

INTERPRETATION OF VOLCANIC GAS DATA FROM
THOLEIITIC AND ALKALINE MAFIC LAVAS*

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The chemistry of magmatic volatiles is of significance to several fundamental geochemical questions, including aspects of the origin of magmas, ore deposits, and the atmosphere, hydrosphere, and biosphere. In recent years, environmental problems and the need for an eruption prediction and monitoring technology have also contributed to an interest in the chemistry of magmatic gases.

The extreme range of compositions displayed by volcanic gas analyses has complicated attempts to apply volcanic gas data to the above problems. This obstacle persists even in analyses of gases collected at high temperatures in the source regions of actively degassing lavas. The variability is partly from chemical alterations imposed on samples during collection, which are often related to the trying circumstances under which the collections are obtained.

Several computational techniques have recently been introduced for identifying imposed alterations and for restoring the analyses to compositions more representative of the erupted

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gases (Gerlach, 1979, 1980A, 1980B, 1980C, 1980D, 1980E). Approximately 150 restored analyses have been obtained for previously reported collections of high-temperature volcanic gases from basic lavas. The data sources, collection temperatures, and pertinent petrological information are presented in Table I. Consideration has been restricted to those samples collected from actively degassing lava at temperatures above 950°C in the vicinity of vents. These restrictions increase the probability of a magmatic origin; they do not insure, however, that the gases are juvenile (i.e., reaching the surface for the first time).

Note that the restrictions employed here limit consideration to gases associated with tholeiitic and alkaline lavas. Unfortunately, high-quality gas data for calcalkaline lavas, which probably exhale the largest proportion of the earth's outgassed product, are much less abundant.

Chemical Characteristics of Volcanic Gases from Mafic Lavas

Secondary alterations imposed on volcanic gas samples produce much of the variability in the reported analyses of gases from mafic lavas (Table I). The common alterations include:

- (1) contamination by the atmosphere, organic matter, and meteoric water;
- (2) oxidation of H_2 , H_2S , S_2 , SO_2 , and CO by atmospheric O_2 ;
- (3) reactions of HCl , H_2O , CO_2 , SO_2 , and H_2S with metallic components sometimes used in sampling devices;
- (4) condensation and reevaporation of water and sulfur in lead-in tubes to sample containers.

Analytical errors, especially for H_2O , are also common, and in several instances the analyses are incomplete with respect to important minor species such as H_2 , CO , H_2S , COS , HCl , and HF .

The restoration procedures for imposed secondary alterations are discussed in detail elsewhere (Gerlach, 1979, 1980A, 1980B, 1980C, 1980D, 1980E).

Table II summarizes the maximum and minimum concentrations of individual species in the highest quality restored analyses for each series of contemporaneous samples from a common collection site. The variations remaining after corrections for secondary alterations are emphasized by this tabulation procedure. Where samples in a collection series are from different sites, the variations remaining in the results are indicated by selected restored analyses. For example, J-8, J-13, and J-11 in Table II are respectively the most CO_2 -rich, H_2O -rich, and SO_2 -rich restored analyses for the Kilauea J-series samples, which were collected from several sites around Halemaumau in 1918 and 1919. Further explanatory details can be found in the notes to Table II.

In addition to the species shown in Table II, the restored analyses also contain minor and trace amounts of COS , SO , S_2O , and HS . The erupted gases undoubtedly also contained minor amounts of N_2 , HF , HBr , HI , rare gases, and metal halogens. Hydrocarbons and organohalogenes (e.g., CH_3Cl) are not present.

The O_2 and S_2 fugacities of the restored analyses are shown at the collection temperatures in Figures 1 and 2. Lavas tend

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to have O_2 fugacities ranging from somewhat below the quartz-magnetite-fayalite O_2 buffer (QMF, Wones and Gilbert, 1969) to the nickel-nickel oxide O_2 buffer (NNO, Huebner and Sato, 1970). This range is illustrated in Figure 1 and has been established from experimental studies (e.g., Fudali, 1965), field measurements on degassing lavas (e.g., Sato and Wright, 1966), and microprobe investigations of iron-titanium oxides (e.g., Carmichael and Nicholls, 1967; Carmichael, et al., 1974). The O_2 fugacities calculated for the restored volcanic gas analyses (Figure 1) corroborate these results.

The dotted line in Figure 1 traces the change in O_2 fugacity for the closed system system cooling of ^atypical volcanic gas from Erta Ale lava lake. The f_{O_2} of the cooling gas decreases less sharply than f_{O_2} along NNO or QMF. This characteristic is typical of calculated closed system f_{O_2} -T paths for volcanic gas compositions. The restored series of samples collected over a range of temperatures, however, have O_2 fugacities (Figure 1) more or less paralleling the buffer curves (e.g., the data for Hawaii, Nyiragongo and Erta Ale). This suggests lavas tend to buffer the O_2 fugacities of their associated gases.

Gerlach and Nordlie (1975A, 1975B) calculated the limiting compositions of volcanic gases by bounding all atomic compositions in the C-O-H-S tetrahedron with O_2 fugacities between QMF and NNO for the temperature range 1250°C to 800°C. The restored analyses in Table II are consistent with their results, which may be summarized as follows:

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- (1) A wide range of compositions is possible from H₂O-rich to CO₂-rich to SO₂-rich.
 - (2) H₂O and CO₂ are the principal hydrogen and carbon species at any reasonable temperature and O₂ fugacity.
 - (3) The concentrations of minor species (H₂, CO, S₂, COS, SO, S₂O, HS; etc.) are extremely sensitive to temperature and O₂ fugacity within the QMF-NNO bounded region.
 - (4) SO₂ and H₂S can be a major or minor species, depending on temperature, O₂ fugacity, and water content of the gas. SO₂ is favored by temperatures above 800°C, O₂ fugacities above QMF, and relatively anhydrous conditions; H₂S is increasingly favored by lower temperatures, lower O₂ fugacities and higher water content. (e.g., Nyiragongo restored data).
 - (5) Hydrocarbons, including CH₄, are virtually non-existent at all conditions investigated.

Evidence for short-term variations almost disappears after corrections are made for secondary alterations. Each series of restored analyses for Surtsey, Erta Ale, Ardoukoba, Mount Etna, and Nyiragongo gives consistent compositions. This is quite unlike the original analytical data, which frequently display large chemical variations for gases sampled over periods of minutes to hours from a common collection site. For example, the reported H₂O content ranged from 8% to 52% for the 1971 Erta Ale analyses,

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From 70% to 85% for the 1974 Erta Ale analyses, and from 0% to 30% for the Mount Etna analyses.

Problems for Future Research

The hazards and uncontrollable circumstances under which volcanic gases are collected give rise to many of the secondary modifications in volcanic gas data. There is no practical way to completely circumvent these problems, even with modern collection and analytical equipment. It will continue to be necessary, therefore, to use restoration procedures such as those developed by the author to assess and remove secondary alterations from analytical data. Modern equipment (e.g., LeGuern et al., 1979A) will, however, undoubtedly decrease concern over analytical errors, and allow geochemists studying volcanic gases to focus on broader problems in addition to those of analytical technique.

There are, nevertheless, several problems that will foster further interest in analytical methods. Perhaps the most important of these is the need to routinely obtain stable isotope data (C, H, O, S) along with chemical analyses of high temperature volcanic gases. There is little such data at present, and they are essential to identifying the ultimate source of volcanic volatiles. They would also be a valuable aid to restoration calculations.

The restoration of volcanic gas data for imposed modifications causing disequilibrium compositions (e.g., mixing of magmatic gases with meteoric steam) requires accurate data for H_2 , CO , H_2S , and S_2 . These species are generally present at low

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concentrations, and are often not reported in analyses. Restorations are impossible without these data, and every effort should be made to obtain them in future studies. Restorations of volcanic gas data would also be greatly aided by O_2 fugacity measurements in the gas streams from which collections are made. An example of the utility of O_2 fugacity data can be found in the restoration of the 1970 Mount Etna data (Huntington, 1973; Gerlach, 1979).

There are several minor and trace species that have environmental and scientific significance, and that should be measured more often than they have been in the past. These include CO_S , CS_2 , HCl , HF , hydrocarbons, and halogenated hydrocarbons. Thermodynamic calculations indicate that hydrocarbons and halogenated hydrocarbons would not be stable under most volcanic conditions (Gerlach, 1980D). These compounds have, nevertheless, been reported in volcanic gas analyses. It is presently unclear whether they are magmatic in origin, or the products of interactions between lavas and near surface sources of organic material. The latter appears to be the case, but more data are needed. There is a great need for data on metal halogens in order to appraise the significance of volcanic gas transport of metals. These data would also have potential applications to ore deposit geochemistry. Finally, there is little chemical or isotopic data available for nitrogen and inert gases released by erupting lava. It must be stressed that

data for minor and trace species in volcanic gases have severely limited scientific value if they are not obtained in conjunction with data for major species.

Past experience is consistent with the hypothesis that volcanic gases are initially near equilibrium and that reaction equilibria are essentially quenched during collection. This hypothesis needs to be checked in detail with modern field analytical equipment to determine the temperature limits for which equilibrium can reasonably be assumed and to examine the extent of retrograde reactions in sampled gases. It would be of interest to know if various gas reaction equilibria tend to quench at similar or dissimilar temperatures, and whether certain sampling and analytical devices cause catalytic effects giving a misleading impression about the approach of erupted gases to equilibrium.

Several experimental studies in recent years have demonstrated that partial melts of mantle peridotite in the presence of high CO_2 pressures are poorer in silica than those formed at low CO_2 pressures, and it appears that CO_2 may play an important role in the generation of alkalic subsilicic magmas (Wyllie, 1979). The restored analyses (Table II) suggest a tendency for alkaline lavas to be associated with higher CO_2 concentrations, but much more data are needed for statistically significant generalizations. The gases from relatively alkaline lavas at Mount Etna and Nyiragongo are comparatively rich in CO_2 , and those from tholeiitic lavas tend to be H_2O rich. Tholeiitic lavas are not necessarily CO_2 poor, however; Kilauea gases can contain up to

50% CO_2 . It should also be noted that the Surtsey gases are very H_2O rich in spite of their association with alkali basalt lavas.

Calcalkaline lavas of volcanic arcs and continental margins are probably responsible for most of the volatiles released from the earth's interior. Gas data for these lavas are very limited, and every effort should be made to sample gases from such lavas in the future. It is interesting to note that the restored analyses for alkaline and tholeiitic lavas (Table II) bear no resemblance to the "excess volatiles" of the earth, which require an abundant source with a distinctly different composition ($\text{H/C} = 36$, $\text{S/C} = .02$).

Thermodynamic calculations indicate that the total sulfur content of exsolved gases from mafic lavas will increase with melt O_2 fugacity (Gerlach, unpublished calculations). And indeed, a correlation exists in the restored analyses (Table II) between total sulfur and relative O_2 fugacity (Figure 3). The data in Figure 3 have been normalized for the strong temperature dependence of O_2 fugacity (Figure 1) by calculating f_{O_2} of the restored analyses relative to the QMF buffer at the collection temperatures:

$$\text{Log}(f_{\text{O}_2}/\text{QMF}) = \text{Log}(f_{\text{O}_2})_{\text{sample}} - \text{Log}(f_{\text{O}_2})_{\text{QMF}}$$

Because most of the sulfur released from erupting mafic lavas is SO_2 , and therefore environmentally hazardous, future observations should be directed towards testing and refining the relationship

suggested in Figure 3 between total sulfur and lava O_2 fugacity.

There is little reason to expect a single gas composition to be exhaled from all basic magmas, even if they initially contained similar concentrations of volatile components. Differences in the solubilities of volatile components, in the extent of crystallization and differentiation, in the depths of degassing, in the rates of magma resupply and circulation in shallow magma chambers or lava lakes, and in the time elapsed since emplacement or extrusion are all factors that can cause chemical variations in the gases exhaled during an eruption. Indeed, it is probable that during a period of degassing at a fixed depth or during upward migration of magma, a wide spectrum of gas compositions develops in terms of the principal magmatic volatiles - H_2O , CO_2 , SO_2 .

Diagrams of atomic H/C vs. S/C (Figure 4) clearly illustrate major trends related to variations in the principal magmatic volatiles of the restored analyses (Table II). Variations related chiefly by H_2O content produce vertical trend lines on such diagrams; those related by SO_2 content follow horizontal trend lines; and those related by CO_2 content follow diagonal lines. When the original analyses for the gas collections under consideration are plotted on these diagrams, a scattered result is obtained. Plots of the restored analyses display consistent and revealing trends.

It is evident from Figure 4 that the variations within the restored analyses from each volcano are primarily due to

differences in CO_2 content. The variations in atomic H/C and S/C show a relationship to CO_2 content indicated in Figure 4 by dashed control lines. The increasing H/C and S/C along each control line reflects the changes in the atomic composition of an initial gas as CO_2 decreases, or as H_2O and SO_2 progressively increase. The CO_2 -related trends, although crude in some cases, are obviously more conspicuous than are trends due solely to changes in H_2O or SO_2 .

The CO_2 control line for the Surtsey data is based on the restored analysis for the most CO_2 -rich 1964 sample, which is related to the 1965 and 1967 restored analyses by progressive decrease in CO_2 . The control line for the Erta Ale data is based on the means of the restored 1971 and 1973 data. It nearly passes through the mean of the 1974 data after a small decrease in CO_2 . It is significant that the Ardoukoba gases are lower in CO_2 than the Erta Ale gases and lie near an extension of the Erta Ale CO_2 control line. The Erta Ale and Ardoukoba gases have a similar origin in certain respects; each was erupted from similar basaltic lavas under conditions of crustal spreading in the Afar Triangle region. Unlike the Erta Ale gases, however, which were released from a large resupplied lava lake, the Ardoukoba gases were collected during the last stage of an eruptive event involving a small body of lava. The atomic H/C and S/C for the restored Kilauea J-series show a rough relationship to a CO_2 control line based on removal of CO_2 from J-8, the most CO_2 -rich gas of the series. An extension of this control

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line also passes near two samples taken from Makaopuhi lava lake; these two samples were reported to be the "best" samples, i.e., most representative, obtained from the Makaopuhi lava (Finlayson et al., 1968). It has been shown (Gerlach, 1979D) that other Kilauea gas samples reported by Heald, et al. (1963) also plot near this CO_2 control line. The restored analyses from Mount Etna and Nyiragongo show relatively constant compositions. There is some suggestion, however, of a trend parallel to a CO_2 control line in the Mount Etna data.

There are several interpretations that can be advanced for the tendency of gases from a given volcano or common eruptive source to follow CO_2 control lines. All such interpretations invoke the much lower solubility of CO_2 , compared to water and sulfur, in mafic silicate melts at low to moderate pressures. For example, the progressive decrease in CO_2 with time in the Surtsey gases may be due to preferential degassing (fractionation) of CO_2 from magma at depth over the period 1964 to 1967. Likewise, the comparatively CO_2 -poor Ardoukoba gases may approximate the equivalent of gases from nearly degassed lava of Erta Ale lava lake. Alternatively, the more CO_2 -rich Surtsey gases may simply represent volatiles exsolved at greater depths compared to shallower degassing depths for the more CO_2 -poor and H_2O -rich gases. And, the differences between the Ardoukoba and Erta Ale gases may indicate a greater depth of gas exsolution for the latter.

In some cases a more complex explanation involving both the above interpretations appears necessary. There is no

evidence, for example, of a simple time- or depth-related variation in the 1918 and 1919 Kilauea gases. These gases were collected from several sites around Halemaumau, and the restored analyses indicate that a considerable range of gas compositions was outgassing from the lava lake on each occasion. The variations in these gases are probably related to differences in the rates of supply of gas-saturated melt to various locations around Halemaumau, to channeling of bubbles exsolved from saturated melt at different depths, to differences in degree of lava crystallization, and to differences in the time elapsed since extrusion of lava at the various sites from which the samples were obtained.

While it is unlikely that the ranges of compositions shown by the restored analyses in Figure 4 includes the complete spectrum of gas compositions released by mafic lavas, they do suggest certain features of erupted gases that may characterize the initiation, continuation and termination of volcanic activity. Gases released just preceding eruptions are likely to originate from gas-charged magma at depth. These gases may be richer in CO_2 than any of the restored analyses in Table II and have compositions at lower atomic H/C and S/C along extrapolations of the CO_2 trend lines in Figure 4. The gases released during the termination of activity are likely to be more "evolved", or of shallower origin, and have compositions extrapolated to higher atomic H/C and S/C along the CO_2 trend lines in Figure 4. During a prolonged continuation of volcanic activity, gases from resupplied shallow magma chambers or lava lakes, such as Erta

✓ Ale, may oscillate on CO₂ control lines as fresh magma is periodically added and subsequently degasses^d.

The above explanation appears to account in large part for the CO₂ trends observed in the restored volcanic gas data and for the observation that submarine tholeiite basalts contain CO₂ rich vesicles, while surface eruptions of similar material (e.g., Erta Ale and Ardoukoba) produce gases richer in H₂O and sulfur. The increasing total sulfur with relative f_{O₂} (Figure 3) for the Surtsey, Erta Ale-Ardoukoba, Kilauea, and Etna gases, respectively, is tentatively interpreted to be partly responsible for the progressive shift in the CO₂ control lines for these gases towards higher atomic S/C in Figure 4.

Further studies need to be made to confirm the CO₂ degassing trends and to evaluate their application in volcano monitoring and eruption prediction. Detailed studies of CO₂ trends during the complete course of a single eruption are particularly desirable. It will undoubtedly prove more tractable to develop monitoring techniques during eruptions of mafic lavas, eruptions of more siliceous lavas being too dangerous for such purposes. sp

u In addition to the research problems outlined above dealing with the composition of volcanic gases and their relationship to lava chemistry, there is also a need for accurate data on the volume of gases released during eruptions. It would be especially interesting to know if the volumes of gases released during eruption periods are compatible with the volumes of lava involved in the eruption, or if they require much larger sources at depth.

If the latter is true, then distillation of volatiles from magma bodies at depth - and possibly from the mantle - during volcanic eruptions could be an important mechanism in magmatic evolution and in causing eruptions.

REFERENCES

- Allard, P., Tazieff, H. and Dajlevic, D., 1979. Observations of Sea Floor Spreading in Afar During the November 1978 Fissure Eruption. *Nature*, 279:30-33.
- Carmichael, I. S. E., Turner, F. J., and Verhoogen, J., 1974. *Igneous Petrology*. McGraw-Hill, Inc., New York, 739 pp.
- Carmichael, I. S. E. and Nicholls, J., 1967. Iron-Titanium Oxides and Oxygen Fugacities in Volcanic Rocks. *Jr. Geoph. Res.*, 72:4665-4687.
- Chaigneau, J., Tazieff, H. and Febre, R., 1960. Composition des Gaz Volcaniques du Lac de Lave Permanent due Nyiragongo (Congo Belge). *C. R. Acad. Sci. Paris*, 250:2482-2485.
- Eugster, H. P. and Wones, D. R., 1962. Stability Relations of the Ferruginous Biotite, Annite. *Jr. Petrol.*, 3:82-125.
- Finlayson, J. B., Barnes, I. L., and Naughton, J. J., 1968. Developments in Volcanic Gas Research in Hawaii. In: *The Crust and Upper Mantle of the Pacific Area*, Amer. Geophys. Un., Geophys. Monogr. No. 12:428-438.
- Fudali, R. F., 1965. Oxygen Fugacity of Basaltic and Andesitic Magmas. *Geochim. et Cosmochim. Acta.*, 29:1063-1075.
- Gerlach, T. M. 1979. Evaluation and Restoration of the 1970 Volcanic Gas Analyses from Mount Etna, Sicily. *Jr. Volc. Geoth. Res.*, 6:165-178.
- Gerlach, T. M., 1980A. Investigation of Volcanic Gas Analyses and Magma Outgassing from Erta Ale Lava Lake, Afar, Ethiopia. *Jr. Volc. Geoth. Res.*, in press.
- Gerlach, T. M., 1980B. Evaluation of Volcanic Gas Analyses from Surtsey Volcano, Iceland, 1964-1967. *Jr. Volc. Geoth. Res.*, in press.
- Gerlach, T. M., 1980C. Chemical Characteristics of the Volcanic Gases from Nyiragongo Lava Lake, and the Generation of CH₄-Rich Fluid Inclusions in Alkaline Rocks. *Jr. Volc. Geoth. Res.*, in press.
- Gerlach, T. M., 1980D. Evaluation of Volcanic Gas Analyses from Kilauea Volcano. *Jr. Volc. Geoth. Res.*, 7, 295-317.
- Gerlach, T. M., 1980E. Restoration of New Volcanic Gas Analyses from Basalts of the Afar Region: Further Evidence of CO₂-Degassing Trends. *Jr. Volc. Geoth. Res.*, in press.

- Gerlach, T. M. and Nordlie, B. E., 1975A. The C-O-H-S Gaseous System, Part I: Composition Limits and Trends in Basaltic Gases. *Am. Jr. Sci.*, 275:353-376.
- Gerlach, T. M. and Nordlie, B. E., 1975B. The C-O-H-S Gaseous System, Part II: Temperature, Atomic Composition and Molecular Equilibria in Volcanic Gases. *Am. Jr. Sci.*, 275:377-394.
- Giggenbach, W. F. and LeGuern, F., 1976. The Chemistry of Magmatic Gases from Erta Ale, Ethiopia. *Geochim. et Cosmochim. Acta*, 40:25-30.
- Heald, E. F., Naughton, J. J. and Barnes, I. F., 1963. The Chemistry of Volcanic Gases. 2. Use of Equilibrium Calculations in the Interpretation of Volcanic Gas Samples. *Jr. Geophys. Res.*, 68:545-557.
- Huebner, J. S. and Sato, M., 1970. The Oxygen Fugacity - Temperature Relationships of Manganese Oxide and Nickel Oxide Buffers. *Am. Mineral.*, 55:934-952.
- Huntingdon, A. T., 1973. The Collection and Analysis of Volcanic Gases from Mount Etna. *Phil. Trans. R. Soc. Lond.*, A274:119-128.
- Irvine, T. N. and Baragar, W. R. A., 1971. A Guide to the Chemical Classification of the Common Volcanic Rocks. *Can. Jr. Earth Sci.*, 8:523-548.
- LeGuern, F., Biccocchi, P., Nohl, A., and Tazieff, H., 1979A. Analyse directe des gaz volcaniques. *C. R. Acad. Sci. Paris*, 288D:867-870.
- LeGuern, F., Carbonnelle, J. and Tazieff, H., 1979. Erta Ale Lava Lake: Heat and Gas Transfer to the Atmosphere. *Jr. Volc. Geoth. Res.*, 6:27-48.
- LeGuern, F., Tazieff, H., Vavasseur, C., and Carbonnelle, J., 1977. Heat and Gas Transfer from Nyiragongo Lava Lake. (Abst.), *EOS, Trans. Am. Geoph. Un.*, 58:920.
- LeGuern, F., Giggenbach, W. F., Tazieff, H. and Zettwoog, P., 1975. Etude des Fluctuations de la Phase Gazeuse à l'étang de Lava Erta Ale (Ethiopia) (Janvier 1973). *D. R. Acad. Sci. Paris*, 280D: 1959-1962.
- Sato, M. and Wright, T. L., 1966. Oxygen Fugacities Directly Measured in Magmatic Gases. *Science*, 153:1103-1105.

Shepherd, E. S., 1921. Kilauea Gases, 1919. Hawaiian Volcano Observatory Bull., 9:83-88.

Sigvaldason, G. E. and Elisson, G., 1968. Collection and Analysis of Volcanic Gases at Surtsey, Iceland. Geochim. Acta, 32:797-805.

Tazieff, H., LeGuern, F., Carbonnelle, J. and Zettwoog, P., 1972. Etude Chimique des Fluctuations des Gaz Eruptifs de Volcan Erta Ale (Afar, Ethiopia). C. R. Acad. Sci. Paris, 274D:1003-1006.

Wones, D. R. and Gilbert, M. C., 1969. The Fayalite-Magnetite-Quartz Assemblage Between 600°C and 800°C. Am. Jr. Sci., 267-A:480-488.

Wyllie, P. J., 1979. Magmas and Volatile Components. Am. Min., 64:469-500.

TABLE I. RESTORABLE HIGH TEMPERATURE VOLCANIC GAS ANALYSES

	<u>Lava¹ Type</u>	<u>Collection Temperature (°C)</u>	<u>Restorable Analyses</u>	<u>Sources of Data</u>
Surtsey (1964)	Alkali Basalt	1125	2	Sigvaldason and Elisson (1968)
Surtsey (1965)	" "	"	3	Sigvaldason and Elisson (1968)
Surtsey (1967)	" "	"	3	Sigvaldason and Elisson (1968)
Erta Ale (1971)	Tholeiite Basalt	1075	20	Tazieff et al. (1972) LeGuern et al. (1979)
Erta Ale (1973)				
hornito 1	" "	1100	22	LeGuern et al. (1975, 1979)
hornito 2	" "	1210	25	" "
Erta Ale (1974)	" "	1130	41	Giggenbach and LeGuern (1976), LeGuern et al. (1979)
Ardoukoba (1978)	Tholeiite Basalt (?)	1070	3	Allard et al. (1979)
Kilauea (1918-19)	Tholeiite Basalt	1185-1085	7	Shepherd (1921)
Mount Etna (1970)	Hawaiite	1075	9	Huntingdon (1973)
hornitos 1 and 2				
Nyiragongo (1959)	Melilite Nephelinite	1020-960	3	Chaigneau et al. (1960)
		Total =	138	

1. Lavas classified according to system of Irvine and Baragar (1971).

TABLE II. COMPOSITION RANGES FOR RESTORED HIGH-TEMPERATURE VOLCANIC GASES (Mole %)

	H ₂ O	H ₂	CO ₂	CO	SO ₂	S ₂	H ₂ S	HCl	T (°C)
Surtsey ^a									
1964	81.13	2.77	9.29	0.69	3.15	0.13	0.64	0.81	1125
	81.98	2.80	9.79	0.71	4.12	0.25	0.89		
1965	87.40	2.27	5.01	0.36	2.43	0.03	0.24	0.40	1125
	87.88	3.12	6.43	0.39	2.72	0.10	0.63	0.43	
1967	91.11	1.42	1.21	0.05	2.81	0.01	0.06	0.52	1125
	92.47	1.74	3.31	0.11	3.74	0.02	0.15	1.16	
Erta Ale ^b									
1971	66.99	1.51	16.13	0.71	7.80	0.41	0.85	nd	1075
	71.65	1.62	18.88	0.83	10.17	0.68	1.10	nd	
1973(1)	71.28	2.09	19.42	1.17	4.91	0.28	0.82	nd	1100
1973(3)	70.35	2.36	18.42	1.55	6.74	0.15	0.38	nd	1210
1974	75.06	1.39	10.92	0.44	6.46	0.21	0.68	0.42	1130
	78.28	1.76	13.08	0.60	8.34	0.36	1.08		
Ardoukoba ^c									
	76.05	1.68	3.39	0.14	12.94	1.07	1.57	nd	1070
	78.71	1.73	4.02	0.17	15.38	1.51	1.80	nd	
Kilauea ^d									
J-8	37.09	0.49	48.90	1.51	11.84	0.02	0.04	0.08	1170
J-13	69.29	1.01	17.82	0.62	10.93	0.03	0.08	0.21	1175
J-11	40.14	0.55	36.69	1.03	21.06	0.25	0.20	0.00	1100
Mount Etna ^e									
	43.09	0.46	17.08	0.36	24.86	0.21	0.20	nd	1075
	49.91	0.54	26.06	0.54	33.54	0.38	0.27	nd	
Nyiragongo ^f									
2	43.50	1.29	48.55	2.20	2.02	0.62	1.72	nd	970
12	45.90	1.59	45.44	2.70	2.30	0.55	1.41	nd	1020
nd: not determined									

Table II Footnotes

a. Based on Gerlach (1980B).

b. Based on Gerlach (1980A). Erta Ale gases also can contain up to 0.03 mole % COS. 1973(1) and 1973(3) are means of restored analyses for data reported by LeGuern et al. (1975, 1979) for hornitos 1 and 3, respectively.

c. Based on Gerlach (1980E).

d. Based on Gerlach (1980D). Restored analyses given for most CO₂-rich (J-8), most H₂O-rich (J-13), and most SO₂-rich (J-11). Sample numbers same as Shepherd (1921).

e. Based on restored 1970 analyses for hornitos 1 and 2 (Gerlach, 1979). Etna gases also contain up to 0.04 mole % SO.

f. Restored 1959 analyses for samples 2 and 12 (Gerlach, (1980C). Results are corroborated by analyses obtained for Nyiragongo lava lake gases in 1972 (LeGuern et al., 1977). Sample numbers same as Chaigneau et al. (1960).

FIGURE CAPTIONS

Figure 1

Representative O₂ fugacities at collection temperatures for restored volcanic gas analyses, Tables I and II: + (Surtsey 1964, 1965, 1967); ○ (Erta Ale lava lake 1971, 1973, 1974); □ (Ardoukoba 1978); ◇ (Kilauea 1918, 1919); × (Mount Etna 1970); △ (Nyiragongo 1959). The Nyiragongo analyses yielded several O₂ fugacity estimates even though only two analyses gave reliable restorations. The dotted line shows the O₂ fugacity of a typical Erta Ale lava lake volcanic gas during cooling from 1150°C at 1 bar total pressure. NNO, QMF, and MW refer to the nickel-nickel oxide, quartz-magnetite-fayalite, and the wustite-magnetite O₂ buffers, respectively (Huebner and Sato, 1970; Wones and Gilbert, 1969; Eugster and Wpnes, 1962).

Figure 2

Representative S₂ fugacities at collection temperatures for restored volcanic gas analyses, Tables I and II: △ (Surtsey 1964, 1965, 1967); □ (Erta Ale lava lake 1971, 1973, 1974); ○ (Ardoukoba 1978); + (Kilauea 1918, 1919); ◇ (Mount Etna 1970); × (Nyiragongo 1959).

Figure 3 Total sulfur vs O₂ fugacity for the restored volcanic gas analyses (Tables I and II) normalized to the quartz-magnetite-fayalite O₂ buffer (QMF, Wones, and Gilbert, 1969). The normalized O₂ fugacity is given by $LOG(f_{O_2}/QMF) = Log(f_{O_2})_{SAMPLE} - Log(f_{O_2})_{QMF}$ at the collection temperatures for the samples: □ (Surtsey 1964, 1965, 1967 mean values); X (Erta Ale lava lake 1971 mean value); † (Erta Ale lava lake, hornitos 1 and 3, 1973 mean values); ▽ (Erta Ale lava lake 1974 mean value); △ (Ardoukoba 1978 mean value); ⊠ (Kilauea 1918, 1919); ◇ (Mount Etna 1970 mean value); ○ (Nyiragongo 1959). The ranges in total sulfur and LOG(fO₂/QMF), where mean values have been used, fall within symbol areas unless otherwise indicated by horizontal and vertical dashed lines.

Figure 4 Atomic H/C vs atomic S/C for the restored volcanic gas analyses, Tables I and II: △ (Surtsey 1964, 1965, 1967, all restored data); □ (Erta Ale 1971, 1973, 1974, means of restored data); ○ (Ardoukoba 1978, all restored data); X (Kilauea 1918, 1919, all restored data); † (Kilauea 1965, "best" samples of Finlayson et al., 1968); ◇ (Mount Etna 1970, all

restored data for fumaroles 1 and 2); ▽ (Nyiragongo
1959, points show range in H/C and S/C for restored
analyses). Dashed lines are control lines showing
increase in H/C and S/C resulting from removal of
CO₂ from Surtsey sample 13, from the mean of the
1971-1973 Erta Ale lava lake gases, and from Kilauea
sample J-8.

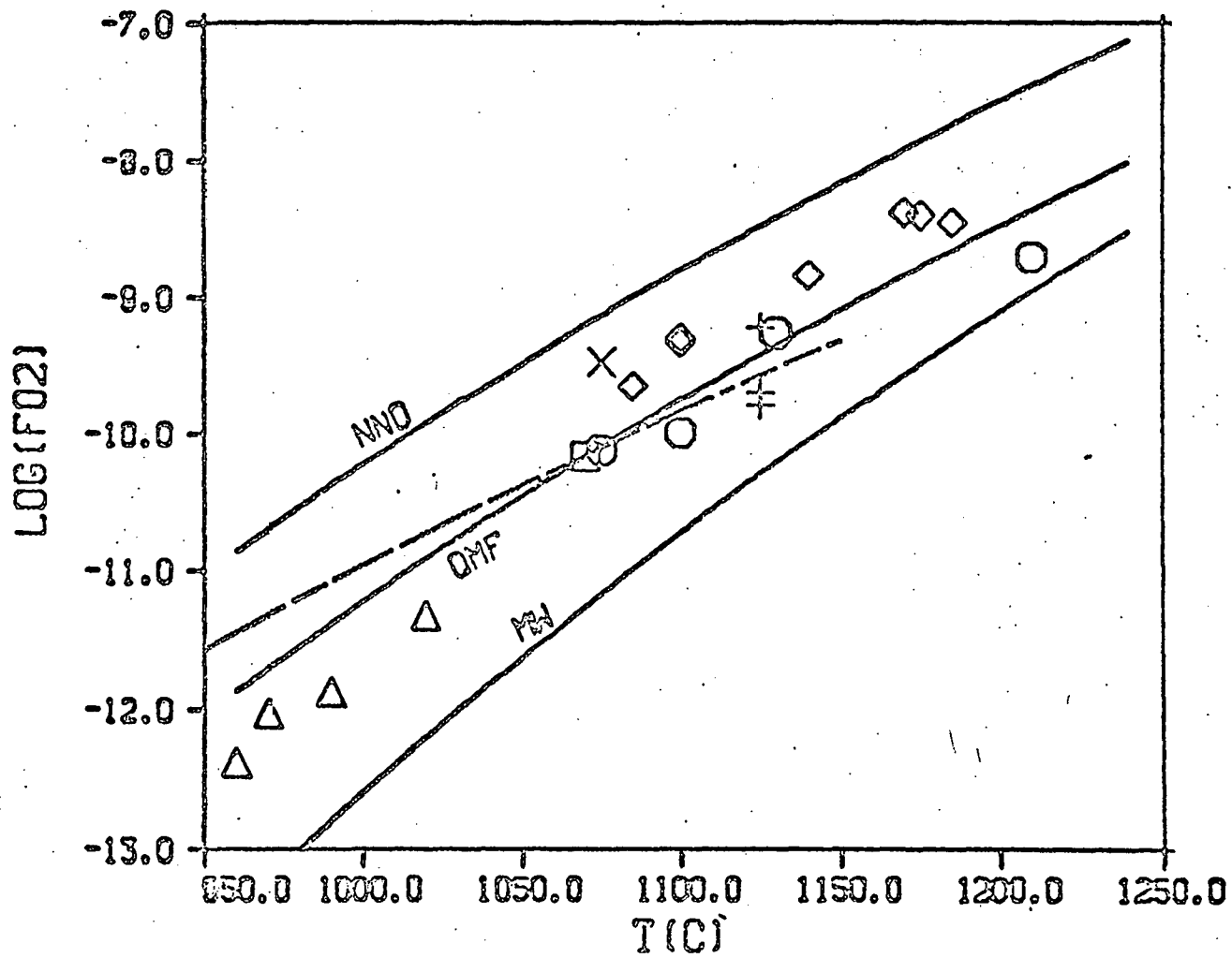


Figure 1

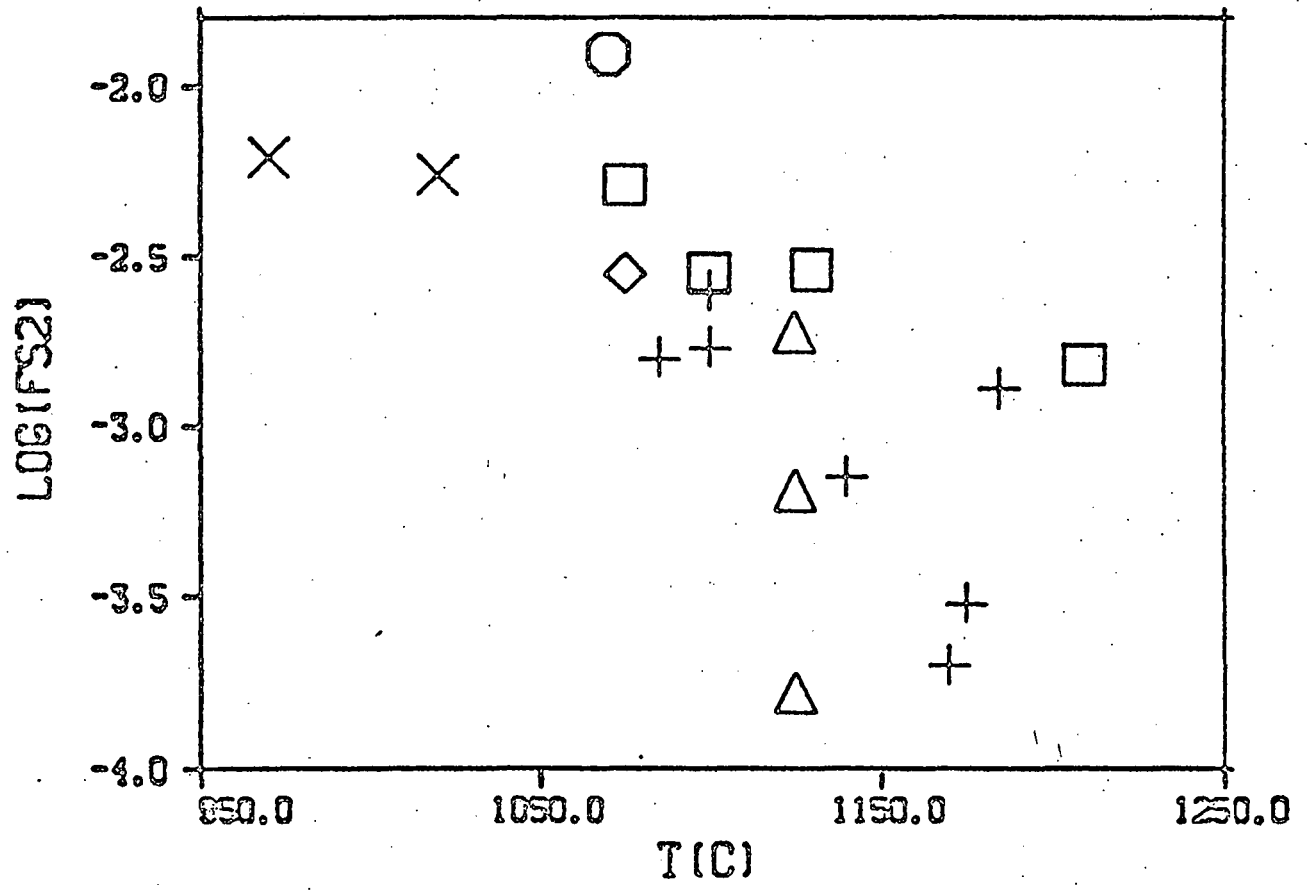


Figure 2

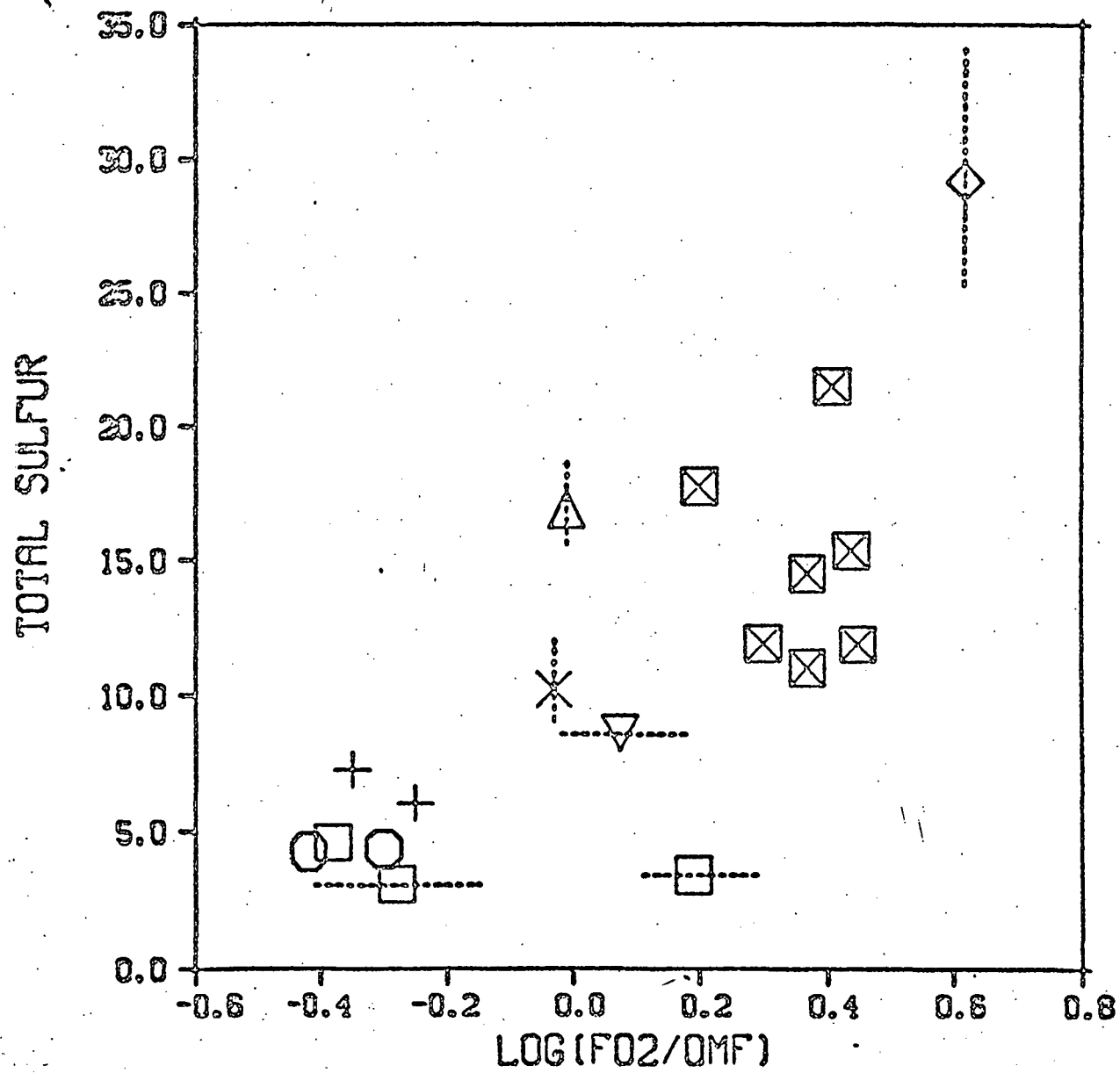


Figure 3

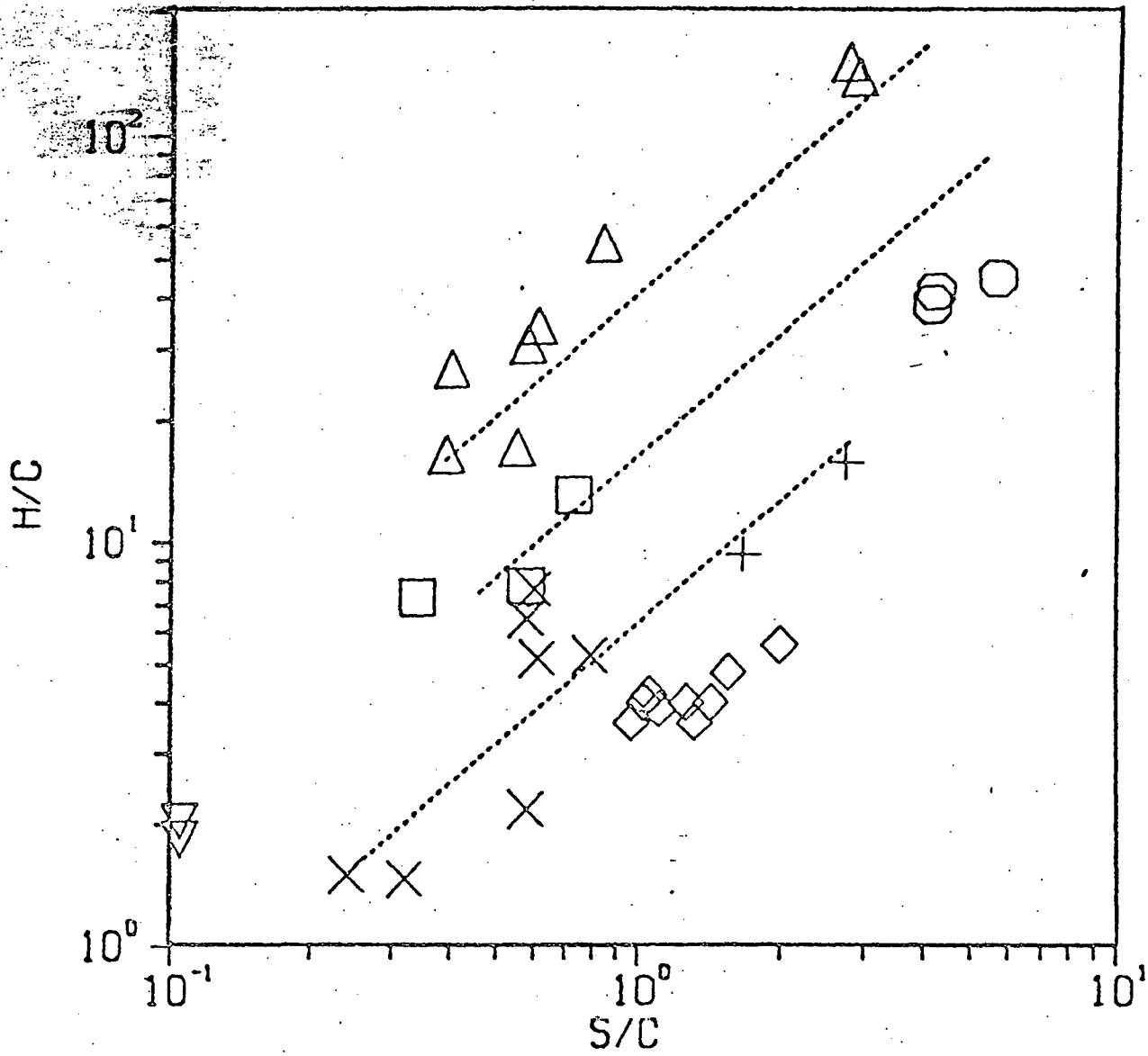


Figure 4