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MAGMATIC GASES.

T. A. JAGGAR.

ABSTRACT. This investigation is the volcanologist's field attempt to arrange volcano gases systematically, as collected in Hawaii, and analyzed by Doctor Shepherd. The new comparisons in the recent statement of the latter author[1] and his earlier publications with Doctor Day, the latter permanently honored in the pregnant A. L. Day volume of the Geophysical Laboratory, deserve extended notice by volcano observers. The present contribution is an offshoot of a larger report on "Craters," and is designed as a critique of the buried truths in the fifty-two tubes, more or less, wherein gases in Hawaii have been collected from liquid lava. The vacuum tube specimens are arranged critically in relation to quality, to volcanic versus atmospheric gas constituents, to the elements, and in relation to serial showings. The results lead to revision of the author's former conclusions.[2]

INTRODUCTION.

THE observatory worker who has lived a quarter of a century with Hawaiian lavas frothing in action, cannot fail to realize that gas chemistry is the heart of the volcano magma problem. Brun[3] showed that Kilauea is an excessively hot volcano. Daly[4] opened the book of the volcano furnace, and closed the volume of steam-engine analogy, so far as magma[5] is concerned. Day and Shepherd[6] followed with real collection of magmatic gases burning with flame at a lava cupola. Shepherd[7]

[1] Shepherd, E. S.: The Gases in Rocks and some related problems. This Journal, 311, 1938.

[2] Jaggar, T. A.: Volcanologic Investigations in Hawaii. This Journal, 165, 1917.

[3] Brun, Albert: L'Exhalaison Volcanique. Paris-Geneva, p. 234, 1911.

[4] Daly, R. A.: Nature of Volcanic Action. Proc. Amer. Acad. Arts and Sci., Vol. 47, No. 3, 1911.

[5] Groundwater steam accounts for so-called "explosive" eruptions.

[6] Day, A. L., and Shepherd, E. S.: Water and Volcanic Activity. Bull. Geol. Soc. Amer., 24, 573, 1913.

[7] Shepherd, E. S.: Composition of the Gases of Kilauea, Bull. Hawn. Volc. Obsy. July 1919: Two Gas Collections from Mauna Loa, same, May 1920: Kilauea Gases 1919, same, May 1921.

and Jaggar [8] carried this forward with vacuum tubes, of which twenty-six analyses of the contained gases are assembled here and in Shepherd's recent paper (loc. cit. 1938). This Hawaiian history of the twentieth century is what we are concerned with.

The writer is not a mathematician, and in the following he attempts no more than orderly arrangement and arithmetic. Averages of good and bad together result in error. Averages are useful when coupled with logical arrangements of numerical data which otherwise appear heterogeneous. There is here given trial a real study of the ten gases, the twenty-six collectings, and the published data of quantitative gas analysis[9] that has been applied to these specimens, comparing all of this to field notes and processes, which the Hawaiian Volcano Observatory has made, measured, and recorded for twenty-eight years. The object is to discover whether analyses arranged in the order of increasing content of such truly magmatic gases as CO_2, SO_2, H_2, S_2, and CO, will throw light on the correlated doubtful gases H_2O, N_2, Cl_2, A, and SO_3; and on the probable reactions that are dominant in Hawaiian bubbling basalt.

MAGMA IN HAWAII.

The petrologist who has not seen Kilauea, Etna, Reunion, Savaii, Mauna Loa, or Nyamlagira in fountaining effervescence at night, will have difficulty in envisaging magma. Magma is not a hand-specimen or a thin slice of rock with silicate minerals. Magma is not granite, diorite, gabbro, or diabase, nor is it obsidian or pitchstone that foams up when heated. No specimen can any more exhibit magma than can a glass of water exhibit the eruptive prominences on the edge of the sun. Both are made in part of hydrogen. In fact the student of geology can come nearer to knowing magma by looking at the rim of the sun with a spectroscope, than he can hope to do by looking into a polarizing microscope. The sun and moon ought to be intimately known to every petrologist. For their surfaces are sculptured by gas. So was the surface of the primitive earth. And the dominant gas of the universe of matter, for physicist, astronomer, biologist, and geologist, is hydrogen.

This is no mere rhetoric. The physical chemists who have studied Kilauea find the water-carbon reaction, the water-

[8] Jaggar's discussion, same, pp. 89-91.

[9] Shepherd, E. S.: The Analysis of Gases. Jour. Geol. Supplement April-May 1925.

sulphur reaction, and the water-iron reaction[10] the three heat makers. These reactions are all actuated by hydrogen as prime mover. Of free hydrogen the amount in our collected flame or melting samples of volcano gas and out-gassed rocks reaches 10.2 and 13.4 per cent and the superlatively dominant gas of both is hydrogen monoxide or water vapor. There is no question of dissociation at the temperatures of liquid lava: the temperature is too low.[11] There is no evident mechanism near the surface of reversing reactions to absorb heat, for the same reason.

The reader who has never seen "boiling lava" lakes should know that Kilauea fire-pit in 1917, 1918, and 1919[12] was a full cauldron. No "cloud of steam" rolled off. A brimming pit 1,400 feet (427 meters) in diameter was easily accessible, with ponds of molten basalt vesiculating with rising gas bubbles. The melt partially congealed on the surface and heavy skins of silvery slag migrated with the currents impelled by convection. Clustered big gas-bubbles burst out in so-called "fountains." Flames played through cracks in the crusts, through spatter cones at local flow sources, through domes built up at border grottoes, through cracks in stiff lava covers, over molten lakes. At all these places, changing from day to day, the collectors stood on crusted living magma shorelines and plied their trade by thrusting vacuum-tube tips behind flames, seeing the tubes rupture, hiss and become cloudy, and then trying to seal the intake hole of the glass bulb effectively. To leeward was the smell of sulphur dioxide. The trioxide is sometimes generated and is irrespirable. So cracked and porous are the lavas that carbon dioxide, though present in considerable amount, never troubles the visitor, because it flows down into pores. Hydrogen sulphide is almost unperceived. There is plenty of visible condensed water-vapor at low temperature cracks outside the crater—rain water—but no such condensation shows anywhere in the puffs of lava-gas. It is all too hot, it is flaming; the flames are not conspicuous, they are only seen at night. The best collecting is done at twilight. The slag pools are very silent, always in motion, fed by wells, streaming to sink-holes.

[10] Day and Shepherd, loc. cit., 1912. Allen, E. T.: Chemical Aspects of Volcanism, Jour. Frankl. Inst., pp. 29-80, 1922.

[11] Fouqué, F., in 1867 (p. 230), at live lava of Santorin, collected oxygen and 56 per cent hydrogen over water, and assumed dissociation. "Santorin," Paris, Masson, 232, 1879.

[12] Bull. Hawn. Volc. Obsy. for these years.

Spatter grottoes make a fiery surge. The semi-solid lava column containing the wells and puddles rises and falls through the weeks.

The writer has been quoted[13] as advocate of "surface combustion[14] at Kilauea, and has suggested repeatedly[15] that hydrogen may be the dominant volcano gas, oxidizing partially under abyssal conditions. Doctor Shepherd's recent chapter (Arthur L. Day Volume) draws together twenty-six analyses from vacuum tube collections in Hawaii of 1917, 1918, and 1919. The vacuum tube collections by Shepherd, December 4, 1912 (Day and Shepherd 594), were at a spatter dome on Halemaumau floor "which permitted the entrance of air and a partial combustion of the gases within the dome." Six tubes were filled, three analyses by weight-percentage published, which re-computed for volume at 100° give:

	Tube 2	*Tube 3*	*Tube 5*
CO_2	33.0	22.15	29.98
N_2	25.3	33.36	22.25
H_2O	41.6	41.73	46.83
SO_3	00.0	2.76	00.94
Cl.	trace	00.00	trace
F.	00.0	00.00	00.00
	99.9	100.00	100.00

The fifty-two tubes mentioned in the abstract are made up by twenty half-liter tubes filled by pumping from a dome in Halemaumau May 28, 1912 (Day and Shepherd 588), in addition to the thirty-two vacuum tubes cited. Five analyses by volume with solubles mostly absorbed in the condensed water, gave for tubes 1, 2, 8, 10, 17 in order

CO_2	24 to 74 per cent
CO	6 to 4 "
H_2	7 to 10 "
N_2	63 to 12 "

Vacuum Tube Collections in Hawaii.

The tubes of 1918-1919 were collected for the Geophysical Laboratory by the writer, two of them from an active fissure

[13] Allen and Shepherd, loc. cit.: and Shepherd, E. S.: Jour. Washn. Acad. Sci., 418, 1925.

[14] Not to be confused with W. A. Bone's activation by hot surfaces.

[15] Bull. Seis. Soc. Amer., 167, 1920; Nat. Res. Council U. S. A. Bull. 77, 55, 1931; This Journal, Sept. 165, 1917; Hawn. Volc. Obsy. Bull., p. 89, May 1921.

on Mauna Loa in time of outflow, October 9, 1919, the others from Kilauea in March of 1918 and March of 1919 from varied sources about Halemaumau pit, especially flame-holes hissing, over lava fountains inside cupolas. All these were accompanied by critical notes of poor, fair, good, or excellent conditions of manipulation, of handling and sealing the tubes, or of variably favorable volcanic flames or jetting vapors. The ideal was always to open the evacuated glass tube (250 cc. or 500 cc.) in confined volcanic gas back of a flame (see Table I for details), and before combustion of gas in air; and to seal tube promptly by melting the glass (Bull. Hawaiian Volcano Observatory, May 1921). The Shepherd collections from Halemaumau of 1917 (Bull. Hawn. Volc. Obsy. July 1919, 94) were made about July of that year, chiefly by thrusting the tip of a vacuum tube into a flaming rupture of folded skin along lava-lake margin. This was followed by prompt sealing in the volcanic flame or plumber's torch. The vacuum tubes were prepared at a factory: vacuum efficiency is not involved, as free oxygen was always calculated out as contamination.

Before discussing the specimens of gas, this is a suitable place to give the reader a table of all twenty-six original vacuum-tube collections in the order of field numbering, and to show the reasons for considering them excellent, good, fair, or poor in conditions of locality, collection, manipulation, and analysis.

There is included at the beginning a compiled statement of methods from the writings of Doctor Shepherd and the author. The quality of each specimen is shown at the right.

Shepherd's work was that of skilled glass-blower and gas chemist. Jaggar's work was that of unskilled non-chemist. There were 16 Jaggar tubes and ten Shepherd tubes. The average per cent hydrogen in Shepherd tubes was 1.39; in Jaggar tubes 0.29; water in Shepherd tubes 64.56; Jaggar tubes 70.83. There is possibility but no evidence the volcano had changing products 1917, 1918, 1919. There was much evidence Jaggar 1919 was more skilled than in 1918, but still slow in sealing. There is every evidence Shepherd was still more skillful in 1917, and quicker in sealing. There was a general trend of more hydrogen and less water from Jaggar 1918; to Jaggar 1919; to Shepherd 1917. In other words, the better the manipulation, the more combustibles trapped and the less of combustion products. Also the lake-edge specimens

TABLE I.

Jaggar-Shepherd Vacuum-tube Specimens, Hawaii.

Number		*Field and Laboratory Records*	*Ab*	*Oxygen Summation*	*Quality*
S-Series.	June-July, 1917.	"Vacuum tubes with soft glass plugs were wired to bamboo rods and the fusible end inserted into promising flame holes as the lava crusts swept along the edge of the Halemaumau lava lake." "The 1917 tubes were more frequently contaminated with air owing to less favorable sources than those of the J-series." Glass of tube is constricted at one place, making it easier to seal off with gasoline torch, necessarily used in the open air, and often in the wind and rain. The collector stood on the edge of the lava lake, and as the soft crust floated by, the tip of the tube was thrust as deeply as possible into the small opening from which small, hissing flames were rising. The bulb is held in this opening until the soft glass plug pulls through and there is sudden clouding of the vessel. When feasible the tip is left in the hot orifice until its glass has softened sufficiently to permit sealing it off by touching it against the hot lava and thereby sealing the tube. Under the most favorable conditions this secured an excellent sample. Not infrequently the tube will crack in pulling it off, and then the tip must be covered with a soft-rubber cap previously dipped in wax, until it can be sealed with a torch. For cooler vents a thin round tip is crushed in against rock wall, and then capped. In the analysis, free oxygen is treated as due to air. From any gas composition, as analyzed, oxygen and the normal equivalent of nitrogen, carbon dioxide, and argon are subtracted, before			

computing the composition of the volcanic gas. Air as such is considered a contamination. Oxygen as volcanic has no place in a mixture of combustible gases issuing from a vent at 1000° or more: evolution of free oxygen as a transient phase has never (see Fouqué) been discovered. The values for argon are analysis residues, and include all the rare gases, krypton, xenon, neon and helium, the last two spectroscopically recognized, not in notably greater quantity than in air residues. Fluorine and selenium are present at Kilauea in small amounts. Methane is in small amount not exceeding 0.2 per cent when present. Concentrated violet-brown sulphur vapor appears in exceptional lava bubbles bursting, shown in erratic analyses; probably a product of old crater-wall concentrates. Ab = ratio Co_2+SO_2 to the figure for O. SO_3 not separated from SO_2 in S-series.

S 1	This tube, A and Cl_2 not determined (udt). CO_2+SO_2 low. (volcanic gases) Water normal. Combustibles high.	udt	19	99.98	Fair
S 2	A and Cl_2 not determined. Water low, volcanic gases normal, combustibles high.	udt	19	99.98	Excellent
S 3	Water very low, volcanic gases very high, combustibles very high, summation inferior.	udt	8	99.55	Excellent
S 4	Water above normal, N_2 and SO_2 not determinable, S_2 and CO excessive, summation poor, Ab probably low.	udt	20	103.10	Poor
S 5	Water normal, volcanic gases moderate, combustibles high.	udt	19	99.99	Excellent

TABLE I (*cont'd*).

Jaggar-Shepherd Vacuum-tube Specimens, Hawaii.

Number		*Field and Laboratory Records*	*Ab*	*Oxygen*	*Summation*	*Quality*
S 6		Water high, volcanic gases low, combustibles low.	udt	18	99.99	POOR
S 7		Water normal, volcanic gases high, combustibles high.	udt	9	99.94	EXCELLENT
S 8		Water above normal, volcanic gases moderate.	udt	11	99.98	GOOD
S 9		Water sub-normal, volcanic gases moderate, combustibles moderate, summation inferior.	udt	19	100.43	GOOD
S 10		Water high, volcanic gases very low, combustibles low.	udt	20	100.00	POOR
ML 1 9 p.m.	Oct. 9, 1919	Water above normal, volcanic gases low, combustibles very low, atmospheric gases high.	udt	udt	99.99	POOR
ML 2 9 p.m.	Oct. 9, 1919	Water normal, volcanic gases low, combustibles low, atmospheric gases high, SO_3 excessive.	udt	udt	99.93	POOR
J 2 7:30 p.m.	Mar. 1, 1918	Blue flame Halemaumau, crust edge of lava lake, 500 cc., break tip, rubber cap.	0.7	20.7	100.05	POOR
J 3 12:45 p.m.	Mar. 2, 1918	Hissing flame crack 2 inches wide NE fill Halemaumau, 2-foot crust, 500 cc. Satisfactory.	16.0	16.0	100.09	POOR
J 4 1 p.m.	Mar. 2, 1918	Hissing flame crack farther out on NE fill, Halemaumau, 1 inch wide.	22.0	15.0	99.99	POOR

J 6	12:40 p.m.	Mar. 5, 1918	SE glowing wall-crack Halemaumau, sulphur odor and fume, yellow deposit, white when cold.	1.4	13.0	99.99	Poor
J 8	4 p.m.	Mar. 25, 1918	Flaming hissing crack NE fill Halemaumau, cone at flow-source, 500 cc., fusible tip, sealed in volcanic flame: deliberate. Opalescent whitish cloud in tube.	80.0	3.0	100.00	Excellent
J 10	5 p.m.	Mar. 25, 1918	Flaming crack SE fountain grotto roof, brilliant cupola: Halemaumau. Broke tip 2 inches down: deliberate. Opalescent gray fume in tube.	32.0	11.0	99.98	Excellent
J 11	5 p.m.	Mar. 13, 1919	Flaming crack south cone Halemaumau hissing strongly, orifice 1 inch, thrust in back of flame, 250 cc. tube, broke tip, sublimates and drops of water. Sealed with cork, fused glass 20 hours later. Smoke in tube.	58.0	6.0	100.06	Excellent
J 12	6 p.m.	Mar. 13, 1919	Flame from 1-inch hissing hole SW side W heap cone, Halemaumau, sealed glass in flame at hole, 250 cc., broke tip for collecting. Resealed 20 hours later.	8.0	18.0	99.98	Poor
J 13	6 p.m.	Mar. 15, 1919	Flame hole 4 inches across N side summit E cone Halemaumau, paraffined rubber seal on 250 cc. tube, fusible tip. Satisfactory. Fused glass 9:30 p. m. Sublimates and fume in tube.*	46.0	9.0	100.59	Excellent

* J 13 "Note that collection of gas from wall-crack cones over lava makes more sublimates in tube, and more fume when hot, than the collections from the lake margin crusts or the lake margin grottoes."

TABLE I (*cont'd*).

Jaggar-Shepherd Vacuum-tube Specimens, Hawaii.

Number		*Field and Laboratory Records*	*Ab*	*Oxygen*	*Summation*	*Quality*
J 14 11 a.m.	Mar. 16, 1919	Flame hole, closed grotto curtained off NE side N lake Halemaumau, small hole summit grotto dome, lava splashing within. Appears ideal for lava lake gas. Rubber cap, 250 cc., fusible tip, sealed by fusion next day. No sublimates.	13.0	17.0	99.98	FAIR
J 15 noon	Mar. 16, 1919	Flame spurt from crack in crust N side N lava lake. Lava stuck on end, broke it off and sealed with rubber tube and copper wire. No sublimates. 250 cc., fusible tip. Sealed by fusion next day. Appears satisfactory.	23.0	14.0	99.98	FAIR
J 16 2 p.m.	Mar. 17, 1919	Flame hissing out from 3-foot lid lifted in spasms 1 or 2 inches, over vent of flow from N base of E cone, Halemaumau, 250 cc., fusible tip, held lid up with stick, rubber cap, sealed by fusion same evening. Satisfactory.	46.9	9.0	99.99	EXCELLENT
J 17 3 p.m.	Mar. 17, 1919	Tip into soft bursting lava bubble through skin of W lava pond, Halemaumau, 250 cc., fusible tip, perfect conditions, rubber cap, sealed by fusion same evening. This the conduit well of rising new lava.	33.0	13.0	99.97	GOOD
J 18 4 p.m.	Mar. 17, 1919	Tip into very small orifice, hissing, on top of a curtained dome over a heavy lava fountain, N side of N lava lake of Halemaumau. A flame hole. Perfect conditions, 250 cc., rubber cap, sealed same evening by fusion. Small crack in tube, but no leak. Collection by breaking tip.	43.0	9.0	100.00	EXCELLENT

of Shepherd were less burned than the flame-crack specimens of Jaggar. But the 1912 collection of Day and Shepherd, by *pumping* from a flame-crack, gave still higher hydrogen and carbon monoxide, suggesting that manipulative method is of greatest importance, though the still earlier date might have been influential. Shepherd reports for 1912 pumped collection "Ab value 73, the O value 0.7" (1921, 83). "Ab" is explained in next section.

The question of tube contamination can be left aside, for all the analyses eliminated free oxygen and its appropriate amounts of nitrogen, carbon dioxide, and argon, all to be treated together as an extraneous systematic error. The percentage of free oxygen recorded by the analyst was, however, a useful criterion of manipulation. The residue was the volcanic product analyzed to a summation, and the summations are mostly good. Straight treatment of the hydrogen of a single tube, as in inverse proportion to water, discords with the facts. (See Plate IV.) Analyses Jaggar-8 and Shepherd-3, with only 36 and 18 per cent water respectively, have these low values balanced by excessive carbon dioxide and sulphur dioxide, not by anything extraordinary for the combustibles. The reversible hydrogen-water reactions are suggested, for these two gases. The single tube is unreliable. On the other hand, the general trend of analyses in series probably points toward a fundamental gas mixture. Burning in air is not the main process.

The supposition of fixed gases in solution in magma, of infinite variability of bubble reactions and equilibria, has been cited (Day and Shepherd, 1913 and loc. cit. Shepherd, 1938) to justify the conception of multiple sources and improbability of a magmatic gas anywhere constant. This is based on the apparent inconstancy of the proportions of all the gases, and on belief in water as fundamentally volcanic. There is no slightest question that hydrogen monoxide is a magmatic product. The vacuum-heating of all igneous rocks proves it. For years the writer has tried arrangement of analyses in series, to learn whither we would be led experimentally by better manipulation, and to learn whether such leading would discover something approaching an ideal volcanic gas mixture, capable of being dissolved in basaltic glass under pressure, but reacting with evolution of heat when released to free vesiculation. This hope was originally justified by the gases falling naturally into

three combustibles, their three oxides, and four residual products characteristic of the hydrosphere or of atmospheric oxidation. The two enigmas are how to get enough hydrogen, and how to burn it without explosion.

The reason why the author dissents from the notion of great variability of the fundamental gas mixture in Hawaiian basaltic magma is that Hawaiian volcanism is uniform, Hawaiian silicate chemistry is uniform, and Hawaiian lavas in action impelled by gas show within measurable limits the same vesiculation and crystallinity, the same gas reactions, and the same viscosities and temperatures. The ten volcanic gas products are with as much right the constituents of magma as the magnesium and iron. As Doctor Shepherd's recent paper shows, a rock analysis from Marvin laccolith in the Henry Mountains records "CO_2 -none," when a cubic centimeter of the same rock (Shepherd No. 29) heated in vacuo yields 9.46 per cent CO_2 within 93 cc. (rock 3 grams equals 1 cc.) of all gases, among them 13 per cent of hydrogen. When a cubic meter of rock (Utah) can produce 130 liters of live hydrogen and 94 liters of carbonic acid, those ingredients were originally magmatic reagents competent in definite proportions to yield water and raise temperature. They have done so at the surface of Kilauea volcano for a century, and their action is not fortuitous. The two pots of lava dipped up in different years from splashing basalt, one analyzed twice, and a clot pulled out on a sounding rod,[16] are sufficiently alike to indicate uniformity beneath the zone of surface contamination.

ARRANGING ANALYSES IN SERIES.

The first arrangement tried was the following (Table II) of the writer's 1918-1919 collections, in the order of increasing $\frac{Ab}{O}$, where Ab is the sum of the volcanic gases CO_2 and SO_2, (gas absorbed by KOH) and O is the percentage of free oxygen that the analyst eliminated. The greater the first two the more volcanic the gas, the greater the O the more air contamination (Shepherd, 1921, 84). The ratio $\frac{A}{A+N}$ is the excess or defect of the argon group including helium, in the presence of nitrogen; unusual quantity being any figure depart-

[16] Shepherd: Samples 15, 16, 17, 22, Table II, pp. 326-337, 1938.

TABLE II.

Fourteen Hawaiian Gas Analyses by Shepherd, $\frac{Ab}{O}$ Order, Volume Percentages at 1,200°, 760 mm. Pressure, Jaggar Collections 1918-19.

	J 2	J 6	J 12	J 14	J 3	J 4	J 15	J 17	J 10	J 18	J 16	J 13	J 11	J 8
CO_2	5.79	0.87	1.42	14.81	6.63	6.79	11.53	11.61	16.44	17.55	18.03	16.96	20.93	47.68
CO	0.00	0.16	0.05	0.47	0.22	0.14	0.13	0.37	0.11	0.74	0.56	0.58	0.59	1.46
H_2	0.00	0.07	0.08	0.17	0.15	0.17	0.10	0.58	0.10	0.83	0.67	0.96	0.32	0.48
N_2	7.92	20.01	0.68	2.91	2.37	2.33	6.20	1.29	15.03	4.50	3.11	3.35	4.13	2.41
A	udt	0.00	0.05	0.00	0.56	0.00	0.16	0.04	0.21	0.12	0.08	0.66	0.31	0.14
SO_2	4.76	0.01	0.51	3.65	3.23	1.38	6.14	6.48	13.57	10.81	8.53	7.91	11.42	11.15
S_2	0.00	0.00	0.07	0.10	0.00	0.15	0.03	0.24	0.05	0.22	0.15	0.09	0.25	0.04
SO_3	2.41	0.13	0.00	1.03	5.51	3.43	1.70	0.00	3.56	3.22	2.53	2.46	0.55	0.42
Cl_2	4.08	0.03	0.03	0.00	1.11	0.62	0.10	0.05	0.03	0.13	0.08	0.10	0.00	0.04
H_2O	75.09	78.71	97.09	76.84	80.31	84.98	73.89	79.31	50.88	61.88	66.25	67.52	61.56	36.18
SUM	100.05	99.99	99.98	99.98	100.09	99.99	99.98	99.97	99.98	100.00	99.99	100.59	100.06	100.00
$\frac{Ab}{O}$	0.03	0.11	0.44	0.76	1.00	1.47	1.64	2.54	2.91	4.78	5.11	5.11	9.50	26.67
$\frac{A}{A+N}$ ..... (air .012)	.000	.000	.068	.000	.191	.000	.025	.030	.013	.026	.025	.139	.069	.054
Quality	P	P	P	F	P	P	F	G	E	E	E	E	E	E

ing from 0.012, the ratio for air, if these gases are non-juvenile. If they are atmospheric and excessive, oxygen has been abstracted; if they are juvenile, any proportions are possible; if they are atmospheric and in anomalous proportions, either one has been removed or one has been added to.

Inspection of Table II is sufficient to show that with general increase of CO_2 and SO_2 $(\frac{Ab}{O})$ there is tendency to increase of hydrogen, carbon monoxide, and sulphur, and toward erratic decrease of the derivative atmospheric or hydrospheric gases water and chlorine, with some similar tendency to decrease of sulphur trioxide as atmospheric oxidation product of sulphur dioxide. Argon is erratic though generally increasing, and notably in the "Excellent" collections reaching amounts sixteen times that required for the air ratio, implying either volcanic origin, or nitrogen removal that is unexplained, or addition of the other noble gases grouped as argon, or volcanic origin of both nitrogen and argon unrelated to atmospheric proportions. Helium and neon have been identified spectroscopically by Shepherd (loc. cit. 1921), who cites volcano argon-nitrogen ratio reaching *twenty* times the air proportions.

This inspection of Table II suffices to show that CO_2 comes next to water vapor in volume, that it is consistent in sequence with $\frac{Ab}{O}$, the volcanic quotient, and that it increases with CO and not inversely to it, so that it is not in this respect a derivative like water. Water vapor trend is inversely as hydrogen, but CO_2 trend is directly as CO. A preliminary trial of the material of Table II suggested that smooth curves might be plotted for each gas.

Arrangement in Order of Constituents.

The best way to begin is to make ten different arrangements of the twenty-six analyses (Table V), each in the order of one of the constituent gases. This has been done in Plate I, giving the field name of each gas and a letter from P to E (poor, fair, good, excellent) with each name, and all of these lists of names are entered in column opposite the accompanying curve of increase for each gaseous constituent. Thus the hydrogen sequence (Table III) proceeds from P-J 2 to F-S 1, and from 0.0 per cent to 4.22 per cent. The upper belt of curves is

drawn to twenty times the scale of those in the lower belt (excepting SO_3). The curve SO_3 is one-half the scale of the upper belt, and ten times the scale of the others; the light curve at the left shows what SO_3 would be like if drawn to the scale of CO_2, etc. The distances on the ordinate corresponding to separate analyses are made equal, and those on the abscissa represent the quantitative percentage by volume at 1,200° C., 760 mm. pressure, for that particular constituent in the analysis in question. A single curve, then, beginning at the bottom shows what a succession of twenty-six actual analyses yields in the increase of that gas. It is as though twenty-six lava bubbles, progressively richer in one constituent, had been collected and their content analyzed.[17]

Throughout this paper, Tables III and V may be used to read the chemical composition of each specimen under its field name, J 2, etc.

Progress from Poor to Excellent.

The first fact that stands out in Plate I is that CO_2 and SO_2 progress from poor to excellent, while H_2O progresses from excellent to poor. The less water vapor, the more of the two voluminous volcanic gases, which when added to water vapor make up with nitrogen the greater part of 100 per cent of any analysis. If the H_2O curve is reversed, all the E-specimens will be opposite each other, and something approaching reasonable summations horizontally will be begun. The form of the water curve also, with long extension to the right, will match the upper part of the other curves. CO and H_2 clearly progress from poor to excellent and are undoubtedly magmatic gases like CO_2 and SO_2. On the other hand, SO_3 and Cl_2 progress from good to poor, and for summations horizontally should be inverted like H_2O. The bulk of S_2 is very small for the greater part of the curve, with a great showing of erratic excessive amounts possible at the top of its curve in poor, fair, good, and excellent collections; as a whole it progresses from

[17] Justification for treatment in series goes further than excellence of manipulation. Serial arrangement in geology always may stand for succession in juvenility versus maturity, abyssal versus superficial, unaltered versus altered, the minute of surface arrival versus the hour or year after circulation. Differences of one element in two boiling springs may be difference in age of outbreak, i.e. geological series. Serial arrangement is thus partly a clue to evolution in minutes or years or millennia.

poor to good and is in the volcanic group of gases. There remain N_2 and A, curves remarkably alike, though N_2 is quantitatively much greater; these are quite erratic in distribution of "excellence" and will need further study to place them among volcanic products. The amount of argon is negligible for summation, amounting in any analysis to only a fraction of one per cent; its maxima, however, are greatly in excess of the air proportion for the nitrogen which is present. As will be seen in the curves of the E analyses (the upper ten of later plates), nitrogen progresses to increasing amounts, and shows no tendency to progress toward zero when volcanic gases are increasing.

Excessive Amounts.

The excessive quantity that each gas except argon can show for the upper three analyses of its own arrangement of the twenty-six specimens is very conspicuous. This bend to the right at the top of each curve is partly an exhibit graphically of systematic error. These excesses in one or two analyses of each curve are from fifty to seventy-five per cent of the entire quantity range, for most of the ingredients. Taking the three upper analyses only of each curve, in percentage of the total range for that gas, we get the following:

Cl_2	75%
CO	71 "
H_2	69 "
S_2	69 "
CO_2	63 "
SO_2	62 "
SO_3	56 "
N_2	56 "
A	23 "
H_2O	15 "
H_2O inverse (four intervals)	42 per cent

If one asks why the gas quantities show increase more rapidly at the upper end of the curves, the explanation is twofold: the superficial gases are approaching maximum vitiation of the volcanic collections, while the magmatic gases are approaching maximum excellence of technique and location. At the minimum quantity end of the curves there is no room for sudden decrease: there are eight gases where the amount is zero; the other two are H_2O (17.97 per cent) and CO_2 (0.87 per cent).

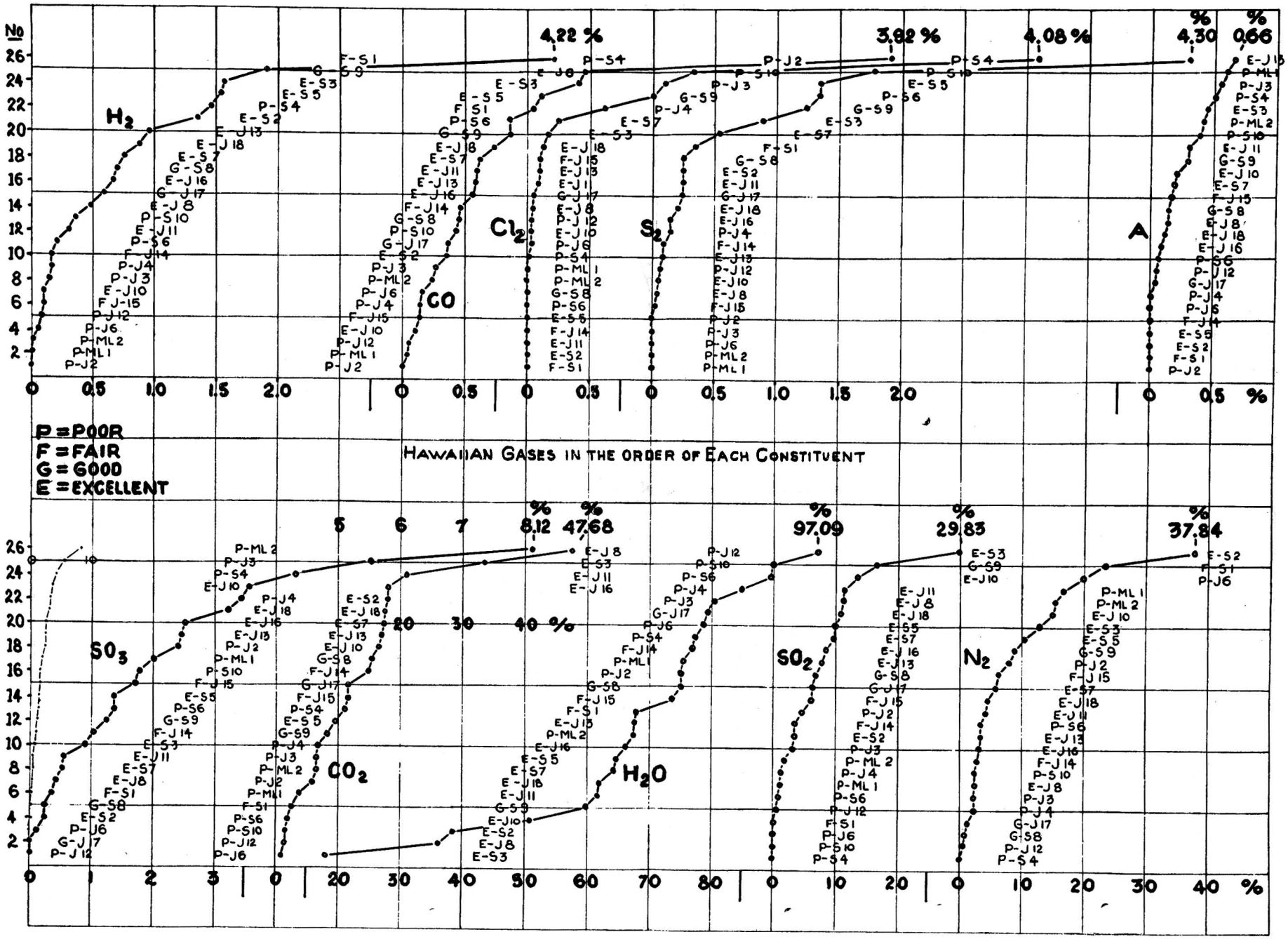

PLATE I. Increase of each constituent, Numbers 1 to 26.

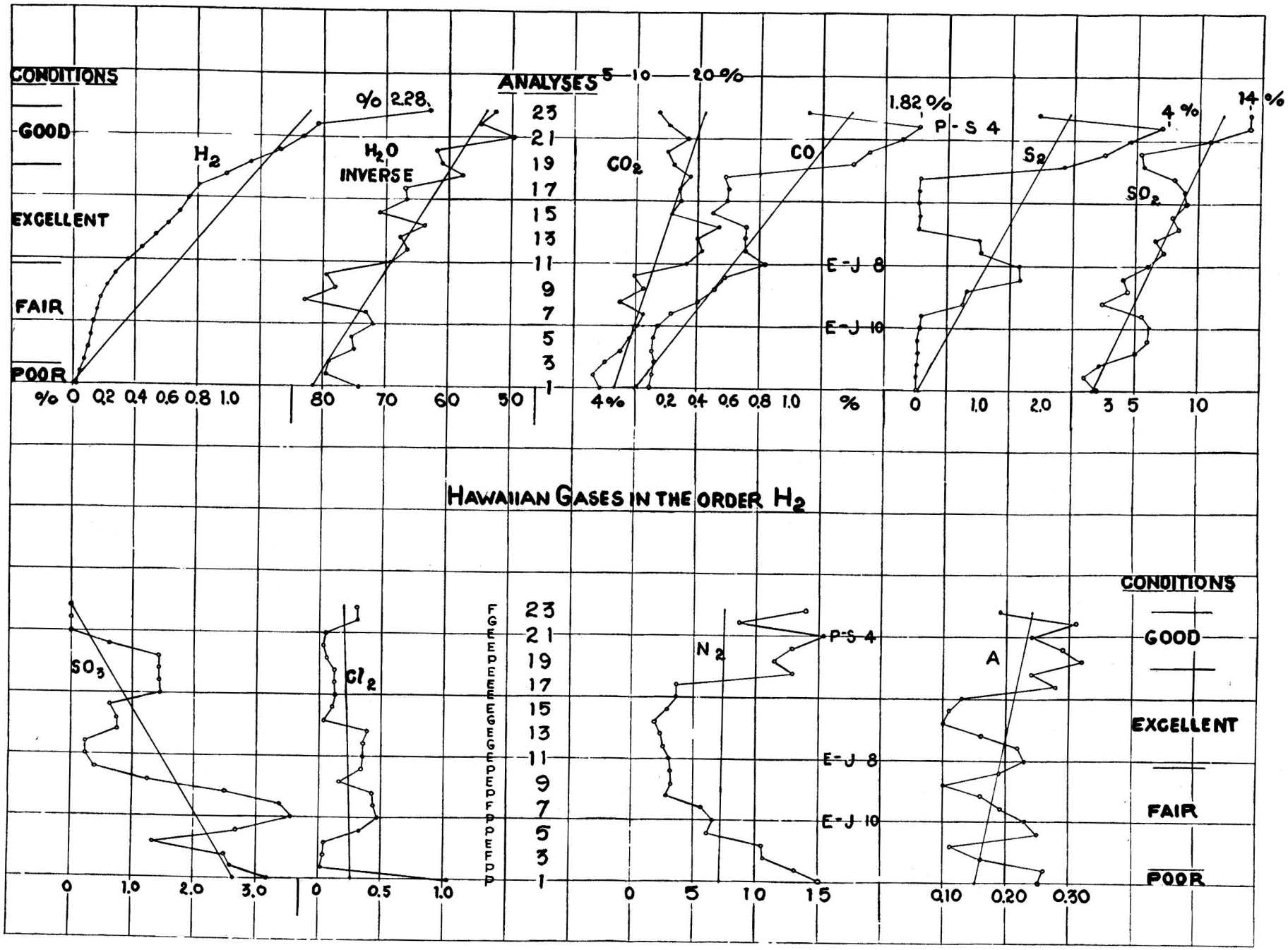

PLATE II. Smoothed curves of each constituent following hydrogen order.

Of the eight, each has from one to nine analyses zero at the origins of single curves. If Cl_2 did not begin with zero, it would doubtless become sigmoidal like H_2O.

Experiment in Summations.

As we are to examine a succession of plates where the numbered units of analyses (shown at the left in Plate I) are horizontally identical specimens with the same field name carried across the chart, it is of some interest that with proper inversions, the summations across Plate I all approach one hundred with the exception of three, and these are end members. If we supposed the assembled minima of number one to make an analysis from left to right, the addition would be numerous zeros and the sum CO_2+H_2O equals 18.84, instead of 100.00. To make a summation equivalent to an analysis out of the highly diversified specimens of all these columns, we must invert H_2O, SO_3, and Cl_2 whose maxima, along with poorness of conditions, are in the direction of the zero of the volcanic gases. Number twenty-six of H_2O, SO_3, and Cl_2 now becomes number one. So arranged the following are the summations of Plate I, and most of the 100-class are in the E-group Nos. 16-24:

No. 1	110.16	No. 14	92.85
2	98.91	15	94.30
3	97.67	16	98.16
4	93.15	17	100.02
5	90.06	18	101.07
6	90.21	19	104.12
7	91.13	20	105.04
8	90.76	21	108.78
9	91.35	22	108.85
10	91.44	23	101.88
11	92.89	24	98.02
12	94.54	25	115.32
13	96.41	26	146.42

It thus appears that an approximately parabolic curve for all the gases except water vapor, mostly starting at zero, with two of them inverted, and H_2O inverted and somewhat sigmoidal, may be a possibility for the grouping of these analyses in series. H_2O inverse would be a parabolic imitation of its neighbors if 80 per cent were its vertical starting line (zero). Turn plate upside down, and compare with CO_2.

TABLE III.

Twenty-six Hawaiian Gas Analyses by Shepherd H_2 Order, All the Vacuum Tube Collections.

Volume Percentages at 1,200°, 760 mm. Pressure.

	J 2	ML 1	ML 2	J 6	J 12	J 15	J 10	J 3	J 4	J 14	S 6	J 11	S 10
CO_2	5.79	3.84	6.42	0.87	1.42	11.53	16.44	6.63	6.79	14.81	1.97	20.93	1.54
CO	0.00	0.03	0.19	0.16	0.05	0.13	0.11	0.22	0.14	0.47	0.82	0.59	0.43
H_2	0.00	0.00	0.01	0.07	0.08	0.10	0.10	0.15	0.17	0.17	0.21	0.32	0.37
N_2	7.92	16.80	15.39	20.01	0.68	6.20	15.03	2.37	2.33	2.91	3.50	4.13	2.44
A	udt	0.58	0.42	0.00	0.05	0.16	0.21	0.56	0.00	0.00	0.07	0.31	0.39
SO_2	4.76	1.22	1.95	0.01	0.51	6.14	13.57	3.23	1.38	3.65	0.95	11.42	0.00
S_2	0.00	0.00	0.00	0.00	0.07	0.03	0.05	0.00	0.15	0.10	2.70	0.25	3.56
SO_3	2.41	2.08	8.12	0.13	0.00	1.70	3.56	5.51	3.43	1.03	....	0.55	....
Cl_2	4.08	0.00	0.00	0.03	0.03	0.10	0.03	1.11	0.62	0.00	0.00	0.00	1.34
H_2O	75.09	75.44	67.43	78.71	97.09	73.89	50.88	80.31	84.98	76.84	89.77	61.56	89.93
SUM	100.05	99.99	99.93	99.99	99.98	99.98	99.98	100.09	99.99	99.98	99.99	100.06	100.00
Quality	P	P	P	P	P	F	E	P	P	F	P	E	P

TABLE III (*Cont'd*).

	J 8	J 17	J 16	S 8	S 7	J 18	J 13	S 2	S 4	S 5	S 3	S 9	S 1
CO_2	47.68	11.61	18.03	15.27	17.25	17.55	16.96	17.95	11.12	9.54	33.48	8.32	2.65
CO	1.46	0.37	0.56	0.45	0.62	0.74	0.58	0.36	3.92	1.12	1.42	0.82	1.04
H_2	0.48	0.58	0.67	0.70	0.76	0.83	0.96	1.35	1.42	1.53	1.56	1.82	4.22
N_2	2.41	1.29	3.11	0.87	5.88	4.50	3.35	37.84	....	10.47	12.88	8.92	23.22
A	0.14	0.04	0.08	0.14	0.18	0.12	0.66	udt	0.51	0.00	0.45	0.29	udt
SO_2	11.15	6.48	8.53	6.98	9.75	10.81	7.91	3.51	....	9.90	29.83	16.80	0.16
S_2	0.04	0.24	0.15	0.49	1.07	0.22	0.09	0.49	8.61	2.72	1.79	2.48	0.70
SO_3	0.41	0.00	2.53	....	0.00	3.22	2.46	....	....	....	....	....	....
Cl_2	0.04	0.05	0.08	0.00	0.25	0.13	0.10	udt	0.02	0.00	0.17	1.01	udt
H_2O	36.18	79.31	66.25	75.08	64.18	61.88	67.52	38.48	77.50	64.71	17.97	59.97	67.99
SUM	99.99	99.97	99.99	99.98	99.94	100.00	100.59	99.98	103.10	99.99	99.55	100.43	99.98
Quality	E	G	E	G	E	E	E	E	P	E	E	G	F

ARRANGEMENT IN THE ORDER OF HYDROGEN.

Supposing that hydrogen and the inverse of H_2O are the two leading chemical controls in volcanic gas action, related to CO_2 and SO_2 in the reactions that have been mentioned, let us take H_2 curve from Plate I, and construct Plate II, smoothed by overlapping means, with the analyses of the H_2 curve as guide for the sequence of the other constituents. The table (Table III) was drawn up, arranging all the gases in the order of increasing H_2. This table shows water, chlorine, and sulphur trioxide decreasing; carbon dioxide,[18] carbon monoxide, sulphur, and sulphur dioxide all increasing; while nitrogen and argon seem erratic.

Overlapping Averages.

The curve exhibits these comparisons graphically, with twenty-three analyses instead of twenty-six. This number of specimens is arrived at by calling "No. 1" the average, for each of the ingredients, of the first four volume percentages in the hydrogen order, namely of J 2, ML 1, ML 2, J 6 (see H_2 curve, Plate I). No. 2 is averaged from 2-5, No. 3 from 3-6, No. 4 from 4-7 and so on. This process of overlapping averages was used by Cargill Knott[19] for statistics in seismology. The resulting series has less unevenness than when original data are used, and the summations of the averaged percentages are equally good $\left(\frac{a+b+c+d}{4}, \frac{b+c+d+e}{4}, \frac{c+d+e+f}{4}, \text{etc.}\right)$.

Progress from "Poor" to "Good."

The first fact that emerges from the hydrogen order is that the other two combustibles, CO and S_2, slope with H_2, as does *H_2O inverse.* Sulphur dioxide increases with hydrogen, CO_2 with less rapidity. Nitrogen and argon increase weakly, suggesting that atmospheric impoverishment in oxygen is not

[18] The author retracts his suspicion of CO_2 being secondary from burnt forest charcoal, limestone, and coal (The Mechanism of Volcanoes, Bull. Natl. Research Council No. 77, 1931, p. 59), so far as basalt is concerned. Carbon gases appear to be just as deep-seated as hydrogen. Nitrogen as air residue and sulphur as wall-rock concentrate may be secondary in solfataric and migmatitic processes adjacent to extrusive and intrusive magma as discussed hereafter under "surface gas mixture," but carbon is more fundamental. The quantitative discussion of carbon monoxide in the depths is important technical chemistry (see Ferguson, J. B., Equilibrium between CO, CO_2, SO_2, S_2. Jour. Am. Chem. Soc. XL, No. 11, 1918), and the extraordinary volume of this gas at Niuafoou, 1929 (Shepherd, 1938, 326), shown by vacuum-heating the lava, is unexplained.

[19] Physics of Earthquake Phenomena, Chapter VII, page 110, Oxford, 1908.

greatly concerned with hydrogen increase. SO_3 strongly diminishes, confirming decrease of atmospheric effect (on SO_2). Cl_2 decreases, probably a contamination in the poor collections, from salt water under the island in accordance with the Ghyben-Herzberg principle.[20]

Aberrant Quantities.

An allowance to be made for emergent zigzags in curves like Plate II is that in the "Excellent-Good" series there are suggestive smooth lines of points as in CO, S_2, SO_2, Cl_2 and N_2, interrupted by groups of errant analyses that make the curves leap to the right or left. Thus specimen J 10 (as shown) affects analyses 4-7 and is notably rich in CO_2, N_2, A; rich in both SO_3 and SO_2; and poor in water. So with J 8, a carbon-rich volcanic E specimen (see Table III), affecting the averages of Nos. 11 to 14, and pulling to the right CO_2, CO, SO_2 and A, in a pattern rather uniform and somewhat followed by S_2 and Cl_2. SO_3 like water makes an opposed pattern. Finally at the top of the curves, specimen S 4 strongly affects with identical pattern CO and S_2, No. 23 restoring these curves to normal, while hydrogen makes its final leap by reason of the exceptional tube S 1.

Straight-line Reduction.

The straight-line reduction of the curves of Plate II is drawn, like the original analyses, to make accurate summations to 100.00 of all the analyses horizontally. This was done by ruling free-hand lines, measuring the intersections, and distributing the resulting percentage error proportionally to each of the 23 analyses intersected (Table IV, end members Nos. 1 and 23).

The figures so corrected make the straight-line curves shown. The essential difference from parent curve is that intervals are equal. The slope would be more truthful if the lower eight analyses, the poorer collections, were eliminated. The superficial gases would point closer to zero, and nitrogen and argon would increase more vigorously.

ARRANGEMENT IN THE ORDER OF CARBON DIOXIDE.

It appears from the hydrogen plate (Plate II) that CO_2 and CO increase with hydrogen, and the oxides of carbon are funda-

[20] Wentworth, C. K.: The Specific Gravity of Sea Water and the Ghyben-Herzberg Ratio at Honolulu. Occas. Paper 39, Univ. Hawaii, 1939.

mental gases in a volcanic system. As CO_2 comes next to water vapor in volume, it will be instructive to build a set of curves using the CO_2 curve as leader for the order of averaged analyses. This was done, by overlapping fours, in the same manner as with H_2, and the resulting curves are in the new plate (Plate III).

TABLE IV.

Hawaiian Gas Analyses H_2 order, Straight-line Reductions of end members from Plate II, summations 100.

	1	23
CO_2	6.54	20.72
CO	0.02	1.38
H_2	0.00	1.51
N_2	7.16	7.48
A	0.15	0.24
SO_2	1.61	11.86
S_2	0.05	2.42
SO_3	2.65	0.00
Cl_2	0.26	0.18
H_2O	81.56	54.21
SUM	100.00	100.00

Progress from Poor to Excellent.

The sequence, as shown by the quality letters of the CO_2 curve, is better than that of the hydrogen curve for progress in the direction of improving quality. The progress is POOR-FAIR-POOR-GOOD-EXCELLENT, whereas the progress for hydrogen was POOR-FAIR-EXCELLENT-GOOD. The middle series of Plate II shows the smoothest sequences in such gases as CO and Cl_2, while the upper ten in Plate III show smoothness. The upper ten ought to be used for showing trends, but for logical consistency the entire curve has been used in reducing to straight lines, the intersections of which as before add up to 100.

Taking the upper ten, CO_2, SO_2, H_2, CO, N_2 and A progress toward increasing amounts; H_2O progresses toward decrease. S_2, SO_3, and Cl_2 are more or less constant with slight tendency to increase; their general trend for the 23 analyses is toward decrease, as is that of N_2 and A.

Aberrant Quantities.

Again there is an instructive pattern in the curves whereby the three combustibles increase to the right on analyses No. 2 and No. 10, where qualities "fair" and "good" alternate with "poor." The atmospheric constituents extend to the right on analysis No. 6, where the upper volcanic group extends to the

left. In the same way on analysis No. 10, the lower group influenced by atmospheric action ("poor") bends back to the left. The specimens that produced these effects are indicated. Specimens S 1, S 9, S 5, and S 4 are notably rich in volcanic gases and deficient in atmospheric gases and water, while ML 1 was influenced by atmospheric oxidation of SO_2, and is rich in SO_3 and residual N_2 and A.

Summary of CO_2 Order.

The more upright slopes of curves following CO_2, as compared with the hydrogen order of Plate II, indicate that atmospheric combustion is here notably pronounced in the specimens collected under poor conditions, but in the excellent specimens it does not increase as much as when hydrogen is the guide. On the other hand the volcanic oxide gases and the inflammables increase throughout the curves, with due allowance for the erratic effect on sulphur of the poorer specimens. The patterns of the entire series of curves are strikingly consistent, and the inverse of H_2O makes bends accordant with the volcanic gases. The water-gas reaction and the hydrogen sulphur-dioxide reaction are indicated consistently in analyses Nos. 14-23.

ARRANGEMENT IN THE ORDER OF WATER-VAPOR.

It was shown in experimenting with summations across Plate I that the greatest error lies at the two ends of the curve. It is possible to distribute this error and make of the inverse of H_2O a parabolic curve retaining the decrease of water in the "excellent" group, starting with 90 per cent as equivalent of 0.0 per cent for most of the constituents. We will use the H_2O inverse curve as guide for an order of actual analyses for all the gases, and for comparison will apply to the drawing so made the corrected curves of increase of all the constituents from Plate I. This comparison is shown in Plate IV.

Here twenty-six actual analyses follow the leadership of H_2O inverse. There is no smoothing by overlap, and the full number of original analyses are shown, on smaller scales than those of the other plates. The solid line curves show the facts of all the original analyses without reduction by averaging, and a single analysis labelled with the field name on the H_2O curve of Plate I, beginning at the top, corresponds to the same analysis with reversed numbering in Plate IV.

Comparison of Corrected Curves for All Constituents.

The line of crosses for each gas is the curve corrected to summations of 100.00 taken from Plate I, but in the order of increase or decrease required by the regular summations of the analyses horizontally. The proportional distribution of error leaves the curves of the crosses so that their summations come out exactly 100.00. The lion's share of correction fell upon H_2O, and yet as shown in Plate IV the correspondence of curve of crosses with the curve of actual analyses is strikingly close in H_2O and in all the fundamental volcanic gases. S_2 is erratic as usual. The curve of the crosses is much nearer quantitatively to actual facts than the straight-line reductions of earlier plates. It contains proportions from actual analyses of the sequences of Plate I and Plate IV combined.

The object is to get material, as suggested in the "Experiment in Summations," for a final diagram drawn to common scale for all constituents that will contain true range of percentages, near to maximum gradations for each gas, preserving real proportions in series. The scientific aim is to disclose origins from, or trends toward, zero and maximum, for each Hawaiian gas artificially trapped at a vent under conditions weighted for accuracy.

Outstanding Features of H_2O Order.

As shown by column "Quality," it would be hard to find an arrangement P to E more satisfactory than the sequence of 26 analyses H_2O inverse. The first impressive feature is that the inflammables fluctuate throughout, just as water fluctuated in the H_2 sequence, remembering that Plate II was a *smoothed* curve. In Plate IV, H_2, S_2, CO and Cl make violent leaps in the poorly collected specimens, showing as stated under "Vacuum Tube Collections" that hydrogen is not inversely as water in single tubes; this is now seen to be more or less true of all the volcanic gases, and only general trends proceed in sympathy with H_2O inverse. This would better be studied in analyses above No. 12, all good quality specimens.

Specimen No. 14 was the first vacuum-tube of Doctor Shepherd's 1917 collection, only "F" in quality, interesting for excessive hydrogen; in this "S 1," A and Cl_2 were not determined, CO_2 and SO_2 were low, H_2O and N_2 were high; like S 4 it is combustible but defective. It is the extreme manifestation of the raggedness of the H_2 curve in relation to water-vapor. The

same defect is in S 4 for all three inflammables. Neglecting such anomalies, the E curves above No. 12 are accordant with H_2O inverse, N_2 and A falling into the volcanic group, as in Plates II and III, for the upper numbers. SO_3 and Cl_2 go in the opposite direction and end with zero, and H_2O decreases from 97 to 18 per cent.

COMPARISON OF ADJUSTED CURVES.

The curves of crosses on Plate IV now become more intelligible. Considering these curves above No. 10 for those gases that increase upward with "Excellence," and those below No. 15 for those that increase downward with defectiveness (P), their range by adjustment to 100 per cent has been contracted from the extreme excursions. These parabolic curves are reasonable in their balance with the ragged excursions.

If the curves of crosses are compared in the same sense with the upper and lower numbers of Plates II and III, with due regard for the more restricted scales of Plate IV, the agreement is good. The crosses stand for an idealized sequence of 26 analyses with diminishing oxidation-hydrous constituents and increasing magmatics.

These curves have been determined by critical investigation of the range of ten gases, in comparison with quality of collection for 26 vacuum-tube specimens from live Hawaiian basalt, in four different methods of arrangement, collected in three successive years by two operators. Therefore, we may next use them to find the composition of the Hawaiian gas mixture below the plane of suface burning.

Projected Curves.

The drawing of Plate V is to combine the assembled data on a common percentage scale. The upper limit of the H_2O curve is 17.97 per cent (E-S3) ; and the lower dotted line 97.09 per cent (P-J 12). The lower scale right to left is that of the three atmospherics, the same upper left to right that of the magmatics. The atmospherics vanish in zero, the magmatics start in zero. Projecting the curves upward only two points eliminates the atmospherics and water.

Any analysis across the middle of these curves has its counterpart in some specimen. If we had 100 collections instead of 26, with better apparatus and variable surface location, a specimen analysis could be found approximating each of these

26 units, from poor to favorable gas jets of merged vesicles, variously burned to water-vapor in CO_2, SO_2 or air.

The argon-helium curve is shown to the left of S_2 (maximum A, 0.66 per cent, E-J 13). The diagram brings out the three combustibles, alike in reaching less than four per cent; the three fundamental magmatics, SO_2, N_2 and CO_2, 30 to 45 per cent; and the two vanishing superficials, SO_3 and Cl_2, seven and three per cent declining to zero. Across the whole sweeps water-vapor, the refuse product of magmatic reactions and atmospheric burning, 97 per cent declining to 18 per cent. This does not mean a steam jet at the origin of the curve. It means a contaminated poor collection of moist air. At the upper end of the curve it means that perfect collection technique would show no H_2O, after oxygen and its air correlatives were removed. Reference to Table III shows the actual gradations of H_2O percentages covered 97, 89, 79, 68, 60, 50, 39, 36, 18. The 1912 collection of water adds one lower step, as the gas pumped by Day and Shepherd could not have exceeded ten per cent[21] of water-vapor. Doctor Day roughly estimated four per cent.

Surface Gas Mixture.

An imaginary analysis, No. 28, obtained by producing the curve of crosses of Plate IV two points gives the following gas composition:

Surface Gas.

CO_2	44.00
CO	3.50
H_2	3.80
N_2	24.04
A	0.66
SO_2	20.00
S_2	4.00
	100.00

Each of these figures is exceeded in some analysis in Table III, except that for argon, here identical with E-J 13. The fundamental gas is merely moderately rich in volcanic ingredients, without water, sulphuric acid, or chlorine. It is rich in hydrogen from a steady source to react with CO_2 and SO_2,

[21] Jaggar: This Journal, 1917, p. 166. The author then attached too much importance to atmospheric burning. The reactions of hydrogen with carbonic acid and sulphurous acid are non-explosive and more important.

yielding water, sulphur, and carbon monoxide, when eruptive vesiculation is permitted. Nitrogen and argon are too abundant, the latter (with its helium) in notable excess. There appear to be too much of these gases and too little of hydrogen. The search for more H_2 to produce the water yielded is found in the nitrogen and sulphur groups. Shepherd's total of these groups ($S_2+SO_2+SO_3$ calculated as S_2, and N_2+A) from all the Hawaiian rocks heated in vacuo is generally only one or two per cent, and in other rocks much less. The 24 per cent of sulphur gases in the above composition is possibly largely from crateral concentrates, or fumed ancient chimney, to be replaced with hydrogen in figuring a deep gas solution. The constituent N_2, also 24 per cent, is properly partly attributable to air carried down into the lava mechanism by convectional overturning, losing oxygen by contact with combustibles; it would be replaced in deep magma by carbon and hydrogen.

THE DEEP GAS PRESSURE.

This doctrine agrees with phenomena apparent when Kilauea and Mauna Loa burst into effervescence. Vesiculation heating and liquefaction propagate powerful convection, with great flaming of gases and involvement of air. The higher the temperature, the more violent is gas release, which vesiculates the slag even to pumice during outfling. Only deep loss of such dissolved gas as heating agent brings eruption to an end. This process all reheats and oxidizes crateral sulphur, sulphates and sulphides and sucks down air in exhausted vesicles. Deep under the island a little salt water is drawn in by breakage. If hydrogen and carbon dioxide were the deep gases in solution in some volume, everything that happens would agree with the conception of hydrogen burning in a CO_2 atmosphere within a vitreous and ferruginous froth. The temperature goes to 1,200°. What is unexplained[22] is the condition of repose of the com-

[22] Bowen, N. L.: Geology and Chemistry, Science, 137, 1939. Doctor F. E. Hance, chief chemist, Hawaiian Sugar Planters' Association, makes the following comment:

"Do volcanic gases always exist in the molecular form at the moment of combustion? Oxidation, or reduction reactions perhaps catalyzed at high temperatures and pressures in the lower magma may result in the liberation of momentarily ionized gaseous atoms such as nascent hydrogen which might force reaction in one direction at enormous speed and hence influence markedly the gaseous phase before or after its composition. For instance, hydrogen monoxide as steam and gaseous molecular sulfur S_2 are potent reagents at high temperatures and pressures."

pressed melt and its gaseous solutes between eruptions. There is little question but that the rise of the internal magma is continuous, and that eruption is due to the edifice yielding. Probably slow intrusion never ceases except during eruption, which is a surficial accident to a continuous accretion.

The surface of the earth, 510 million square kilometers, if imagined over a shell 50 km. thick, might possess from inside a magmatic pressure outward. At Hawaii 1912-1921 over possible 5,000 sq. km. there was tumescent energy applied to lift surfaces,[23] probably .01 meter in ten years. This pressure appears to be a volcanic constant in Hawaii, more effective at the rift centers. If intrusion is general under the oceanic three quarters of the earth, or from the oceanic area to the continental quarter, impelled by magmatic accretion, this is a force to be reckoned with, more measurable experimentally than gravity compensation or contraction. Of the Yellowstone magmatic gases, hydrogen monoxide as superheated steam made 99 per cent, permanent gases including CO_2 and H_2 one per cent; and the contribution of magmatic H_2O made 12 per cent of the supply of hot spring water (Allen and Day, 1939, pp. 40 and 87; The Hot Spring Problem, Day, A. L., Bull. Geol. Soc. Amer., 317, 1939). This impressive gas emission could hardly fail to be an index of the stress that keeps the Yellowstone plateau high. And *subterranean* magmatic water is characteristic perhaps of the whole earth.

THE LAVA REACTIONS.

I am indebted to Professor J. H. Payne of the University of Hawaii for comments on the following oft-quoted reactions:

Atmospheric reactions:

$$S_R + O_2 = SO_2 + 69\ 300 \text{ calories} \quad (1)$$
$$CO + \tfrac{1}{2}O_2 = CO_2 + 68\ 000 \text{ calories} \quad (2)$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (gas)} + 57\ 800 \text{ calories} \quad (3)$$

In (1), S_R refers to the rhombic form of sulphur, stable up to 96° C., where it changes to the monoclinic which exists to the melting point. The heat of fusion of S_R is 300 calories and the heat of vaporization 11 600 calories. With the combustion of sulphur vapor still more heat is evolved. The above oxidations

[23] Wilson, R. M.: Ground Surface Movements Kilauea. Univ. Hawaii Publ. No. 10, 1935.

would necessarily proceed in the direction indicated with evolution of heat at 1,000° in Kilauea lava if air were available.

Intra-magmatic reactions:

$$H_2+CO_2=CO+H_2O+10\ 000 \text{ calories} \quad (4)$$
$$2H_2+SO_2=2H_2O+S+11\ 500 \text{ calories} \quad (5)$$
$$3\ FeO+H_2O=Fe_3O_4+H_2+15\ 400 \text{ calories} \quad (6)$$

Reaction (4) would proceed in this direction at 1,000°-1,200° with release of heat and is probably the most important magmatic process, in view of the volumes of the constituents on both sides of this equation found in volcanic collections. Whatever there may be in the depths, no surface temperature has been measured high enough to speed this reaction to the left with absorption of heat.

No reaction in (5) occurs below 280° C. H_2S is always a product, but unstable at the temperatures of Kilauea lava: it is found in the andesite volcanoes, at fumaroles, and at volcanic springs.

Reaction (6) takes place above 570° C. and is appreciable at 1,000° C. Discussed by Day and Shepherd as the reaction between gas and lava, it may be reversed, with high temperatures of indrawn air and mixtures of gases in a volcanic system. Also the Fe_3O_4 may go over to Fe_2O_3 with atmospheric oxygen, a reaction that has been observed on hot aa flows and in glowing lava caverns. The catalytic effects of iron oxides in presence of hydrogen may be very important in the peculiar differentiation of vesicular glassy basalt to its crystalline forms that occurs with convectional and "Bessemer" stirring[24] in Hawaiian craters and flows. This mode of thinking is useful in considering solfataric action and heat source for phreatic explosion.

MEASURED RANGE OF VOLCANIC HYDROGEN.

In Table V are shown besides hydrogen and water all the Hawaiian vacuum-tube data of the 26 analyses, and quality of collection, in the order of each gaseous component as on Plate I. In Table VI a comparison is made of field collection of hydrogen by seven investigators (Day, Shepherd, Jaggar, Lacroix, Bunsen, Thorkelsson, Fouqué) in Hawaii, Martinique, Iceland,

[24] Emerson, O. H.: The Formation of Aa and Pahoehoe. This Journal, Vol. 11, 109, 1926.

TABLE V.

Twenty-six Hawaiian vacuum-tube analyses, constituents arranged in the order of increase, with field name and Quality[1] of each specimen. H_2O, SO_3[2], and Cl_2 are shown in inverse order.

H_2		CO		Cl_2		S_2		A	
P-J 2	0.00	P-J 2	0.00	P-J 2	4.08	P-ML 1	0.00	P-J 2	udt
P-ML 1	0.00	P-ML 1	0.03	P-S 10	1.34	P-ML 2	0.00	F-S 1	udt
P-ML 2	0.01	P-J 12	0.05	P-J 3	1.11	P-J 6	0.00	E-S 2	udt
P-J 6	0.07	E-J 10	0.11	G-S 9	1.01	P-J 3	0.00	E-S 5	0.00
P-J 12	0.08	F-J 15	0.13	P-J 4	0.62	P-J 2	0.00	F-J 14	0.00
F-J 15	0.10	P-J 4	0.14	E-S 7	0.25	F-J 15	0.03	P-J 6	0.00
E-J 10	0.10	P-J 6	0.16	E-S 3	0.17	E-J 8	0.04	P-J 4	0.00
P-J 3	0.15	P-ML 2	0.19	E-J 18	0.13	E-J 10	0.05	G-J 17	0.04
P-J 4	0.17	P-J 3	0.22	F-J 15	0.10	P-J 12	0.07	P-J 12	0.05
F-J 14	0.17	E-S 2	0.36	E-J 13	0.10	E-J 13	0.09	P-S 6	0.07
P-S 6	0.21	G-J 17	0.37	E-J 11	0.08	F-J 14	0.10	E-J 16	0.08
E-J 11	0.32	P-S 10	0.43	G-J 17	0.05	P-J 4	0.15	E-J 18	0.12
P-S 10	0.37	G-S 8	0.45	E-J 8	0.04	E-J 16	0.15	E-J 8	0.14
E-J 8	0.48	F-J 14	0.47	P-J 12	0.03	E-J 18	0.22	G-S 8	0.14
G-J 17	0.58	E-J 16	0.56	E-J 10	0.03	G-J 17	0.24	F-J 15	0.16
E-J 16	0.67	E-J 13	0.58	P-J 6	0.03	E-J 11	0.25	E-S 7	0.18
G-S 8	0.70	E-J 11	0.59	P-S 4	0.02	E-S 2	0.25	E-J 10	0.21
E-S 7	0.76	E-S 7	0.62	P-ML 1	0.00	G-S 8	0.25	G-S 9	0.29
E-J 18	0.83	E-J 18	0.74	P-ML 2	0.00	F-S 1	0.35	E-J 11	0.31
E-J 13	0.96	G-S 9	0.82	G-S 8	0.00	E-S 7	0.54	P-S 10	0.39
E-S 2	1.35	P-S 6	0.82	P-S 6	0.00	E-S 3	0.89	P-ML 2	0.42
P-S 4	1.42	F-S 1	1.04	E-S 5	0.00	G-S 9	1.24	E-S 3	0.45
E-S 5	1.53	E-S 5	1.12	F-J 14	0.00	P-S 6	1.35	P-S 4	0.51
E-S 3	1.56	E-S 3	1.42	E-J 11	0.00	E-S 5	1.36	P-J 3	0.56
G-S 9	1.82	E-J 8	1.46	E-S 2	udt	P-S 10	1.78	P-ML 1	0.58
F-S 1	4.22	P-S 4	3.92	F-S 1	udt	P-S 4	4.30	E-J 13	0.66

[1] P = poor, F = fair, G = good, E = excellent.

[2] As SO_3 was not computed in the S-specimens, one-half the S_2 was subtracted and here assigned to SO_3.

TABLE V (*cont'd*).

Twenty-six Hawaiian vacuum-tube analyses, constituents arranged in the order of increase, with field name and Quality[1] of each specimen. H_2O, SO_3[2], and Cl_2 are shown in inverse order.

SO_3		CO_2		H_2O		SO_2		N_2	
P-ML 2	8.12	P-J 6	0.87	P-J 12	97.09	P-S 4	udt	P-S 4	udt
P-J 3	5.51	P-J 12	1.42	P-S 10	89.93	P-S 10	0.00	P-J 12	0.68
P-S 4	4.31	P-S 10	1.54	P-S 6	89.77	P-J 6	0.01	G-S 8	0.87
E-J 10	3.56	P-S 6	1.97	P-J 4	84.98	F-S 1	0.16	G-J 17	1.29
P-J 4	3.43	F-S 1	2.65	P-J 3	80.31	P-J 12	0.51	P-J 4	2.33
E-J 18	3.22	P-ML 1	3.84	G-J 17	79.31	P-S 6	0.95	P-J 3	2.37
E-J 16	2.53	P-J 2	5.79	P-J 6	78.71	P-ML 1	1.22	E-J 8	2.41
E-J 13	2.46	P-ML 2	6.42	P-S 4	77.50	P-J 4	1.38	P-S 10	2.44
P-J 2	2.41	P-J 3	6.63	F-J 14	76.84	P-ML 2	1.95	F-J 14	2.91
P-ML 1	2.08	P-J 4	6.79	P-ML 1	75.44	P-J 3	3.23	E-J 16	3.11
P-S 10	1.78	G-S 9	8.32	P-J 2	75.09	E-S 2	3.51	E-J 13	3.35
F-J 15	1.70	E-S 5	9.54	G-S 8	75.08	F-J 14	3.65	P-S 6	3.50
E-S 5	1.36	P-S 4	11.12	F-J 15	73.89	P-J 2	4.76	E-J 11	4.13
P-S 6	1.35	F-J 15	11.53	F-S 1	67.99	F-J 15	6.14	E-J 18	4.50
G-S 9	1.24	G-J 17	11.61	E-J 13	67.52	G-J 17	6.48	E-S 7	5.88
F-J 14	1.03	F-J 14	14.81	P-ML 2	67.43	G-S 8	6.98	F-J 15	6.20
E-S 3	0.90	G-S 8	15.27	E-J 16	66.25	E-J 13	7.91	P-J 2	7.92
E-J 11	0.55	E-J 10	16.44	E-S 5	67.71	E-J 16	8.53	G-S 9	8.92
E-S 7	0.53	E-J 13	16.96	E-S 7	64.18	E-S 7	9.75	E-S 5	10.47
E-J 8	0.42	E-S 7	17.25	E-J 18	61.88	E-S 5	9.90	E-S 3	12.88
F-S 1	0.35	E-J 18	17.55	E-J 11	61.56	E-J 18	10.81	E-J 10	15.03
G-S 8	0.24	E-S 2	17.95	G-S 9	59.97	E-J 8	11.15	P-ML 2	15.39
E-S 2	0.24	E-J 16	18.03	E-J 10	50.88	E-J 11	11.42	P-ML 1	16.80
P-J 6	0.13	E-J 11	20.93	E-S 2	38.48	E-J 10	13.57	P-J 6	20.01
G-J 17	0.00	E-S 3	33.48	E-J 8	36.18	G-S 9	16.80	F-S 1	23.22
P-J 12	0.00	E-J 8	47.68	E-S 3	17.97	E-S 3	29.83	E-S 2	37.84

[1] P = poor, F = fair, G = good, E = excellent.

[2] As SO_3 was not computed in the S-specimens, one-half the S_2 was subtracted and here assigned to SO_3.

and Santorin, reducing analyses to the same standard of collection-over-water used by Bunsen and Fouqué. This removes H_2O, SO_2, SO_3, S_2, and Cl_2. Also in Fouqué's collection oxygen was present in the gases that bubbled up in sea-water, containing 56 per cent of hydrogen, directly over the vents of an andesitic lava flow that showed pale flames on its rough surfaces above lea-level. Both Lacroix[25] and Fouqué found methane.

The Mont Pelée locality of Lacroix was 800 meters from the shore on the right bank of the Rivière Blanche: blue fume rose on the side of a talus four meters high, where there were numerous orifices giving out gas and producing intense heat. The openings were between large boulders, and two different kinds of vents were coated respectively with sulphur or with sal-ammoniac. The latter reached temperatures of 410° C. and the collections were made June-July, 1902. In the valley higher up on the left bank were found more of these intensely hot fumaroles with what appeared to be realgar.[26] Hydrogen sulphide was the principal odor; Lacroix considered that hydrocarbons might come from buried vegetation, but the sal-ammoniac and excess of argon were believed due to "deep origin."

Fouqué used a bell-jar connected through a stop-cock and rubber tubing to a gas tube with its end in a basin, all completely filled with water, which the rising gases displaced. After collecting, the gas tube was sealed off by melting at its constrictions. Specimens 1866-F 3 and F 4 were collected in March in canals between spurs of the flaming heap of andesite, in highly sulphurous milky waters at temperatures 78° and 61°. Specimen 1867-F 3 a year later was collected March 7, from where incandescent flows plunged into the sea with sharp hissing and great rising of gas; a test of this specimen with a match showed that the gas burned with a strong explosion. The gas rising through the water was the product of the rapid chilling of the crust of the liquid lava by the sea-water, with contraction, and cracking; the place of bubbling up followed the progress of the moving front of the flow; quoting Fouqué, "this ebullition can only be explained by supposing the gas came from the fused lava and was rapidly squeezed out." Fouqué's anomalous explanation of the excessive oxygen along

[25] Lacroix, A.: La Montagne Pelée. Paris. Masson. 396, 1904.

[26] This disappeared in transport: may it not have been selenium?

Table VI.

Partly recomputed analyses showing hydrogen at lava or fumaroles of active volcanoes, as though collected over water. (Air, water and water-absorbable constituents eliminated.)

	1918 *Hawaii*[1] J 8	1917 *Hawaii*[1] S 3	1917 *Hawaii*[1] S 4	1912 *Hawaii*[1] DS 17	1917 *Hawaii*[1] S 1	1871 *Iceland*[2] A 231	1902 *Pelée*[3] A 196	1906 *Iceland*[2] A 259	1902 *Pelée*[3] A 197*
H_2; HYDROGEN	0.92	3.18	7.76	10.20	13.54	15.59	19.33	21.70	21.76
$CO_2 + CO$	94.19	70.07	84.60	78.00	11.86	68.80	36.02	66.90	47.47
$N_2 + A$	4.89	36.75	7.64	11.80	74.60	9.72	44.65	3.10	30.77
CH_4	....	....	....	....	....	....	....	0.90	....
H_2S	....	....	....	....	....	5.89	....	7.40	....
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	1902 *Pelée*[3] A 195	1902 *Pelée*[3] A 199	1866 *Santorin*[4] F 3	1866 *Santorin*[4] F 4	1902 *Pelée*[3] A 198	1906 *Iceland*[2] A 244	1867 *Santorin*[4] F 3('67)	1867 *Santorin*[4] F 3('67)*
H_2; HYDROGEN	22.46	26.28	29.93	32.72	38.65	52.00	77.20	56.70
$CO_2 + CO$	46.37	55.14	36.99	38.68	58.35	39.50	0.30	0.22
$N_2 + A$	31.17	0.82	32.21	27.78	3.00	6.20	0.00	21.90
CH_4	....	17.76	0.87	0.82	....	....	0.10	0.07
H_2S	....	....	....	....	....	2.30	....	....
	100.00	100.00	100.00	100.00	100.00	100.00		
							O_2.. 22.40	21.11
							100.00	100.00

* Fouqué's figures.

[1] Hawaii specimens of Jaggar, Shepherd, Day and Shepherd: Kilauea volcano live lavas 1,200°. Shepherd numbers, 1938.

[2] Iceland specimens of Bunsen 1871, and Thorkelsson, 1906, Allen numbers, Jour. Frankl. Inst., Jan. 1922. Fumaroles 90°.

[3] Pelée, Martinique, specimens of Lacroix, Moissan analyst, Allen numbers: Rivière Blanche fumaroles 400°.

[4] Santorin specimens, F. Fouqué monograph, collected over live andesite flow, in sea-water, the lava at about 1,000°: Fouqué numbers. In Spec. F 3 ('67), oxygen and nitrogen were collected cool with hydrogen, *oxygen in excess*. N_2 and apportionate O_2 here eliminated. Fouqué's H_2 was 56.70%, the most remarkable hydrogen collection ever made. The lava dome was flaming profusely, the specimen was explosive, and Janssen identified hydrogen spectroscopically in the flames. Fouqué believed volcanic H_2O dissociated, unquestionably an error. His scientific technique was excellent.

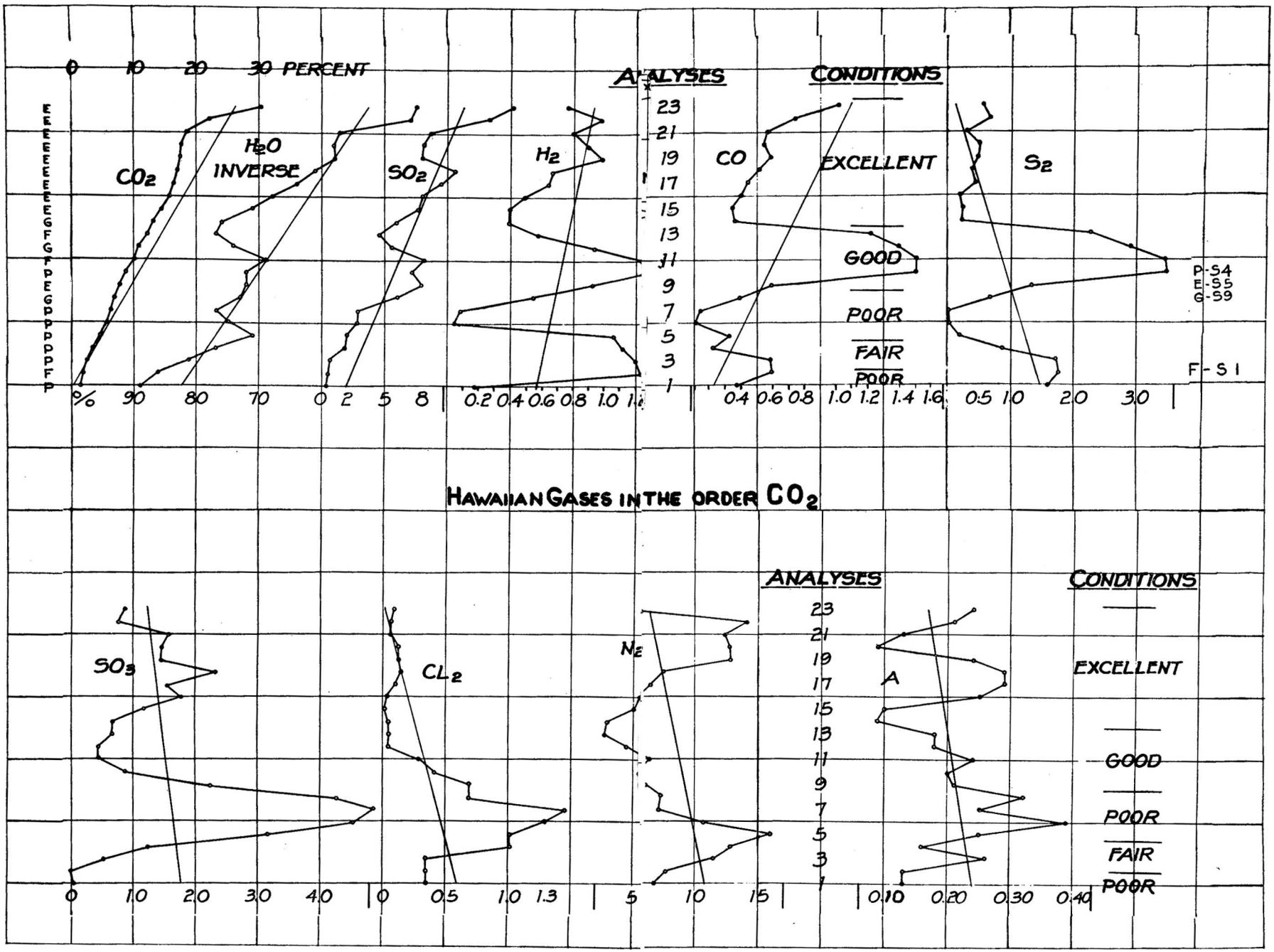

PLATE III. Smoothed curves of each constituent following carbon dioxide order.

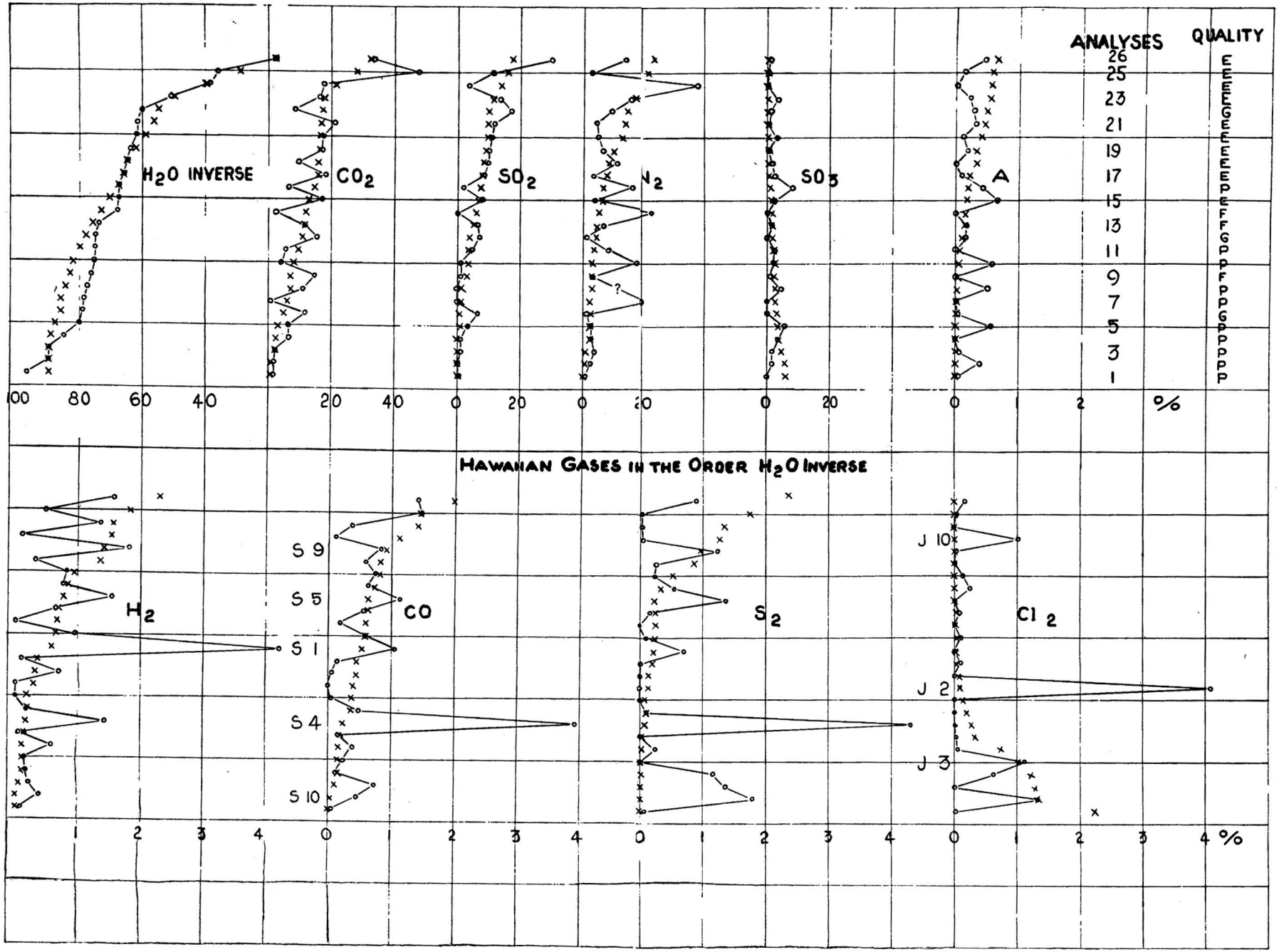

PLATE IV. Actual and theoretical curves following inverse of water-vapor.

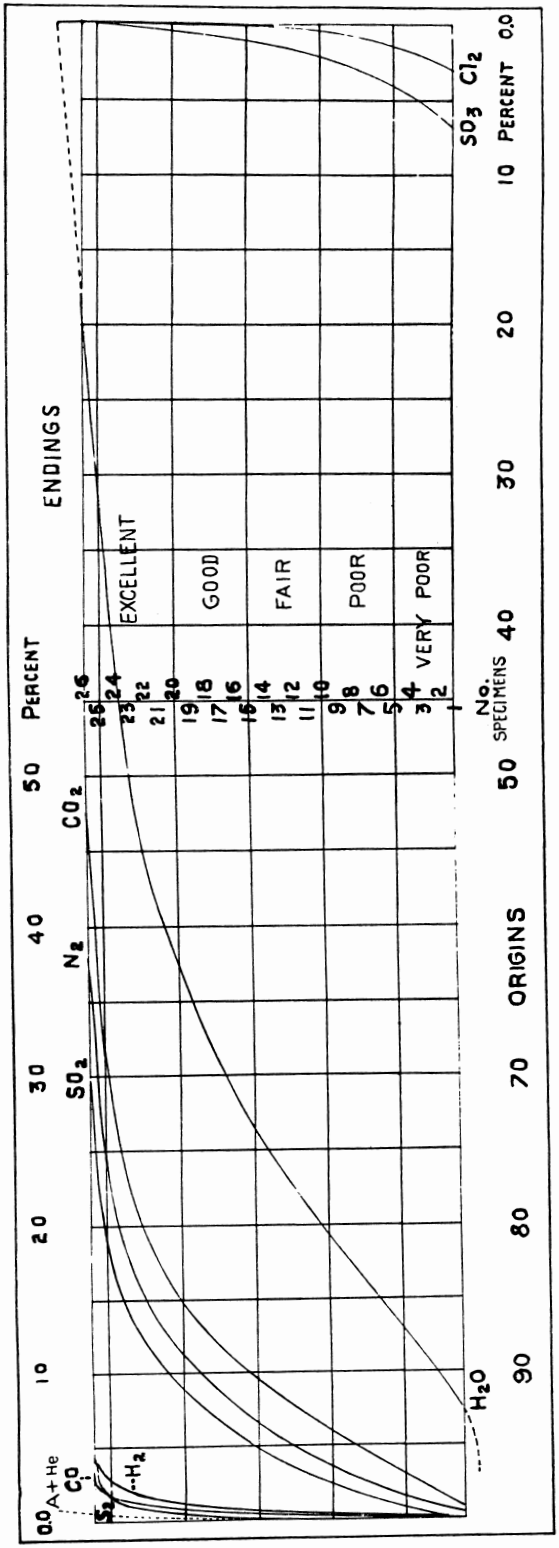

PLATE V. Theoretical derived curves approaching ideal Hawaiian gas sample.

with free hydrogen rising through sea-water, is that they must have been together in the enclosing lava without combining, "probably because of the high temperature." This makes the flame jets from the dome essentially oxy-hydrogen flares. Fouqué concluded that the pasty lava of an andesite dome can trap its enclosed combustible gases in a flow for several hundred meters, and the evidence of the collections was that the volcanic gases and hydrogen were more and more abundant, to such extent as the collection was made "in lava of the highest possible temperature, and as close as possible to the point of emergence." He was more successful than his successors of 1925.[27] As chemist and petrologist, Fouqué in the Santorin monograph takes second place to no one in the history of science. He set a standard for all time in field vigor, laboratory precision and completeness, and literary output. It was Fouqué and Michel-Lévy who wrote the first text on laboratory synthesis of rocks.

DISCUSSION OF PERMANENT GASES.

The measured range of volcano hydrogen from 0.92 per cent to 77.20 per cent, where the solfataric, hydrous, and water-soluble products are eliminated, is consistent with the doctrine derived above, to the effect that Kilauea sulphur and nitrogen may be largely replaced with hydrogen in deep magma. The disclosure of high hydrogen in Icelandic fumaroles, and elsewhere in andesite-dacite domes, agrees with high hydrogen in Shepherd's and Gautier's[28] outgassed plutonics and laccolithic rocks. They got $H_2 = 30$, 56, and 77 per cent apart from water. The range is identical with Table VI if the lavas are included, where in the obsidians the H_2 is only one or two per cent after eliminating water. The elimination of water for computing permanent gases alone was done by Gautier, and by Allen and Day in the Yellowstone,[29] and is essential for any comparisons with a hot-spring volcano district like Iceland, as the underground water removes solubles. It is striking that the low-hydrogen end of Table VI approaches the constitution of *deep gas for a solfataric district* computed by Allen and Day:

[27] Reck, Hans.: Santorin. Berlin. Vol. II, p. 74, 1936.

[28] Gautier, A.: Genesis of Thermal Waters. Econ. Geol., July-Aug., 690, 1906. La genèse des eaux thermales. Ann. des Mines, Vol. 9, 316-370, 1906.

[29] Allen, E. T., and Day, Arthur L.: Hot Springs of the Yellowstone National Park. Carnegie Institution Publ. 466, 88, 1935.

Yellowstone, Allen and Day, H_2 0.11: CO_2 98.26: N_2+A 0.86: H_2S 0.66: CH_4 0.11

Kilauea, Jaggar, J 8, 1918, H_2 0.92: CO_2 94.19: N_2+A 4.89: H_2S 0.00: CH_4 0.00[30]

Table VI shows that geographically the arrangement of collections in a progression following one element is useful, and that even without water and the soluble gases, H_2 is relatively low and CO_2 high in incandescent Hawaiian basalt, while these two are abundant and become equal in Iceland, and in Santorin and Pelée andesite, with nitrogen diminishing. Here is a contrast perhaps between high-temperature sub-oceanic magma and low-temperature continental refractory slag, between "substratum" basalt and "assimilation" differentiate, between vanishing water and condensed water: the deep, steaming andesite plugs are breakable and contaminated and cooled like granites with much vadose water, and their own consumption of hydrogen is far less than that of the free-frothing, exothermically heated basic lavas encased in a furnace of water-tight selvage shells of glass, using up irregularly by convectional overturn much atmospheric oxygen. Remnant nitrogen is a measure of this irregularity, large in some of Shepherd's collections (S 1, 2, 3, 5) gathered right in the midst of the convection currents. Low-temperature siliceous magmas doubtless have irruption assisted by surrounding rock water, as suggested by all the water-absorption theories and experiments.[31]

A corollary of this view is that Hawaiian olivine basalt is representative of "substratum," while granite is representative of cool concentrate contamination. There is no knowledge of what this word "substratum" means, whether 70 or 700 kilometers down or both, whether at a boundary or a transition or both, and whether the boundary is a gas-tight limit to a kinetic world within, the mantle being locally fissured. There is a tendency in the "rigid as steel" theorists to attempt reconciliation of such diversified analogies as melting experiments, and moduli of compression and rigidity, and of a non-isotropic mantle bearing seismographs, with an isotropic globe. This is

[30] 0.20 cited by Shepherd as maximum for Hawaiian specimens among fixed gases *that include the soluble gas* SO_2 (Bull. Hawn. Obsy. July 1919).

[31] Goranson, R. W.: Solubility of water in granite magmas. This Journal 481, 1931; 227, 1932. Day, A. L.: Causes of Activity Lassen Peak. Jour. Frankl. Inst., p. 578 seq., 1922. Morey, G. W.: Development of Pressure in magmas. Jour. Washn. Acad. 12, 219, 1922. Day and Allen. Lassen Peak. Carnegie Inst. Publ. 360, pp. 76, 164, 1925.

not knowledge. Melting something solidified bears no relation to a never-cooled dynamic system essentially solar and atomic, if not indeed sub-atomic. "Volcanic eruptions occasioned by the sudden heating of rock masses"[32] appears to be as improbable as the partly cooled intrusive body underground of Daly for Kilauea, of Day for Lassen Volcano. I can see no objection to a system of increasing hydrogen-carbon nitrogen-metals under the great volcanic fractures, in transition to something at 2,000 kilometers, for which we have only the ancestral sun for analogy, with the physics of the future for use in guiding new progressions of disclosed analytical facts. "Magmatic gas" refers as much to a progressively changing physical state as to a mere melt. Lassen and Kilauea are valves to a centrosphere controlled by solar cycles.

WORKING HYPOTHESES.

There are three working hypotheses that I would recommend to volcanologists in considering the progressive data developed in this paper.

Hypothesis (1). Intrusion is the principal volcanic process at the present day, and indication of its *irruptive* power by dissolved gases is afforded by basaltic *eruptions* at those volcanoes that emit frothing magma. This basaltic magma is worldwide and mostly submarine, is primal and hottest, and the event in time of its observed foaming gas-emission is like the event in time of any underground intrusion.

This means that the injection of an andesite porphyry laccolith is a short-lived temporary violent vesiculate irruption of a volcanic dome in the midst of soft shales that would have been a Santorin eruption if it had been on the surface. It means further that the injection of a granite body is a similar irruption in the midst of diastrophic continental material, also a sudden event and vesiculate with gases.

If injections and intrusions are recognized as sudden events, and basaltic magma in action volcanically on seven-tenths of the earth's surface, the little known sea-bottom, is the fundamental magma, capable of occasional ejection of alkaline types

[32] Gautier review, loc. cit. Econ. Geology, p. 693. It is curious that a world "as rigid as steel" resists tidal stress but yields agreeably to *isostatic* adjustment. One wonders why tidal change is kinetic and isostasy is static as the name implies. A condition of "isokinesis" might fit better the volcanologist's experience of seisms and microseisms, and a world that is neither thermally nor chemically in repose.

through continental crust as shown by Nyamlagira, while carbon,[33] oxygen, and hydrogen are the centrosphere gases; then three stages of magma in the mantle are basaltic matter hottest and deepest, partly assimilated andesitic matter cooler and less widespread, and granitic matter coolest, highest, and continental. Any of these may break through the surface volcanically, the basaltic matter doing it most freely along maintained primitive widespread ruptures, mostly unknown, because geologists know no rock geology or its processes over seventy per cent of the earth.

The injection of granite now becomes just as fiery an eruption as Mauna Loa's performance with its 500-foot froth fountains. But it is *irruption*, beginning somewhere in excessively hot basaltic stages, and assimilating somewhere and somehow concentrates of silica and other elements. Novarupta with 70 per cent silica flowed up as a magma at Katmai. Just as on Mauna Loa, the exhaustion of contained gases, at first in violent breakage, thereafter in very slow transfusion of surroundings, is the principal process. This is the "transfusion in petrogenesis," of Holmes and Harwood,[34] "activating emanations protean in their geochemical range." They might have spelled it "*protein*" and found the same gases in the same order. The greatest event of a Mauna Loa episode, in time, bulk, and expenditure of energy, is what happens underground in the four years following an eruption; this magmatic transfusion of the under-earth may have affected many thousand square kilometers with ground surface movement and thermal change only barely perceived seismically by the volcano observatory, or the seismometrical geodesists.

On the other hand the overwhelming violence of a few hours of Krakatoa August 1883, Pelée May 1902, or Vesuvius April 1906, is a phenomenon of crustal recession of magma and phreatic geyser action. It is true that pumice and magma follow, because the disruption and release of pressure set loose rhythms of magma flow. It has been repeatedly shown that the main jet of temporary duration was pure steam and not the asphyxiating gas of magma, and that the initial magma move-

[33] The boiling point of carbon 4,200° is 1,600° above that of silicon, and is only exceeded by platinum, iridium, osmium, and tungsten, with several of the rare earths unknown. The reaction $C+O_2=CO_2+94\,400$ calories.

[34] Holmes, A., and Harwood, H. F.: Geol. Surv. Uganda Mem. 3, Volcanic Area of Bufumbira Part II, 1937; also Nature, April 15, p. 650, 1939.

ment was downward. The sequent magma movement is whole decades of rising.

Hypothesis (2). Probably hydrogen and carbon monoxide are the fundamental exudations to impregnate magma, these arising from the inner earth of unknown atomic conditions, and creating by unknown process of oxidation the fundamental fluid with carbon dioxide, hydrogen, and nitrogen in solution. Here the chemical imagination is at liberty to play freely with compounds ending in -ide. The volcanic evidence would fit best a centrosphere atomic and kinetically active: a mantle ruptured and variable, in thickness, and in sub-continental and sub-oceanic constitution. Possibly it has large relief on its bottom surface, if there is any surface, and is a thick-shelled rigid box with ruptures that resemble a spectroheliogram. While we have the sun and stars to measure, they appear physically to be safer guides than imaginative static terrestrial cosmology, seismology, and theories of geological investigators who have as yet no *knowledge* of what an earthquake is.

Hypothesis (3). Volcanism of flowing magma is frankly admitted to be deep in origin, and every volcano observable where magma flows is capable of producing measurements in series indicative of evolutional progress. This is true of measurement of all earth processes, and a series of measurements compared with time relations and experimental variables is better than an assemblage of averages. The author started these tabulations fully expecting water and sulphur to carry him into the depths. He arrived there with carbon and hydrogen in somewhat equal amounts, nitrogen diminished, argon-helium increased. Oxygen as intratelluric element is devoured by carbon and we know nothing more. The mere names of these elements suggest the names of Eddington, Bethe, Gamow, Van de Graaff, and Lawrence, and I would like to see the concepts of Arrhenius revived. Radio-activation may be terrestrially important apart from radium. Geophysics may be expected to keep pace with physics, and to depart from any notion of a static or moribund earth. Possibly "gravity layers" is too static a conception, and fluid convection quite inappropriate except near the surface.

SUMMARY OF MAGMATIC GASES.

(1) By arranging analyses of gaseous constituents of Hawaiian active lava in the order of each gas, guided by

progress from poor to good collections, it was found that increasing amounts of H_2O, SO_3, and Cl_2 moved from good to poor. Of those that went from poor to good, CO_2, SO_2, and N_2 were the leaders, and in much smaller volume H_2, CO, and S_2. Argon is in excess of its air ratio to nitrogen in the better collections.

(2) These conclusions were tested by smoothed curves of analyses in sequence following respectively the order of hydrogen, carbon dioxide, and the inverse of water-vapor. It was found that these three constituents vary together and that in general the volcanic gases start from zero values in the poor collections. They increase to the good collections in somewhat parabolic curves, and all the constituents are capable of extraordinary amounts in certain specimens. This means diversity of mixtures in a turbulent surface convection in contact with air, and in contact with surface concentration of sulphur and chlorine.

(3) The curves are summarized in a single diagram, Plate V, showing that in Hawaiian lavas under surface conditions water-vapor vanishes in excellent collections along with chlorine and sulphur trioxide, while the volcanic gases and the argon group increase to a mixture making perfect summation without water-vapor, in volumes much less than actual maxima in the analyses.

(4) Comparing the proportions of inflammables and the oxide gases in the interpretation of the several curves, it is obvious that the principal chemical process is the water-gas reaction, and the two secondary ones are exhaustion of atmospheric oxygen from air with inflammables to yield excessive nitrogen, and the reaction of SO_2 with hydrogen.

Study of the outgassing of rocks in vacuum at red heat shows that nitrogen and sulphur are minor constituents in the deeper regions. To account for the large quantity of water by reaction of CO_2 with H_2, the hydrogen must be greatly increased for the deeper gas. This is accomplished by nitrogen in less amount, as a residue from air, below the convection level, which is probably shallow; and by sulphur dioxide much less below the crateral level, where most of the sulphur comes from concentrates in fumed rock. Sulphur is concentrated because it is the least volatile of the ten gases. The deep gas then becomes H_2 and CO_2 in equal amounts, N_2 less, and the other gases in small volume.

(5) The fact that vacuum-heating yields more hydrogen in plutonic rocks suggests a comparison of all gas collections in series at the magmas and fumaroles of Hawaii, Iceland, Martinique, and Santorin. Analyses recomputed to collection-over-water proportions, as in hot-spring regions, show hydrogen increasing to seventy-seven per cent and carbon gases decreasing from similar figures to nearly zero. Nitrogen fills the gaps but in general decreases. The magmas involved range from fifty per cent to sixty-two per cent of silica, the surface temperatures decreasing approximately from 1,200° to 1,000°. Increase of unconsumed hydrogen goes with more viscous lava and lower temperature. This checks with Gautier's determination of similar increase of hydrogen to seventy-seven per cent in rocks increasingly siliceous, when heated to red heat in a vacuum, and the analyses computed without water. The low-hydrogen Hawaiian end of our list may be thought of as an analysis approaching the magmatic gas under hot springs, as computed for the Yellowstone. The explanation of hydrogen rising without explosion is that it is in equal large volume with CO_2, and reaches no free oxygen. Doctor Hance suggests that this assumption might also include reasoning as deduced from the gas laws in that even were complete chemical reaction to occur in this case, there would be no resultant changes in gas volumes on either side of this equation. Hence no explosive phenomenon. The condition of hydrogen and carbon dioxide in solution under pressure in magma, so as to react in vesiculation, but not before, is worthy of extended investigation.

(6) The positions of nitrogen and argon are peculiar, in that partly they are only superficially volcanic by the convectional downsucking of air, and transfused use of its oxygen. Partly they are abyssal, and the ratio $\frac{A}{A+N}$ increases to many times that of air. The argon group includes helium. The sequence of elements hydrogen, carbon, nitrogen, oxygen, and helium occurs in exothermic transmutation on the sun. It would be of interest to know whether indication of atomic alteration can be detected in the isotope relations of volcanic products.

Dr. E. T. Allen says "Jaggar's evidence even at Kilauea is by no means sufficient to prove that hydrogen is more important than water in the original volcanic gases" (Frankl. Inst. 1922, 46). "He has no evidence bearing on the *amount* of

oxidation of hydrogen" (ibid. 45). "It has not been shown that the conditions at Kilauea are characteristic of other volcanic craters" (45).

The answer to the first point is that *even at Kilauea* Plate V shows water vanishing, and *even Kilauea* with small hydrogen content in Table VI matches Allen's own computation for Yellowstone magmatic gas as shown above in "Discussion of Permanent Gases": and the still more *original* earth emanation, by vacuum-heating from Pelée and Santorin and granite, shows increase of hydrogen for intrusive and siliceous rocks. The *amount* of hydrogen oxidized is pretty clear in Table VI. The same table certainly does not make Kilauea unique by excess of hydrogen, and the volumes of that gas from the other volcanic districts named are mostly from Allen's valuable tabulation. Let us exorcise forever this bogey of Kilauea's isolation, and recognize with Dana that the Hawaiian volcanoes are splendidly typical of Iceland, Italy, Central Africa, and the South Seas, with the added advantage of continuity of action.

Prof. N. L. Bowen has called my attention to the fact that no laboratory utensil will hold hydrogen at 1,200°. He has stressed[35] the importance of volatiles in volcanism. "The investigation of these reactions in the laboratory is a special field of high-temperature and high-pressure chemistry that is warranted to tax the ingenuity of the most accomplished experimenter, and the theoretical treatment of the results will require a most facile mind." The earth is a utensil that holds hydrogen. Carbon dioxide apparently is hydrogen's restraining neighbor. The crystallization of basalt with the aid of these volatiles will bear extensive experimental investigation in the field.

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[35] Bowen, N. L.: Geology and Chemistry. Science No. 2303, p. 137, 1939.

HAWAIIAN VOLCANO OBSERVATORY,
HAWAII NATIONAL PARK.