the mission, at which time spacecraft maneuvers will be curtailed in order to minimize extraneous factors.

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25 August 1966

Oxygen Fugacities Directly Measured in Magmatic Gases

Abstract. *An electrochemical device was used to measure the fugacity of oxygen* (f_{O_2}) *in holes drilled through the crust of Makaopuhi lava lake, Kilauea Volcano, Hawaii. Results obtained within 6 months of the lake formation show that log* f_{O_2} *normally varies linearly with the reciprocal of the absolute temperature, and that chemical changes occurring in the cooling tholeiitic basalt are reflected in the* f_{O_2} *values measured in the holes.*

Knowledge of the fugacities of volatile components in magmas at various stages of crystallization is vital to clear understanding of the mechanisms of igneous and associated processes. Particularly emphasized recently is the fugacity of oxygen (f_{O_2}); it is now realized that oxygen fugacity is one of the more important factors in determining the course of differentiation in basaltic magmas (*1, 2*). Most work on this subject to date, however, has concentrated on laboratory studies of simple mineral assemblages under controlled atmospheres; experiments with natural rock samples are few (*3, 4*). Other approaches to the problem depend on thermodynamic extrapolations of equilibrium oxygen fugacities of analyzed volcanic and fumarolic gases (*5, 6*), or of observed mineral assemblages (*7*), to high temperatures.

To obtain data in a more direct way, a project was launched (*8*) to develop a reliable, rugged, and sensitive probe to measure oxygen fugacities of magmatic gases above and within a body of crystallizing basaltic magma. While the laboratory work was still in progress, an eruption occurred on the upper east rift of Kilauea Volcano, Hawaii, 5 March 1965; a circular lava lake of tholeiitic basalt was created, approximately 400 m across and 82 m deep, in the west pit of Makaopuhi Crater. During the eruption, the lava varied little in bulk chemical composition (SiO_2, 50.06 to 50.19 percent; MgO, 8.33 to 8.49 percent by weight), and except for minor settling of crystals of olivine it has not since differentiated appreciably.

Wright observed that minerals began to crystallize at the following temperatures: olivine, about 1200°C; augite clinopyroxene, 1180° ± 10°C; plagioclase, 1160° ± 5°C; and opaque minerals (ilmenite followed by magnetite), 1070° ± 10°C. The solidus with 3 to 5 percent residual glass was estimated at 990° ± 10°C.

After the lava solidified to a depth of a meter or two, a number of holes were drilled through the crust and an oxygen probe (later described) was inserted. The results of the first series of measurements, between 3 and 6 months after the eruption, revealed interesting and previously unknown features of oxygen fugacities over a crystallizing basalt magma.

The oxygen probe is an electrochemical oxygen-concentration cell arranged

Ni–NiO mixture, Pt |
reference f_{O_2} |
$(ZrO_2)_{0.85}\,(CaO)_{0.15}$ |
solid electrolyte for O^{2-} ion |
Pt, gas phase
unknown f_{O_2}

which operates reversibly at temperatures above approximately 600°C and at oxygen fugacities above 10^{-22} atm (*9*). The zirconia-lime solid solution is a chemically unreactive and highly refractory material that becomes a good oxide-ion conductor at elevated temperatures because of oxygen vacancies in its fluorite-type structure (*10*). It is very useful, therefore, as the electrolyte in a high-temperature oxygen-concentration cell (*11*) and is commercially available for fuel-cell application. The electrode reactions at the boundaries of the electrolyte correspond to the reaction

$$O_2 + 4e \rightleftarrows 2O^{--} \qquad (1)$$

and the emf of the above cell is therefore given by the relation:

$$E = (RT/4F)\ln [f_{O_2}\,(\text{unknown})/f_{O_2}\,(\text{reference})] \qquad (2)$$

where R is the gas constant, T the absolute temperature, and F the Faraday constant. An equation describing the equilibrium oxygen fugacity of the mixture Ni–NiO was given by Eugster and Wones (*12*); by substitution of it for the reference oxygen fugacity and by use of proper numerical values for the constants, Eq. 2 reduces to

$$\log f_{O_2}\,(\text{unknown}) = \{[(2.02\,E - 2.47) \times 10^4]/T\} + 8.94 \qquad (3)$$

from which the oxygen fugacity of the gas phase is determined by substituting the measured values of the emf and the temperature.

In construction the oxygen probe resembles a design suggested by Schmalzreid (*9*). A powdered mixture of nickel and green nickel oxide (2:1 mole) is packed in the lower one-third of a flat-bottomed, impervious tube of the zirconia-lime solid solution, which is 3.8 cm long and 8.5 mm in outer diameter. The mixture is electrically connected to a platinum wire by way of a column of nickel powder. The tube is sealed with mullite cement and a fired pyrophyllite plug having a small hole in the center for the platinum wire. Another platinum wire is wound around the lower exterior wall of the tube for several turns and insulated from the rest of the tube by sheathing with a small alumina tube.

For insertion into drill holes the probe is fitted into the lower end of a 61-cm-long alumina tube in which slits are cut for better exposure to the magmatic gases. The alumina tube is attached in turn to stainless-steel tubing; inside the tube, the platinum wires of the probe are connected to a pair of long platinum leads sheathed with mullite beads and mullite spaghetti.

The probe is tested and calibrated in the laboratory before use in drill holes. The probe lasts for several hours in air at approximately 1000°C if the seal is tight and thermal shocks are avoided; it fails to operate properly when the column of nickel powder, oxidized by oxygen leaking through the pyrophyllite plug, can no longer protect the reference mixture from the atmosphere. It also fails when the zirconia tube is cracked by thermal shock or by increase in volume of the nickel column by oxidation. Its lifespan is greatly extended in the reducing atmosphere of an uncontaminated magmatic gas.

When the emf is measured with a vacuum-tube voltmeter of a high input impedance, the probe responds almost instantaneously and reproducibly to changes in external oxygen fugacity at temperatures as low as 500°C. The high impedance of the electrometer reduces polarization error and expands the range of measurement at low temperatures at which the resistivity of the electrolyte increases sharply.

The accuracy of the probe depends on the extent of internal equilibration of the reference Ni–NiO mixture; for a temperature change of less than 50°C, the equilibration is achieved within several minutes above 800°C, but several hours are required at 500°C. With equilibration periods of 1 hour, the maximum deviation of observed emf values from those calculated from Eq. 3, for pure oxygen gas at 1-atm pressure, was: 2 percent between 1050° and 800°C; 5 percent between 800° and 600°C; and 8 percent between 600° and 500°C. Below 500°C the probe is ineffective because of poor reproducibility.

The following procedure was used to measure f_{O_2} in the drill holes. The temperature profile of each hole was determined by means of a chromel-alumel thermocouple, immediately either before or after use of the oxygen probe; the profile was stable during the several hours required to complete a set of oxygen-fugacity measurements within a hole. The probe assembly was lowered slowly to the bottom of the hole to avoid thermal shock. When a constant emf reading was obtained on a battery-operated electrometer of 10^{14}-ohm input impedance, the assembly was raised, held till the reading again became constant, and raised—usually in steps of 30 cm. The measurement was terminated when the temperature became too low to produce a constant reading within a reasonable period.

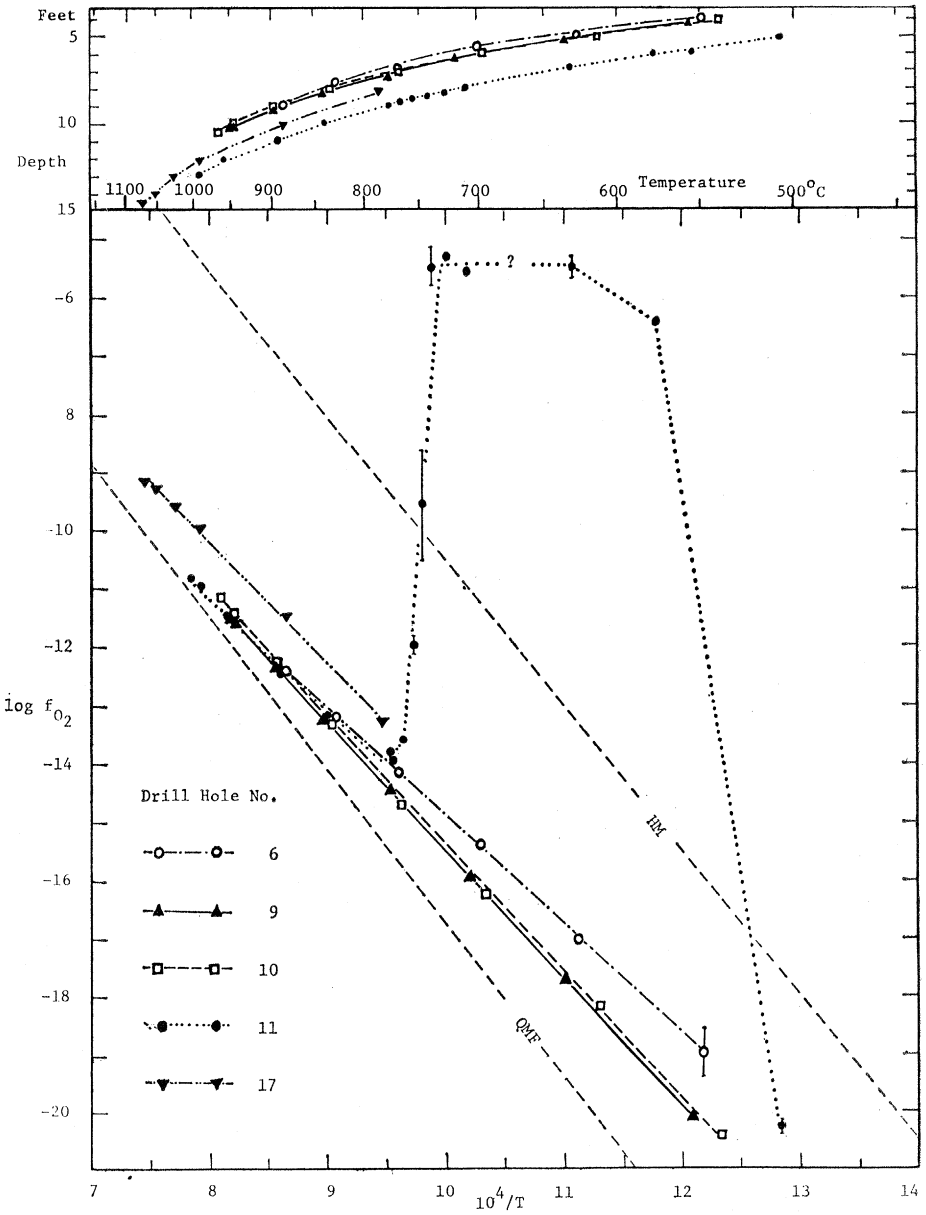

Fig. 1. Logarithms of oxygen-fugacity (f_{O_2}) values measured in drill holes plotted against the reciprocals of the absolute temperatures (T). Identification numbers, distances from the edge of the lake, and depths of the holes are, respectively: No. 6, 165 m, 3.14 m; No. 9, 64 m, 3.2 m; No. 10, 30.5 m, 3.23 m; No. 11, 13.7 m, 3.93 m; and No. 17, 198 m, 44 m. The vertical lines placed on several plots indicate the ranges of error resulting from uncertainties in the emf readings; all other readings are within 1 percent. *HM* and *QMF* are the univariant curves along which hematite + magnetite and quartz + magnetite + fayalite coexist at 1 atm total pressure, respectively. The depth-temperature relations of the reading locations are shown above.

To check the function of the probe, one measurement was repeated at the end of each day of the investigation. Equilibration times at the bottom of a drill hole varied from 60 to 90 minutes. Succeeding emf readings higher in the hole became constant after only 10 to 15 minutes at temperatures as low as 600°C. Below 600°C the equilibration time increased greatly; below 500°C, no readings were steady. Laboratory tests with several probes established that the sluggish responses to the first high temperature, and at low temperatures, mainly resulted from the sluggishness of the Ni–NiO mixture in attaining internal equilibrium.

Oxygen fugacities in the drill holes were calculated from Eq. 3, using the measured values of emf and temperature. The error introduced by uncertainties in the emf readings never exceeded 1 percent of the final log f_{O_2} value, except for a few measurements associated with abrupt change in f_{O_2} (hole No. 11, up to 10 percent) and one measurement made in the lowest temperature range (hole No. 5, 2.6 percent).

More than 50 measurements in the temperature range 500° to 1065°C were made in 8 of the 17 available drill holes with the first probe assembled; five holes yielded sufficient detailed data to reveal the following features of the oxygen fugacity patterns:

1) Oxygen fugacity changes as a function of temperature according to the relation:

$$\log f_{O_2} = (a/T) + b \qquad (4)$$

where T is the absolute temperature. This relation was obeyed in holes No. 6, 9, 10, and 17 throughout the temperature ranges investigated—884° to 548°C (2.71 to 1.19 m), 950° to 555°C (3.125 to 1.3 m), 963° to 538°C (3.17 to 1.19 m), and 1068° to 784°C (4.42 to 2.44 m), respectively; and in hole

No. 11 between 1002° and 775°C (3.91 to 2.74 m) and apparently at 505°C (1.52 m) (Fig. 1). Hole No. 11 showed an anomalous feature (to be discussed presently): this relation was interrupted by a zone of exceptionally high oxygen fugacity. Data from other holes, not described here, also conform with the above relation. Because of the general occurrence of this linear relation for plots of log f_{O_2} versus $1/T$, holes that closely follow the relation may be said to have a "normal" oxygen pattern. The slope coefficient a and the constant b, calculated by the least-squares method, are, respectively: No. 6, -1.86×10^4 and 3.73; No. 9, -2.19×10^4 and 6.44; No. 10, -2.19×10^4 and 6.48; No. 17, -2.08×10^{-4} and 6.47; and No. 11 (excluding the data between 775° and 505°C), -1.87×10^4 and 3.73. The negative slope coefficients correspond to decreasing oxygen fugacity with decreasing temperature, a relation compatible with Osborn's model (*2*) for a basaltic system of constant total composition.

2) The oxygen fugacities at any given temperature above 850°C are almost identical in all holes save No. 17, which shows relatively high f_{O_2} values; its measurements were made only 6 days after drilling, whereas those in other holes were made from 4 to 6 weeks later.

3) Except for the anomalous zone of hole No. 11, all measured f_{O_2} values fall within the stability field of magnetite, outlined in Fig. 1 as the area between the hematite-magnetite (*HM*) and (quartz + magnetite)–fayalite (*QMF*) stability boundaries, according to the data of Eugster and Wones (*12*).

4) The zone of exceptionally high oxygen fugacity observed in hole No. 11 is apparently related to a zone of highly altered basalt. The drill core taken from this hole showed reddish color and markedly high magnetic susceptibility at approximately the same depth.

Our present conclusion is that the gases in the drill holes reacted continuously with the basalt wall as they ascended; thus the measured oxygen fugacities reflected local chemistry and mineralogy of the adjacent wall throughout the temperature spectrum investigated. This conclusion was reached primarily because the observed f_{O_2} anomalies can be explained only in terms of influence by the local irregularities in the basalt wall. Calculations based on homogeneous volcanic gas equilibria (*6*) show that the oxygen fugacity of a closed volcanic gas system varies with temperature like our normal oxygen pattern (observation 1). This closed-system model, however, fails to explain the high-f_{O_2} zone in hole No. 11. Atmospheric contamination would explain the abrupt rise in f_{O_2} but not the steep return to the normal pattern. The best explanation of the high zone seems to be the presence of an oxidized-basalt layer at the corresponding depth, indicated by the mineral alteration and high magnetic susceptibility observed in the core from this hole (observation 4).

Additional evidence of the equilibration of the gas phase with the basalt comes from the similarity of the extrapolated value of a normal oxygen pattern to an independently determined f_{O_2} value from a similar basalt at 1200°C. The f_{O_2}–temperature relation described by Eq. 4 is characteristic of an oxidation-reduction reaction implicating a pair of oxide or silicate minerals (or both) of a transition element in two oxidation states (for example, magnetite-hematite). If a normal oxygen pattern is the result of the f_{O_2} control of the gas phase by such reactions in basalt of constant total composition, the equilibrium oxygen fugacity of the basalt at a higher temperature should equal the extrapolated value of the normal pattern at this temperature. Extrapolation of the normal oxygen patterns from the holes yields f_{O_2} values very similar to Fudali's (*4*) experimental value for tholeiite basalt from the 1921 Kilauea flow: for example, the extrapolated value for hole No. 9 at 1200°C, $10^{-8.43}$ atm, agrees well with Fudali's value of $10^{-8.2}$ atm. The specific oxidation-reduction pairs responsible for f_{O_2} control in the holes remain unknown, but it is likely that combinations of ferromagnesian olivines and pyroxenes, magnetite, ilmenite, and the melt (at liquidus temperatures) were involved.

The oxidized-basalt layer and the associated high-f_{O_2} zone in hole No. 11 deserve further discussion because more-recent measurements with different probes have shown that similar high-f_{O_2} zones developed in several other holes within the same temperature range (750° to 550°C) and migrated downward as the lake cooled; the slope coefficient always remained approximately the same outside the anomalous zone.

Temperature-controlled oxidized-basalt layers characterized by a high $Fe_2O_3:FeO$ ratio, altered olivine and ilmenite, and high magnetic susceptibility were found in Alae lake in the core collected between 650° and 400°C (*13*). A similar oxidized layer was also observed in Kilauea Iki lava lake (*14*); the oxidation was evidently followed by reduction, at least partially, at lower temperatures. In Alae lake, the core collected at 100° to 200°C had a lower $Fe_2O_3:FeO$ ratio than the core collected in the temperature range mentioned above.

A plausible mechanism to account for the zones of high f_{O_2} in Makaopuhi lake is one in which a certain horizon of the lake gradually cools to the temperature range in which oxygen and water molecules can no longer diffuse through the basalt freely, while hydrogen continues to escape toward the surface because of its greater diffusion rate. In other words, the basalt acts as a semipermeable membrane for hydrogen in this temperature range. This preferential escape of hydrogen induces further thermal decomposition of water and locally generates high oxygen fugacities, so that oxidation of the basalt occurs in the horizon. A simple calculation shows that, if hydrogen alone escapes, only 1 (weight) percent of water is required to oxidize as much as 8 (weight) percent of FeO to Fe_2O_3. As the temperature of the horizon decreases further, even the diffusion of hydrogen becomes difficult, and the hydrogen ascending from underlying layers begins to react with, and possibly reduce, the previously oxidized basalt.

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15. We thank D. Peck, H. Shaw, B. J. Skinner, D. B. Stewart, D. R. Wones, and E-an Zen, all of U.S. Geological Survey, for help, advice, or criticism. Publication authorized by the director, U.S. Geological Survey.

30 June 1966