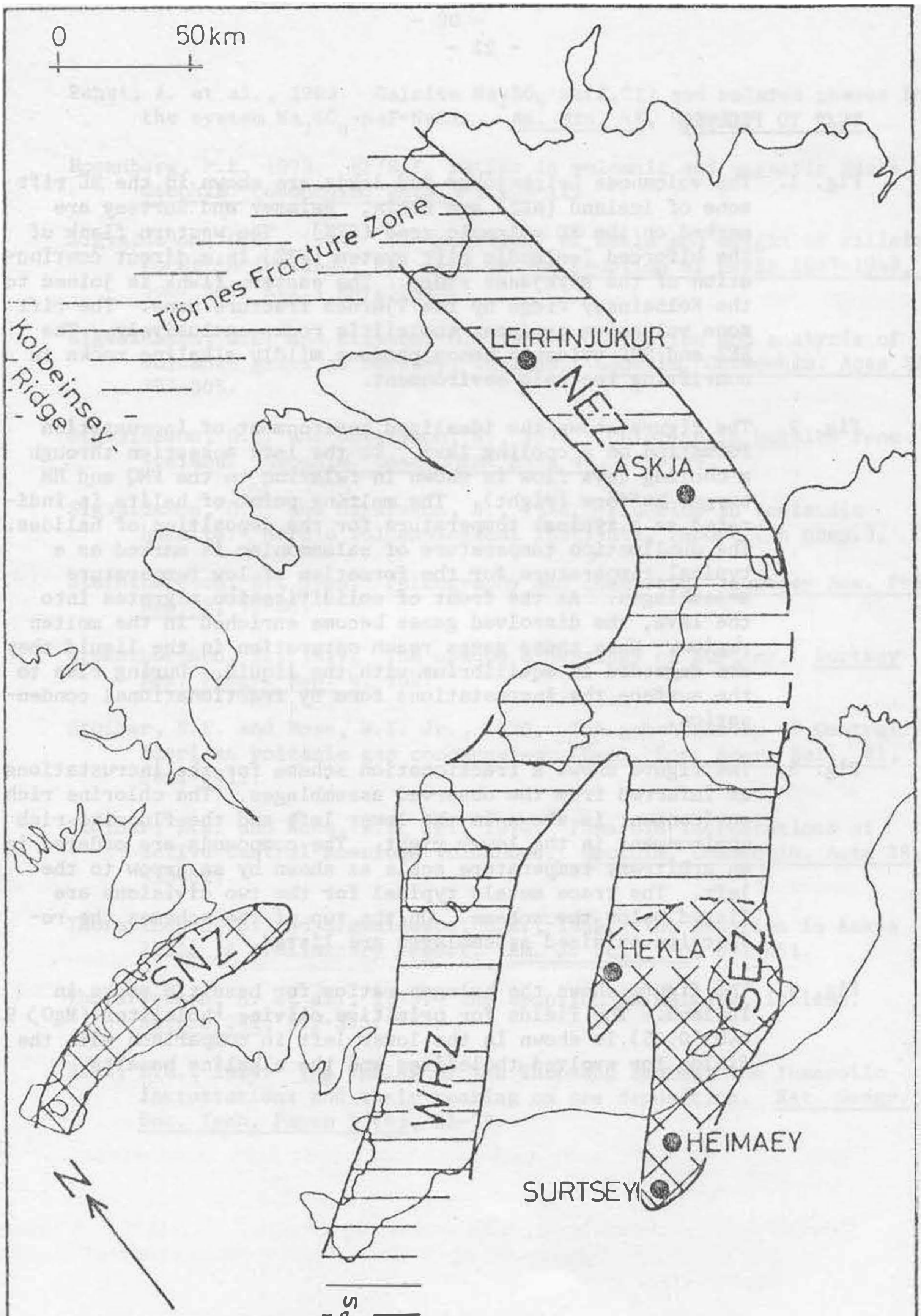
0
50km
Tjörnes Fracture Zone
Kolbeinsey Ridge
LEIRHNJÚKUR
NEZ
ASKJA
SNZ
HEKLA
SEZ
WRZ
HEIMAEY
SURTSEY
N
Reykjanes Ridge

FIG. 1

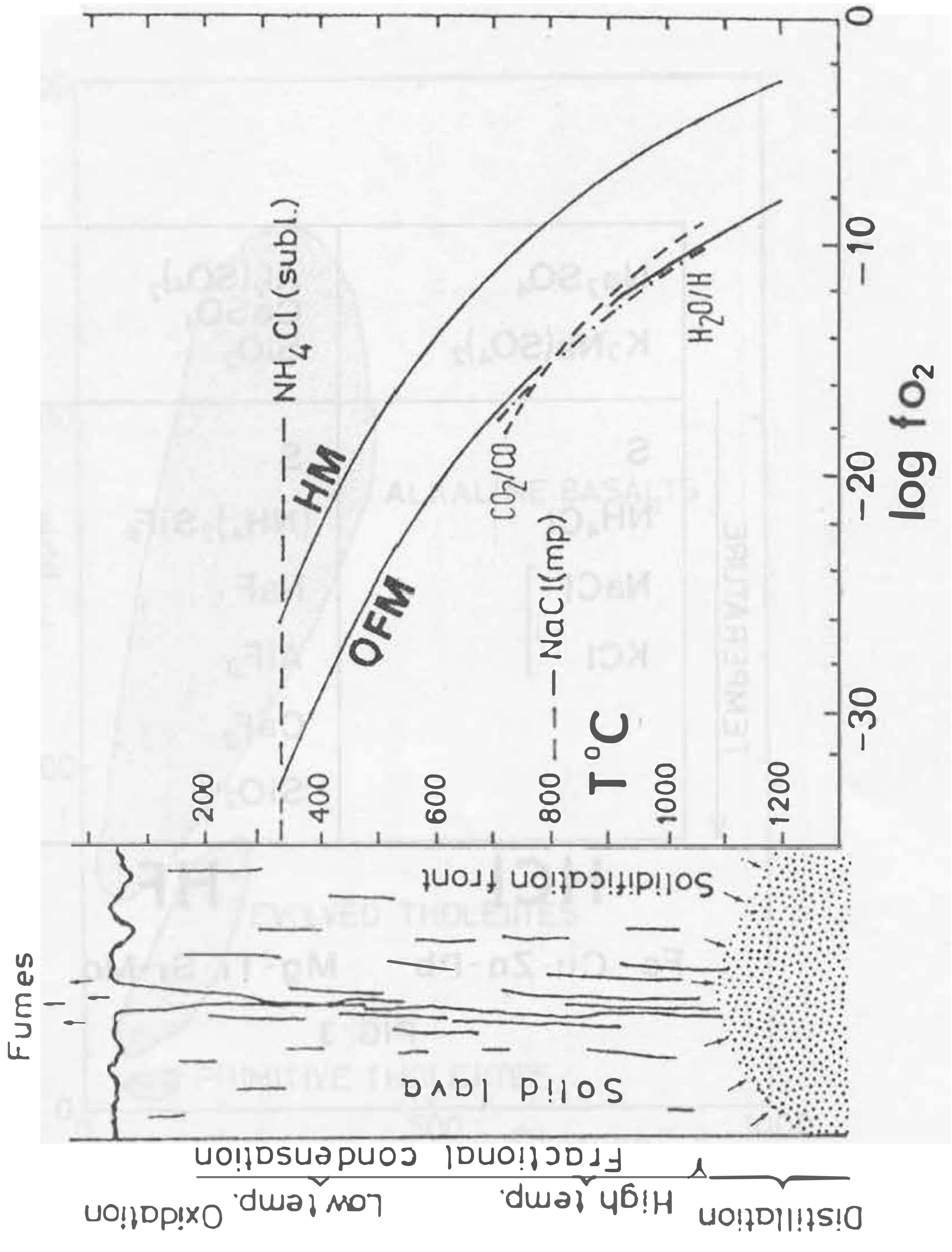
Fumes
Solid lava
Solidification front
Distillation
High temp.
Low temp.
Oxidation
Fractional condensation
HM
OFM
$NH_4Cl$ (subl.)
NaCl(mp)
$CO_2/CO$
$H_2O/H$
T°C
200
400
600
800
1000
1200
−30
−20
−10
0
log $fO_2$

FIG. 2

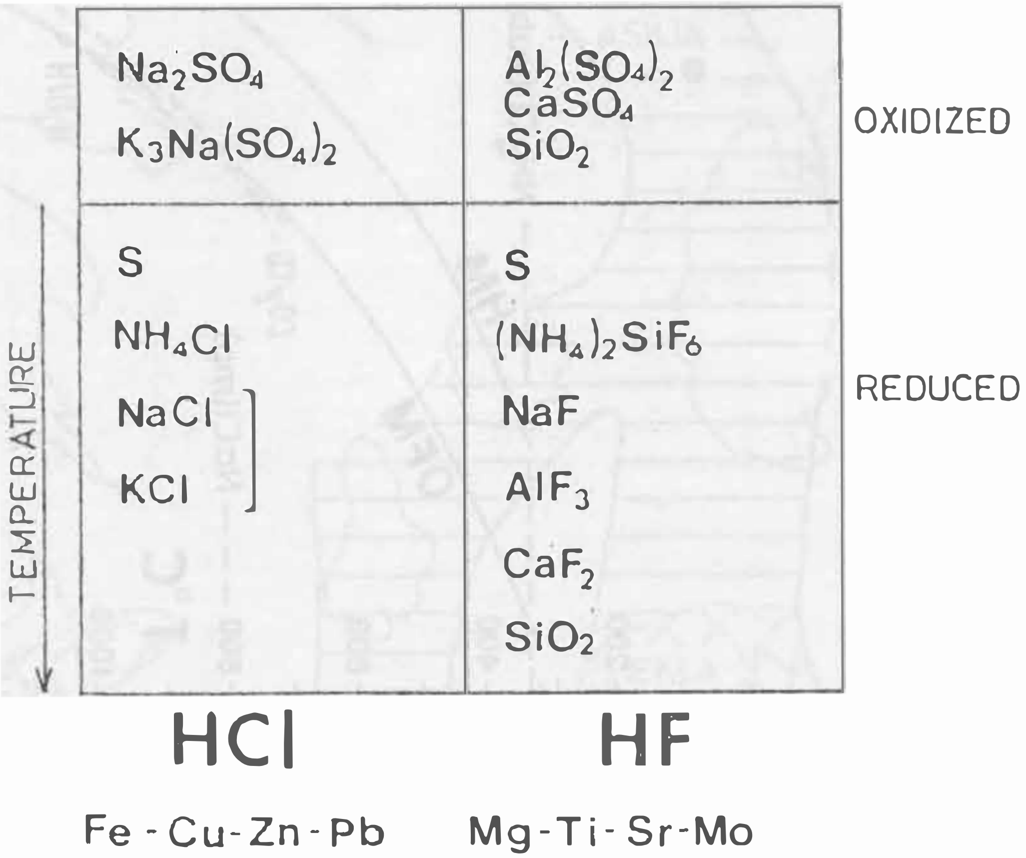
$Na_2SO_4$
$K_3Na(SO_4)_2$
$Al_2(SO_4)_2$
$CaSO_4$
$SiO_2$
OXIDIZED
S
$NH_4Cl$
NaCl
KCl
S
$(NH_4)_2SiF_6$
NaF
$AlF_3$
$CaF_2$
$SiO_2$
REDUCED
TEMPERATURE
HCl
HF
Fe - Cu - Zn - Pb
Mg - Ti - Sr - Mo

FIG. 3

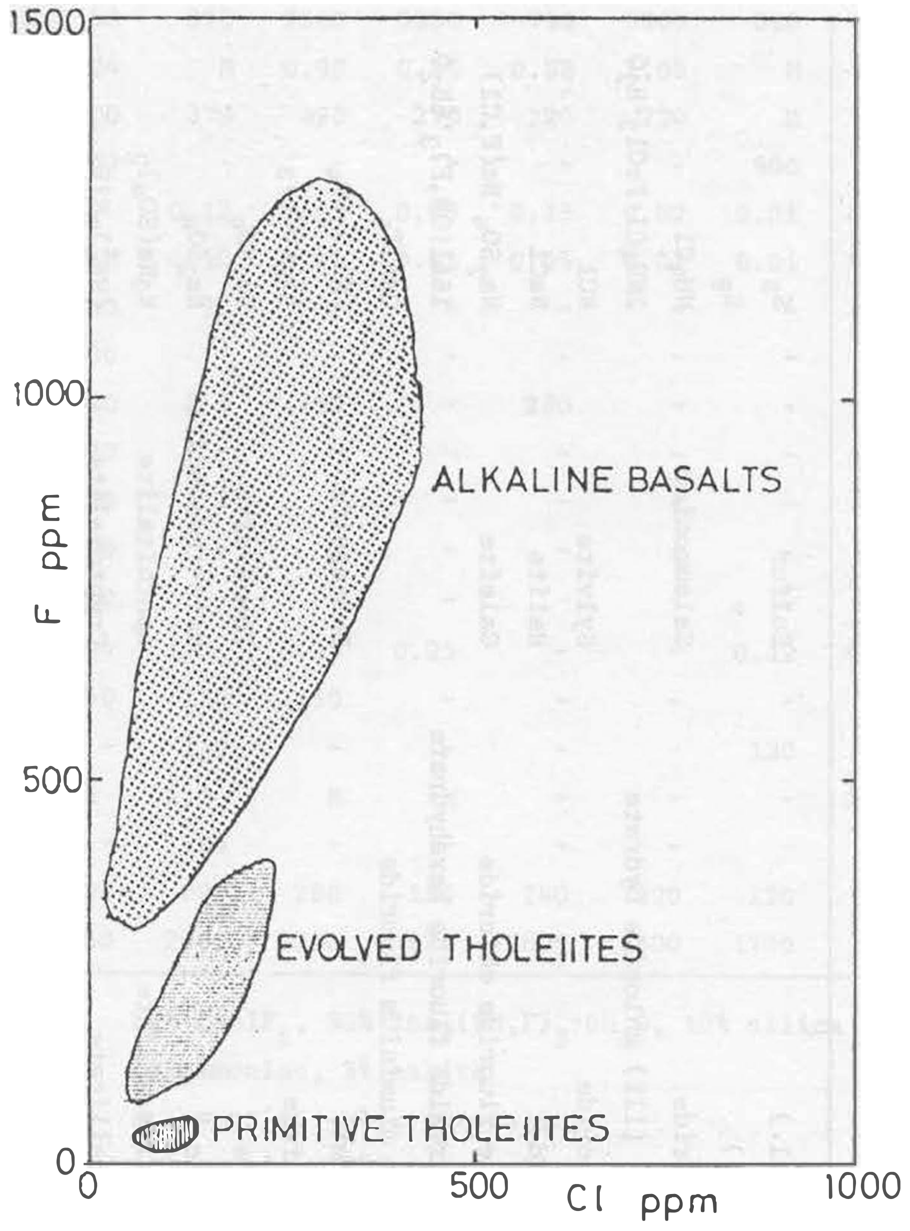
1500
1000
500
0
F ppm
0
500
Cl ppm
1000
ALKALINE BASALTS
EVOLVED THOLEIITES
PRIMITIVE THOLEIITES

FIG. 4

TABLE I SOLID PHASES OF INCRUSTATIONS

| Solid phase | Mineral name | Composition |
|---|---|---|
| 1. Sulfur (monocl.) | Sulfur | $S_8$ |
| 1a. Sulfur (orth.) | " | $S_8$ |
| 2. Ammonium chloride | Salammoniac | $NH_4Cl$ |
| 3. Ammonium iron (III) chloride hydrate | | $2NH_4Cl\cdot FeCl_3\cdot H_2O$ |
| 4. Potassium chloride | Sylvite | $KCl$ |
| 5. Sodium chloride | Halite | $NaCl$ |
| 6. Sodium sulfate fluoride chloride | Galeite | $Na_2SO_4\cdot Na(F,Cl)$ |
| 7. Aluminium hydroxide fluoride hexahydrate | | $16Al(OH,F)_3\cdot 6H_2O$ |
| 8. Alpha-calsium aluminium fluoride | | $CaAlF_5$ |
| 9. Ammonium sulfate | Mascagnite | $(NH_4)_2SO_4$ |
| 10. Aluminium sulfate | | $Al_2(SO_4)_3$ |
| 11. Sodium sulfate | Thenardite | $Na_2SO_4$ |
| 11a. Sodium sulfate | Meta-thenardite | $Na_2SO_4$ |
| 12. Potassium sodium sulfate | Aphthitalite | $K_3Na(SO_4)_2$ |
| 13. Ammonium fluosilicate | Cryptohalite | $(NH_4)_2SiF_6$ |
| 14. Silicon dioxide | Amorphous silica | $SiO_2$ |

TABLE II CHEMICAL COMPOSITION OF HALIDES (M = major element)

| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| % | F | M | 1.8 | M | M | 0.4 | 0.2 | 0.2 | 2.5 | M | 0.2 |
| % | Cl | 0.19 | M | M | M | M | M | M | M | 5.7 | M |
| ppm | Br | 50 | 320 | 2500 | 3500 | 790 | 5300 | 580 | 4500 | 450 | 480 |
| % | Na | 3.24 | M | 0.96 | 0.96 | 0.88 | 1.05 | M | 0.88 | 0.88 | 0.88 |
| ppm | K | 7800 | 370 | 320 | 270 | 220 | 220 | M | 370 | 530 | 220 |
| ppm | Rb | 150 | | | | | | 800 | | | 100 |
| % | Mg | 1.7 | 0.12 | 0.03 | 0.03 | 0.15 | 0.02 | 0.01 | 0.04 | 0.04 | 0.02 |
| % | Ca | M | 0.10 | 0.01 | 0.01 | 0.05 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 |
| ppm | Sr | 1240 | 90 | | | | | | | | |
| ppm | Y | 2900 | | | | | | | | | |
| ppm | Ti | 1600 | 350 | 350 | | 280 | | | 110 | 250 | 740 |
| ppm | Zr | 820 | | | | | | | | | |
| ppm | Mo | 160 | 20 | | | | | | | | |
| ppm | Nb | 190 | | | | | | | | | |
| ppm | Ni | 100 | | | | | | | | | |
| % | Fe | 0.94 | 1.0 | 0.13 | 0.25 | | | 0.12 | 0.05 | | 0.51 |
| ppm | Cu | 150 | 130 | 1150 | | | | | | | |
| ppm | Zn | | 130 | | | | | 130 | | | |
| % | Si | 4.5 | 1.4 | M | M | | | | 0.5 | M | |
| ppm | Sn | | 580 | | | | | | | | |
| ppm | P | 730 | 270 | 280 | 150 | 240 | 220 | 120 | 200 | | 260 |
| ppm | S | 350 | 2600 | 3200 | 920 | 3600 | 4500 | 1700 | 210 | 2200 | 690 |

| | | |
|---|---|---|
| 1) | Hekla | 60% $CaAlF_5$, 30% $16Al(OH,F)_3 \cdot 6H_2O$, 10% silica |
| 2) | Hekla | salammoniac, 3% halite |
| 3) | Hekla | salammoniac, 4% cryptohalite |
| 4) | Hekla | salammoniac, 7% cryptohalite |
| 5) | Leirhnjúkur | salammoniac |
| 6) | Leirhnjúkur | salammoniac |
| 7) | Heimaey | 79% halite, 21% sylvite |
| 8) | Heimaey | salammoniac |
| 9) | Heimaey | cryptohalite |
| 10) | Askja | salammoniac |

TABLE III CHEMICAL COMPOSITION OF SULFATES (M = major element)

| | | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| % | F | 0.10 | 0.10 | 0.20 | 0.4 | 1.6 | 0.60 |
| % | Cl | .019 | .014 | .006 | .012 | 0.39 | 0.46 |
| ppm | Li | 20 | 10 | 10 | 5 | 20 | 10 |
| ppm | K | M | M | M | 6300 | 1400 | 3500 |
| ppm | Rb | 470 | 400 | 300 | | | |
| % | Mg | 0.05 | 0.03 | 0.03 | 0.94 | 0.26 | |
| % | Ca | 0.02 | 0.01 | 0.01 | 1.8 | 0.02 | |
| ppm | Sr | | | | 130 | 130 | |
| ppm | Y | 730 | | 360 | | | |
| ppm | Ti | | | | 6200 | 530 | |
| ppm | Zr | | | | 350 | | |
| ppm | Nb | | | | 70 | | |
| ppm | Mo | | | | 780 | | |
| ppm | Ni | 80 | 80 | | | | |
| % | Fe | 1.09 | 0.67 | 0.91 | 2.96 | 0.67 | |
| ppm | Cu | 3340 | 5530 | 1340 | 130 | 130 | 330 |
| ppm | Zn | 1460 | 1290 | 730 | 2970 | 65 | 20 |
| ppm | Cd | 12700 | 8100 | 6900 | 20 | | |
| ppm | Tl | | | | 760 | | |
| % | Si | | | | 1.6 | | |
| ppm | Sn | 1850 | | 1390 | | | |
| ppm | Pb | 1100 | 1300 | 800 | 20 | | |
| ppm | P | 130 | 120 | 150 | 2900 | 450 | 130 |
| ppm | As | 300 | 400 | 300 | 100 | | |
| ppm | Bi | | | | 100 | | |

1) Surtsey 98% aphthitalite, 2% thenardite
2) Surtsey 91% " 9% "
3) Surtsey 89% " 11% "
4) Hekla 80% Al-sulfate, 15% thenardite, 3.4% silica
5) Hekla thenardite
6) Askja thenardite

## TABLE IV PHASE ASSEMBLAGES OF INCRUSTATIONS

### ASKJA 1961 (coll.: G.E. Sigvaldason)

1. Salammoniac + amm. iron (III) chloride
2. Salammoniac + sulfur
3. Thenardite
4. Sulfur

### SURTSEY 1963-1967 (coll.: H. Sigurdsson)

1. Thenardite ± galeite
2. Aphthitalite + thenardite
3. Aphthitalite
4. Sulfur

### HEKLA 1970 (coll.: G.E. Sigvaldason)

1. Al. hydroxide fluoride + CaAl-fluoride + silica
2. Halite + salammoniac + sulfur
3. Salammoniac + sulfur
4. Salammoniac + cryptohalite + sulfur
5. Salammoniac + cryptohalite + sulfur + mascagnite
6. Cryptohalite ± sulfur
7. Al. sulfate + thenardite + silica
8. Thenardite
9. Sulfur

### HEIMAEY 1973 (coll.: S. Steinthorsson)

1. Halite + sylvite
2. Halite + salammoniac
3. Salammoniac
4. Salammoniac + cryptohalite ± sulfur
5. Cryptohalite ± sulfur
6. Sulfur

### LEIRHNJÚKUR 1975-1977 (coll.: AE. Jóhannesson & N. Óskarsson)

1. Halite
2. Halite + salammoniac
3. Salammoniac ± sulfur
4. Meta-thenardite
5. Sulfur

## APPENDIX: ANALYTICAL METHODS

PHASE ANALYSIS BY X-RAY DIFFRACTION were performed with the powder method. Hand picked samples were ground in agate mortar and loaded in the specimen holders of the goniometer. Copper $K_{alpha}$ radiation was used at goniometer scanning speed 1/2°2 theta/min. The X-ray tube was operated at 36 kV, 16 mA and intensities measured with scintillation counter. Diffraction patterns were identified by comparison with the ASTM data file.

CHEMICAL ANALYSIS of the light elements Al-Fe were done on pressed pellets of the samples by the XRF method. Using Cr-tube operated at 50 kV, 40 mA the element radiation was resolved on PET analysing crystal and measured in vacuo with flow counter applying PHS. Standardization was done by comparison with synthetic mixtures of the elements in a matrix of the appropriate major compounds. The heavy elements Fe-Bi were analysed by XRF using W-tube operated at 50 kV, 20 mA, LiF analysing crystal and scintillation counter. Standardization was done against mixture of the elements purchased from "SPEX INDUSTRIES", Metuchen N.J. The standard mixtures were diluted with crushed acid washed quartz.

MAGNESIUM AND SODIUM were analysed by AAS-spectroscopy. The samples were dissolved in water (50 mg/50 ml) acidified and filtered. Lithium was analysed by FES-spectroscopy in the same solutions.

FLUORINE was determined by potentiometry using a combined $LaF_3$/calomel-electrode (ORION). The samples were boiled with ZnO in order to separate silica as the zincsilicate. The sesquioxides were separated by boiling with sodium carbonate. After acidification with $HNO_3$ the fluoride activity of the filtrate was measured using TIASB buffer. All the wet-chemical determinations were standarized against solutions of analytical reagents carried through the preparation steps.