Light hydrocarbons in volcanic gases from the Japanese island arc

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Light hydrocarbon contents were determined for volcanic and geothermal gases from the Japanese island arc volcanoes. C₁–C₄ alkanes and C₂ alkene were detected, independent of fumarolic and downhole temperature. On the basis of the abundance ratios of alkanes and alkene relative to methane, the volcanic hydrocarbons are classified mainly into the fumarolic type of inorganic origin and the volcanic geothermal type of thermogenic origin.

Thermodynamic calculations are made for the reactions of inorganic hydrocarbons under redox condition governed by a variety of mineral buffer systems. The results indicate that the amounts of alkanes and alkene depend essentially on the oxygen fugacity rather than temperature or other factors such as $f_{\text{H}_2\text{O}}$ and f_{CO_2} . The concentrations of volcanic light hydrocarbons are probably controlled by redox conditions during the discharge process as well as equilibrium with magma.

INTRODUCTION

Many geochemical studies on volcanic gases have been performed to determine the behavior and origin of volatile discharges such as water, carbon dioxide and sulfur compounds. For example, the magma gas components have been discussed in terms of their thermodynamic equilibrium (e.g., Ellis, 1959; Matsuo, 1960; Gerlach and Nordlie, 1975). Furthermore, the isotopic studies of steam condensates from andesitic volcanoes suggest that the water in these volcanic gases is a mixture of magmatic and meteoric waters (Mizutani, 1978; Viglino *et al.*, 1985; Mizutani *et al.*, 1986; Taran, 1990). However, the origin of carbon and sulfur compounds found in volcanic gases has not yet been made clear.

Except for CH₄, light hydrocarbons are minor components of volcanic gases and have rarely been investigated. Until recently, a few studies on volcanic light hydrocarbons have been reported (Stoiber *et al.*, 1971; Markhim *et al.*, 1977; Nehring and Truesdell, 1978; Giggenbach *et al.*,

1990). The results indicate that alkanes and alkenes were detected as volcanic hydrocarbons and are probably derived from the thermal decomposition of organic matter in the basement sedimentary rocks which surround the volcanoes. However, it is poorly known whether these light hydrocarbons are also of inorganic or thermogenic origin.

In the present study, light hydrocarbons found in volcanic gases from dacitic and andesitic volcanoes in the Japanese islands are analyzed and their origin and evolution are discussed.

EXPERIMENTAL

Sampling

Fumarolic and geothermal well gas samples were collected from some volcanic areas as shown in Fig. 1. More detailed information on the geology and geochemistry of these areas was summarized by Mizutani (1978), Mizutani *et al.* (1986), Kiyosu (1983, 1986), Kiyosu and Yoshida (1988) and Asada (1993). The sampling method used was a modification of that discussed by Ozawa (1966).

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Fig. 1. Locations of volcanoes and geothermal systems, the Japanese island arc, from which gas samples were collected. Open and closed circles represent volcanoes and geothermal systems, respectively.

Gas samples were absorbed in a water-cooled 6 N KOH solution. The dissolved H_2S was immediately fixed as CdS in order to prevent oxidation over short time periods (Kiyosu, 1983). The fumarolic temperature at the time of the gas collection was determined with the use of a thermocouple and/or a mercury thermometer.

Analytical procedures

The analytical method of water, carbon dioxide, sulfur compounds (SO_2 , H_2S), and chloride absorbed into KOH, has been reported in detail elsewhere (Mizutani, 1978; Viglino *et al.*, 1985; Kiyosu, 1983). The alkali residual gases such as H_2 , N_2 , O_2 and CH_4 were analyzed by gas chromatography with a thermal conductivity detector (Kiyosu, 1983). On the basis of O_2 contents, a

correction was made for air contamination in the gas samples. The light hydrocarbons were measured by gas chromatography on a Unibead 1 S column having an argon carrier with a flame ionization detector. The margin (1σ) of error in the determination of the light hydrocarbons was $\pm 2\%$, except for methane ($\pm 1\%$).

RESULTS AND DISCUSSION

Chemistry of volcanic gases in Japanese volcanoes

Figure 2a shows the relative contents in terms of CO_2 , $SO_2 + H_2S$ and HCl from volcanic gases in the Japanese island arc. The water vapour contents were always >90 vol.%. The gases can be classified into three types: high temperature fumarolic gases ($\geq 200^\circ C$) containing HCl (Matsuo,

Fig. 2. a) Relative CO_2 , $\text{SO}_2 + \text{H}_2\text{S}$ and HCl contents of fumarolic and geothermal gases. b) Relative H_2 , N_2 and CH_4 contents of fumarolic and geothermal gases. 1: Showashinzan (Matsuo, 1961; Mizutani, 1978), 2: Nigorikawa (Asada, 1993), 3: Tamagawa (Kiyosu, 1983), 4: Matsukawa (Kiyosu, 1983), 5: Takinoue (Kiyosu and Yoshida, 1988), 6: Onikobe (Kiyosu, 1986), 7: Issaikyo (Kiyosu, 1983), 8: Nasu (Kiyosu, 1983), 9: Kusatsu Shirane (Asada, 1993), 10: Myoko (Asada, 1991), 11: Tateyama (Asada, 1991, 1993), 12: Ontake (Asada, 1993), 13: Kuj-Iwoyama (Mizutani et al., 1986), and 14: Unzen (Asada, 1993). Squares, circles and triangles indicate high temperature fumarolic gases: 1, Usu (Matsuo et al., 1982), 13, Satsuma-Iwojima (Matsuo et al., 1975), low temperature fumarolic gases: 3, 7-12, 14, and geothermal gases: 2, 4, 5, respectively.

Table 1. Distribution of light hydrocarbons, normalised to methane, in volcanic gases from the Japanese island arc

Locality		Temp. °C	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀ m mol/mol	<i>n</i> -C ₄ H ₁₀	C ₂ H ₄
Showashinzan		637	5.76	1.65	4.55	0.539	15.0
		617	1.10	3.26	4.49	2.22	39.0
Kuju Iwoyama		350	0.60	0.24	0.10	0.137	0.67
Tamagawa		101	1.75	0.59	1.31	6.11	2.24
Issaikyo		94	10.37	1.43	2.97	0.937	5.37
Nasu	O-3	102	1.10	0.078	0.043	0.083	0.43
	O-3	101	1.65	0.111	0.022	0.035	0.38
	U-1	95	1.75	0.135	0.017	0.052	0.47
	M-1	171	1.68	0.128	0.090	0.079	1.87
	M-6	140	1.60	0.185	0.015	0.096	0.95
	UW-1	96	1.49	0.139	0.052	0.063	0.52
	T-3	112	1.39	0.088	0.038	0.042	0.65
Kusatsu	Kita 1	102	15.4	4.71	1.24	1.20	0.45
	Kita 2	100	2.03	0.47	—	0.51	—
	Kita 3	101	3.10	2.63	1.45	1.93	2.08
	Sessyou 1	95	0.41	0.48	0.11	0.10	0.14
	Sessyou 2	94	0.58	0.05	0.01	0.02	0.025
Ontake	OT-1	117	2.60	0.306	0.054	0.074	0.10
	OT-2	115	2.47	0.274	0.054	0.101	0.11
Myoko	A-1	92	13.5	3.06	0.394	0.516	0.001
	A-2	94	14.6	3.74	0.484	0.590	0.002
	A-3	116	15.0	3.35	0.403	0.451	0.0002
Tateyama	A-1	104	0.73	0.37	0.335	0.230	2.13
	A-2	105	1.10	0.32	0.335	0.236	1.86
	B-1	109	0.82	0.33	0.046	0.425	1.18
	B-2	93	0.85	0.33	0.199	0.132	0.52
	231	110	0.64	0.03	0.033	0.033	0.11
	241	103	0.73	0.03	0.053	0.053	0.17
	KAJ	102	0.87	0.24	0.027	0.082	0.014
	DAG	107	2.06	0.60	0.112	0.196	0.037
	DAY	108	1.40	0.353	0.136	0.203	0.109
	KAR	26	5.97	0.70	0.096	0.075	0
Unzen	K02	73	7.12	1.34	0.303	0.284	0
	K01	98	5.89	1.05	0.229	0.154	0
	SEID	102	5.77	1.08	0.233	0.189	0
	DAI	94	6.76	1.07	0.222	0.124	0
	HAT	77	11.5	1.08	0.224	0.146	0
	SIMA	25	0.43	0.713	1.092	0.060	0.083
Nigorikawa		250*	39.1	14.7	1.90	0.304	0.332
Matsukawa	M-2	240*	7.27	0.40	0.030	0.016	0.211
	M-3	240*	2.01	0.19	0.050	0.218	—
	M-5	220*	7.22	0.47	0.009	0.055	—
	M-9	230*	4.26	0.19	0.029	0.062	0.172
Takinoue	A	98	43.7	11.9	0.781	3.13	1.88
	B	97	10.4	1.92	0.090	0.210	1.37
Onikobe	A	99	10.1	0.51	0.541	0.118	10.2
	B	240*	12.8	5.61	2.63	1.79	9.95

CH₄ = 1 mol.

—: not measured.

*downhole temperature.

1961; Matsuo *et al.*, 1975, 1982; Mizutani, 1978; Mizutani *et al.*, 1986), low-temperature fumarolic gases containing some HCl (Kiyosu, 1983; Asada, 1991) and geothermal gases containing no HCl (Kiyosu, 1983, 1986; Kiyosu and Yoshida, 1988). Alkanes such as methane are present in volcanic geothermal gases being predominantly composed of carbon dioxide. On the other hand, on the basis of relative H₂, CH₄ and N₂ contents, the high-temperature and low-temperature fumarolic gases and volcanic geothermal gases may be classified as H₂, N₂ and CH₄ rich, respectively (Fig. 2b). However, the Ontake and Nasu low-temperature fumarolic gases and the Onikobe volcanic geothermal gases have high H₂ contents and correspond to the high-temperature fumarolic type, the low-temperature fumarolic gases from the Myoko and Unzen volcanoes contain considerably more methane and belong to the volcanic geothermal type. Thus, in addition to temperature, volcanic gases can also be classified by their chemical composition.

Light hydrocarbon in volcanic gases

The Showashinzan and Kuju-Iwoyama H₂ type fumarolic gases (high-temperature) contain CH₄ ranging from 1.0 to 1.2×10^{-4} vol.% (Matsuo, 1957; Mizutani 1978; Mizutani *et al.*, 1986), while N₂ type fumarolic gases (low-temperature) have methane concentrations between 1.2×10^{-4} and 6.4×10^{-2} vol.% (Kiyosu, 1983; Asada, 1991). The Nigorikawa, Matsukawa, Takinoue and Onikobe CH₄ type geothermal gases have methane from 1.9×10^{-3} to 6.4×10^{-1} vol.% (Kiyosu, 1983, 1986; Kiyosu and Yoshida, 1988; Asada, 1991). The analytical results of other hydrocarbons for gas samples taken from several locations are listed in Table 1.

Volcanic hydrocarbons might deviate considerably from the equilibrium concentrations with magma due to secondary processes such as decreasing temperature, oxidation by air or surface water and contamination of hydrocarbon gases derived from groundwater or sedimentary rocks. In order to clarify the effects of these processes, the hydrocarbon gases from fumaroles in some

volcanoes were examined by Asada (1991). From the results, it was found that the hydrocarbon abundance ratios in each volcano are almost uniform independent of fumarolic temperature. This suggests that the hydrocarbon gases are not affected by processes near surface, but contain information from deep-seated areas.

Several sources including inorganic, thermogenic or biogenic origin were postulated for the origin of light hydrocarbons such as CH₄ associated with volcanic hydrothermal systems. Inorganic and thermogenic gases usually contain CH₄ together with other light hydrocarbons, while biogenic gas predominantly methane (Schoell, 1988; Welhan, 1988). Light hydrocarbons of the East Pacific Rise (E.P.R.) hydrothermal brine were supposed to be inorganic; they have low but similar concentrations of ethane to those of butanes and alkenes such as ethylene (Welhan and Craig, 1982). On the other hand, in the thermogenic gases from oil fields the abundance of hydrocarbons relative to CH₄ decreases from ethane to higher hydrocarbon but contain almost no ethylene (Schoell, 1988).

Figure 3a shows the abundance ratios of hydrocarbons in fumarolic gases from several dacitic and andesitic volcanoes. Although the relative abundance ratios of other hydrocarbons relative to methane are variable in each area, the patterns are similar to each other, suggesting that the hydrocarbon gases are of inorganic origin (Welhan and Craig, 1982), independent of the fumarolic temperature. However, the fumarolic gases from the Myoko and Unzen volcanoes belong to the volcanic CH₄ type geothermal gases. On the other hand, with the exception of ethylene, the abundance patterns in geothermal gases are similar to those of thermogenic hydrocarbons (Chung, 1976; Sakata *et al.*, 1989), as shown in Fig. 3b. One exception are the Onikobe geothermal gases (H₂ type), which indicate an inorganic hydrocarbon pattern.

Thus, almost all of the hydrocarbons in volcanic gases of H₂ and N₂ types have the pattern of inorganic origin, whereas the methane rich fumarolic and geothermal gases are of thermogenic

Fig. 3. Alkane and alkene concentrations relative to methane in fumarolic gases (a) and geothermal gases (b). Square, circle and triangle indicate H_2 , N_2 and CH_4 type, respectively. The symbol $\bullet$ represents E.P.R. geothermal gases (Welhan and Craig, 1982), $\blacksquare$ the Tolbachik subaerial basaltic gases (Markhim *et al.*, 1977), $\triangle$ coal pyrolysis gases (Chung, 1976) and $\blacktriangle$ thermogenic gases (Sakata *et al.*, 1989). The numbers are referred to the sample location shown in the caption of Fig. 2.

origin. In order to identify the contribution of different sources, we use a triangular diagram of alkanes (CH_4 , C_2H_6 and C_3H_8), as shown in Fig. 4.

In a comparison of relative CH_4 , C_2H_6 and C_3H_8 contents, the first end-member to be defined is of biogenic origin (B). The biogenic pole is easily distinguishable from the magmatic pole and thermogenic domain (T). As described later, the magmatic hydrocarbons are buffered by either the fayalite-magnetite-quartz buffer (FMQ) (M_1) or the magnetite-wüstite buffer (MW) (M_2), and plot near the CH_4 and C_3H_8 poles, respectively. The domains of submarine (Welhan and Craig, 1988; Roger *et al.*, 1981; Welhan and Lupton, 1987) and

subaerial (Markhim *et al.*, 1977) basaltic gases are also represented in Fig. 4. Most of the data from these areas can be reasonably attributed to mixing between magmatic and thermogenic hydrocarbons. Furthermore, the magmatic end-members of both basaltic gases are FMQ (M_1) and MW (M_2) buffer types. On the other hand, the samples from andesitic and dacitic gases in Japan are consistent with the domain of submarine basalt. The hydrocarbons from the H_2 and N_2 type fumarolic gases show near magmatic values (M_1), whereas most of the CH_4 type volcanic and geothermal gases contain the thermogenic compound. Therefore, fumarolic (H_2 and N_2 type) and geothermal (CH_4 type) hydrocarbon gases from the Japanese islands

Fig. 4. $\text{CH}_4\text{-C}_2\text{H}_6\text{-C}_3\text{H}_8$ triangular diagram. Symbols are the same as in Figs. 3a and b. The biogenic pole (B) coincides with the CH_4 pole. The magmatic hydrocarbons (M_1 and M_2) have been estimated in the text. The submarine basaltic gases (S) are from Welhan and Craig (1982), Roger et al. (1981) and, Welhan and Lupton (1987). The subaerial basaltic gases (A) are from Markhim et al. (1977). The thermogenic gases (T) are from Chung (1976) and Sakata et al. (1989). E: E.P.R. (Welhan and Craig, 1982), R: Red Sea (Roger et al., 1981), G: Guaymas (Welhan and Lupton, 1987).

are likely to be largely of inorganic and thermogenic origin, respectively.

Factors controlling the abundance of inorganic hydrocarbons in volcanic gases

The possible reactions of inorganic formation of hydrocarbons in magma have been thought to be Fisher/Tropsch reactions (Craig, 1953). We would then have the following series of reactions:

where C_nH_{2n+2} and C_nH_{2n} indicate alkanes and alkenes, respectively.

From Eqs. (1), (3) and (4) the following can be obtained

The equilibrium constant K_n of reaction (5) is

$$K_n = f_{C,H_2O} f_{O_2}^{(3n+1)/2} / f_{CO_2}^n f_{H_2O}^{n+1}, \quad (6)$$

where $n = 1, 2, 3, \dots$.

Then $n = 1$:

$$K_1 = f_{\text{CH}_4} f_{\text{O}_2}^2 / f_{\text{CO}_2} f_{\text{H}_2\text{O}}^2. \quad (7)$$

From Eqs. (6) and (7), it can be determined that

$$f_{C_nH_{2n+2}} / f_{CH_4} = (K_n / K_1) f_{CO_2}^{n-1} f_{H_2O}^{n-1} f_{O_2}^{3/2(1-n)}, \quad (8)$$

where $n > 1$.

Similarly, the formation of ethylene can be written as

The equilibrium constant K_2' of Eq. (9) is:

$$K_2' = f_{C_2H_4} f_{O_2}^3 / f_{CO_2}^2 f_{H_2O}^2. \quad (10)$$

From Eqs. (7) and (10), it can be obtained that

$$f_{C_2H_4} / f_{CH_4} = (K_2' / K_1) f_{CO_2} f_{O_2}. \quad (11)$$

Fig. 5. Comparison of hydrocarbon concentrations relative to methane. Thermodynamic data are from Barin (1989). Temperature = 1000 K, $f_{H_2O} = 2$ kb, and $f_{CO_2} = 1$ kb. $\diamond$ denotes the FMQ (fayalite-magnetite-quartz) buffer system, and $\blacklozenge$ the MW (magnetite-wüstite) buffer system. The shadowed area is the observed values of fumarolic gases.

The alkane and ethylene concentrations relative to methane can then be expressed as a function of temperature, f_{H_2O} , f_{CO_2} and f_{O_2} .

The concentration of CO_2 in magmatic systems may also be defined by carbonate minerals as follows:

and

The lower and upper limits of f_{CO_2} can then be obtained from Eqs. (12) and (13), respectively. Therefore, the alkane and alkene concentrations relative to methane can be expressed as a function of temperature, f_{H_2O} and f_{O_2} .

If the oxygen fugacity of volcanic gases is controlled by the FMQ buffer at 1000°K and

Fig. 6. Temperature effect to magmatic hydrocarbon contents relative to CH_4 (C_i/C_1) when $f_{H_2O} = 2$ kb, $f_{CO_2} = 1$ kb (1000 K) and $f_{H_2O} = 1$ kb, $f_{CO_2} = 0.5$ kb (800 K).

$f_{\text{H}_2\text{O}} = 2 \text{ kb}$, the hydrocarbon content decreases drastically from ethane to butane, as shown in Fig. 5. Alternatively, if f_{O_2} is defined by the MW buffer, the alkane concentrations increase from C_2 to C_4 . That is, the abundance pattern of the hydrocarbon appears to be largely governed by the mineral buffer systems. Therefore, under more oxidizing conditions, saturated hydrocarbons relative to methane decrease from ethane to butane, whereas under reducing condition they increase. A flat pattern with hydrocarbon contents relative to methane nearly constant, corresponds to a position between FMQ and MW oxygen buffer systems.

The effect of temperature was examined by assuming that the oxygen fugacity is controlled by the FMQ buffer (Fig. 6). Although the hydrocarbon contents relative to CH_4 decrease with increasing temperature, the abundance pattern of hydrocarbons varies only slightly. On the other hand, the relationship between the abundance pat-

tern and water vapor is shown in Fig. 7. The alkane and ethylene concentrations relative to methane increase with increasing $f_{\text{H}_2\text{O}}$, but the pattern does not exhibit very much change.

Thus, the relative contents of light hydrocarbons are predominantly controlled by the oxygen fugacity. Most of the inorganic hydrocarbons found in volcanic gases may be formed at redox potentials between those of the FMQ and MW buffer systems are relatively independent of temperatures and $f_{\text{H}_2\text{O}}$.

Magmatic hydrocarbons

Magmatic hydrocarbons are probably controlled by the oxygen fugacity defined by the FMQ (oxidized type) or MW (reduced type) buffer. The redox potential of basaltic magmas which exist in upper mantle is close to the oxidation states of fayalite-magnetite-quartz (Haggerty, 1978; Ballhaus *et al.*, 1990). However, electrochemical measurements suggest that the redox conditions of the upper mantle are heterogeneous, and may approach the oxygen fugacity defined by the MW buffer (Arculus, 1985; Arculus *et al.*, 1984).

Figure 8 shows the oxygen fugacity for volcanic rocks estimated from Eq. (3). The oxygen fugacity of volcanic gases in basalt (Gerlach, 1979, 1980a, 1980b, 1980c, 1981) is consistent with that of the FMQ buffer, while those in dacite and andesite (Matsuo, 1961; Matsuo *et al.*, 1982; Giggenbach, 1982; Guern *et al.*, 1982) are higher than the f_{O_2} of the FMQ buffer estimated from oxide minerals (Ueda and Itaya, 1982) and near the NNO (nickel-nickel oxide) buffer. This suggests that the volcanic gases in dacite and andesite magma are significantly oxidized in the process of being discharged (Ueda and Itaya, 1982).

The isotope compositions of waters from fumarolic gases suggest that most of volcanic gases in Japan are mixtures of magmatic gases and meteoric waters (Mizutani, 1978; Kiyosu, 1983). This fact is supported by fumarolic and hot spring activities at dacitic and andesitic volcanoes in the Japanese island arc. That is, the vapour and liquid phases separate after mixing and produce fumarolic gases and volcanic acid hot springs, re-

Fig. 7. Effect of water vapor fugacity to magmatic light hydrocarbon concentrations relative to methane (C_i/C_1). Temp. = 1000 K, $f_{\text{CO}_2} = 1 \text{ kb}$.

Fig. 8. Comparison of oxygen fugacities for volcanic gases. Basalt: Surtsey (Gerlach, 1980c); Mount Etna (Gerlach, 1979); Kilauea (Gerlach, 1980a); Nyiragong (Gerlach, 1980b); Erta Ale (Gerlach, 1981). Dacite and andesite: White Island (Giggerlbach, 1982); Ngauruhoe (Giggerlbach, 1982); Merapi (LeGuern *et al.*, 1982); Usu (Matsuo *et al.*, 1982); Showashinzan (Matsuo, 1961); Satsuma Iwojima (Matsuo *et al.*, 1975). Abbreviations: H = hematite; M = magnetite; Py = pyrite; Po = pyrrhotite; Q = quartz; F = fayalite; W = wüstite; N = nickel; NO = nickel oxide. Hatched area is the oxygen fugacity estimated from the abundance ratios of hydrocarbons in volcanic gases of H_2 and N_2 types at Temp. = 1000–1200 K; $f_{H_2O} = 2$ kb; $f_{CO_2} = 1$ kb.

spectively (Kiyosu, 1985). When oxidation and cooling of magmatic gases occur during mixing with meteoric waters, CO is presumably more easily oxidized by H_2O than hydrocarbons. In general, the oxidation rate of hydrocarbons is slow, even at temperatures $>500^\circ\text{C}$ (Kiyosu and Krouse, 1989).

Another possible explanation is that volcanic gases from the Japanese island arc are formed by

addition of CO_2 derived from the thermal decomposition of limestone or organic matter in sedimentary rocks (Marty *et al.*, 1989). Therefore, the abundance pattern of light hydrocarbon relative to CH_4 may be similar to that of the thermogenic type. However, the hydrocarbon patterns of fumarolic gases (H_2 and N_2 types) found at island arc volcanoes are of the flat types as described before.

Thus, the inconsistency of the oxygen fugacity defined by FMQ buffer and the observed values in dacitic and andesitic volcanoes estimated from the CO_2 -CO system may be due to oxidation of volcanic gases during mixing with surface waters. The abundance ratios of light hydrocarbons which migrate to vapour phase probably do not change, since the solubility of light hydrocarbons in water is small and similar to each other (Wilhelm *et al.*, 1977). Therefore, the redox potential suggested from the abundance ratio of volcanic hydrocarbons is close to that of the FMQ buffer, as shown in Fig. 8. That is, it may be concluded that the abundance patterns of hydrocarbons found in volcanic gases directly reflect the oxidation state of magmatic gases at depth.

In general the oxygen fugacities of silicic magmas estimated from iron-titanium oxides correspond to the Ni-NiO buffer and are higher than those of basic magmas (e.g., Carmichael, 1991). However, according to the oxygen isotope study of silicic volcanic rocks (Hildreth *et al.*, 1984), it would appear that their magmas reacted with meteoric water. That is, silicic magmas with small amounts of iron and large amounts of water do not reflect original redox states. Accordingly the oxygen fugacities obtained from the abundance ratio of volcanic hydrocarbons in the Japanese island arc may indicate the redox states of lower crust or upper mantle suggesting deeper zones of the magma chambers. An alternative explanation could be that their relative oxygen fugacity, with respect to the FMQ, may be controlled by assimilation of reduced carbon or graphite derived from shallow crust in an ascending silicic magmas. The problem of redox states in silicic magmas require more detailed discussion in future.

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