SENSOR EQUIPMENT FOR MEASURING THE PARAMETERS AND COMPOSITION OF VOLCANIC GASES. RESULTS OF MEASUREMENTS AT KUDRIAVY VOLCANO, ITURUP, SOUTH KURILES

Korzhinsky M.A., Tkachenko S.I., Botcharnikov R.E., Zhdanov N.N., and Osadchii E.G.

Institute of Experimental Mineralogy, Rus. Acad. Sci., Chernogolovka, 142432, Russia
E-mail: korj@iem.ac.ru

An application of sensor equipment and techniques at geochemical studies of volcanic gases allows to conduct direct *in situ* measurements of gas composition and physical parameters (e.g., Sato and Wright, 1966; Gantes et al., 1983). When connected to automatic registering devices, such sensors may be used for continuos monitoring surveillance of volcanic gases and hence may be a useful tool for precise quantitative estimation of changes in volcanic activity (Kazahaya et al., 1988; Vitter, pers. comm., 1999). Such field sensor equipment and technique has been developed in the Institute of Experimental Mineralogy RAS. Sensors were successfully tested both in monitoring operation and in single measurements at high-temperature (up to 940°C) fumaroles of Kudriavy volcano.

Sensor equipment

Oxygen sensor. The oxygen partial pressure (pO_2) in volcanic gases was measured with application of oxygen sensor based on CaO (CSZ) or Y_2O_3 (YSZ) stabilized ZrO_2. The following galvanic cell was arranged as:

$$\text{Pt, Fe(s), FeO(s), } pO_2\text{(g)} \mid \text{CSZ or YSZ} \mid \text{Pt, } pO_2\text{(g)}$$

The sensor design is analogous to one developed by Gantes et al. (1983). Fe-FeO pair was used as an inner reference oxygen buffer.

Sulfur sensor. The sulfur partial pressure (pS_2) was measured using the sensor on a base of Ag β-alumina as solid electrolyte (Sato and Wright, 1966; Osadchii et al., 1997) in the galvanic cell:

$$\text{Pt, Ag(s), } \mathbf{a}_{Ag} \mid \text{Ag } \beta\text{-}Al_2O_3 \mid Ag_{2+x}S\text{(s, l), } pS_2\text{(g), Pt}$$

Chlorine sensor. The galvanic cell of this sensor should be described as:

$$\text{Pt, } Na_xWO_3\text{(s), } \mathbf{a}_{Na} \mid \text{NASICON} \mid \text{NaCl(s, l), } Cl_2\text{(g), Pt}$$

where tungsten bronze is the inner reference sodium buffer, and NASICON is the Na^+-conducting solid electrolyte.

Fluorine sensor. The fluorine partial pressure (pF_2) in volcanic gases was measured by the sensor based on monocrystal of MgF_2 as a F^--conducting solid electrolyte and Al_2O_3-AlF_3-O_2 as an inner reference system. The galvanic cell of this sensor should be described as:

$$\text{Pt, } Al_2O_3\text{(s), } AlF_3\text{(s), } pO_2\text{(g), } pF_2\text{(g)} \mid MgF_2 \mid pO_2\text{(g), } pF_2\text{(g), Pt}$$

in an assumption that pO_2(g) on the left and right sites of the cell above are the same.

Excess gas pressure sensor. This sensor is designed as a quarts tube connected with sensitive pressure transducer via silicon hose and protecting membrane. The excess gas pressure in fumarole outlet is an individual characteristic for each fumarole and depends on a gas head in fumarolic conduit. The accuracy of pressure measurements was estimated as $\pm 2 \cdot 10^{-4}$ bar.

Hydrogen sensor. The action of hydrogen sensor is based on diffusion of hydrogen through platinum membrane at elevated temperatures. Its design is analogous to one described by (Shaw, 1967). The sensor consists of platinum capsule hermetically connected with sensitive pressure transducer via stainless-steel capillary pipe. Remarkable feature of this sensor is the using of high sensitive pressure transducer which allows to measure absolute pressure and does not depend on atmospheric pressure. The accuracy of measurements is $\pm 2 \cdot 10^{-4}$ bar or ±0.02 mol% of hydrogen in a gas phase.

Single measurements

Single measurements were conducted at different fumaroles with temperature range of 350 to 900°C in the Kudriavy crater.

Sulfur. The measurements of pS_2 in volcanic gases of Kudriavy volcano were performed in 1995 (Fig.1). The obtained data are in a good agreement with ones calculated from analyses of gas samples collected according to Giggenbach's method (Giggenbach, 1975) in 1991-93. It implies that this sulfur sensor can be successfully used for direct pS_2 measurements in fumarolic gases. However, the long-term usage of this sensor in gases at elevate temperature leads to recrystallization of Ag_2S and gas penetration to the surface of solid electrolyte. It does not allow to apply such sensors in a long-term monitoring operation at temperature higher then 500°C.

Fluorine. The fluorine partial pressure in volcanic gases was measured in 1999 (Fig.2). The pF_2 values were calculated using temperature dependence of pO_2 in the inner reference system corresponding to one measured earlier in the Kudriavy gases by Osadchii et al.(1997). The obtained values are in a good agreement with the data calculated from analyses of gas samples collected in 1991-95. It allows to suggest that this sensor can be applied for in situ measurements of fluorine fugacity but its usage in long-term measurements requires further testing.

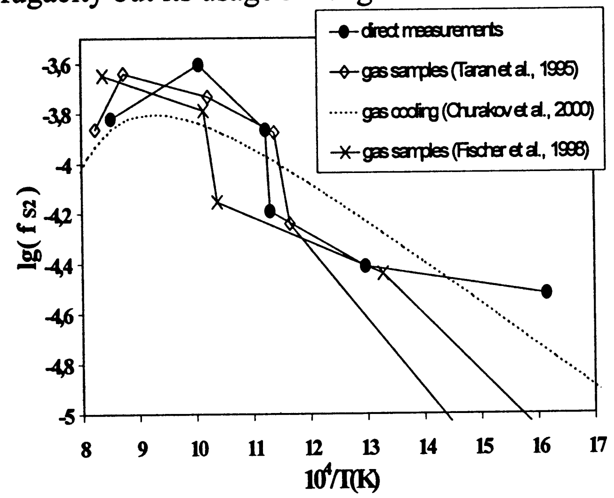


Figure 1. Temperature dependence of sulfur fugacity in fumarolic gases of Kudriavy volcano.

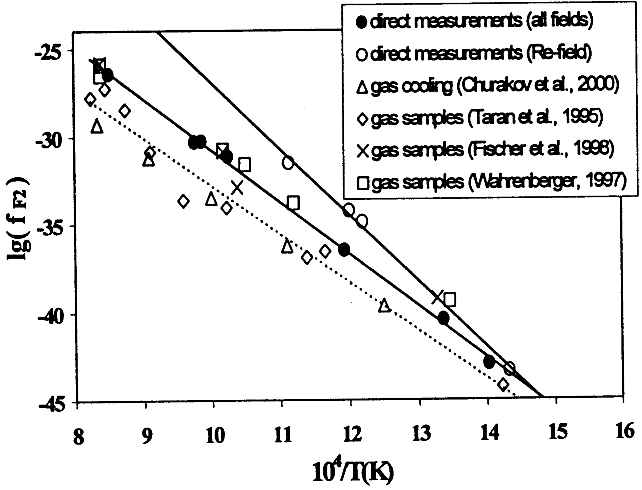


Figure 2. Temperature dependence of fluorine fugacity in fumarolic gases of Kudriavy volcano. Dotted line is the linear trend for data recalculated from (Taran et al., 1995), upper solid line is the linear trend for direct measurements at 'Re' fumarole field, lower solid line is the trend for direct measurements at the other fumarole fields.

Monitoring measurements

Measurements in monitoring operation were conducted at Kudriavy volcano in 1998 and 1999. The measurements were performed applying different kind of sensors including thermocouple, stationary data logger, and portable computer for automatic recording the data. The control measurements of temperature, fugacity of oxygen and gas sampling in the same fumaroles were periodically carried out during monitoring. Seismic activity was measured at the Kudriavy crater in 1999.

The results of measurements in 1998 are presented in Fig.3. The concentration of hydrogen in volcanic gas (mol%) was calculated as follows: $X_{H2} = pH_2 / (P_{total}) \cdot 100$, where pH_2 is the hydrogen partial pressure and P_{total} is the total pressure in fumarole outlet. The data on hydrogen concentrations obtained from analyses of gas samples are also shown in Fig.3. The data displayed relatively constant values of gas parameters during a long time.

Figure 3.

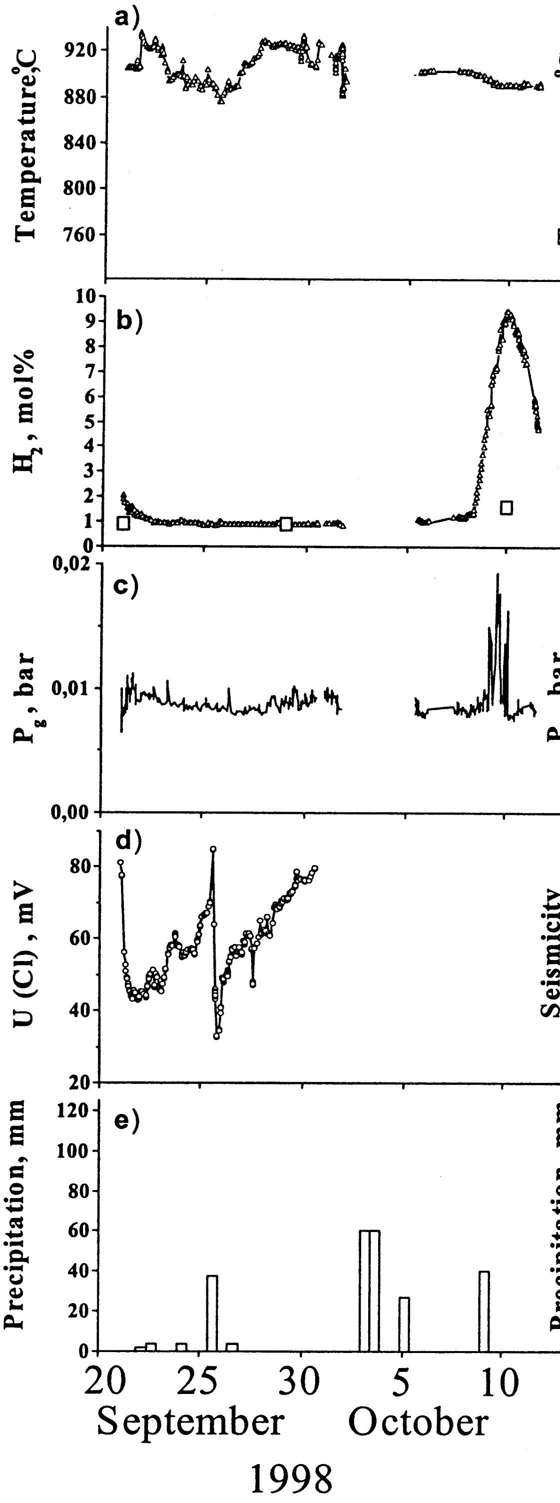
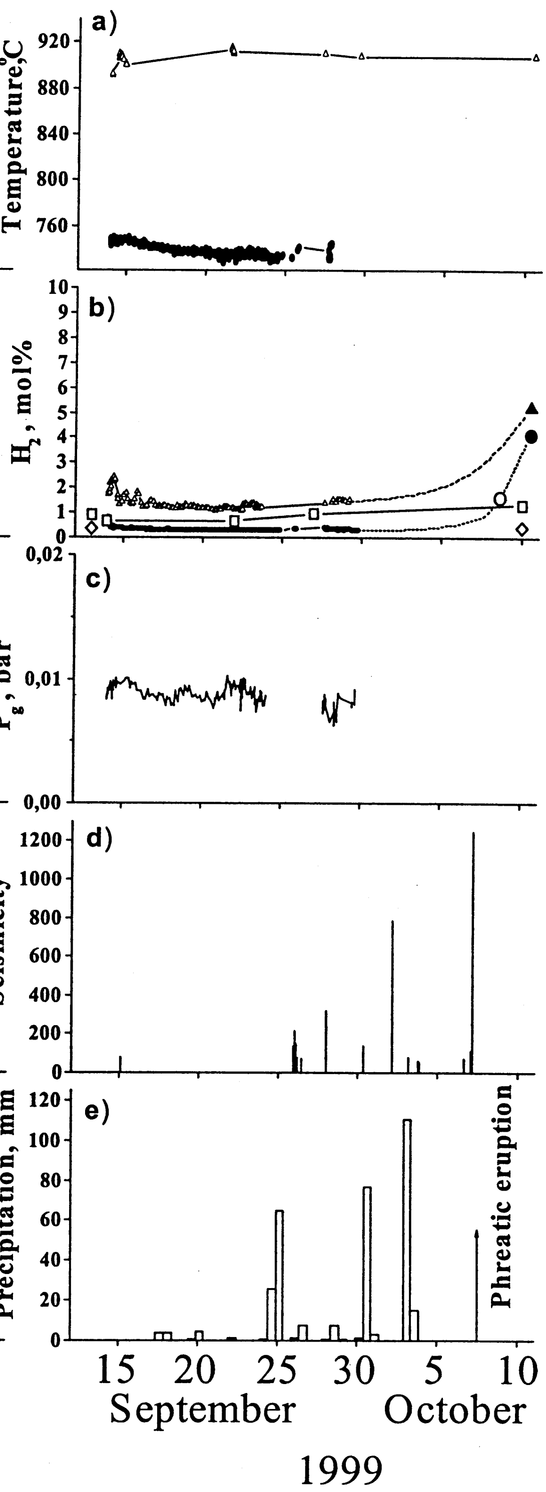


Figure 4.



Date

Figure 3. The results of measurements of gas parameters in 'F-940' fumarole in 1998.

a) Temperature
b) X_{H2} (mol%), open squares are gas samples
c) Excess gas pressure
d) E (Cl_2), mV [the lack of thermodynamic data for Na_xWO_3 does not allow to determine f_{Cl2} value in fumarolic gases yet]
e) Precipitation at the Kudriavy crater

Figure 4. The results of measurements of gas parameters in fumaroles 'F-940' and 'F-750' in 1999.

a) Temperatures
b) X_{H2} (mol%). Open triangles are the results of direct measurements at 'F-940' fumarole while filled circles are the calculated values from measured f_{O2} at 'F-750' fumarole. The large open circle is a directly measured value at 'F-750' fumarole. The large filled circle and triangle are the recalculated values from fO_2 for 'F-750' and 'F-940' fumaroles, respectively. Open diamonds and squares are the analyses of gas samples from 'F-750' and 'F-940' fumaroles, respectively.
c) Excess gas pressure in 'F-940' fumarole
d) Seismicity measured at the Kudriavy summit
e) Precipitation at the crater

However, a dramatic increase in hydrogen concentration was measured from 1 mol% up to 10 mol% from October, 7 to 11. The excess gas pressure had been simultaneously changing from 0.008 to 0.018 bars. Hydrogen concentration in gas sample collected on October, 10 was 1.58 mol%. These changes in gas parameters occurred five days after intense meteoric precipitation (>100 mm).

The results of measurements in 1999 are presented in Fig.4. Measuring gas parameters were relatively constant as ones observed in 1998. The monitoring system switched off because of the drop in power supply on October, 29. Figure 4 also presents single measurements of pO_2 conducted on October, 10, three days after phreatic eruption. The calculated values of hydrogen content in fumarolic gases from measured oxygen fugacity revealed 5.5 mol% and 4.0 mol% in fumaroles with temperature 910°C and 740°C, respectively. Temperature of high-temperature fumarole was relatively constant in the same period.

The studies mentioned above imply that sensor equipment and technique can be successfully applied for direct measurements in high-temperature volcanic gases. It is important that pioneering hydrogen sensor showed its validity in aggressive volcanic gases. However, the significant difference in hydrogen concentration measured by the sensor and analyzed in gas samples can not be clearly explained to date and requires further investigations.

The performed studies revealed changes in gas-dynamic regime of fumaroles and intrinsic seismic activity of the volcano after intense meteoric precipitation. These changes were determined both from sensor measurements (increase in pH_2, P_g, seismicity, and decrease in pO_2) and from conventional methods of gas sampling (decrease in water and increase in gas content respectively). Intense rains led to phreatic eruption in 1999. The observed changes in gas composition and possible causes of phreatic eruption are discussed in details by Korzhinsky et al. (2000).

References

Churakov, S.V., Tkachenko, S.I., Korzhinskii, M.A., Bocharnikov, R.E., and Shmulovich, K.I. Evolution of composition of high-temperature fumarolic gases from Kudryavy Volcano, Iturup, Kuril Islands: the thermodynamic modeling. *Geochem. Intern.*, **38**: 436-451, 2000.

Fischer T. P., Giggenbach W.F., Sano Y., and Williams S. N. Fluxes and sources of volatiles discharged from Kudryavy, a subduction zone volcano, Kurile Islands, *Earth and Planet. Sci. Letters*, **160**, 81-96, 1998.

Gantes, M., Sabroux, J.-C., and Vitter, G. Chemical sensors for monitoring volcanic activity. In: *Forecasting volcanic events* (eds. H.Tazieff and J.C. Sabroux), 337-386, Elsevier, 1983.

Giggenbach W.F. A simple method for the collection and analysis of volcanic gas samples, *Bull. Volcanol.*, **39**, 132-145, 1975.

Kazahaya, K., Takahashi, M., Ohsumi, T., Soya, T., Ando, N., Hirabayashi, J., Kusakabe, M., Hamada, R. Chemical monitoring of volcanic gas from crater of Mt. Mihara, Izu-Oshima. *Bull. Volcanol. Soc Jpn., Ser. 2*, **33**: 13-19 (in Japanese with English abstract).

Korzhinsky, M.A., Botcharnikov, R.E., Tkachenko, S.I., and Steinberg, G.S. Degassing activity of Kudriavy volcano, Iturup, Kurile Islands during 1990-1999. Phreatic eruption of 1999. *Earth, Planets and Space*, (submitted), 2000.

Osadchii, E.G., Lunin, S.E., Korzhinsky, M.A., Tkachenko, S.I., and Taran, Yu.A. fO_2 and fS_2 measurements by electrochemical sensors in high-temperature fumaroles of active volcanoes. *Geochem. Int.*, **35**: 66-73, 1997.

Sato, M. and Wright, T.L. Oxygen fugacities directly measured in magmatic gases. *Science*, **153**: 1103-1105, 1966.

Shaw, H.R. Hydrogen osmosis in hydrothermal experiments. In: *Researches in geochemistry* (ed. P.H. Abelson), John Wiley, N.Y., **2**: 521-541, 1967.

Taran Yu.A., Hedenquist J.F., Korzhinsky M.A., Tkachenko S.I., and Shmulovich K.I. Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril islands, *Geochim. Cosmochim. Acta.*, **59,** 1749-1761, 1995.

Wahrenberger C.M. Some aspects of the chemistry of volcanic gases, *Ph.D. dissertation, Zurich*, 1997.