

## Fluids in volcanic and geothermal systems

GUDMUNDUR E. SIGVALDASON

Nordic Volcanological Institute, Reykjavik, Iceland

**Abstract**—Mineral buffers control the composition of most volatile components of magmas and dissolved species in geothermal fluids. The only element which occurs in significant quantities in volcanic and geothermal fluids and is not controlled by mineral buffers is chlorine. It is argued that in absence of marine influence, geothermal fluids reflect the chlorine content of associated magmatic fluids.

The chlorine content of oceanic volcanic rocks has a positive correlation with elements, which are believed to indicate a heterogeneous source region. Since the source is generally believed to be the Earth's mantle, the implication is that the mantle is heterogeneous with regard to chlorine and other volatiles. Such heterogeneities would have important consequences for genesis and distribution of ore.

All major magma types of the oceanic environment occur in Iceland. Their spatial distribution is closely related to a volcanotectonic pattern, suggesting crustal control. A geophysical model of crustal accretion in a rift zone is used in conjunction with classical petrology to predict geochemical processes in a rift zone crust. The model has two kinematic parameters—drift rate and subsidence rate—which combined describe trajectories of mass particles deposited on the surface. When considering in conjunction with thermal gradients of the rift zone a series of metamorphic reactions and chemical fractionation processes are bound to occur, eventually resulting in a layering of the oceanic crust. The physical parameters result in a derived variable, rift zone residence time, which depends on the width of a rift zone. Long residence times in a wide rift zone lead to multistage recycling of material. Other properties of the model, based on geometric arrangement of productive fissure swarms within a rift zone, explain off-rift volcanism as directly related to rift zone processes, either as plate trapped magmatic domains or a transgressive thermal anomaly into an older crust. Off-rift volcanism is accordingly not fed directly by mantle derived liquids.

The model predicts that all volcanic fluids, with the exception of those which are associated with the most primitive olivine tholeiites, are partly or wholly recycled through all stages of hydrothermal and metamorphic reactions. In that sense associated volcanic and geothermal systems are a part of the same chemical fractionation column.

It is concluded that the chemistry of fluids in volcanic and geothermal systems can be viewed in the perspective of predictable crustal fractionation processes before any conclusion need be drawn concerning more deep seated causes for chemical anomalies.

### INTRODUCTION

The evolution of knowledge of fluids in volcanic and geothermal systems has extended over a long analytical period followed by a short period of syntheses, where experiment and thermodynamic deduction have brought considerable clarity into what previously amounted to confusion.

A major advance in the understanding of the chemistry of volcanic gases and geothermal fluids is the realization that some major chemical components are controlled by mineral buffers. Since the composition of magmas, and rocks in general, vary within relatively narrow limits in terms of their buffer capacity, the associated fluids will always be similar with regard to buffer controlled components at the same *PT* conditions. Dissimilarities are found primarily in those components which are not buffered by the silicate system.

The available knowledge on volcanic emanations was reviewed by White and Waring (1963) and by Sigvaldason (1974). Some additional analytical data has accumulated since then, but the principal advance has been through critical examination of existing data in an attempt to estimate sampling and analytical errors and restore the analysis to a form which is consistent with thermodynamically predicted compositions (Gerlach and Nordlie, 1975a,b,c; Gerlach, 1980a,b,c).

Much data is steadily accumulating on the composition of geothermal fluids due to the economic utilization of geothermal energy. The main effort is directed towards detailed study of solution equilibria between hydrothermal minerals and the fluid. A detailed

Table 8.1. Volcanic gas analyses (mole %)

	Hawaii	Erta'Ale (1974) (mean)	Surtsey	Showa* Shinzan	Katmai* S-16
CO	1.07	0.52	0.69		
CO <sub>2</sub>	33.27	11.70	9.29	65	
H <sub>2</sub>	0.73	1.59	2.80	25	
H <sub>2</sub> O	53.38	77.13	81.13	—	
SO <sub>2</sub>	11.31	7.39	4.12	1.66	
S <sub>2</sub>	0.02	0.29	0.25		
H <sub>2</sub> S	0.05	0.92	0.89	0.1	13
HCl	0.14	0.42	0.81	5.39	74
HF				2.76	13
T(°C)	1175	1150	1125	750	250

The analyses from Hawaii, Erta'Ale and Surtsey have been corrected for sampling and analytical error (Gerlach and Nordlie 1975a,b,c)

\*The analyses from Showa Shinzan and Katmai (White and Waring, 1963) are recalculated to 100% after subtraction of H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub> and Ar. The sum of these components in the original analysis is 99.3% in Showa Shinzan and 99.24% in Katmai.

review of that aspect, as well as overall chemical compositions, is given by Ellis and Mahon (1977) and Yfe *et al.* (1978).

Due to these readily available recent reviews the present paper will emphasize the correlation between fluid composition and geologic environment. It will be argued: (1) that there is a correlation between the chemistry of volcanic fluids and geothermal fluids in the same area, and (2) that volcanic fluids are controlled by processes which can be related to the tectonic environment of the volcanism.

Much of the relevant evidence for the model to be discussed is geological and geophysical rather than chemical. The chemical data on volcanic and geothermal fluids can, however, be used to test the model, but since the chemical evidence is incomplete and tenuous the discussion is bound to be speculative.

### VOLCANIC EXHALATIONS

Volatiles escaping from erupting volcanoes have been successfully sampled on a relatively few occasions. Chemical analysis of these samples have provided knowledge on the composition of volcanic gases from a limited number of magma types, but a wider spectrum of compositions is anticipated. The restriction of the present knowledge is implicit in the correlation between the chemical composition of volcanic products and the hazard involved in obtaining meaningful samples close enough to the erupting vent. Available information is therefore restricted to volatiles escaping from relatively quiet basaltic eruptions, but limited knowledge is available from explosive eruptions, which gave vent to intermediate or silicic lavas and tephtras.

Erupting basaltic liquids have a temperature in the range from 1050 to 1200°C, and represent the hottest natural materials on the surface of the Earth. High temperature, and generally difficult access, make sampling difficult. In addition the infrequent opportunity to obtain samples have generally resulted in each team of people performing this task only once in a lifetime, using improvised and often primitive equipment. The result is an incongruous set of data obtained with different methods of sampling and analysis over a period of the last 70 years.

A comprehensive review of available data up to 1960 was compiled by White and Waring (1963). Up to that time the best available data on volatiles associated with basaltic volcanism had come from Hawaiian volcanoes in the period from 1912 to 1917 (Jaggard, 1940). After 1960 a few other basaltic volcanoes have been sampled with some success (Table 8.1).

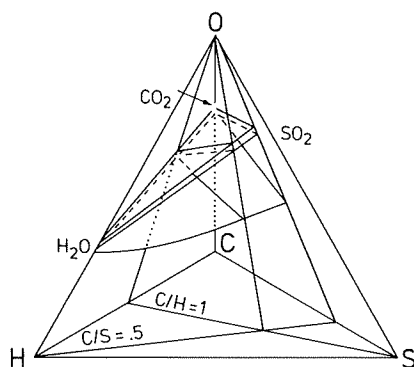


Fig. 8.1. The C—O—H—S tetrahedron. The planes  $C/S = 0.5$  and  $C/H = 1$  delimit known compositions of volcanic gases. Other surfaces shown are defined by mineral buffers. Above the first surface is the HM buffer at  $1250^{\circ}\text{C}$ . Just below comes the QFM buffer surface at  $1250^{\circ}\text{C}$ . The lowest surface is QFM at  $800^{\circ}\text{C}$ . The range of allowed volcanic gas compositions is outlined by the two vertical planes and the HM  $1250^{\circ}\text{C}$  and QFM  $800^{\circ}\text{C}$  buffer surfaces (from Gerlach and Nordlie, 1975a).

First attempts to correlate the observed analytical data with compositions predicted on the basis of thermodynamic calculations were made by Ellis (1957), Krauskopf (1959) and Heald *et al.*, (1963). It soon became evident that many, if not most, of the data were inconsistent. The types and qualities of components could in many cases not have been at equilibrium at the reported temperatures. Two main reasons for this inconsistency were apparent: first, contamination from atmospheric air and meteoric water and second, reaction of the high temperature gases with the sampling equipment.

Nordlie (1971) attempted to evaluate the nature and amount of contamination of volcanic gas samples from Hawaii. He was able to demonstrate an improved correspondence with predicted equilibrium compositions by subtracting atmospheric air and meteoric water from the reported analytical values. Gerlach and Nordlie (1975a,b,c) reviewed existing data on volatiles associated with basaltic volcanism. By carefully selecting only those data which appear to be of high quality they were able to delimit a compositional volume in the C—O—H—S tetrahedron, which is bounded by a  $C/S$  ratio larger than 0.5 and a  $C/H$  ratio smaller than 1 (Fig. 8.1). A further limitation on compositional variation of natural high temperature gases is set by commonly observed oxygen buffers in terrestrial magmas. The extreme limits are the QFM (quartz-fayalite-magnetite) and the HM (hematite-magnetite) buffers. Temperature limits in Gerlach and Nordlie's (1975a) study were set at 1250 and  $800^{\circ}\text{C}$ . Although defined on the basis of best available analysis from basaltic magmas, all analyses of Cl-poor volcanic and fumarolic gases, regardless of petrographic association, have atomic compositions that plot within these limits.

The range of possible atomic compositions can be further constrained. Most igneous rocks are known to have crystallized at a fugacity of oxygen close to the QFM buffer and the majority of gas samples considered to be good to excellent have a composition falling close to that buffer at the respective collecting temperatures. This correspondence between the QFM buffer composition and collecting temperature indicates that the gas is buffered by the magma and not vice versa.

In spite of the relatively narrow compositional volume defined by the above constraint the available volcanic gas analysis may not be representative of the volatile content of a magma at moderate to high pressure. Differential degassing, due to solubility differences of volatile species in the silicate liquid will continuously alter the atomic proportions of the remaining volatiles in solution. If degassing occurs along with cooling and the QFM buffer is maintained, material transfer between liquid and gas phases depends to a large degree on the sulphur content of the gas phase, since the buffer surface in the C—O—H—S volume is considerably inclined towards the S-corner at low temperature. Degassing of

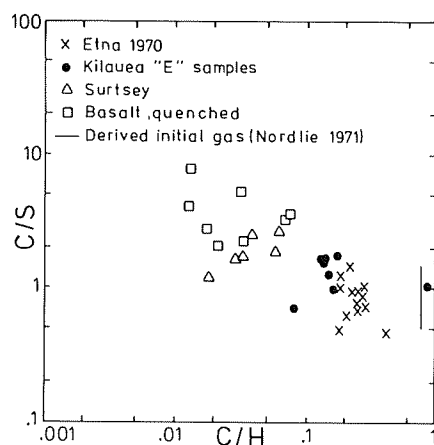


Fig. 8.2. A plot of C/S versus C/H of high quality gas analysis from basaltic lavas. The bar at the right indicates the derived composition of Hawaiian gas after correction for contamination and surface degassing. Ratios derived from residual gases in quenched basalts may show the end stage of a differential degassing process (Gerlach and Nordlie, 1975a).

an intrusion or an ascending magma with only slight lowering of temperature at large decrease in pressure results in a large variation of the relative amounts of the main species  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{H}_2\text{O}$  without substantial material transfer between liquid and gas phases, since the QFM buffer surface in the C–O–H–S volume is nearly parallel to the  $\text{SO}_2$ – $\text{CO}_2$ – $\text{H}_2\text{O}$  plane at high temperature (Gerlach and Nordlie, 1975a).

Gerlach and Nordlie (1975a) compared the highest quality gas samples from Etna, Surtsey and Hawaii and found them to plot within a narrow compositional band in a C/S to C/H diagram (Fig. 8.2). The trend can be interpreted as a compositional evolution as degassing advances. If projected back to an 'initial gas phase' (to the right in Fig. 8.2) the trend indicates that the first gas phase to form would be rich in sulphur (as  $\text{SO}_2$ ) and carbon (as  $\text{CO}_2$ ) relative to hydrogen (as  $\text{H}_2\text{O}$ ). Gerlach (1980a) looked in more detail at the Surtsey gases and found a time dependent evolution, which could be expressed as preferential loss of  $\text{CO}_2$  from the magma reservoir over a period of 3 years of continuous volcanic activity.

While differential degassing may be a dominant factor in shaping the compositional trend of gases sampled from a single volcano, differences between volcanoes may be due to actual differences in the original volatile contents of magmas generated from different sources. Compositional restrictions due to buffering and differential degassing prevent any definite conclusion to be drawn about regional variations in the C–O–H–S system, but the limited data indicate that such variations may exist. In contrast it can be shown with a higher degree of confidence that elements such as chlorine, which are not controlled by mineral buffers, vary significantly between areas. This will be discussed in connection with geothermal fluids.

#### GEOTHERMAL FLUIDS

High temperature aqueous fluids occur in most areas of active or relatively recent volcanism. This close association of volcanism and geothermal activity led early students of the phenomena to believe that both the water and chemicals dissolved in hot spring water and constituents of fumarolic gases were of magmatic origin (c.f. Barth, 1952). First doubts about such direct magmatic derivation of geothermal fluids were expressed by Einarsson (1942), who held the view that hot spring waters of Iceland were of meteoric origin and that the dissolved elements were derived from wall rock leaching. In the early 1960's it became evident from studies on deuterium and oxygen isotopes that most of the water in geothermal fluids was of meteoric origin (Craig, 1963). Furthermore, experimental studies on rock water interaction in the temperature range up to  $300^\circ\text{C}$

Table 8.2. Chemical compositions of high temperature geothermal waters

	1	2	3	4	5
SiO <sub>2</sub>	609	480	805	740	400
Ca	2.0	1.5	2.2	280	2800
Mg	0.5	0	0.1	8	54
Na	156	212	1050	5820	50400
K	15	27	210	1570	17500
CO <sub>2</sub>	90	55	128	1653	7100
F	—	1.9	7.3	—	15
Cl	63	197	1743	10420	155000
SO <sub>4</sub>	178	61	8	0	5
B	1.1	0.6	48.2	12.4	390
T(°C)	(90.5)	216	260	340	340
pH	—	9.6	8.3	—	4.7

Concentration in mg/kg after steam loss due to boiling at 1 atm. pressure. The analyses are selected to show the observed range in salinity of high temperature geothermal water.

1: Hveravellir, Iceland<sup>b</sup> 2: Hveragerdi, Iceland<sup>a</sup>. 3: Broadlands, drill hole 2, New Zealand<sup>a</sup>. 4: Mexicali, Hole 5, Mexico<sup>a</sup>. 5: Salton Sea, Hole 1, California<sup>a</sup>. <sup>a</sup>Ellis and Mahon 1977; <sup>b</sup>Fyfe, 1978).

showed that most of the dissolved elements in geothermal fluids were in solution equilibrium with a mineral assemblage stable at the respective environmental conditions (Ellis and Mahon, 1964, 1967). At the same time it became clear that a few important elements contained in geothermal fluids were not controlled by mineral buffers. Especially chlorine and boron and some cations with very large ionic radius would always favour the aqueous phase relative to any solid. This together with the assumption that all constituents of geothermal fluids were derived from rock/water interaction, led to calculations of rock volumes necessary to provide some of these incompatible elements in amounts enough to sustain present production rates over a geologically estimated lifetime of a geothermal system. The rock volumes needed were truly enormous (Ellis, 1966). Drilling into geothermal areas has not given any convincing proof of thorough leaching of these elements, although substantial decreases have been noted, especially for chlorine. The elements sulfur and carbon are always heavily enriched in hydrothermally altered rocks of geothermal areas and although these elements can be derived from wall rock leaching under hydrothermal conditions there is little or no field evidence of a depleted source rock. The theory that all chemical elements are derived by wall rock leaching is therefore open to question.

Alternatively elements like chlorine, sulphur and carbon could be derived from a degassing magma. Even so, the problem of volume remains if a stagnant magma body is assumed. Episodic refilling of a magmatic reservoir is needed in order to explain the flux of chemicals and heat in a long lived geothermal system. Such episodic magmatic activity has now been observed in Iceland (Björnsson *et al.*, 1979). It is noteworthy that this particular event has established a direct link between the magma and the associated geothermal system. Intense degassing of the magma, as it intrudes to a level at 2–3 km depth in the crust, temporarily exceeds the buffer capacity of the hydrothermal system. Reaction rates are not fast enough to cope with occasional pulses of acid volcanic gases resulting in drastic lowering of pH of the geothermal water from 9 to 1.8 (Óskarsson, 1978; Gíslason and Arnórsson, 1976).

Table 8.2 lists examples of high temperature geothermal waters, demonstrating the observed compositional spectrum. The analyses selected for this Table are all of the sodium chloride type, representing fluids contained in water reservoirs above 200°C. Elements controlled by mineral buffers have a limited concentration range. The most dramatic differences are among the elements chlorine and boron, which are not compatible with any mineral of the wall rock. If the wall rock is supposed to be the source for

the incompatible elements a specific environment or a specific process have to be assumed. High chlorine can result from leaching of marine sediments, or the hydrothermal fluid can be circulated sea water. This can be proven in many cases, but frequently such an origin can only be assumed with different degree of probability. Another possibility is a large rock/water ratio, where very large volumes of rock are leached by small amounts of water. A third possibility is concentration by steam loss from a stagnant water reservoir. Very high chlorine concentrations resulting from steam loss do, however, require high initial amounts of chlorine or large initial water volumes or both.

All these possible mechanisms of brine formation require special conditions which can develop in a number of geological environments. One would therefore not expect any pronounced regional pattern in the distribution of thermal brine versus more dilute geothermal waters associated with volcanism. There is, however, a pattern, on a global scale, which may possibly be related to systematic regional differences in the composition of magmatic fluids.

The evidence for different chlorine concentrations of volcanic gases in oceanic and continental volcanism is indicative but tenuous. Very low concentrations of chlorine are reported in volcanic gases from Hawaii and Iceland, and the chlorine contents of basaltic rocks from Iceland are very low (Sigvaldason and Óskarsson, 1976). In contrast chlorine seems to be present in high concentrations in volcanic exhalations from continental volcanoes (White and Waring, 1963).

The chlorine content of geothermal fluids coincides with this pattern of chlorine distribution in oceanic and continental volcanic fluids. Geothermal waters in Iceland are extremely dilute with respect to chlorine, containing a few tens to maximally a few hundreds ppm Cl. Only where sea water influx is positively proven does the chlorine content exceed this low level. Geothermal fluids associated with submarine ridge volcanism like the Red Sea brine or the recently discovered East Pacific Rise hydrothermal activity (Cyamex, 1979) are examples where sea water plays a dominant role, but as soon as oceanic ridge or intraplate volcanism occurs on land then chlorine is extremely low in the associated geothermal fluid.

In view of the capacity of chlorine to form complexes with a number of rare metals it is noteworthy that Iceland is absolutely barren with regard to any economic deposits of ore, while ore deposits are found on the oceanic bottom in a similar, but submerged, volcanotectonic environment (Cyamex, 1979).

Practically all geothermal areas on continental borders, associated with subduction zone volcanism, produce fluids containing one to three orders of magnitude higher chlorine concentrations than fluids associated with oceanic volcanism. One may speculate that chlorine, and other incompatible elements in hydrothermal processes are captured by marine sediments deposited on the oceanic plate and subducted beneath continental borders. Remelting of the subducted slab would result in magmas highly enriched both in water and other volatiles, which due to the sedimentary involvement would have an entirely different halogen and other incompatible element than magmas of the ocean ridges (Anderson, 1974; Fyfe, 1978). Due to buffering the proportion of components in the C-H-O-S system would, however, be similar in both cases.

#### VOLCANIC AND GEOTHERMAL FLUIDS IN RELATION TO GEOLOGICAL SETTING

Volcanic and geothermal fluids are integral parts of a dynamic system which modern geology attempts to describe in terms of a plate tectonics theory. The formation of a new crust at the ocean ridges by transfer of material from the Earth's mantle is one of the most important steps in the dynamic processes described by the theory. In fact, if any geologic process can be called 'primary' then it would be the crustal accumulation resulting from oceanic magmatism and volcanism.

In the oceanic environment a few general types of magma compositions occur. Each type is characteristic of a well defined volcanotectonic environment, such as a rift zone or



an oceanic island. The oceanic magmas can be grouped into three mineralogic systems, based on coexisting minerals at three different invariant points in the basalt tetrahedron of Yoder and Tilley (1962): olivine tholeiite, tholeiite and nepheline basanite. All three mineral systems are controlled by the same main components—olivine, plagioclase and pyroxene—while orthopyroxene, quartz and nepheline are the fourth phase respectively in each system. None of these minerals exert any control on the composition or amount of volatiles in the system. Another nonvolatile group of elements is incompatible with the structure of these principal mineral components and there seems to be a general positive correlation between volatiles and incompatible elements such as potassium (Sigvaldason and Óskarsson, 1976).

There is currently a heavy emphasis in petrogenetic theory on the occurrence pattern of incompatible elements. They are believed to reflect chemical properties of the source region of oceanic magmas, the Earth's mantle. It is ultimately concluded that the Earth's mantle is heterogenous with respect to incompatible elements, and hence volatiles, both vertically and laterally.

All principal magma types of the oceans occur in Iceland. An occurrence pattern correlates with tectonic properties of the crust. Chemical and isotopic evidence, which elsewhere is thought to indicate mantle heterogeneities, is found in Iceland displayed in a regular, repetitive array. Unless the crust is a fine-scale mirror-image of the mantle, one must assume that crustal processes play a much more important role in controlling the chemical composition of oceanic volcanic rocks than implied from current genetic models.

The details of this pattern are described by Óskarsson *et al.* (1979), who propose a model to explain the petrochemistry of oceanic rocks with special emphasis on Iceland. In its present initial state the model seems capable of eliminating a number of current paradoxes, without creating serious new ones. The model is a frame into which it is possible to incorporate available information on natural fluids at high temperature and pressure and it allows predictions to be made, which can be tested by direct observation. A brief description of the model is given below, but for geological and petrological evidence the reader is referred to the original paper by Óskarsson *et al.* (1979).

#### THE KINEMATIC MODEL OF OCEANIC PETROGENESIS

Bödvarsson and Walker (1964) presented a mode of plate accretion at a rift zone, which was later quantified by Pálmason (1973). In Pálmason's treatment the accretion process is described in terms of two parameters: drift rate away from the rift, and subsidence due to material accumulation at the surface of the rift zone. The subsidence rate, assuming isostatic equilibrium, is directly related to volcanic productivity. Fig. 8.3 is a schematic presentation of the model. It describes the paths of material particles deposited at the surface. Depending on the distance from the rift zone median line, material particles are carried down and sideways at different inclination angles. Numeric values of the kinematic parameters allow isochrons to be calculated, showing that material deposited at the margin of the rift zone 1 Ma ago is at the surface 10 km away from the rift zone margin but material deposited at the same time within the rift zone is at a depth of up to 10 km and still within the rift zone.

We now follow the petrological and chemical development of material particles described in the model. Extrapolated thermal gradients within and outside a rift zone have been estimated by direct measurements in drill holes and by implication from heat flow data (Pálmason, 1973). This allows us to draw a generalized thermal structure. Fig. 8.4 summarizes the result. Material travelling towards higher temperature passes through various stages of metamorphic reactions. Hydrothermal alteration in geothermal systems of the rift zone results in low grade zeolite facies assemblages. Further subsidence carries the material through successive stages of metamorphic reactions establishing greenschist, amphibolite and eventually granulite facies.

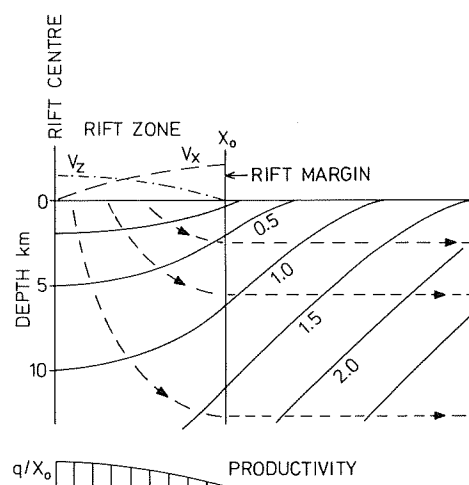


Fig. 8.3. The kinematic model. The broken arrows represent paths of particles deposited at different distance from the rift center. Rate of subsidence ( $V_z$ ) is proportional to the rate of productivity ( $q/X_0$ ) and approaches zero at a distance  $X_0$  from the rift center. Rate of drift ( $V_x$ ) approaches a constant value at  $X_0$ . Solid lines are isochrons (millions of years) calculated for best available data on drift and productivity for the Icelandic rift zones (Pálmason, 1973).

Experimental work on the melting behavior of hydrated basalt by Holloway and Burnham (1972) and Helz (1973, 1976) provides guidelines for some details of the process. Two isotherms represent jumps in the chemical evolution of the subsiding rock pile. The first represents the breakdown of mica and alkali feldspar at about 700°C to form silicic melts. The second is the amphibole breakdown temperature at about 900°C. The forma-

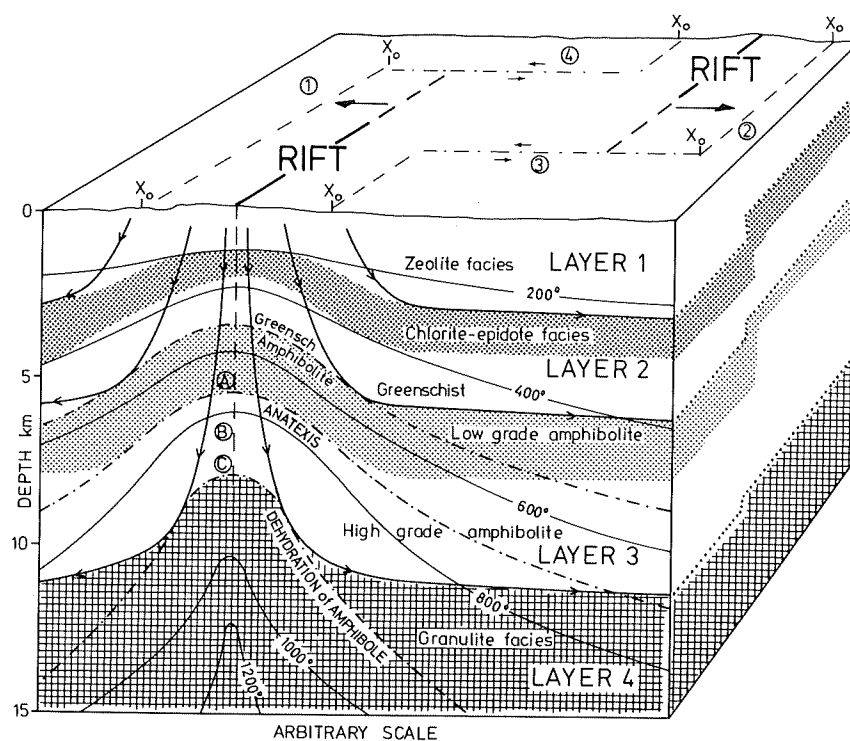


Fig. 8.4. A simplified block diagram through a rift zone. Solid arrows are paths of mass particles. Alternating solid and broken lines are isotherms. Mass particle paths go through temperature maxima at different depths. Where temperature maxima along the path coincide with isotherms of significant metamorphic reaction or melting a contact is established between crustal layers (Oskarsson *et al.*, 1979).



tion of partial melts in the subsiding pile results in chemical fractionation since the melts segregate and move upwards relative to the residue. The result is a layering of the oceanic crust where the composition of each layer is predictable.

While within the rift zone the subsiding crust generates two types of magmas: (1) a magma of the granite system, and (2) a magma of the nepheline basanite system (alkali olivine basalt).

Since the model prescribes the nature of the starting material and the composition of partial melts and melt residues, certain predictions can be made concerning the composition of the volatile content of the magmas. First, however, some further properties of the model have to be described.

Material and energy to drive the model comes from a deep mantle source. As a first approximation the material is assumed to be primitive olivine tholeiite, the most common magma type produced on narrow submarine ridges. No other types of mantle derived magmas are required. This magma is injected into the crust and has three possible evolution paths:

- (1) Direct extrusion to the surface after minimal reaction with the crust.
- (2) Residence in and reaction with silica depleted high grade amphibolite, where the olivine tholeiite mixes with nepheline basanite melts. The mixture will evolve by fractional crystallization towards the olivine tholeiite invariant point as long as the olivine tholeiite is the larger part of the mixture. Incompatible and volatile element content will be entirely but predictably different from the primitive olivine tholeiite.
- (3) Residence in and reaction with silica enriched low grade amphibolite, where the olivine tholeiite mixes with liquids of the granitic system. The mixture will evolve by fractional crystallization towards the quartz tholeiite invariant point. Incompatible and volatile element contents are predictably different from melts of case 1 and 2.

Any combination of the above evolution paths can occur in nature.

Still another property of the model becomes evident when we pass from the simple generalized sketch of Fig. 8.4 to more complicated natural conditions. An oceanic rift zone is usually pictured as a single fissure passing through the crust. In nature this is somewhat more complicated, since there is usually a set of productive fissures, a fissure swarm, running along the rift zone. Most of the world's rift system is a series of fissure swarms arranged end to end with frequent offsets at fracture zones. Occasionally two or more fissure swarms are arranged parallel, or in an en echelon pattern resulting in a considerable widening of the rift zone. This occurs at locations where magmatic productivity is above average—the so-called hot spots of the oceans. This, however, is not associated with higher rate of drift. If two or more fissure swarms are arranged in parallel then interference occurs between the kinematic parameters of individual swarms. Only those fissure swarms which are next to the margin of the rift zone will contribute to plate accretion. The crustal section between the marginal fissure swarms will subside due to accumulation of volcanic products at the surface.

Assuming steady state we can put crustal accretion as equivalent to net input of mantle-derived material into the rift zone crust. Variable rift zone width at constant drift rate then represents a rock reservoir of variable volume. Reservoir volume divided by annual input is the average residence time of material in the reservoir if complete mixing occurs. Chemical fractionation due to the uneven thermal distribution in the reservoir and the effect of interfering kinematic parameters result in large deviations from that average. Chemical elements with affinity for the liquid phase will tend to be captured within the crest of the thermal anomaly and become gradually enriched. The actual residence time of these elements may approach the age of the rift zone. The width of a rift zone therefore adds a time variable to crustal accretion processes, with inevitable consequences for the growth of radiogenic isotopes. The expected result is that the crust of a wide rift zone would evolve to a higher degree and fractionate more completely than the crust of a narrow rift zone. Simultaneously a drastic change in the volatile composition

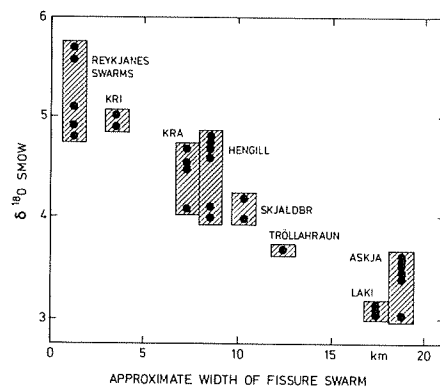


Fig. 8.5. Oxygen isotope ratios of basalts (Muehlenbachs *et al.*, 1974; Muehlenbachs and Jakobs-son, 1979) plotted against width of respective fissure swarms (Óskarsson *et al.*, 1979).

and content of the rift zone magmas occurs, which should also be reflected in the stable isotope ratios of oxygen, sulfur and carbon.

Recycling of material in the rift zone results in repeated hydration of the same material in the uppermost crustal layers, and dehydration as the low melting hydrous minerals break down at depth. One expected result is an accumulative exchange of oxygen isotopes between meteoric water and the rocks of the rift zone. Figure 8.5 shows the correspondence between oxygen isotope ratios of Icelandic basalts and the surficial width of the fissure swarms where they were produced. It should be noted that all basalts plotted in this Figure are completely fresh, a good deal of them between 2 and 200 years old.

If the oxygen isotope ratios are plotted against incompatible elements, such as potassium or other evolutionary indicators, a similar correspondence results. The weight of evidence therefore favors the interpretation that the low oxygen isotope ratios in these evolved basalts result from isotope exchange with meteoric water in a multistage recycling process. If so, then magmatic gases—water as well as sulfur and carbon—contained in basaltic melts are derived to varying degree from the breakdown of hydrated minerals, sulfides and carbonates, formed initially in shallow geothermal systems.

I have so far described processes in the rift zone crust implied by the kinematic model of petrogenesis. These processes are strongly influenced by two possibly interrelated factors; the productivity of the rift zone segment, and the geometrical arrangement of the producing fissure swarms. The geometry has still further implications which influence the chemistry of the volcanic products and allow further testing of the theory.

Figure 8.6 is a map of Iceland showing the pattern of fissure swarms which constitute the rift zone across the country. Injection of mantle-derived olivine tholeiite occurs preferentially at one locality on each fissure swarm and magma is then injected laterally away from that location into the adjacent fissures (Björnsson *et al.*, 1979). The point or area where primitive magmas enter the crust has a surficial expression in so called volcanic centers. Here large amounts of magma are stored and evolve. Such magmatic accumulation are referred to as magmatic domains in the crust.

Rifting at the plate boundary is episodic. I see no reason why rifting should be statistically distributed among many parallel fissure swarms. On the contrary rifting, may be confined to one or two fissure swarms within a broad rift zone for extended period of time. When that happens marginal fissure swarms become an integral part of the drifting plate. A magmatic domain then drifts away from the rift zone and is permanently decoupled from its source of mantle derived magma. Volcanic activity continues on a gradually diminishing scale and becomes increasingly alkaline as the crustal generated magmas became dominant in proportion to the olivine tholeiite inherited from the rift zone. Such decoupled or remnant volcanic centres are prominently evident to the east

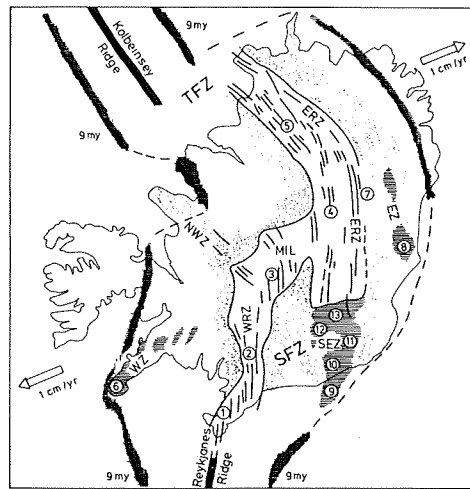


Fig. 8.6. Map of Iceland showing principal volcanotectonic features. Tholeiitic fissure systems of the rift zone are indicated by solid lines. Off-rift alkaline volcanism is shown by horizontal hatching (from Óskarsson *et al.*, 1979).

and west of Icelandic rift zone, and I suggest that alkaline volcanic islands of the oceans may be generated in the same way.

Another implication of rift zone geometry can be deduced from Fig. 8.6 and Fig. 8.4. Due to the broadening and bending of the rift zone across Central Iceland a situation is created where fissure swarms of one part of the rift zone extend into a crustal section which was formed previously by another part of the rift zone. The result is a transgressive heat anomaly which extends from the rift zone termination and causes remelting of the older crust. The isotherms of the anomaly have assumedly a downward inclination away from the rift zone termination and volcanic products observed on the surface correspond to melting of successively deeper layers. Due to the earlier fractionation and layering of the crust the volcanic products of the transgressive zone have a variable but geometrically arranged compositional pattern.

The kinematic model of petrogenesis therefore defines three types of oceanic volcanism:

- (1) rift zone volcanism;
- (2) decoupled or remnant volcanism; and
- (3) transgressive volcanism.

Implicit in this classification is that only the rift zone volcanism has any direct communication with the Earth's mantle.

#### VOLATILES AND THE KINEMATIC MODEL

Several authors have recently questioned the applicability of Rubey's (1951) model of excess volatiles, mainly because of the recycling processes, which inevitably occur as a consequence of subduction at continental margins (Fyfe, 1978).

The recycling of material in a broad rift zone is confined to a geologically monotonous area and is therefore less complicated than the reworking of material in a subduction zone. A few relevant tests can be made. Input of volatiles into the rift zone magma systems comes from two major sources—the Earth's mantle and the atmosphere and hydrosphere. In Iceland the simplifying situation prevails, that the input from the hydrosphere is meteoric water, in contrast to submerged parts of the rift zones where sea water is involved in the hydrothermal alteration of the uppermost crustal layers.

The input of material from the Earth's mantle could be estimated from knowledge on the volatile content of the most primitive olivine tholeiite. Studies on the volatile content

of rapidly chilled glass margins of primitive olivine tholeiite lavas, which extruded under high hydrostatic pressure on the ocean bottom, have shown that the water content of such magmas must be very low. The solubility of water in basaltic magmas (Hamilton *et al.*, 1964) is high enough to prevent the formation of a separate gas phase at the observed water contents and pressure of extrusion (Moore, 1965, 1970). The water content of rapidly chilled glass is in the order of 0.1–0.4%. The lower value may be more realistic, considering that practically all processes of evolution would tend to increase the water content of the melt. Delaney *et al.* (1978) have argued on the basis of very low water contents of glass inclusions in phenocrysts from rapidly chilled glasses, that the water content of primitive olivine tholeiite may be still lower. In contrast, the carbon dioxide contents of chilled olivine tholeiite glasses from the deep ocean are approximately equivalent to what would be expected from CO<sub>2</sub> solubility at the respective hydrostatic pressure (Delaney *et al.*, 1978). Small vesicles found in these glasses are probably due to exsolution of CO<sub>2</sub> gas (Moore, 1965). Evidence for voluminous release of CO<sub>2</sub> from a shallow (3 km) basaltic magma chamber is found in the Krafla area in North Iceland, where a drastic increase in the CO<sub>2</sub> content of fumarole gases is associated with magmatic intrusion from depth (Óskarsson, 1978).

Delaney *et al.* (1978) found that the average molar ratio of CO<sub>2</sub> to SO<sub>2</sub> in chilled glassy borders of olivine tholeiite from the sea bottom is about 3. The molar ratio of CO<sub>2</sub> to H<sub>2</sub>O is in the order of 0.6. This gives a considerably higher ratio of carbon and sulfur to hydrogen than what is found in most analyses of high temperature volcanic gases from basaltic eruptions. Gerlach and Nordlie (1975a) were aware of this difference and concluded that the main reason was different solubilities, which led to early depletion of carbon and sulfur during ascent. That interpretation, however, assumes the same or similar initial composition of volatiles in basaltic magmas in general. The chemical composition of lavas from which it was possible to collect high temperature gases is, however, widely different, although they are all basalts in a general sense. They range from a tholeiite on the island of Hawaii to a basalt transitional between a tholeiite and an alkali basalt from Erta'Ale in Ethiopia and an alkali olivine basalt on Surtsey, Iceland. The kinematic model suggests that these magmas are either crustal derived or heavily contaminated by crustal material in contrast to a primitive mantle-derived olivine tholeiite.

The analysis of components within the C–O–H–S system does not provide any constraints on that theory due to buffering and differential degassing, but the very large decrease in the C/H ratio from the olivine tholeiite to the alkali basalt would be the expected result if the alkali basalt is derived from remelting of hydrated material, which had lost CO<sub>2</sub> in previous fractionation processes. Studies on isotopic ratios of the respective elements, both in volcanic gas samples and residual volatiles in rocks should be able to provide a conclusive test for such processes, but this remains to be done.

The behavior of the halogens, chlorine and fluorine, in volcanic and geothermal systems can be predicted and tested with greater confidence than the C–O–H–S group of elements. In essence the prediction is based on the very great affinity of fluorine to minerals of the amphibole group, and the importance of amphiboles in crustal metamorphism. In contrast, chlorine is truly incompatible with any major mineral phase and will always become concentrated in the liquid phase, be it water or silicate melt.

The Cl/F ratio in primitive mantle-derived olivine tholeiite is approximately 3 (Sigvaldason and Óskarsson, in preparation). Any closed system evolution of a primitive melt by fractional crystallization is unable to alter that ratio. Evolution by reaction with a crustal envelope containing amphibole will, however, tend to decrease the ratio in the magma since residual amphiboles of the crust contain fluorine in excess of chlorine as a result of the separation of crustal derived liquids. The reaction between a primitive olivine tholeiite and a fractionating crust within a rift zone will therefore recycle fluorine in contrast to chlorine, which is continuously lost to the hydrosphere at a much faster rate.

The fractionated crust leaving the rift zone is therefore enriched in fluorine relative to chlorine and any liquids derived by melting of that crust should have much lower Cl/F ratios than the magmas of the rift zone. Unfortunately, none of the analyses of high temperature volcanic gases include determination of fluorine, but some indirect evidence exists.

One of the hazards of volcanic eruptions in Iceland is fluorosis in grazing animals caused by excessive fluorine produced by the volcanoes. A study of records on damage done by various eruptions through the past centuries revealed that in some eruptions there is no mention of fluorosis in spite of the proximity of the volcano or heavy ash falls. Mapping of these cases shows that fluorosis was not reported in connection with eruptions occurring within the rift zone while fluorine poisoning is severe when eruptions occur on the transgressive volcanic belt in South Iceland.

This observation prompted a closer study of halogens in volcanic products of Iceland. Óskarsson (1979) found that sublimates deposited from fumes on cooling lavas were chlorides in the rift zone but fluorides and chlorides in the transgressive volcanic zone and Sigvaldason and Óskarsson (in preparation) find a close correlation between the Cl/F ratio of volcanic rocks in Iceland and their volcanotectonic position.

#### CONCLUDING REMARKS

The kinematic model of oceanic petrogenesis is initially based entirely on geophysical parameters. Chemical and petrological consequences of the model can be followed, and the resulting predictions compared to actual observation. A key conclusion of the model is that volcanic and geothermal fluids form a part of the same system and cannot be treated separately. This will be specially evident when it comes to the interpretation of isotopic ratios in volcanic gases from evolved magmas, where a previous fractionation in a geothermal system has to be considered.

Another implication of the model is that the oceanic crust is fractionated in a heterogeneous manner, depending on the length of the rift zone residence time. As the crust is subducted beneath continental margins, the process of remelting and the resulting volcanic products will reflect the degree of fractionation initially attained during rift zone residence.

In an extended form the model may therefore also apply to continental volcanism, where it might provide guidelines for a better understanding of ore genesis and deposition.

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## DISCUSSION

SIMON:

Concerning the gases you get from the volcanoes, do you have any  $^{13}\text{C}/^{12}\text{C}$  ratios?

SIGVALDASON:

To the best of my knowledge none of these gas samples which are considered to be representative for basaltic magmas have been analysed for  $^{13}\text{C}/^{12}\text{C}$  ratios.

HELGESON:

I'd like to make a comment on your attempt to interpret the bulk composition of gases and fluids at the surface in terms of their origin. It seems to me axiomatic that in order to

do this, one must take account of the kind of immiscibility in the system  $\text{CO}_2\text{--NaCl--H}_2\text{O}$  that Professor Franck discussed (in his presentation). Although the extent of immiscibility is still uncertain, it appears that a  $\text{CO}_2$ -rich gas phase may coexist with an  $\text{NaCl/H}_2\text{O}$ -rich liquid phase over wide regions of pressure/temperature composition space. In fact, Roedder's observations and Hamann's data suggest to me that the miscibility gap may occur at considerable depths in the earth. If so, the components of magmatic gases will be partitioned between the two immiscible phases, and the extent of partitioning will depend on equilibrium constants which themselves change with pressure and temperature. In addition, such partitioning will be affected by nonideal mixing in the two phases. It therefore seems to me tenuous at best to use a simple bulk composition argument to assess the fractionation of, say, chlorine between the solid, gas, and liquid phases in the system.

**SIGVALDASON:**

In magmatic systems there is a large range of immiscibility phenomena which are poorly understood. However, if a volatile component is present in such low concentration in a silicate liquid that it does not form a separate gaseous phase until at very low, near surface, pressure then we may be justified to interpret its amount in terms of the source composition. This is the case for chlorine in primitive oceanic basalts where the chlorine content lies much below its solubility even at atmospheric pressure. By contrast continental magmas are usually chlorine rich and it is difficult to say anything about the chlorine content of the magmatic sources because of the arguments you mentioned. My point is that this difference in chlorine contents of oceanic and continental magmas indicates a fundamental difference in the chlorine content of the sources.

**SHEPPARD:**

I have two interrelated questions. Do you have evidence for amphibole in basalts in Iceland and, secondly, am I correct in believing that the low  $\delta^{18}\text{O}$  basalts are very dry, 0.1–0.2 wt%  $\text{H}_2\text{O}$ ?

**SIGVALDASON:**

In answer to the first question, I can say that there is no evidence for amphibole in basaltic rocks in Iceland. You would expect them to break down easily if included in a water poor tholeiitic magma.

The low  $\delta^{18}\text{O}$  basalts are not especially water-rich. The Laki lavas, for example, which have about 3.8  $\delta^{18}\text{O}$ , have  $\text{H}_2\text{O}$  contents in the order of 0.8–1.0%.

**BURHAM:**

There's a paper that should be coming out very soon by Schilling<sup>1</sup> and co-workers on the fluorine/chlorine ratios of basaltic glasses dredged from the mid-Atlantic ridge extending from Iceland a long distance down the ridge. He has shown, fairly clearly I think, that the fluorine/chlorine ratio changes markedly at water depths of 500 m. The interpretation they placed on that was that eruptions at shallower than 500 m result in the dramatic loss of chlorine to values you find in Iceland, and there is a very low chlorine content of the quench glasses. Whereas at water depths greater than 500 m there's as much, if not more, chlorine than fluorine, something like 250 ppm on the average. How does that fit in to your hypothesis?

**SIGVALDASON:**

Schilling's interpretation of the degassing of chlorine as a function of water depth is not in accord with results obtained on basaltic rocks in Iceland. According to our interpretation (Sigvaldason and Oskarsson, 1976) less than 10% chlorine is lost by degassing at the surface and there can be no dramatic loss of chlorine during the degassing process.

**ROEDDER:**

I like your picture of the origin of several types of basalts very much. I would like to try to ask you a question concerning the correlations of your gas analyses with these



various environments of formation of basalts. The gas analyses you showed indicated a fairly sizeable degree of oxidation—fairly oxidized compared with possible environments, for example, where methane would be rich. Do most of these gases presumably include some surface oxygen?

SIGVALDASON:

Those analyses which I showed are restored analyses. They are calculated to the QFM buffer and corrected for possible errors introduced by atmospheric contamination, by meteoric water contamination or by reaction during sampling. This is a work by Gerlach (1979a,b,c,) which is about to come out. He has restored analyses from different sampling groups and made them internally consistent.

ROEDDER:

But are there any such gas analyses that show highly reduced gases?

SIGVALDASON:

There are no high temperature volcanic gas samples which depart significantly from the QFM buffer. In a few cases highly reduced gases have been reported but their oxidation state was shown to have resulted from reaction with the sampling equipment.

YODER:

I liked your residence time model very much, but it was constrained to only about a quarter billion years for all the activity seen on Iceland. The  $^{87}\text{Sr}/^{86}\text{Sr}$  variance far exceeds that which you would get in that time span. Would you not rather appeal to the fact that the  $^{87}\text{Sr}/^{86}\text{Sr}$  would be partitioned differently, say, between liquid and perhaps a gas and a fluid phase. The gas streaming may produce your variance in  $^{87}\text{Sr}/^{86}\text{Sr}$  rather than the time of residence that the magma sits there; because the magma erupting today would have sat there since the Atlantic first started to part.

SIGVALDASON:

What I am saying is that magma is always present in the crust of an active rift zone. There is a steady state flow of solid material into the accreting plate boundary as well as back to the mantle. At any particular time increment the liquid part of the system will be enriched in those elements which have a higher affinity to the fluid than to the solid phases and the bulk composition of the system becomes enriched in those elements relative to any previous time increment.

YODER:

You have detached the alkali olivine basalt volcanoes from the main olivine tholeiite source, and yet the evidence in the alkali basalts (the nodules) indicates that they have a high-pressure assemblage. The result is that you have now taken them away from the one source for high-pressure phases. I am concerned about your source of alkali basalt.

SIGVALDASON:

But the thing is that, if you move the drift parameter of the model then, of course, the main parameter is only subsidence. So, as you recirculate this material, you are always pushing it further down.

YODER:

But not below, say, 10 km?

SIGVALDASON:

The source rock is the same in the sense that primitive melts are derived from the deep mantle. However, during ascent these isotopically primitive melts have to pass through two barriers which can change their isotopic composition: (1) A shallow mantle material, derived from the crustal fractionation (breakdown of amphibole). This shallow mantle material is in isotopic equilibrium with the crust from which it is derived and in mineralogical equilibrium with the primitive melt from below. The only effect on the melt as it ascends through this crustal derived shallow mantle is isotopic equilibration giving the

primitive melt a new isotopic pattern characteristic for that particular rift segment. (2) Depending on residence time and the amount of crustal fractionation the crust has developed an Rb/Sr ratio higher than the Rb/Sr ratio of primitive melt. Mixing with crustal derived melts will then further modify the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of melts appearing on the surface.

As regards the source for alkali basalts it may be instructive that alkali basalts in Iceland do not carry any nodules with high pressure mineralogy. If alkali basalts are formed in areas where crustal thickness is several tens of kilometers nodules with high pressure mineralogy and crustal magma genesis need not be incompatible.

#### FOOTNOTE TO DISCUSSION

<sup>1</sup>Row E. C. and SCHILLING J.-G. (1979) Fluorine in Iceland and Reykjanes Ridge basalts *Nature* **279**, 33–37.

