

## MAGMATIC EMANATIONS.

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### INTRODUCTION.

A knowledge of the nature of the emanations from cooling igneous magmas is of great importance to the economic geologist. These emanations have been most frequently discussed in connection with theories of vulcanism or of the pneumatolytic deposition of ores, hence an article treating of them directly may prove of value. It will at all events place in the hands of those engaged in the investigation of ore deposits a condensed statement of the facts thus far established.

This paper was undertaken at the suggestion of Professor J. F. Kemp, to whom the writer desires to express his thanks for advice during its preparation.

### CLASSIFICATION.

When our knowledge of magmatic emanations shall have become wider, it will doubtless be found advisable to classify them according to origin, but at present such a classification is impracticable, if not actually impossible. For the purposes of the present paper, a classification of emissions made along the line of our sources of information respecting them will be most satisfactory. In 1903, Weed<sup>1</sup> stated that our knowledge of magmatic emanations had been derived from "(1) analyses of the gaseous emanations of volcanoes and lava-flows; (2) analyses of the gases occluded in cold rocks; (3) analyses of the sublimation products formed by fumaroles; and (4) evidence of contact metamorphism of included masses of sediments entirely surrounded by the igneous rock." Other sources of information are now available, which, taken in conjunction with those noted by Weed, suggest the following classification of magmatic emanations:

<sup>1</sup> *Trans. A. I. M. E.*, 33, 739.

- I. ACTUAL EMANATIONS.
  - 1. From lava-flows.
  - 2. From volcanoes.
  - 3. From deep-seated magmas.
- II. FOSSIL EMANATIONS.
  - 1. Inclusions in minerals.
  - 2. Minerals in druses and lithophyses.
  - 3. Minerals at igneous contacts.
  - 4. Minerals in veins.
- III. REPRESSED EMANATIONS.
  - 1. Of volcanic rocks.
  - 2. Of plutonic rocks.
- IV. POTENTIAL EMANATIONS.
  - 1. Of igneous rocks.
  - 2. Of sedimentary rocks.

Actual emanations are those actually in process of emission from cooling igneous magmas. Fossil emanations are remains or traces of past actual emanations which have been preserved in some manner. Repressed emanations are those which would have been generated by igneous rocks at the time of their formation had the pressure upon them not exceeded that of the atmosphere and had they remained at a high temperature for a sufficient length of time. Potential emanations are those which rocks are capable of producing if heated to a high temperature under atmospheric pressure. In the case of igneous rocks potential emanations necessarily include repressed emanations.

#### ACTUAL EMANATIONS.

Actual emanations may be observed rising as gases and vapors from lava-streams, expelled from volcanic vents, and issuing forth as springs generated by deep-seated magmas. Upon recent lava-flows and at active vents, the emissions are susceptible of direct observation at or shortly after the time of their expulsion, but plutonic emanations cannot be seen until long after they have left their source.

Notwithstanding the accessibility of volcanic craters there are obvious difficulties in the way of obtaining samples of the gases concerned in great volcanic eruptions. Under favorable conditions, the gases given forth during the less violent out-

breaks of volcanoes may be determined qualitatively by means of the spectroscope. It is occasionally possible during quiet eruptions to take samples directly above the volcanic vent (*e. g.*, Table I, Emanation 19), but quantitative determinations of emissions from volcanoes in eruption are usually made upon samples from side-wall crevices, lava fumaroles or submarine vents, while analyses of gases from the eruptive center are of samples obtained during periods of quiescence.

Janssen<sup>1</sup> studied the volcanic flames of Santorin spectroscopically in 1867 and found the chief combustible gas to be hydrogen. Sodium was always noted and the presence of copper, chlorine and carbon was also indicated. At Stromboli the flames were found to be of similar composition. In 1883 Janssen<sup>2</sup> had an opportunity to examine the flames of Kilauea with a spectroscope. He found in them sodium, hydrogen and hydrocarbons. Libbey<sup>3</sup> investigated the Kilauean flames independently in 1893. With a pocket spectroscope he was able to detect carbon dioxide and hydrocarbons.

Volcanic emanations are collected in the form of gases and vapors, but upon cooling the sample may be found to include gases, liquids and solids. The principal liquid is water. This is usually noted as "a little," "much," or "an enormous quantity," but since this water is an essential part of the emanation (except in the case of submerged vents), its quantitative relations with the gas should be stated, as has been done in Emanations 12 and 29 of Table I. It is also customary not to subject this water to a quantitative determination, but simply to test it qualitatively. It would be better, whenever possible, to make a quantitative analysis, figuring gaseous constituents in solution, like HCl, back into the gas analysis, stating the proportions of any liquids present, and figuring dissolved solids in with sublimates. Sublimates and dissolved solids are usually present in such minute amounts proportionally to the gases and water, that the quantity of emanation taken for the sample is

<sup>1</sup> *Comptes Rendus*, 64 (1867), 1303.

<sup>2</sup> *Comptes Rendus*, 97 (1883), 371.

<sup>3</sup> *Amer. Jour. of Sci.*, [3], 47 (1894), 371.

not sufficient for a satisfactory determination. Fortunately, however, these solids frequently collect about the mouths of fumaroles, and thus coatings which have taken hours or days to form may be obtained and analyzed. The analyses of sublimations as given in Table I have been made upon this class of material.

Out of a collection of over two hundred distinct volcanic emanations, fifty have been selected and placed in Table I. These fifty were selected (1) to show geographic range and (2) to show variety of chemical composition. The average of these fifty emanations does not represent a typical volcanic gas, but is simply of value for purposes of comparison and as roughly indicating the nature of the composite volcanic gas poured into the earth's atmosphere.

From this average, it would appear that nitrogen, with an average percentage of 44.361 in the cases cited, is the most important volcanic gas. The question arises, however, as to how much of this nitrogen has actually come from the lava and how much has been derived from air which has become mixed with the true volcanic emanations after their ejection from the lava and before their collection in the sample. The same question may be asked with regard to the oxygen which makes up 9.026 per cent. of the average. A considerable proportion of this nitrogen and oxygen may be due to contamination by air, but it seems almost certain that some of each gas is original. For in the case of submerged vents like those which gave Emanations 2, 18, 41 and 42, one seems forced to the conclusion that both oxygen and nitrogen are original; although in cases where sea-water is concerned, as in Emanations 17, 46 and 47, one is at liberty to question whether these gases may not, at least in part, have been driven from solution in circulating sea-water by the heat. In Emanation 3, from a high pressure fumarole, it would also appear that part at least of the oxygen and nitrogen must be original. Additional evidence of a confirmatory nature is offered by Emanations 2, 3 and 18 when their content of argon is considered; for the ratio of argon to nitrogen is higher than

TABLE I. VOLCANIC EMANATIONS.

No.	Volcano (or Locality).	Conditions.	Temperature. °C.	Composition of Gas in Parts per Hundred.											Water.	Accompanying Substances.	Sublimates.	
				CO <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	H <sub>2</sub>	HCl	H <sub>2</sub> S	SO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	A				He
1	Pelée.	Low pressure fumarole.	400	15.38	1.60	0	5.46	8.12	Tr.	0	0	13.67	54.94	0.71	—	Water.	NH <sub>4</sub> Cl, S, tr. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ?	As sulphide.
2	Soufrière.	Inundated	96	52.8	0	0	0	0	Tr.	2.7	7.5	36.07	0.73	—	Water with Ca and Fe salts:	S	S	
3	"	High pressure	95-96	69.5	0	0	0	0	0	4.5	2.7	22.32	0.68	—	Water with Ca salts and Fe <sub>2</sub> O <sub>3</sub> .	S	S	
4	Tolima.	Fumarole.	50	14	—	—	—	—	0	Tr.	17.2	68.8	—	-a	"	"	"	
5	Puracé.	"	86.5	85	—	—	—	—	0	0	3.15	11.85	—	-a	"	"	"	
6	Pasto.	"	78	85	—	—	—	—	0	0.5	4.4	17.6	—	-a	"	"	"	
7	(Tuquerres).	"	(Melted Bi, not Pb)	99.5	—	—	—	—	0	0	—	—	—	—	"	"	"	
8	Cumbal.	"	86	99.9	—	—	—	—	0	0	—	—	—	—	"	"	"	
9	Hekla.	"	<85	2.44	—	—	—	—	0	0	1.54	—	—	—	"	"	"	
10	"	"	—	0.56	—	—	—	—	0	0	14.21	81.81	—	—	Water with tr. HCl.	NaCl 5.65%, CaSO <sub>4</sub> 62.41%, MgSO <sub>4</sub> 12.68%, Na <sub>2</sub> SO <sub>4</sub> 16.78% and K <sub>2</sub> SO <sub>4</sub> 0.88%	Alum and CaSO <sub>4</sub> .	
11	"	Lava fumarole.	—	87.43	—	—	—	—	0	0	16.86	82.58	—	—	Water with tr. HCl and H <sub>2</sub> SO <sub>4</sub> .	NH <sub>4</sub> Cl and other chlorides (i).	S	
12	(Iceland).	Fumarole.	—	50.00	—	—	—	—	0	6.60	20.09	78.90	—	—	Water	"	"	
13	"	"	—	8.92	—	—	—	—	0	0.38	24.12	1.67	—	—	"	"	"	
14	(St. Paul Is.).	Great Geyser.	92	94.71	—	—	—	—	0	0	16.67	68.81	—	—	"	"	"	
15	"	"	78-80	2.27	—	—	—	—	0.32	0	12.21	68.45	—	—	"	"	"	
16	(Terceira Is.).	Thro' 205 fathoms sea-water.	—	92.400	—	—	—	—	0	16.75	0.125	68.45	—	—	Water with tr. H <sub>3</sub> BO <sub>3</sub> .	"	"	
17	(Larderoello).	Suffioni.	(Melted Ag)	10.50	—	—	—	—	Tr.	0	9	91	—	—	Water with FeCl <sub>3</sub> , NaCl (tr. CoCl <sub>2</sub> ), FeCl <sub>3</sub> , K salts, tr. CuO.	"	"	
18	Vesuvius.	Directly above vent.	(Melted Zn)	Tr.	—	—	—	—	—	—	17.24	72.26	—	—	Water.	"	"	
19	"	"	305-400 ±	2.80	—	—	—	—	—	0	13.76	86.24	—	—	A little water.	NaCl 96.566%, KCl 1.281%, Cu <sub>2</sub> Cl <sub>2</sub> 2.157% (g).	"	
20	"	"	66-154	0	—	—	—	—	—	0.10	20.49	79.32	—	—	No water.	NaCl with a little of other salts (g).	"	
21	"	"	218	5.38	—	—	—	—	2.37	2.06	19.17	73.60	—	—	Enormous quantity water with HCl and H <sub>2</sub> SO <sub>4</sub> .	"	"	
22	"	"	89	7.43	—	—	—	—	—	1.60	19.08	79.32	—	—	Enormous quantity of water.	"	"	
23	"	"	—	90.2	—	—	—	—	—	Tr.	18.46	76.16	—	—	"	"	"	
24	"	"	—	85.38	—	—	—	—	—	0	18.62	73.95	—	—	"	"	"	
25	"	"	—	99.1	—	—	—	—	—	0	2.85	9.38	—	—	"	"	"	
26	"	"	112	80.2	—	—	—	—	—	0.05	2.85	9.38	—	—	"	"	"	
27	"	"	87	8.02	—	—	—	—	Tr.	0	14.2	56.7	—	—	About 95% of gas was steam.	"	S	
28	"	"	99	—	—	—	—	—	9.1	—	18.71	73.27	—	—	Enormous quantity of water.	"	FeCl <sub>3</sub> .	
29	La Solfatara	High pressure fumarole.	—	5.00	—	—	—	—	—	0.45	17.27	77.28	—	—	Water with HCl and H <sub>2</sub> SO <sub>4</sub> .	"	S	
30	"	Fumarole.	—	10.6	—	—	—	—	—	0.30	15.2	74.2	—	—	"	"	"	
31	Etna.	"	41-82.5	92.53	—	—	—	—	—	0.99	0.12	4.70	—	—	Water with many salts in solution (i).	"	"	
32	"	"	46	95.35	—	—	—	—	—	0.30	0.58	2.28	—	—	Water with HCl and H <sub>2</sub> SO <sub>4</sub> .	"	"	
33	"	"	—	23.40	—	—	—	—	73.80	—	Tr.	0.52	—	—	Water with many salts in solution (i).	"	"	
34	"	"	—	68.8	—	—	—	—	—	—	24.40	14.54	—	—	Saline water.	"	"	
35	"	"	100	86.0	—	—	—	—	—	—	6.1	16.9	—	—	FeCl <sub>3</sub> .	As sulphides, NH <sub>4</sub> Cl. (No S or H <sub>3</sub> BO <sub>3</sub> .)	"	
36	Vulcano.	Fumarole.	360	68.8	—	—	—	—	—	—	0.7	11.2	—	—	S, NH <sub>4</sub> Cl (tr. I)	As sulphides (Se and tr. P), H <sub>3</sub> BO <sub>3</sub> .	"	
37	"	Flaming fumarole.	(Melted Pb, not Ag)	81	—	—	—	—	—	—	2.6	8.3	—	—	"	"	"	
38	"	Fumarole.	60-120	86.0	—	—	—	—	—	—	0.1	13.9	—	—	"	"	"	
39	"	Water-filled depression.	100	81	—	—	—	—	—	—	12.0	—	—	—	"	"	"	
40	"	"	82	86.0	—	—	—	—	—	—	16.41	70.45	—	—	"	"	"	
41	"	"	25	68.5	—	—	—	—	—	—	14.12	66.47	—	—	"	"	"	
42	Santorin.	Fumarole.	115	12.24	—	—	—	—	19.4	0.90	1.64	66.47	—	—	Water with HCl and less H <sub>2</sub> SO <sub>4</sub> .	"	S	
43	"	"	160	17.28	—	—	—	—	—	—	Tr.	1.46	—	—	"	"	"	
44	"	"	61	35.60	—	—	—	—	—	—	10	30.09	—	—	"	"	"	
45	"	Sea-water milky with S.	—	38.4	—	—	—	—	—	—	57.1	2.4	—	—	Water	"	"	
46	"	Fumarole.	—	49.2	—	—	—	—	—	—	1.0	5.2	—	—	"	"	"	
47	(Nisyros).	"	100	39.4	—	—	—	—	—	—	18.1	74.8	—	—	"	"	"	
48	"	"	70	7.0	—	—	—	—	—	—	0	—	—	—	"	"	"	
49	"	"	—	36.903	0.692	0.601	0.638	1.601	2.037	4.991	0.966	9.026	44.360	—	—	"	"	"
50	Average.	"	—	—	—	—	—	—	—	—	—	—	—	—	"	"	"	

NOTES.—a "Air" computed to O<sub>2</sub> and N<sub>2</sub>. b NH<sub>4</sub>Cl 78.00%, FeCl<sub>3</sub> 5.90%, AlCl<sub>3</sub> 2.00%, MgCl<sub>2</sub> 3.57%, CaCl<sub>2</sub> 2.58%. c Average of analyses of three different sublimates. d Of four. e Of five. f Average of analyses of three different sublimates. NaCl 84.3%; MgCl<sub>2</sub> (tr. Fe) 0.6%; Na<sub>2</sub>SO<sub>4</sub> 0.2%; K<sub>2</sub>SO<sub>4</sub> 1.0%; MgSO<sub>4</sub> 0.4%; CaSO<sub>4</sub> 2.7%; Hyg. H<sub>2</sub>O 0.8%. i Bases, Na, K, Ca, Mg, Al, Fe, tr. Li, tr. Cs, tr. Rb; acids; H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>(PO<sub>4</sub>), HNO<sub>3</sub>, HCl, HBr, HI, HF.

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43. Gorceix: *l. c.*, 270.
44. Fouqué: *C. R.*, 64 (1867), 186-7.
45. *Ibid.*
46. *Ibid.*
47. *Ibid.*, 667.
48. Gorceix: *C. R.*, 78 (1873), 1309.
49. *Ibid.*, 445.
50. *Ibid.*

in air. Moreover in Emanation 18 the ratio of helium to argon and nitrogen is enormously greater than it is in air. Special arguments may be advanced for the originality of the nitrogen. The proportion of nitrogen to oxygen is usually greater than in air and at times nitrogen is present entirely unaccompanied by oxygen. While a small amount of oxygen might readily be removed by secondary reactions after the emanations had been set free from the lava, such an explanation would hardly account for the more pronounced instances of low or lacking oxygen content. As we shall see later, nitrogen has been found in both fossil and repressed emanations, though the presence of oxygen in either case has not as yet been noted. It seems probable that, could the proper deductions be made for introduced air, nitrogen would be reduced to at least second place and oxygen would either be entirely lacking or present as one of the minor constituents only.

Conceding this to be the case, one may look upon carbon dioxide as the most important volcanic gas. A small amount of this gas may come from introduced air, but as it is present in air to the extent of only 0.03 per cent., the amount so introduced is almost negligible. Carbon monoxide has been found in one instance,—Emanation 1,—accompanying the carbon dioxide. Next in importance come the sulphurous gases, with hydrogen sulphide making up 4.991 per cent. of the average and sulphur dioxide, which may all have been derived from hydrogen sulphide by combustion, making only 0.966 per cent. Then, in order come hydrochloric acid, hydrogen and methane, with a trace of ethane.

Of the non-gaseous constituents of volcanic emanations, water heads the list, while the more important solids are sulphur, salt, sal ammoniac, gypsum and ferric chloride. The nature of the solids present in lesser quantities has been studied most thoroughly in the Æolian Isles and at Vesuvius. Abich<sup>1</sup> found that at Stromboli hydrochloric acid was the principal acid of the sublimations with lesser quantities of sulphuric acid. The bases were ammonium, iron, calcium, aluminum, and magnesium, with traces of sodium, potassium, copper, nickel and tin. Native sulphur was also present. At Vulcano<sup>2</sup> there have been found: sulphur, tellurium, realgar, boric acid, salt, sal ammoniac, ferric chloride, glauberite, lithium sulphate, glauber salt, alum with thalium, rubidium and cæsium, hieratite ( $2\text{KFl}\cdot\text{SiFl}_4$ ), cobalt, zinc, tin, bismuth, lead, copper, iodine and phosphorus. In the Vesuvian eruption of 1895, Matteucci<sup>3</sup> noted among the products of the fumaroles: hydrochloric acid, sulphurous anhydride, hydrogen sulphide, carbon dioxide, sulphur, calcium sulphate, various sulphates and chlorides of iron and of copper, erythrosiderite, chlorides and sulphates of sodium and of potassium, sal ammoniac, tenorite, and hematite, together with selenium, hydrofluoric acid, hydriodic acid, hydrobromic acid, and sodium bicarbonate. In the eruption of 1900 iron nitrate was produced at the same time as sal ammoniac.<sup>4</sup> In the last eruption of Vesuvius the fumaroles produced, according to Lacroix:<sup>5</sup> chlorides of iron, sodium, calcium, magnesium, etc., including erythrosiderite; realgar, sulphur, galena, magnetite, hematite, pyrrhotite, pyrite, and cotunnite; tenorite, chlorides and sulphates of potassium, sodium and copper, with a little calcium and magnesium. Thus the minor constituents of volcanic emanations have been shown to include all the economic metals with the exception of gold and silver.<sup>6</sup>

<sup>1</sup> *Zeit. deutsch. geol. Ges.*, 9 (1857), 403.

<sup>2</sup> Bergeat, *Abh. Munich Akad. Wiss., math.-phys. classe*, 20 (1900), 193.

<sup>3</sup> *C. R.*, 129 (1899), 65-6.

<sup>4</sup> Matteucci, *C. R.*, 131 (1900), 963-5.

<sup>5</sup> *C. R.*, 143 (1906), 727-730.

<sup>6</sup> The galena in the ejected marble blocks of Monte Somma is argentiferous, as noted by Matteucci, *Centralblatt f. Min. Geol. u. Pal.* (1900), 47, so that of the Vesuvian fumaroles may contain silver.



Actual plutonic emanations cannot, of course, be observed at the time of their emission. Many mineral springs may be of magmatic origin, but since their starting points are inaccessible they can be proved to be juvenile only by showing that they cannot be meteoric. Thus it has been argued that the Karlsbad Springs must originate from a cooling magma because they are situated in the midst of a large granite area and the quantities of water, carbon dioxide, and sodium salts which they contain cannot be explained by the infiltration of surface waters and leaching of the granite.<sup>1</sup> These springs are therefore probably actual plutonic emanations. The Karlsbad Springs hold in solution salts containing the elements chlorine, fluorine, boron, phosphorus, sulphur, selenium, thalium, rubidium, caesium, arsenic, antimony, zinc, sodium, potassium, lithium, calcium, magnesium, strontium, barium, iron, manganese, aluminum, and silicon.

#### FOSSIL EMANATIONS.

Fossil emanations are the more or less well preserved remains and traces of actual emanations. The complete preservation of past emissions is often seen in inclusions in minerals, while partial preservation is common in druses and lithophyses, at contacts and in veins.

Gases, liquids and solids enclosed in impermeable original cavities in the crystals of igneous rocks constitute samples of emanations from the magma at the time those crystals were formed. Sorby<sup>2</sup> found that the fluid in the cavities of the quartz of elvans and granites which he examined was water holding in solution chlorides of sodium and potassium and sulphates of sodium, potassium and calcium. Sometimes one salt, sometimes another, was in excess; occasionally there was more salt than the water could hold in solution; and often there was an excess of acid. Vogelsang and Geissler<sup>3</sup> found water and carbon dioxide in the cavities of the quartz of a granite from

<sup>1</sup> Suess, *E. and M. J.*, 76 (1903), 52.

<sup>2</sup> *Jour. Geol. Soc.*, 14 (1858), 487.

<sup>3</sup> *Pogg. Annal.*, 137 (1869), 56.

Saxony. Pfaff<sup>1</sup> conducted an interesting series of quantitative experiments in this line. He prepared samples by heating them to a low red heat and cooling in a desiccator. He then determined the water by grinding the specimens very fine in a current of dry air and weighing the moisture gathered up by this air. He concluded that granites, gneisses, etc., and the crystals of quartz and feldspar from granites, etc., all contain mechanically enclosed water and sodium chloride. The minimum quantity of water was found in a syenite from Meissen which contained 0.11 per cent. and the maximum in a mica schist from Davos with 1.8 per cent. Lava, obsidian and basalt were found to contain no mechanically enclosed water. Wright<sup>2</sup> analyzed the inclusions so plentiful in the pegmatitic quartz of Branchville, Conn. The gas from these cavities was 1.31 times the volume of the quartz and the water was 0.163 per cent. of the weight of the quartz. The gas consisted of 98.33 per cent. carbon dioxide and 1.67 per cent. nitrogen with traces of hydrogen sulphide, sulphurous anhydride, ammonia, fluorine and possibly chlorine. In addition to the gas and water, there were present in the cavities sodium chloride and a hydrocarbon of the nature of bitumen.

In druses in the nevadite of Chalk Mountain, Colorado, Cross<sup>3</sup> found sanidine, quartz, biotite, a few ore grains, and occasionally a topaz crystal. The appearance of these associated minerals suggested to him that they might be all sublimation products. Upon examining the minerals of lithophyses in rhyolite from Nathrop, Colorado, Cross<sup>4</sup> found a similar series of minerals. But in addition to the minerals found at Chalk Mountain, spessartite was discovered and some of the ore grains were believed to be hematite. Cross decided these minerals were "primary, and produced by sublimation from presumably heated solutions, contemporaneous, or nearly so, with the final consolidation of

<sup>1</sup>*Ibid.*, 143 (1872), 610.

<sup>2</sup>*Amer. Jour. of Sci.*, [3], 21 (1881), 209.

<sup>3</sup>*Ibid.*, 27 (1884), 94.

<sup>4</sup>*Ibid.*, 31 (1886), 432.

the rocks." Iddings<sup>1</sup> has identified quartz, tridymite and fayalite in lithophyses of obsidian and rhyolite from the Yellowstone National Park. Roth<sup>2</sup> mentions augite as occurring in druses.

The other varieties of fossil emanations, minerals at some igneous contacts and in some veins, have been so often and ably described in works upon ore-deposits that it seems unnecessary to discuss them at length in the present paper. It is well to remember in this connection that while the minerals of veins and contacts frequently appear to be in whole or in part of magmatic origin, in any individual instance it is almost as difficult to prove this to be the case as it is to prove that a certain hot spring is juvenile. For heat from an intruded magma will set free as secondary emissions part of the potential emanations of the rock into which it is forced, will start new circulations of meteoric waters and will stimulate old ones and thus effects may be produced similar to those which magmatic emanations would bring about. Thus in order to prove that the emissions from cooling magmas have contributed in an important way to the composition of contact zones and mineral veins, it is not only necessary to show that they might have done so but also that no other agent could have.

Ore deposits probably of pneumatolytic origin contain all the metals and mineralizers which have been found in actual emanations together with a few which up to the present time have not been so found.

#### REPPRESSED EMANATIONS.

When unaltered igneous rocks are heated to a high temperature: (1) absorbed gases and gasifiable substances may be driven off, (2) the gases and gasifiable substances in cavities may be set free and (3) some of the solids present may decompose or react upon one another to form new gases. These latter gases, the gases of composition, may be designated as repressed emanations because had the igneous rock containing them remained at a suffi-

<sup>1</sup> *Ibid.*, 30 (1885), 58.

<sup>2</sup> "Allgemeine u. Chemische Geologie" (1885), Vol. 2, p. 215.

TABLE II. REPRESSED GASES OF IGNEOUS ROCKS.

Rock.	Locality.	Authority.	Volumes Gas per Vol. Rock.	Percentage Composition of Gas.						Water	
				CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub>	Parts by Weight per 1000.	Lost During Preliminary Heating.
1. Granite . . . . .	Skye.	Tilden.	2.2 (c)	23.60	6.45	3.02	61.68	—	5.13	—	—
2. Gabbro. . . . .	Lizzard.	Tilden.	6.4 (b)	5.50	2.16	2.93	88.42	—	1.90	—	—
3. Basalt . . . . .	Antrim	Tilden.	8.0 (b)	32.08	20.08	10.00	36.15	—	1.61	—	—
4. Basalt . . . . .	Skye.	Travers.	.49	0	0	—	100.00	—	—	—	—
5. Granite. . . . .	Vire.	Gautier (a).	8.4	12.73	5.18	1.77	78.79	0.80	0.55 (d)	—	—
6. Quartz Diorite Porphyry.	Esterel.	Gautier.	7.4	59.25	4.20	2.53	31.09	0	2.10	—	2.29
7. Ophite . . . . .	Villefranche.	Gautier (a).	7.6	31.49	4.40	1.35	59.49	3.15	0.29	—	5.80
8. Lherzolite. . . . .	Lherz.	Gautier.	15.7	78.35	1.99	.01	7.34	11.85	Tr.	—	—
<b>Average . . . . .</b>			<b>7.024</b>	<b>30.375</b>	<b>5.558</b>	<b>2.589</b>	<b>57.870</b>	<b>1.975</b>	<b>1.448</b>	<b>12.903 (e)</b>	<b>4.045 (f)</b>

NOTES.—a. Average of three analyses; b. From another sample of same rock; c. Average of analyses of two other samples; d. Rich in argon; e. Average of last four analyses only; f. Average of analyses of gases 5 and 6 only.

CITATIONS.—Tilden, *Proc. Roy. Soc.*, 60 (1897), 455; Travers, *Ibid.*, 64 (1899), 130; Gautier, *Comptes Rendus*, 132 (1901), 58.

ciently high temperature and low pressure for a sufficient length of time they would have been generated as magmatic emanations. The nature and quality of repressed emanations are evidently dependent upon the composition of the rock, the temperature and the pressure.

According to Brun,<sup>1</sup> nearly all lavas emit gases when remelted, often in such quantities as to cause veritable explosions. The gases so generated are: Nitrogen and ammonia, chlorine and hydrochloric acid, hydrocarbons and substances derived from them by decomposition and combustion. Only insignificant quantities of steam are formed.

The repressed emanations of some igneous rocks have been investigated quantitatively and the results appear in Table II. A glance at this table shows water to be the principal substance generated in igneous rocks by the action of heat. Then, in order, follow hydrogen, carbon dioxide, carbon monoxide, methane, hydrogen sulphide and nitrogen. The main points of difference between these gases and volcanic gases are such as can be explained by the introduction of air into the gases generated by the volcanic magma. In this way the amount of hydrogen in a generated gas would be reduced by the formation of water, the amount of carbon dioxide would be increased and of carbon monoxide decreased by the oxidation of the latter, and sulphur dioxide and water would be formed by the combustion of hydrogen sulphide while at the same time the quantity of nitrogen would be increased and oxygen, if not entirely consumed, would be added to the list of gases.

#### POTENTIAL EMANATIONS.

Potential emanations exist in all rocks. They are the gases which would be evolved by a rock if it were heated to a high temperature under atmospheric pressure. Looked at in another way, they are the largest quantity of secondary emanations which can be produced from a rock as a result of the intrusion of a magma. From still another point of view, they are the

<sup>1</sup>"Quelques recherches sur le volcanisme," *Arch. Sci. phys. et nat.* [4], 19, 439-450 and 589-606.

greatest amount of gases which a rock could evolve if it were in any way converted into a magma. Were a magma derived from a rock by fusion, the potential emanations of the rock would be separated into two portions, one being expelled as actual emanations and the other being retained as repressed emanations.

The potential emanations of an igneous rock are present as repressed emanations, absorbed substances, and fossil emanations. Repressed emanations and fossil emanations have already been discussed. The principal absorbed substance is water which is present in extremely variable amount. In Table II the amount of absorbed water in connection with gases 5 and 6 is given.

The potential emanations of sedimentary rocks are of somewhat similar nature to those of igneous rocks. They are present as substances in chemical combination, substances in cavities and absorbed substances. No data as to their chemical composition are available, but it is evident that a pure sandstone would give rise to but little gas, a limestone to immense quantities of carbon dioxide, and that in general much more steam would be generated than from igneous rocks.

Potential emanations are the source of the secondary magmatic emanations induced in rocks by the heat from intruded magmas. The relative amounts of primary and secondary emanations evolved in any particular case are not known, and the ratio probably varies widely. Investigation is greatly complicated because magmas may absorb by contact substances of the nature of potential emanations and give them forth later as direct magmatic emanations.

#### SOURCE OF THE EMANATIONS.

Travers<sup>1</sup> has said: "In the *majority of cases* where a mineral substance evolves gas under the influence of heat, the gas is the product of the decomposition or the interaction of its *non-gaseous* constituents at the moment of the experiment." There seems to be little doubt that the emanations derived from dry

<sup>1</sup> *Proc. Roy. Soc.*, 64 (1899), 142.

unaltered igneous rocks are due to the decomposition or interaction of minerals which compose the rock. The following explanation of the observed facts seems reasonable. In order that certain rock minerals shall produce emanations two conditions must be fulfilled: the heat must be high and the pressure must be low. Lavas retain potential emanations because they have cooled so rapidly that they have not had time to generate them while plutonic magmas retain them because they are under such great pressures.

Brun<sup>1</sup> believes the generators in the case of the Mediterranean volcanoes to be: For nitrogen, nitride of iron and nitride of silicon,—“Marignacite,”—for chlorine, the combined silicate and chloride of calcium; for hydrogen and carbon, heavy hydrocarbons; and for oxygen, polybasic ferric silicates. Reactions between these generated substances give rise to the gases observed. Brun's theory is founded upon both analytic and synthetic investigations.

Gautier<sup>2</sup> conducted analytic and synthetic work which led him to somewhat different conclusions as to the nature of the generators. Water set free at a high temperature reacts upon ferrous silicates and analogous compounds to form ferrous-ferric and ferric compounds and free hydrogen. Water reacting upon siderite at temperatures even below red heat sets free carbon monoxide, carbon dioxide and hydrogen. Hydrogen sulphide is formed (*a*) by the decomposition of iron and manganese sulphides by water; (*b*) by the reduction of sulphates by nascent hydrogen to sulphides and their destruction as in (*a*), and (*c*) by the decomposition of sulphosilicates by water. Nitrogen, ammonia, argon and helium result from the decomposition of nitrides, argonides and helides. Traces of nitrides and cyanides are present and are decomposed by water at red heat forming nitrogen and ammonia. Methane and traces of petroleum are formed from metallic carbides decomposed by water at high temperatures.

<sup>1</sup>*Op. cit.*

<sup>2</sup>*Bull. Soc. Prim.* [3], 29 (1903), 191. In more recent work (*Ec. Geol.*, 1, 688), Gautier has complicated his results by introducing exhalations from a supposed incandescent metallic nucleus of the earth.

Thus Gautier attributes the formation of the repressed emanations mainly to the action of water while Brun explains the formation of the same gases without water. Each was doubtless correct within the range of his own experiments, for considerable difference must exist between the generators left in the intrusive rocks and those left in the extrusive rocks, since the repressed emanations are retained under such different conditions in the two cases. It should be borne in mind, however, that while Gautier was dealing with solid rocks Brun was dealing with melted lavas. Brun's analyses were upon solid generators and lavas, his experiments upon melted ones. When these solids melted and dissolved in one another, the nature of the generators may have been somewhat different, ions rather than compounds becoming of importance.

It is apparent that primary magmatic emanations are of similar origin to repressed emanations, if the view advanced here that repressed emanations are simply actual emanations kept back by cooling or pressure or both cooling and pressure is true. Thus the magma may best be looked upon as an extremely complicated system of liquids and gases. Any relief of pressure leads to a rearrangement of this system whereby emanations are given forth and a part of the generators are destroyed in giving birth to more of the gas. Increased pressure causes the absorption of gas and the formation of more of the generators. Cooling of the magma will cause it to solidify, but the formation of emanations may continue till a temperature slightly below red heat is reached, providing the pressure is low.

#### CONCLUSIONS.

Magmas contain certain substances which decompose or interact unless prevented by pressure or cooling. These generators give rise to primary magmatic emanations. Cooling or pressure or both cooling and pressure prevent the complete destruction of the generators, hence igneous rocks contain repressed emanations which may be expelled by heating them to red heat at atmospheric pressure.

Intruded magmas by heating the adjoining rocks induce sec-



ondary emanations which consist of part of the potential emanations of these rocks. The ratio of primary to secondary emanations is an unknown quantity.

Magmatic emanations which are expelled as gases and vapors become at the ordinary temperatures of the earth's surface solids, liquids and gases. The principal gases are carbon dioxide, methane, hydrogen, hydrochloric acid, hydrogen sulphide, sulphur dioxide, nitrogen and oxygen, with less carbon monoxide and ethane and a very little hydrofluoric, hydriodic and hydrobromic acids. Water is the only important liquid, and it makes up a large percentage of the total emanation. The solids are chiefly chlorides and sulphates of the alkalies and alkaline earths and of iron, together with a much smaller quantity of metals and mineralizers.