

Chemical and isotopic composition of magmatic gases from the 1988 eruption of Klyuchevskoy volcano, Kamchatka

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ABSTRACT

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Gas samples have been collected at the place of magma effusion during the 1988 flank eruption of Klyuchevskoy, for the first time in the course of studies at this volcano. The high-temperature gases (1000–1100°C) are rich in water and halogens but depleted in sulphur. Their molar composition is close to chemical equilibrium at the collection temperature, while their oxidation state corresponds to redox conditions between FMQ and NNO buffers. The isotopic composition of the water ($\delta D = -71$ to -44‰ ; $\delta^{18}O = +6.3$ to $+8.4\text{‰}$, versus SMOW) plots within the field of “primary magmatic” waters. The isotopic composition of H_2 ($\delta D = -187\text{‰}$ to -160‰) is consistent with isotopic equilibrium between H_2 and H_2O in the conditions of emission. Both the chemistry of the gases and the low $\delta^{13}C$ of carbon dioxide (-11.6‰ , PDB) suggest extensive magma outgassing occurred during the course of the eruption.

Introduction

In spring and summer 1988, during a flank eruption of Klyuchevskoy volcano, we succeeded in collecting high-temperature gases from the mere place of magma outpouring. It is the first time such a sampling could be done at Klyuchevskoy, after more than half a century of systematic observation. Previous conditions of eruptions had allowed to collect gases from only the surface of cooling lava flows or from cinder cones (Basharina, 1963; Serafimova, 1979). These samples were by 95% or more contaminated by air and their temperatures were lower than 600°C.

Klyuchevskoy volcano, a huge strato-volcano (the height of the volcano is 4750 m a.s.l. and the volume of the edifice is more than 250 km³) belongs to the so-called

Klyuchevskoy volcanic group which is located in the Central Kamchatkan Depression, at the junction of the Kurile-Kamchatka and Aleutian island arcs. Lately, a wealth of data have been systemized on geophysics, petrology, on geochemistry of solid products of eruptions as well as on the dynamics of the activity of volcano (Kirsanov et al., 1973; Fedotov et al., 1988; Khrenov et al., 1989). The age of Klyuchevskoy is about 7 thousand years (I.V. Melekestsev, pers. commun., 1989). Its products are typical calc-alkaline basalts of aluminous to magnesian character. Cyclicity in the eruptive activity of the volcano has been noted. The last eruptive cycle, with simultaneous flank eruptions and explosive-effusive activity at the summit crater, was characterized by an upward migration of the vents of flank eruptions. Since 1980 all flank eruptions

were purely effusive

The 1988 eruption occurred on the southern slope of Klyuchevskoy at an elevation of 4,100 m and lasted for more than 7 months (from January 29 to September 14). It was the longest of the cycle and the closest to the summit crater. The eruptive center, formed at the intersection of a radial fissure and ring fissure, opened on the upper slopes of the mountain. Lava flowing took place from the base of a small cinder cone which was formed during the course of the eruption. The width of the flow at the vent was 1.2–1.5 m and in May its rate was about 0.4 m/s.

Sampling and analysis

Sampling

Several gas samples were collected during the eruption. The present paper deals with four of them (air content is lesser than 95%). Sample 1 (May 4) and sample 2 (July 18) were collected from the cone of splashing lava (hornito), approximately 3 m above the head of the lava flow. The diameter of the vent was about 0.7 m in May. Its inner part was incandescent and up to bright orange in color. Under the pressure of the gas, pieces of liquid lava were thrown up. The velocity of the gas jet in May was estimated at 15 m/s and the gas discharge at about 6 m³/s. The gas velocity varied according to occasional collapses of lava walls into the vent. These portions either were further blown out by the gas to heights of 6–10 m or were squeezed from the hornito in small lava flows. After clearing of the channel, the regime of gas release reconstituted. This type of activity persisted in July. In August, only a few narrow fissures at the top of lava cone occurred, but lava flowing rate was not changed. Samples 3 and 4 (August 21 and August 25, respectively) were collected from one of the fissures. At the time of sampling, gas from fissures escaped with a typical hissing. Flames of light blue color, the height of

which was 10–30 cm, were observed at night at the places of gas issue.

For sampling, a ceramic pipe, 40 mm in diameter, was plunged into the orifice of the hornito or into fissures of the lava cone. Inside this pipe we inserted a silica tube, connected to a series of gas absorbers by teflon and rubber links. Temperature at the sampling points was measured with an optical pyrometer.

Most gas samples were collected in evacuated bottles containing an alkaline solution (NaOH, 4*N*). The gas was also aspired using a glass syringe of 100 cm³ through bubblers which were cooled by snow in order to sample both water condensate and gas into 230-cm³ glass vessels.

Analysis

Unabsorbed gases in the bottles with alkaline solution (O₂, N₂, H₂, CO, CH₄) were analyzed by chromatograph, using a 4-m-long molecular sieve column and a thermal conductivity detector. Argon was determined on a composite column with molecular sieves CaA and NaX (at room temperature, after Tsitsishvili et al., 1975). For isotopic analysis we separated CO₂ (by freezing with liquid nitrogen) and H₂ (by burning and subsequent reduction on uranium) from the other gases collected into the glass vessels.

“Acid” gases (CO₂, H₂O, SO₂, HCl and HF) in alkaline solutions were determined by wet chemistry and the proportions of H₂O and SO₂ were calculated by method of Giggenbach (1975). In samples 1 and 3 precipitation of elementary sulfur was noticeable. Because of poor knowledge of the redistribution of H₂S, S₂ and SO₂ in these two samples, only a total sulfur was reported.

Results

The analytical results are listed in Table 1. Chemical compositions are given in

TABLE 1

Chemical and isotopic composition of magmatic gases from Klyuchevskoy volcano (1988 eruption)

Date of sampling:	May 4	Jul 18	Aug 21	Aug 25
Number of sample:	1	2	3	4
$T(^{\circ}\text{C})$	1050	1070	1100	1100
<i>Chemical composition ($\mu\text{mole/mole}$)</i>				
H ₂ O	940000	908400	976000	977300
H ₂	11600	17000	6200	5900
CO ₂	24600	44700	500	1200
CO	1100	1550	<5	12
H ₂ S	1700	500	1500	20
SO ₂		1000		900
HCl	20200	22500	15300	14200
HF	740	2900	3000	2500
N ₂	*	**	80	40
Ar	*	**	0.38	0.32
CH ₄	7	13	<1	<1
<i>Isotopic composition (‰)</i>				
¹⁸ O _{H₂O}	-	+8.4	+6.3	+7.8
D _{H₂O}	-	-44	-71	-59
D _{H₂}	-	-164	-187	-160
¹³ C _{CO₂}	-	-11.6	-	-
<i>Atomic ratios</i>				
H/C	77	41	9800	1640
S/C	0.066	0.035	3.0	0.76
Cl/F	27	7.8	5.1	5.7
N ₂ /Ar	*	**	210	125

Air content in dry gas (volume %); * -83; ** -41.

$\mu\text{mole/mole}$, isotopic ones in δ per mil deviations with respect to international standards (SMOW for H₂O and H₂, PDB for carbon).

In samples 1 and 2 collected directly from hornitos, air contamination amounts to 83% and 41% of the anhydrous phase, respectively. Samples 3 and 4, collected from fissures of lava cone, contained almost no air. In those water-rich samples CO concentrations were close to the detection limit of our chromatographic technique. Methane has been detected only on samples 1 and 2 and its concentration is close to that corresponding to air addition, as inferred from the N₂ content ($\sim 10^{-4}\%$ in dry gas). The N₂/Ar ratio of samples 3 and 4 is much higher than atmospheric ratio (83). Therefore elemental and isotopic analysis of noble gases could be done only for these two samples, the results of which will appear elsewhere.

The isotopic composition of water (Table 1) plots into the field typical of "primary magmatic" waters (Taylor, 1979) and, particularly water in the "driest" sample 2 is isotopically characteristic of "andesitic" magmatic waters (Sakai and Matsubaya, 1977; Allard, 1983; Poreda, 1985; Taran et al., 1989). Its magmatic origin thus is likely. The δD of H₂ ranges from -187 to -160‰ and allows to calculate equilibrium temperatures of about 1000–1199°C for isotopic exchange in the system H₂-H₂O (Table 2). Thus both species were in equilibrium at the emission.

The $\delta^{13}\text{C}$ of CO₂ (-11.6‰), measured only in sample 2, differs from "normal" mantle values (-8 to -5‰). It also differs from $\delta^{13}\text{C}$ of some high-temperature gases of island arcs and continental margins volcanoes (Allard, 1980, 1983; Javoy et al., 1986). Specially, it is comparable to the $\delta^{13}\text{C}$ of CO₂ from

TABLE 2

Apparent equilibrium temperature of Klyuchevskoy gas samples, as inferred from either chemical or isotopic reactions, and calculated oxygen and sulfur fugacities

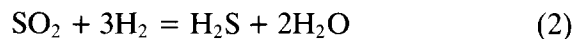
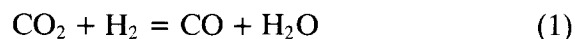
Sample number:	1	2	3	4
$T^{\circ}\text{C}$, measured	1050	1070	1100	1100
T_C	1359	1047	–	1007
T_S	–	983	–	960
T_H	–	994	998	1089
$\log f_{\text{O}_2}(\text{H})$	–9.96	–10.03	–8.75	–871
$\log f_{\text{O}_2}(\text{C})$	–10.53	–10.00	–	–8.40
$\log f_{\text{O}_2}(\text{S})$	–	–10.73	–	–9.70
$\log f_{\text{S}_2}$	–	–4.98	–	–6.68

Note: T_C and T_S were calculated from eqs. (6) and (7), respectively; T_H was calculated from isotopic equilibrium $\text{H}_2 - \text{H}_2\text{O}$ (eq. 12) $\log f_{\text{O}_2}(\text{H}, \text{C}, \text{S})$ inferred from eqs. 8–10 and $\log f_{\text{S}_2}$ from eq. 11. See text.

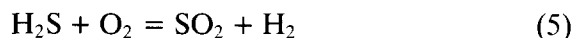
several Kamchatkan and Kurile volcanoes in fumarolic stage of activity (e.g. Menyailov et al., 1983; Taran, 1985; Taran et al., 1991).

Gas and isotopic equilibria

Based on thermodynamic constants for the following two reactions:



one can estimate “apparent” equilibrium temperatures of gas mixtures. Then, once this temperatures calculated, we can estimate the corresponding “apparent” oxygen fugacity of the gas using the following equilibria:



The purpose of these calculations, whose results are given in Table 2, is to check whether the Klyuchevskoy magmatic gases were in equilibrium in the conditions of sampling, to evaluate the redox conditions of the melt-fluid system, and to elucidate the reasons of possible deviations from equilibrium.

In our case, such calculations were of interest since, on one hand, the gases collected and particularly samples 3 and 4 are rich in water - a feature rather typical for low- and mid-temperature fumaroles of volcanoes in inter-eruptive stage, - on the other hand, this water, according to its isotopic composition, suffered no or little contamination by meteoric waters (ice and snow at this elevation have mean $\delta^{18}\text{O} = -20\text{‰}$ and $\delta\text{D} = -150\text{‰}$; Y. Muraviev, pers. commun., 1990).

Formulas for temperature and f_{O_2} calculations were obtained through interpolation of data from Robie et al. (1978), as $\log K = A + B/T$. Their accuracy is no less than 0.05 log units.

$$T_C(^{\circ}\text{C}) = 1778/(1.61 - \log K_C) - 273 \quad (6)$$

where $K_C = x_{\text{CO}} \cdot x_{\text{H}_2\text{O}}/x_{\text{CO}_2} x_{\text{H}_2}$ and x_i are mole fractions;

$$T_S(^{\circ}\text{C}) = 11907/(4.75 - \log K_S) - 273 \quad (7)$$

where $K_S = x_{\text{H}_2\text{O}}^2 \cdot x_{\text{H}_2\text{S}}/x_{\text{H}_2}^3 \cdot x_{\text{SO}_2}$

$$\log f_{\text{O}_2}(\text{H}) = -25932/T + 5.72 - 2 \log(x_{\text{H}_2}/x_{\text{H}_2\text{O}}) \quad (8)$$

$$\log f_{\text{O}_2}(\text{C}) = -29487/T + 9.05 - 2 \log(x_{\text{CO}}/x_{\text{CO}_2}) \quad (9)$$

$$\log f_{\text{O}_2}(\text{S}) = -14025/T + 1.08 + \log(x_{\text{SO}_2}x_{\text{H}_2}/x_{\text{H}_2\text{S}}) \quad (10)$$

$$\log f_{\text{S}_2} = -4722/T + 2.56 - 2 \log(x_{\text{H}_2}/x_{\text{H}_2\text{S}}) \quad (11)$$

For the isotopic fractionation factor between H_2 and H_2O in the temperature range 800–1300°C, interpolation of Richet et al. (1977) data give:

$$\Delta_{\text{H}} = 1000 \ln \alpha_{\text{H}_2-\text{H}_2\text{O}} = -151.6 + 361842/T \quad (12)$$

The calculations show that the high water content of our samples is consistent with equilibrium temperatures close to but lower than

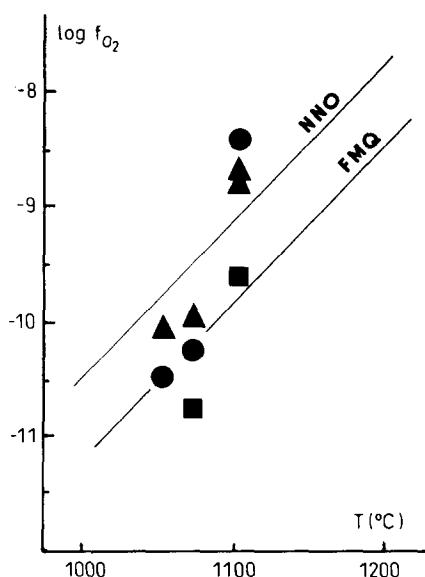


Fig. 1. Relationship between the measured temperature and oxygen fugacity f_{O_2} of the gases calculated from oxidation reactions (3–5). The curves correspond to the FMQ and NNO oxygen buffers, respectively. f_{O_2} values from: triangles – x_{H_2}/x_{H_2O} ratio; circles – x_{CO}/x_{CO_2} ratio; squares – x_{H_2S}/x_{SO_2}

the measured temperatures. Temperature T_C is higher than T_S , though unrealistically high for sample 1. T_S temperatures are lower by about 100°C than the measured ones, which most probably reflects losses and/or redistribution of sulfur species in the sampling system. Lower f_{O_2} low f_{S_2} values correlate with low “sulfur” temperatures.

Figure 1 shows the relationship between the measured temperatures and values of oxygen fugacity calculated from equations (8 to 10). The spread in calculated f_{O_2} values is within one log unit for samples 1 and 2, and somewhat higher for samples 3 and 4 which also are much more oxidized (low CO, H₂ and H₂S). The points for samples 1 and 2, calculated from ratio x_{H_2}/x_{H_2O} , lie between the fayalite-magnetite-quartz (FMQ) and nickel-nickel oxide (NNO) oxygen buffers, i.e. in the redox field typical of most basaltic and andesitic gases (Allard et al., 1977; Gerlach, 1983).

The values of f_{O_2} calculated from equation (10) prove once again that the use of sulfur species for thermodynamical calculations is less reliable. In our case, one cannot exclude errors in analytical determinations, due to the very small amount of sulfur in the gases from the 1988 eruption of Klyuchevskoy.

Chemical evidences of magma degassing

The main chemical features of our samples are their high water content, high Cl and F content, and low sulfur content. In that respect, they look very similar to the gases sampled by I.A. Menyailov et al. during the Southern Breakthrough of the Large Tolbachik Fissure eruption (LTFE) (Menyailov et al., 1984). In Table 3, these data on both Klyuchevskoy and Tolbachik are compared with other magmatic gases from basaltic volcanoes. It is noteworthy that these basaltic gases generally contain not less than 3 mole % sulfur, not less than 5% CO₂, while H₂O does not exceed 92.5% in the most hydrous gases (Surtsey, Iceland). In contrast, the Klyuchevskoy gases as well as the gases from the Southern Breakthrough of LTFE, contain no more than 0.2% S but up to 98% H₂O. We stress again that isotopic evidences support that this water is of magmatic origin and exclude any significant admixture of meteoric water. A likely explanation of the chemical peculiarity of Klyuchevskoy samples is that they reflect the late degassing of basaltic magma previously depleted in carbon dioxide. Indeed, the solubility of CO₂ in basalt is many times lower than that of water and halogens (Kadik et al., 1971; Stolper and Holloway, 1987). Figure 2 shows the correlational dependencies of atomic ratios H/C and S/C for the basaltic gases listed in Table 3, as constructed by Gerlach (1983), as well as for both Klyuchevskoy and Tolbachik gases. It can be seen that the plots for all concerned volcanoes follow a similar linear trend, with a slope of about 1. The Klyuchevskoy and

TABLE 3

Chemical composition (mole %) of high-temperature basaltic gases (modified from Gerlach, 1983)

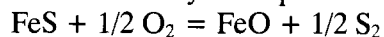
Volcano	Year of sampling	H ₂ O	H ₂	CO ₂	CO	SO ₂	S ₂	H ₂ S	HCl	t(°C)	H/C	S/C
Surtsey	1964	81.13	2.37	9.29	0.69	3.15	0.13	0.64	0.81	1125	16.7	3.34
	1965	87.88	3.12	6.43	0.39	2.72	0.10	0.63	0.43	1125	26.7	1.98
	1967	92.47	1.74	3.31	0.11	3.74	0.02	0.15	1.16	1125	55.1	1.14
Erta Ale	1971	71.65	1.62	18.88	0.83	10.17	0.68	1.10	–	1075	7.43	1.65
	1973	70.35	2.36	18.42	1.55	6.74	0.15	0.38	–	1210	7.28	0.35
	1974	78.28	1.76	13.08	0.60	8.34	0.36	1.08	–	1130	11.8	0.72
Ardoukoba	1978	78.71	1.73	4.02	0.17	15.38	1.51	1.80	–	1070	38.4	4.46
Kilauea	J-8 ^a	37.09	0.49	48.90	1.51	11.84	0.02	0.04	0.08	1170	1.49	0.24
	J-13 ^a	69.29	1.01	17.82	0.62	10.93	0.03	0.08	0.21	1175	7.62	0.60
	1982 ^b	47.07	0.57	6.24	0.13	44.32	–	1.68	–	1070	15.26	6.94
	1983 ^b	85.85	1.45	1.43	0.05	10.61	–	0.61	–	1110	118	7.58
Mauna Loa ^c	1984	69.40	0.66	4.57	0.16	24.7	–	0.38	0.015	1130	296	5.30
Etna	1970	49.91	0.54	26.06	0.54	38.54	0.38	0.27	–	1075	3.79	1.47
Nyiragongo	1959	45.90	1.59	45.44	2.70	2.30	0.55	1.41	–	1020	1.97	0.09
Tolbachik ^d	NB 1976	78.56	3.01	4.87	0.39	0.03	–	0.16	0.57	1000	31.0	0.036
	SB 1976	97.77	0.76	0.08	0.001	0.13	–	0.11	0.74	1100	2433	2.96
Klyuchevskoy ^c	Jul 18, 1988	90.84	1.70	4.47	0.16	0.11	–	0.005	2.02	1050	40.0	0.025
	Aug 25, 1988	98.73	0.59	0.12	0.0001	0.09	–	0.0002	1.42	1100	1640	0.76

Notes: ^a Gases of so-called J-series from classical collection of Jagar 1918–1919; ^{b, c} after Greenland (1987); ^d after I.A. Menyailov et al., 1984; ^e authors' data.

Tolbachik samples display specially high H/C ratios, due to their higher water content.

Such a pattern is typical of a progressive depletion of CO₂ in the melts, with gradual and concomitant enrichment of both water and sulfur in the gas released during the course of eruptions (Gerlach, 1983). Nevertheless, it remains to explain why the sulfur content of both Klyuchevskoy and Tolbachik gases are so low compared to most other basaltic gases. Gerlach (1980) noted relatively low sulfur content in gas from Nyiragongo (Africa), which he explained by low *f*_{O₂} conditions, (lower than FMQ buffer) of the gas-melt system, rather than by a depletion of sulfur in the magma, since Nyiragongo lavas contain up to 0.5 wt.% S, i.e. much more than mid-ocean ridge basalts (~0.1 wt.% S). It is known that the solubility of sulfur in silicate melts depends on various parameters, among

which the Fe content and the oxygen fugacity of the melt (Haughton et al., 1974; Katzura and Nagashima, 1974; Whitney, 1985). At low *f*_{O₂} sulfur occurs in the melt mostly as Fe-sulfides (pyrrotine) and the sulfur fugacity is controlled by the equilibrium:



i.e. by the (FeO/FeS) ratio of the melt independently to its total sulfur content.

From the above considerations, we may propose the following interpretation of the chemical features in the gases from Klyuchevskoy. As a result of eruptive activity and degassing at the summit crater of Klyuchevskoy during the last eruptive cycle ending in 1988, considerable loss of CO₂ and sulfur occurred from the feeding magma. Such degassing resulted in a relative enrichment of water and halogens (HCl, HF) in the residual magma and gases. Sulfur in out-

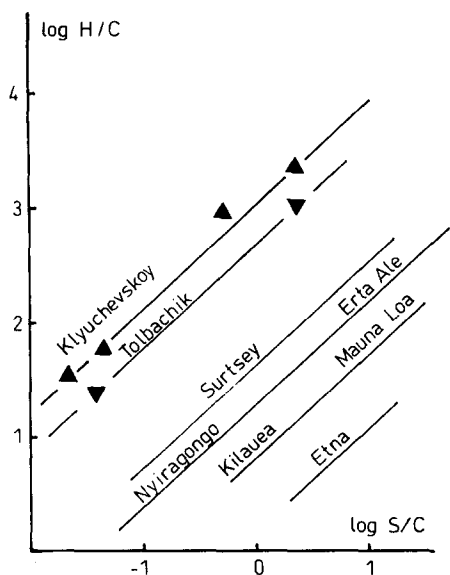


Fig. 2. Correlated variations of H/S and S/C atomic ratios in high-temperature gases of basaltic volcanoes. After Gerlach (1983), except for data on Klyuchevskoy (this paper), Tolbachik (Menyailov et al., 1984) and Mauna Loa (Greenland, 1987a), which were added.

gassed, crystallizing basalt would occur as sulphide, while in the gas phase its fugacity will be controlled by both f_{O_2} and $(FeS/FeO)_{melt}$ ratio. Further analysis of volatile abundances and oxygen fugacity in basaltic glasses from the 1988 flank eruption of Klyuchevskoy will allow to verify this point.

Carbon isotopes and outgassing degree of the melt

Our data on carbon isotopes provide further insight into the above discussion. The $\delta^{13}C$ measured on one sample of CO_2 (sample 2) was -11.6‰ (PDB). It is known that mantle-magmatic carbon dioxide has an average isotopic composition of $-6 \pm 1\text{‰}$ (Allard, 1983; Des Marais and Moor, 1984; Javoy et al., 1986). $\delta^{13}C$ in magmatic gases from basaltic volcanoes range from -6‰ in Afar (Allard et al., 1977; Allard, 1979), -4‰ at Etna (Allard, 1983), to -4 to -2.5‰ in Hawaii (Friedman et al., 1987). Menyailov et

al. (1984) reported a $\delta^{13}C$ of -3.4‰ for high-temperature gases from the Northern Breakthrough of the LTFE.

Now, there is a significant isotopic fractionation of about 4‰ between basalt melt and CO_2 at magmatic temperatures, in favour of the CO_2 (Javoy et al., 1978). New experiments of Belomestnykh and Shilobreeva (1989) with basalts from the Klyuchevskoy volcano at $1250^\circ C$ and 3 kbar pressure give the average value of $\Delta^{13}C$ (melt - fluid) $+4.2 \pm 0.8\text{‰}$. Accordingly, assuming the CO_2 released with $\delta^{13}C_{CO_2} = -11.6\text{‰}$ was in equilibrium with the CO_2 dissolved in the melt, this latter would have had a $\delta^{13}C$ of about -16‰ , i.e. much lower than the "normal" magmatic values. Considering a Rayleigh distillation mechanism for CO_2 degassing from the melt (no extraneous source of CO_2), we can estimate the degree of melt outgassing:

$$\Delta_C^{13} = -6 - (-16) = \Delta_0^{13}C \ln(1 - F) \quad (13)$$

where Δ_0 is the equilibrium isotopic fractionation factor of -4.2‰ and F is the degree of outgassing. Hence $F \approx 91\%$.

If our assumptions are true, then the CO_2 -outgassing degree of the Klyuchevskoy melt in July was of about 90% .

Our arguments from carbon isotopes are based on only one figure and thus are rather speculative. However, this assumption is consistent with both the features of the Klyuchevskoy eruption and the chemical characteristics of the collected gases. A value of -30‰ was obtained by Menyailov et al. (1984) for $\delta^{13}C$ of CO_2 from the Tolbachik Southern Breakthrough, during the latest stage of the eruption (October 1976). Such a low $\delta^{13}C$ may also indicate a large outgassing degree of the corresponding melt toward the end of the eruption.

On the other hand, one may propose that low $\delta^{13}C$ of CO_2 from the Klyuchevskoy gases is due to some contribution of crustal reduced carbon from metamorphic rocks of the basement to the magmas. The enrichment of the

magmatic water in deuterium (sample 2) may also be connected with crustal contamination.

Conclusions

(1) High-temperature (1000–1100°C) basaltic gases from the Klyuchevskoy 1988 flank eruption are particularly rich in water and poor in sulfur. Their chemical composition was close to chemical equilibrium at sampling temperatures. Their oxygen fugacity, calculated from their molar composition, ranges between the FMQ and NNO oxygen buffers.

(2) Although particularly enriched in this gases, water has an isotopic composition typical of “primary” magmatic water. The isotopic composition of molecular hydrogen is consistent with isotopic equilibrium between H₂O and H₂ at the emission temperatures of 1000–1100°C.

(3) The amounts of carbon and sulfur in the gases, the correlated trend of H/C and S/C ratios, as well as, the occurrence of isotopically light CO₂ compared to mantle carbon, are taken as indication that considerable outgassing of the melt took place prior to or during the 1988 flank eruption of Klyuchevskoy.

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