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THE COMPOSITION OF AIR AND SPONTANEOUS GASES IN THE DEATH VALLEY IN KAMCHATKA

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In 1975, a number of dead beasts and birds, lying in postures indicative of sudden death, were discovered in the valley of a brook, the source of Geĭzernaya River, 850–900 m above sea level, at the southeast base of Mount Zheltaya. It is associated with the volcanic massif of Kikhpinych strato-volcano. As reported by the Kronotskiĭ Wildlife Reserves, lost in this Death Valley in the last five years were 13 bears, 3 wolverines, 9 foxes, one hare, 86 mice, one sea eagle, 19 crows, and more than 40 smaller birds. Regular observations showed that the death of the larger animals mostly coincided with the thaw, which lasts here from May to mid–July.

In 1976, V. L. Leonov and V. A. Voronkov, of the Institute of Volcanology, noticed outlets of thermal springs in the Death Valley. The spontaneous gases of these springs consisted mostly of carbon dioxide, with a small admixture of hydrogen suflide. It was assumed that the death of the animals could have been caused by the accumulation of carbon dioxide in the depressed parts of the valley. Similar instances were recorded also in other areas of volcanic activity. Thus, dead grizzly bears were found in the Dead Canyon, near the Yellowstone National Park, USA. Bodies of suffocated boars and other animals were repeatedly found near outlets of carbon dioxide jets (mofettes) in the Death Valley in Jawa. Each time carbon doixide [5], which accumulates in depressions, in the absence of convective mixing of the air [10], was held responsible.

The Kamchatka Death Valley is confined to the Kikhpinych volcanic massif exhibiting solfataric and fumarolic stage of activity. The young Savich cone, in the northeast part of the massif, has an active fumarole near its summit. The solfataric fields on the south and southwest slopes of Kikhpinych Volcano, composed of variegated clay and alunite rocks streaked with sulfur, are dotted over with outlets of steam and gas jets, the latter containing chiefly CO_2 and H_2S, with some SO_2 and other gases [3, 6].

The Death Valley overlies a deep fracture running west wardly across the Uzon caldera; its hydrothermal system is known to be of sulfide type, hydrogen sulfide constituting up to 8.0 vol. % [4, 7].

The area where dead animals were found is confined to a narrow valley 2 km long and 100–500 m wide. There is, however, a small space, 100 x 30 m large, where dead birds and animals are found most often. It is on the lower boulder-and-shingle terrace of the brook, 0.5–0.7 m high. The edges are composed of argillized rocks, with abundant inclusions of sulfur. Deposits of practically pure native sulfur occur in the upper course of the small brooks running down to this space from the east.

On the left bank of the brook a very strong sulfuric acid leaching of the sulfur-bearing rocks is noted, which is due to the oxidation of sulfur by thiobacteria lowering the pH of the solutions to values below 2. Downward from the area the brook carrying acid water, received an inflow of snow melt water, and large quantities of ocherous iron oxides are deposited in its channel. Downstream, on both banks of the brook, outlets of mofettes with a noticeable smell of hydrogen sulfide, are observed, but only a few carcasses of small birds were found there.

In the Death Valley itself, the oxidative activity of thiobacteria is suppressed; their concentration on sulfur samples was only 10^3 cells/g, i.e., several orders of magnitude lower than usual in sulfuric-acid leaching. Both, weak evolution of the bacterial processes of sulfur oxidation in this area and the presence of hydrogen sulfide in the gases of the mofettes suggested that hydrogen sulfide was the principal cause of the animals' death.

Surveying the Death Valley early in May, 1979, we found a dead fox. The traces in the snow, which had fallen the day before, showed that the fox had come down the steep bank and died suddenly; a dead snow bunting lay in front of it. In that place the snow had caved in, forming a peculiar well. Descending into it, we felt the smell of hydrogen sulfide and had to put on our gas masks to stop the dizziness and tachycardia.

Air samples taken 10–15 cm above the water table contained 21 and 23 mg/liter (1.41 vol. %) of hydrogen sulfide and were extremely low in oxygen (Table I, sample 10^b–c/79). Hydrogen sulfide content at a level of 50 cm above water table decreased to 10.2 mg/liter (0.69 vol. %). Hydrogen sulfide content of the water in the cold brook was 105.4 mg/liter; all stones in the brook were thickly coated with collodial sulfur. The snow around the "well" was also saturated with hydrogen suflide. A second survey of this place, in the fall of 1979, showed that the brook had died up, the sulfur deposit had disappeared, and no gas jets concentrated or gassing springs could be found in the neighborhood. Nevertheless, in the niches beneath sulfur mounds, the air contained higher hydrogen sulfide concentrations. No hydrogen sulfide was found this time in the air in the open wind-swept places.

Surveying the Death Valley in August 1981, in the peiod of final melting of the névé and strong winds blowing through the valleys, we found no fresh evidence of animals' death. Dead small birds and mice were scattered about the gas-emitting fissures, while hundreds of dead insects marked out the gas outlets. The delivery of hydrogen sulfide over these zones was evidenced by the intense blackening of the lateral rocks, due to the formation of iron disulfide. In an 80-ml air sample injected with a rubber bulb into a vessel containing cadmium acetate (sample parallel to sample 2106, Table I), 1.3 vol. % of H_2S was determined. On the other hand, two air samples (Table I, samples 2101 and 2107) taken at the same place using an electric pump (pumping 30 liters of gas through a 500-ml vesse for one hour) were found to contain no hydrogen sulfide, apparently because of its further oxidation by oxygen. In samples 2103 and 2105, taken at the same place and analyzed at different laboratories, and in sample 2106, a certain excess of oxygen in respect of nitrogen (oxygen ratio) was detected, probably due to the entrance of oxygen and nitrogen with meteoric ground water. Upon its contact with the jets of hot gas, the water undergoes degasation, the N_2/O_2 ratio in the emerging gas stream changes accordingly, since nitrogen and oxygen solubility (as well as concentration) in water differs from that of oxygen noticeably. A similar fact was observed earlier at Ebeko Volcano [9].

To verify the assumption that gases may be generated by the heated mass of sulfur deposits an analysis was made of the occluded gases in two samples of native sulfur taken from sulfur mounds in the area where dead animals were found. The samples were placed in glass ampoules and evacuated. At 10^{-6} Torr, the ampoules were sealed and kept in a tube furnace for one h at $100 \pm 1°C$. Then they were placed into the

TABLE I

Composition of the Air and Spontaneous Gases in the Death Valley

Analysis No.	Sample No.	Sampling date	T, °C	Gas composition, vol. %														
				H_2	O_2	N_2	CO_2	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	Ar	H_2S	He	COS	SO_2	Σ
1	10^b–c/79	May 14, 1979	4	0.0	8.65	53.90	36.80	0.0	0.6525	0.0008	0.0	0.0002	–	0.0	0.0	–	–	100.00
2	10–c/79	May 14, 1979	4	0.0148	16.07	74.09	2.69	0.0	0.0717	–	0.00033	0.0	0.666	0.0	–	–	–	93.60
3	11–c/79	May 14, 1979	46	0.891	0.028	5.62	82.18	–	0.452	–	0.0	0.021	–	6.76	–	–	–	95.93
4	12–c/79	May 14, 1979	28	0.0	0.0	5.92	82.44	–	4.29	–	0.0	0.0026	–	7.35	–	–	–	100.00
5	2101	Aug. 21, 1981	12	0.0	20.95	77.52	0.019	–	0.00091	0.0	0.0	0.0	–	0.0	0.0	–	–	98.49
6	2107	Aug. 21, 1981	12	0.0	20.71	78.09	0.063	–	0.00043	0.0	0.0	0.0	–	0.0	0.0	–	–	98.86
7	2103	Aug. 21, 1981	98	0.0	20.70	76.70	1.140	0.0	0.38	0.0	0.0	0.0	0.95	0.012	0.0	0.0001	0.008	99.89
8	2105	Aug. 21, 1981	98	0.0	21.78	78.09	0.031	0.0	0.0035	0.0	0.0	0.0	–	0.0	0.0	–	–	99.90
9	2106	Oct. 21, 1981	32	0.0	24.6	73.8	0.14	0.0	0.34	0.0	0.0	0.0	–	0.016	0.0	0.0004	0.0092	98.90
10	2104	Aug. 21, 1981	12	0.263	0.0	2.26	93.45	0.0	1.66	0.0	0.0	0.0	0.156	1.739	0.0	–	–	99.54

Note. Sampling sites: 10^b–c/79 – air 0.5 m from the ground in the area where dead animals were found; 10–c/79 – same, 1 m above the ground; 11–c/79 – griffon on the left bank of the Geĭzernaya River, 0.8 km below the area; 12–c/79 – griffon near the 11–c/79 point; 2101 – ground air in the area where dead animals were found; 2107 – same, 1 m above the ground; 2103, 2105 – hot gas from the collapse sink-hole in the sulfur mound; 2106 – air from the fissure zone where iron sulfide is formed; 2104 – spontaneous gas of the source in the brook bed. Analyses 1–6, 8, 10 were performed by N. Ya. Nepomnyashchaya at the Laboratory of Volcanic Chemistry, Institute of Volcanology, Far-East Scientific Center, USSR Academy of Sciences, on a *Gazokhrom* chromatograph; analyses 7, 9 were performed by Yu. M. Miller at the Institute of Microbiology, USSR Academy of Sciences, with an MI–2101 mass spectrometer. Dash – not analyzed for; 0.0 – not detected. In gas samples containing oxygen, hydrogen sulfide is unstable and completely oxidized to elemental sulfur. Therefore, regardless of its abundant liberation on the Death Valley site, the presence of hydrogen sulfide in the air, analyzed 1.5 months after sampling, was not confirmed.

evaculated let-in system of a mass spectrometer and opened. The liberated gas entered the ionization zone of the ion source.

The mass spectra were taken in a 2–250 a.m.u. range covering all the gas components expected to be present in the samples. As the sensitivity of the mass spectrometer varied selectively, depending on the compound, the results were adjusted by introducing coefficients of relative sensitivity. Particular attention was paid to the molecular peaks of CH_4, H_2S, CO_2, COS, and SO_2. It was not possible to determine the CO content because of the superposition of an intense peak of N_2. For the same reason, the upper limit, 10^{-3} %, for HCN can be determined to a rough approximation.

In composition, the evolved gas (Table II) is, to a certain extent, intermediate between ordinary air and the samples of spontaneous gas taken in the Death Valley. It is probable that this gas composition originated as a result of the diffusion of the stream of fumarole gases, and of atmospheric oxygen and nitrogen, into the sulfur deposit. The presence of sulfur dioxide, carbonyl sulfide (COS), and carbon disulfide, in the occluded gases is noteworthy; carbonyl sulfide was found earlier in pyroclastic flows of Bezymyannyĭ Volcano [1, 2] but carbon disulfide was never found on volcanoes before.

TABLE II

Composition of Occluded Gases, vol. %

Sample No.	N_2	O_2	Ar	CO_2	SO_2	COS	CS_2	H_2S†
1044/1	56.9	16.6	0.69	23.9	0.16	0.16	0.45	0.21
1044/2	51.0	14.1	0.65	30.6	0.37	0.14	0.38	0.19
Air (reference)	78.0	20.9	0.93	0.0	–	–	–	–

Note. Samples: 1044/1 – disintegrated to particle size 5–10 μm; 1044/2 – not disintegrated; 1044/1 – 3.44 g weight, contained 62.5 ml of gas; 1044/2 – 3.86 g weight, contained 63.6 ml of gas; the dagger refers to the approximate values of hydrogen sulfide content, obtained allowing for the superposition of the mass spectrometric peaks of oxygen isotopes. The specimens were analyzed by Yu. M. Miller with an MI–2101 mass spectrometer. The total amount of gas was determined on the basis of the air reference.

Thus, apart from carbon dioxide in fairly high concentrations, the air in the Death Valley has been found to contain also H_2S, SO_2, COS, and CS_2. These substances seriously affect the central nervous system: 0.1% of H_2S in the air causes bad poisoning and paralyzes animals; 0.2% of SO_2 produces syncope; 0.5% of CS_2 affects the central nervous system and different organs, although it does not show at once; COS is similar in its toxic effect to H_2S but acts more slowly [8, 11].

Considering that the air sampling in August, 1981, was accompanied by strong wind blows through the Valley, it is quite possible that in calm weather concentrations of heavy toxic components like CO_2, H_2S, SO_2, COS, and CS_2 in the ground air may be higher. Stable stratification of gas layers sharply differing in chemical composition (chemical meromixy) depends on the microrelief of the locality, and on the weather [10]. In the Death Valley, this phenomenon must have been triggered off by the inversion of atmospheric temperature during the snow melt, followed by the accumulation of carbon dioxide and sulfur compounds in the ground air.

References

1. L. A. Basharina, *Tr. Lab. Vulkanol. AN SSSR* 19: 69–79 (1961) (in Russian).
2. O. G. Borisov, in: *Sovremennyĭ vulkanizm* (Recent volcanism) (Moscow: Nauka, 1966): 153–160 (in Russian).
3. V. I. Vlodavets and B. I. Piĭp, *Byul. Vulkanol. St.* No. 25: 37–40 (1957) (in Russian).
4. G. A. Karpov and A. L. Pavlov, *Uzon-Geĭzernaya gidrotermal' – naya rudoobrazuyushchaya sistema Kamchatki* (The Uzon-Geĭzernaya hydrothermal rock-forming system of Kamchatka) (Novosibirsk: Nauka, 1976) (in Russian).
5. G. A. Macdonald, *Volcanoes* (Englewood Cliffs N.J.: Prentice-Hall, 1972).
6. S. I. Naboko, *Byul. Vulkanol. St.* No. 20: 52–59 (1954) (in Russian).
7. S. I. Naboko and S. F. Glavatskikh, *Dokl. AN SSSR* 191, No. 3: 684–688 (1970) (in Russian).
8. B. V. Nekrasov, *Osnovy obshcheĭ khimii* (Fundamentals of general chemistry) 1 (Moscow: Khimiya, 1973): 323, 329, 571 (in Russian).
9. K. A. Skripko, E M. Fil'kova, and G. G. Khramova, *Byul. Vulkanol. St.* No. 42: 42–55 (1966) (in Russian).
10. K. A. Skripko, *Byul. Vulkanol. St.* No. 51: 64–69 (1975) (in Russian).
11. *Encyclop. gas et l'air liquide* (Amsterdam: Elsevier, 1976).