consistent estimates of the wind and buoyancy forcing should be available from the re-analysis activities now underway at international forecasting centres. It should also provide a useful testbed for development of coupled atmosphere–ocean models of climate change. ☐

Received 15 November 1993: accepted 23 March 1994.

1. Fuglister, F. C. *Atlantic Ocean Atlas* (Woods Hole Oceanographic Instn, Woods Hole, 1960).
2. Roemmich, D. & Wunsch, C. *Deep-Sea Res.* **32,** 619–664 (1985).
3. Manabe, S., Stouffer, R. J., Spelman, M. J. & Bryan, K. *J. Climate* **4,** 785–818 (1992).
4. Mikolajewicz, W., Santer, B. D. & Maier-Reimer, E. *Nature* **348,** 589–593 (1990).
5. Roemmich, D. & Wunsch, C. *Nature* **307,** 447–450 (1984).
6. Joyce, T. M. *Deep-Sea. Res.* (in the press).
7. Fine, R. A. & Molinari, R. L. *Deep-Sea Res.* **35,** 1441–1450 (1988).
8. Lavin, A. M., Thesis, Massachusetts Inst. Technol. (1993).
9. Bindoff, N. L. & Church, J. A. *Nature* **357,** 59–62 (1992).
10. Bindoff, N. L. & McDougall, T. J. *J. Phys. Oceanogr.* (in the press).
11. Mantyla, A. W. *Deep-Sea Res.* (in the press).
12. Bryden, H. L. in *Interactions Between Global Climate Subsystems* (eds McBean, G. A. & Hantel, M.) 65–75 (Geophys. Monogr. No. 75, Am. Geophys. Un., Washington DC, 1993).
13. Broecker, W. S. *Oceanography* **4,** 79–89 (1991).
14. Levitus, S. *Climatological Atlas of the World Ocean* (NOAA Prof. Pap. No. 13, Us Govt. Print. Off., Washington DC 1982).
15. Schlesinger, M. E. & Mitchell, J. F. B. *Rev. Geophys.* **25,** 760–798 (1987).
16. Bretherton, F. P., Bryan, K. & Woods, J. D. in *Climate Change The IPCC Assessment* (eds Houghton, J. T., Jenkins, G. J. & Ephraumus, J. J.) 173–193 (Cambridge Univ. Press, 1990).
17. Manabe, S. & Stouffer, R. J. *Nature* **364,** 215–218 (1993).
18. Read, J. F. & Gould, W. J. *Nature* **360,** 55–57 (1992).
19. Manabe, S., Bryan, K. & Stouffer, R. J. *J. Phys. Oceanogr.* **20,** 722–749 (1990).
20. Dietrich, G. *Atlas of the Hydrography of the Northern Atlantic Ocean* (Conseil International Pour L'Exploration de la Mer, Charlottenlund Slot, Denmark, 1969).
21. Lehman, S. *Nature* **365,** 108–110 (1993).

ACKNOWLEDGEMENTS. We thank Junta de Gestión del B.I.O. *Hespérides* for its support and collaboration in carrying out the 1992 transatlantic section, and we appreciate the assistance of the captain, officers and crew of the *Hespérides*. We also thank, J. Molinero for help with the measurements and with the data processing and C. Wunsch, D. Roemmich, J. Read, J. Price and T. Joyce for their comments. This work was supported by the Instituto Español de Oceanografía and Comisión Interministerial de Ciencia y Tecnologia, by the US NSF and NOAA, and by the UK NERC.

Discovery of a pure rhenium mineral at Kudriavy volcano

M. A. Korzhinsky*, S. I. Tkachenko*,
K. I. Shmulovich*, Y. A. Taran† & G. S. Steinberg‡

* Institute of Experimental Mineralogy, Russian Academy of Sciences,
142432 Chernogolovka, Russia
† Institute of Volcanic Geology and Geochemistry,
Russian Academy of Sciences, 683006 Petropavlovsk-Kamchatsky,
Bulv. Piipa 9, Russia
‡ Institute of Volcanology and Geodynamic ANSRF,
693008 Yuzhno-Sakhalinsk, Box 18, Russia

KUDRIAVY volcano on Iturup island in the Kuril arc is an active calc-alkaline volcano. It has not erupted this century; its current volcanic activity is characterized by hot (up to 910 °C) gas jets which have been stable for at least 30 years. The composition of the gaseous emissions is typical of high-temperature fumaroles, but we report here the discovery of unusual subsurface sublimates associated with one gas jet—a sulphide mineral containing rhenium as the only cation. To our knowledge, this is the first reported occurrence of a pure rhenium mineral. The concentration of rhenium in the fumarole gas is only 2–10 p.p.b., so the condensation of pure rhenium sulphide from this gas requires both enrichment of rhenium by eight orders of magnitude and remarkable selectivity. Rhenium is generally believed to exist in only trace amounts at the Earth's surface, but our findings demonstrate that it can be readily mobilized, dispersed and concentrated by degassing magmas.

The andesito-basaltic Kudriavy volcano (986 m) is located on the northern tip of Iturup island in the Kuril volcanic arc, which divides the Okhotsk sea and Pacific ocean. The last recorded explosion took place in 1883. (A later date of 1949 attributed[1] to the last eruption is probably not correct, as remains of an early twentieth century Japanese sulphur mine can still be seen in the crater.)

The volcano was visited for a field trip in 1961, and since 1989 annual field work has been undertaken. We have made temperature measurements on the volcano since 1990. In that year the highest temperature measured was ~770 °C; in 1991 we managed to penetrate into the 'hot zone' which yielded a fumarole temperature of ~910 °C (Fig. 1). In 1992, this fumarole yielded the same temperature, and a new fumarole with a temperature of 940 °C was identified. This is probably the maximum stable temperature of fumaroles measured over a continuous period.

No noticeable changes of temperature or the power of gas emission have been detected since 1961 and during 1989–93. Repeated temperature measurements of individual fumaroles over the last 5 years gave the same results, within the error of measurement. As the temperature of the jets and the power of the gas emission appear to be constant, we conclude that the process of magmatic degassing is itself essentially constant.

Gas samples were taken using the Giggenbach method[2], trapping H_2S by cadmium acetate. Gas compositions[3] of the high-temperature fumaroles are typical of the island arc volcanoes: 95 mol% H_2O, 3–4 mol% CO_2, ~1 mol% SO_2, 0.4–0.7 mol% H_2S, with H_2, HCl and HF present in smaller quantities. CO, CH_4 and so on are present in minimal amounts. Excluding H_2O and CO_2, a constant content of HCl and HF is found ($20\pm1\%$ and $1\pm0.1\%$, respectively). This constancy of the concentrations of salt hydrolysis products in a gas phase provides further evidence that the source area of the gas is approximately isothermal.

Oxygen fugacity measurements were made[4] of gas emitted from a fumarole at 890 °C (Fig. 1) over a period of 4 h, using a cell with a solid electrolyte, and yielded $\log f_{O_2} = -12.4\pm0.1$. Values of f_{O_2} calculated from the ratios $H_2S/H_2/SO_2$ and CO/CO_2 in the gas phase from this and other fumaroles are in agreement with the direct measurements, and over the temperature range 500–950 °C approximate to $\log f_{O_2} = 0.0212T - 31.02$, where T is the temperature in °C. Within this temperature interval the f_{O_2} of the gas jets are close to the Ni/NiO buffer. So, the main fluid components are water and carbon dioxide.

Samples of condensed vapour from hot gas jets were analysed by the inductive coupled plasma (ICP) approach[5]. The condensates were collected using a water-cooled glass vessel. The

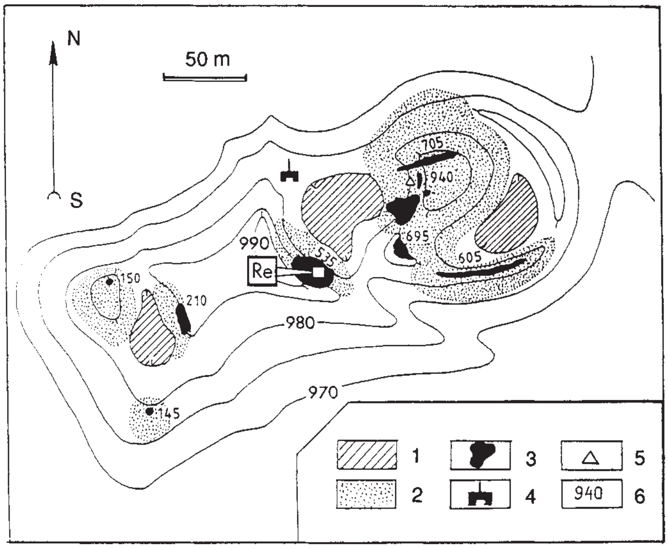

FIG. 1 Map of fumarole fields at the crater of Kudriavy volcano, Iturup island, Kuril arc (148° 45′ E, 45° 41′ N). Legend: 1, detrital deposits; 2, sulphur deposits; 3, fumarole fields; 4, remains of Japanese sulphur mine; 5, location of f_{O_2} measurements; 6, temperatures of fumaroles (°C) and altitude (on contours, m). Location of Re mineralization indicated by Re symbol and white square.

condensates are rich in sulphur, which both separates out as a precipitate, and is present in solution in the form of H_2SO_4 with a concentration in the range 200–4,000 p.p.m. Chlorine was not analysed by ICP, but appears to be mainly in the form of HCl. The concentrations of trace components are: Si, 80–200 p.p.m.; B, 20–40 p.p.m.; Na, 10–50 p.p.m.; K, 10–100 p.p.m.; and Ca, Fe, Al from 2 to 20 p.p.m.. Analyses of the pure aqueous solution phase of the condensate gave variable contents of ore metals; for example, the content of Ag ranges from 2 to 6 p.p.b.. However for the same sample, analyses of the aqueous solution together with the sulphur-rich sediment (shaken sample without any additions) yield metal concentrations that are some two orders of magnitude higher than in the aqueous phase alone. This is observed for Cu, As, Sb, Te, Tl, Pb and Bi. Most of these elements precipitate at sampling together with sulphur, possibly in the form of sulphides. The Re content in both the aqueous solution and the sulphur-rich precipitate is 2–8 p.p.b..

After complete condensation of fumarole gases and the subsequent evaporation of the water from the hot ground, a dry residue should remain containing up to 100 kg of ore metals per ton of residue (that is, up to 18 kg of Tl, ~1 kg of Ag + In + Pd, and several kilograms each of Sn, Bi, Te, Hg and Zn).

Before sampling the gas, we usually removed the rubble from around the jet to insert a marker pipe. When one fumarole with a temperature of 535 °C (Fig. 1) was prepared in this way for sampling, we found sublimates on the rubble at a depth of 25–40 cm. The mineral covers fragments of pyroclastic debris, lava and altered rocks with a solid crust 1–2 mm thick, and is light-grey, graphite-like and soft. The scanning electron micrographs of the deposits (Fig. 2) reveal a plate-like morphology typical of sublimates.

On the basis of its appearance, the mineral was diagnosed initially as molybdenite, MoS_2, which is often found in volcanic sublimates. In the field, we therefore did not see any need for a detailed investigation of the sequence of mineral precipitation. But during subsequent microprobe studies of the mineral, we found that it does not contain any Mo.

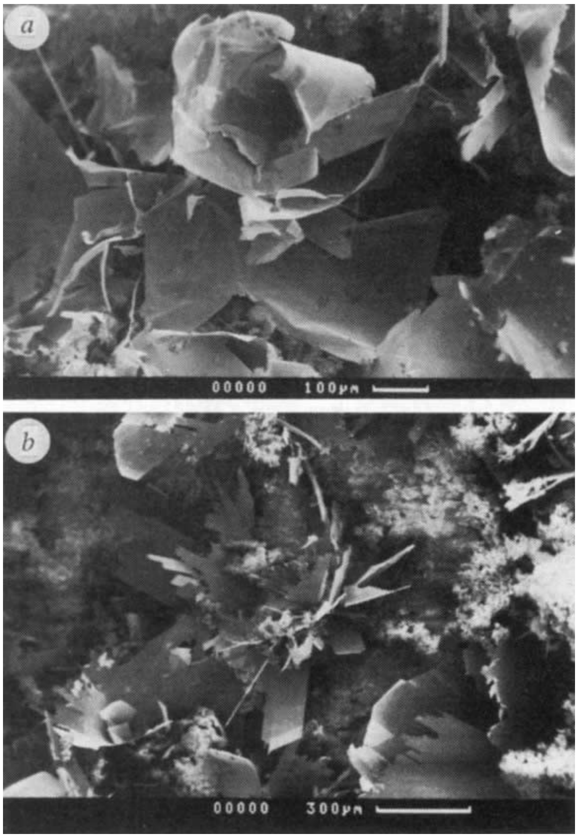

FIG. 2 Scanning electron micrographs of thin plates of rhenium sulphide. *a*, In the form of a rose, *b*, as radial clusters. (Scale bar is 100 µm in *a*, and 300 µm in *b*.)

More that 50 analyses of different samples of this sublimate have now been made. Well pressed and polished samples yield 76–78 wt% Re and 23–24 wt% S, that is, between the theoretical compositions of ReS_2 (74.4% Re) and Re_2S_3 (79.5% Re). The basal spacing is 6.11 ± 0.01 Å. The mineral is currently being analysed in detail at the Institute of Ore Deposits and Mineralogy at the Russian Academy of Sciences. A number of samples representing compositions intermediate between molybdenite and rhenium sulphide were also found; samples containing 5–12% of Mo are quite common. Molybdenite with a significant Re content has also been reported[6].

The samples of sublimates were also collected on glass tubes (25 mm diameter, 1 m long) placed in the marker pipes. These tubes, cooled by wind and rain, became incrusted with rhenium sulphide, molybdenite and intermediate compositions of solid solutions ReS_n–MoS_2 over a period of 2 months. A variety of other minerals were also deposited, including halite, sylvite and magnetite.

Previously, Re minerals have been observed only as inclusions in pyrrhotite, pentlandite[7] and other sulphides[8,9]. Moreover, they contain Cu, Mo or Pb in addition to Re, and this appears to have precipitated from solid solutions. To the best of our knowledge, the sublimates from Kudriavy volcano are the first natural mineral with Re as the only cation and the first example of macroscopic Re mineralization.

It is of interest to note that in the condensate solution the amount of Re does not exceed 10 p.p.b.. Thus, the process of condensation of rhenium sulphide from the gas which also contains high concentrations of other metals, requires not only Re enrichment by almost eight orders of magnitude, but also a remarkable selectivity.

The discovery of rhenium mineralization in sublimates is a clue to the form of Re transport. It takes place in the gas phase as no liquid solutions exist under crater conditions. The industrial technology of rhenium production is based on extracting it from gases emitted during copper and molybdenum processing. We can see here how nature partly reproduces an industrial process. The Re oxides have remarkably high vapour pressures ($p =$ 1 atm is reached at 1,400 °C for ReO_2, at ~600 °C for ReO_3 and at ~350 °C for Re_2O_7 (ref. 10)), itself sufficient for mass transport. Unfortunately, we cannot determine for certain the exact forms in which Re and other elements are transported. The concentration of each of the halogens (Cl, F, I) is greater than of all the ore elements together and might therefore play a role in transporting the rhenium. Industrially, gas transport of metals often uses iodide, chloride or fluoride complexes. Any of all of these processes may be significant at Kudriavy gas jets.

The scale of rhenium transport is hard to estimate, but to a first approximation, if the total steam emitted is ~10–100 tons per day, rhenium precipitation should be measured in grams per day. ☐

Received 17 November 1993; accepted 3 March 1994.

1. Gorshkov, G. S. *Volcanism of Kuril Island Arc*, (Nauka, Moscow, 1967).
2. Giggenbach, W. F. *Bull. volcan.* **39,** 132–145 (1975).
3. Tkachenko, S. I. *et al. Dokl. Akad. Nauk SSSR* **325,** 823–828 (1992).
4. Rosen, E., Osadchii, E. & Tkachenko, S. *Chem. Erde* **53,** 219–226 (1993).
5. Korzhinsky, M. A., Tkachenko, S. I., Romanenko, I. A., Steinberg, G. S. & Shmulovich K. I. *Dokl. Akad. Nauk SSSR* **330,** 627–629 (1993).
6. Bernard, A., Symonds, R. B. & Rose, W. I. *Appl. Geochem.* **5,** 317–326 (1990).
7. Tarkian, M., Houslay, R.M., Volborth, A., Greis, O. & Moh, G. H. *Europ. J. Miner* **3,** 977–982 (1991).
8. Jedwab, J. & Fletcher, T. Terra (Abstr.) **3,** 107 (1991).
9. Mitchel, R. H., Laflamme, J. H. G. & Cabri, I. J. *Miner. Mag.* **53,** 635–637 (1989).
10. Bolshakov, K. J. (ed.) *The Technology of Rare and Trace Elements* Vol. 2 613–663 (Vishaya Shkola, Moscow, 1969).

ACKNOWLEDGEMENTS. We thank G. Lloyd for the SEM pictures of Re sulphide.