Studies on Volcanic Gases and Gases from Hydrothermal Fields in Kamchatka

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ABSTRACT

This paper describes the main lines of investigation for the volcanic and geothermal research in Kamchatka. Methods of gas sampling in the field and gas extraction from rocks are also described.

INTRODUCTION

In Kamchatka, investigations on volcanic gases begun just after the organization of volcanologic stations in 1936. Since then, Soviet volcanologists have published a number of works dealing with volcanic gases and interpretation of field sampling of volcanic gases at numerous Kamchatka volcanoes. Despite the difficulties in obtaining precise analyses of volcanic gases, after the Second World War several summary works were printed where foreign and our own experiences were used.

The first state, namely the «prechromatographic epoch» in Kamchatka is associated with the names of such investigators as B.I. Piip, V.I. Vlodavets, A.I. Menyailov, S.I. Naboko, E.K. Markhinin, L.A. Basharina, etc. (BASHARINA, 1961, 1963; IVANOV, 1938, 1941; MENYAILOV and NABOKO, 1939; NABOKO, 1959, 1959a; PIIP, 1956; VLODAVETS, 1940).

After the organization of the Institute of Volcanology, Academy of Sciences of URSS in Kamchatka, systematic investigations on volcanic gases became a constituent part of volcanologic programmes.

MAIN DIRECTIONS OF INVESTIGATIONS

At present, all Soviet groups studying volcanoes and related phenomena, follow a few major directions in studies on volcanic gases.

1) Sampling and interpretation of «magmatic» gases, gases emanating from «hornitos» and from fresh effusive and pyroclastic material during volcanic eruptions. The main achievements in this direction concern volcanic gases from lateral eruptions of the basaltic Klyuchevskoy volcano, the Kurile basaltic volcanoes of Alaid and Tyatya, the andesite-dacitic Karymsky and andesitic Bezymianny volcanoes. The greatest success was achieved by Menyailov, Nikitina, Shapar, Markhinin, and Ponomarev during the Tolbachik fissure eruption in 1975-1976 (AVDEIKO *et al.*, 1974; MENYAILOV, 1976, 1976a; MENYAILOV *et al.*, 1980; PONOMAREV *et al.*, 1977; VAKIN *et al.*, 1966).

2) Periodic surveillance of the gas composition of «fumarolic fields» at volcanic centers like Shiveluch, Mutnovsky, Koshelevsky, Ebeko and Mendeleev volcanoes where the temperature of «regime» fumaroles is above 200°C, as well as single observations at numerous volcanoes displaying gas activity, such as Avachinsky, Koryaksky, Kizimen, Kambalny, Golovnin, Komarov, etc. Contemporaneously, investigations on fumarolic incrustations (sublimates) and ore-forming processes as well as temperature meas-

urements are carried out at these volcanoes.
(Byulleten Vulkanologicheskikh Stantsii, from 1937 to 1979; Vulkanologiya i seismologiya, 1979-1980).

3) Constant surveillance of the gas composition of high-temperature hydrothermal systems carried out in order to get answers to some questions on the origin of such systems and their relationship with volcanic activity. At sites having a large thermal potentiality from the economic point of view, these observations help in determining the energetic resources as well as in planning drilling works. Great attention is paid to these investigations because they are of practical (industrial) importance.
(AVERIEV *et al.*, 1965; AVERIEV 1966; BELOUSOV and SUGROBOV, 1976; VAKIN *et al.*, 1970, 1976).

4) Studies on post-magmatic processes were carried out on fresh scoria cones and lava flows. Observations on the gases released from ejected rocks were made and studies were performed on the evolution of gas and mineral composition of sublimates.
(BASHARINA, 1968; NABOKO, 1963; NABOKO *et al.*, 1980; VERGASOVA, 1977; SERAFIMOVA, 1979).

5) Studies on free and dissolved gases from numerous Kamchatka hot and cold springs confined to certbain volcanic or tectonic systems have also been carried out.
(IVANOV, 1966; PIIP, 1937).

6) Finally, studies are carried out on the origin of the gases in inclusions and on the interaction between gases and volcanic rocks.
(PILIPENKO *et al.*, 1979; PILIPENKO, 1980).

In conclusion, in terms of methods of gas sampling, we may distinguish the following four main lines:
1. Gas sampling from natural outlets with temperatures of 100°C and above (up to 1050°C at the large Tolbachik fissure eruption).
2. Gas sampling from boreholes of hydrothermal deposits (from 70°C to 300°C).
3. Sampling of spontaneous gas from thermal springs (100°C).
4. Gas extraction from rocks (700° to 1100°C).

METHODS OF GAS SAMPLING

Gas Sampling from Natural High Temperature Outlets

a) Gas sampling with intermediate absorbers.

In this case, if the precise volume of pumped gas is known, we may determine, from the change of the volume of water, the gas-condensate ratio. NaOH(KOH) absorbs the « acid » part of CO_2, SO_2, H_2S, HCl and HF, which are then analysed by weight (volumetric) analysis. The content in H_2S is determined with $Cd(CH_3COOH)_2$ after iodemetric titration. Absorbers are prepared beforehand in the laboratory.

b) Gas sampling with preliminary condensation.

In this case the gas-condensate ratio is determined first, and then one works with known gas volumes and different absorbers: $Cd(CH_3COOH)_2$, HCl, Ba(OH), etc.

One problem lies with lock-up liquids. Method (b) is suitable when gas emanates under pressure and gas discharge is very high.
Both these methods cannot solve the problem of the change of composition with changing temperature.

Gas Sampling from Steam Gas Pressure Wells.

Such a system is applied to continuous observations of gas emanating from wells. Gas and condensate pass along their own lines. Sensors, chromatographs and thermometers are placed on each line. There are a lot of problems. The main problem is as follows. When H_2S is abundant (0.5 vol.%), electrochemical and chromatograph sensors break in a short period of time. It is then necessary to install a scrubber (absorber) with NaOH. When the gas discharge is high a special absorber and a lot of NaOH are necessary.

Another very important problem is the absence of electrochemical sensors operating reliably for a long time with a short response time for small disturbances and with a good zero line, not speaking of selectivity. Gases and condensates are very «dirty» in the chemical sense. It is necessary to undertake frequent calibrations or special routine discrete measurements.

Much time has been spent to solve this important methodical problem, and we are in contact with designers of sensors (of electrodes) and with producers of special measuring instruments who operate in our complex field conditions.

Spontaneous Gas Collection

While collecting spontaneous gas, particular problems do not arise, which instead arise when the results of the analysis are to be interpreted. We have concluded that it is very useful to carry out complex sampling in each point of gas sampling: gas, dissolved gas, temperature, composition of water, pH and Eh.

Gas Extraction from Rocks

Gas extraction from rocks is a separate line of investigation with its own problems concerning both the methods of extraction and interpretation of results, radioactivity and isotopic ratios of D, O_2, He, Ar, Ne.

INSTRUMENTS AND METHODS OF ANALYSIS

We have the difficulties arising from our geographical isolation from scientific and industrial centres and from severe natural conditions. However, our laboratories are equipped with the minimum necessary. We analyse almost everything by ourselves, and only highly precise investigations such as isotopy of rare gases, chromatomassospectrometry and activation analyses are made in the scientific centres of the Siberian Department of the Academy of Sciences of USSR, in Moscow or Leningrad.

The chemical-analytical methods used include titration, potentiometric titration, polarography, spectrophotometry, atomic absorption and i.r. spectroscopy. We also analyse $^{13}C/^{12}C$, He, Rn and Hg. A great number of modern gas chromatographs are available at the Institute of Volcanology.

Unfortunately, we often have to design instruments for field works ourselves and produce them with the help of other institutions. For these reasons there are no such instruments in serial production.

At present, we carry out field gas investigations using two field instruments. The first is a gas chromatograph, which together with the electrical feed, cylinders with gas-bearers and recorders, weighs about 15 kg. It is rated at continuous operation for approximately 120 hours. It is equipped with 3 columns and two detectors (catarometer and combustion heat detector) and permits analysing N_2, O_2 (0.5 vol.%); H_2 (10^{-4} vol.%); CO (10^{-3} vol.%); CO_2 (0.2 vol.%); CH_4 (0.02 vol. %); H_2S (0.1 vol.%); He (10^{-3} vol.%) (with satisfactory precision).

The second field gas instrument represents a system with diaphragm gas electrodes to H_2 and O_2. It is distinguished by its small dimensions (1 kg) and realiability (especially for O_2) in operation within the temperature interval from 0 to 70°C. Its sensitivity is up to 0.05 vol.%. For its continuous operation a portable recorder is added. These new devices still require adjusting but at present they have already yielded results which have been published (Pilipenko, Taran, this volume).

WAYS OF INTERPRETATION OF RESULTS; SCIENTIFIC PROBLEMS

At present, at our Institute, there are groups of researchers involved in solving problems related to the interpretation of the observed gas composition. Often single problems overlap each other considerably, which requires standardization of methods of sampling and of interpretation to be avoided.

We will enumerate a few major directions, and will comment on our interpretation of field data for each direction.

1) Detection of the latent regularities of the observed gas composition in terms of the following eruption parameters: eruption dynamics, depth, energy and composition of solid products. Study of the degassing conditions of the mantle, crustal and mixed materials. Migration of ore material to the surface (NIKITINA, 1978; VERGASOVA, 1979; OKRUGIN, 1979; SERAFIMOVA *et al.*, 1979; NABOKO and GLAVATSKIKN, 1980).

2) The richest and reliable material was sampled in the thermal crateric fields and in the regions of hydrothermal deposits. Our task is that of correlating the observed variations in time of gaseous and hydrous compositions with the structure, dimensions, and depth characteristics of the studied hydrothermal system; of identifying the «deep-seated» endogenic component and of understanding which deep-seated magmatic process is related to it and how it responds to this process and to its development in time and space (AVERIEV, 1966; VAKIN and KUTYEV, 1979; TRUKHIN and SHUVALOV, 1979).

Judging from major components, it is clear that in most cases gas responds with a good precision to the equilibrium at the temperature and pressure available during sampling. For some systems, such as Mutnovsk, considerable variations of the composition of gas in time are noted, against a background of which «signals», *i.e.* abrupt changes in the gas composition, sometimes appear. A comprehensive study of all parameters of such systems in close cooperation with geophysicists and thermophysicists and a strict statistical treatment of the observed sequences will help us in identifying both the nature of «signals» and the general internal regularities and nature of the proper «noise» of the studied systems.

3) One of the problems we have been dealing with for many years is the origin and evolution of Carbon compounds in the magmatic process. At present, in addition to field sampling, we are trying to consider it from a chemical point-of-view.

Field sampling provides us with data on the distribution of C-H-O bearing components in volcanic gases. Particular attention is paid to the relations between hydrocarbons, and to the search of complex organic compounds in deliberately sterile samples with the help of high-sensitive chromass-spectrometers. In the last few years we began to pay great attention to isotopic ratios. Now many summary papers concerning this problem have appeared (ROZHKOV, 1979; KAMENSKII, 1976).

This problem causes us to face the next problem, *i.e.* that of determining the catalytic properties of the erupted materials in contact with C-H-O bearing gases. We compare data on the hydrocarbon distribution obtained by different ways, namely equiponderant calculations, reactions in weak and strong electrical discharges, cracking, catalytic transformation and hydrocarbons of inclusions in erupted rocks. At present we have gathered sufficient material to draw preliminary conclusions. Catalytic properties are studied by us using standard technological procedures (TARAN, 1980).

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