PAPERS READ BEFORE THE CHEMICAL SOCIETY.

VI.—*Observations on Fluid-cavities.*

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I. *On the probable Temperature incident to the Formation of Topaz.*

SINCE the publication of my last paper on the variations in the critical point of carbon dioxide in minerals, I have made an examination of the splendid collection of topazes in the British Museum. With the kind permission of Professor Storey-Maskelyne, I selected all those specimens which from their appearance were most likely to contain fluid cavities. The following were from the Ilmen Mountains, Ural :—

1. Colourless crystal of small size, with many cavities.
2. Colourless crystal, with cavities.
3. Colourless crystal of large size, full of fissures, very few cavities.

From Nertchinsk, Irkutsk, Siberia :—

4. Large crystal of slightly greenish-blue colour.

From the River Urulga, Nerchinsk, Irkutsk :—

5. A large crystal.

From Murchinsk :—

6. Blue topaz, piece of large crystal.

Each of these specimens contained cavities with a single fluid enclosed. This fluid was not affected by a temperature of 90° C., and hence was most probably water.

From Saxony :—

7. A yellow crystal.
8. The same.
9. The same.
10. The same.

Each of these specimens contained cavities with a single fluid therein. This fluid was unaffected at 90° C., and was most probably water.

Brazilian topazes, Minas Novas, Minas Geraes:—

11. }
 12. }
 13. } These were rounded pebbles. Two of them contained no flaw
 14. } or blemish whatever. Any cavities noticed were empty.
 15. }
16. A crystal. Contained what appeared to be water cavities only. From the nature of the specimen it was difficult to make a good observation.
17. A pebble split in two. Large cavities containing one liquid, apparently water, and a bubble which was at least half the size of the cavity.
18. A sliced specimen from New Holland, of a greenish tinge. Many large cavities with one liquid in each, which did not occupy quite one-half of the cavity. The liquid, for reasons already stated, was presumably water. About 1,000 cavities were examined in this specimen.

Cairngorms from Scotland:—

19. A polished slice, much fissured.
20. A magnificent crystal, cut and polished at one part. It contained what were apparently water cavities. These were few in number.
20. A slice off a large crystal, much fissured and full of cavities, many of large size. The slice contained liquid which appeared to be water. It occupied a little more than half the space in each cavity.

Topaz, a fluosilicate of aluminium ($\text{AlF}_3 \cdot \text{SiF}_4 \cdot 5\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), may possibly be formed, as Bischof has suggested, from the alteration of mica and felspar. The frequent association of topaz with granites in Brazil, in the Mourne Mountains, Ireland, with the decomposed granites of Scotland, and of the Ilmen Mountains, favours this view entirely. It is most probable that the process of conversion has been effected by the action either of alkaline fluorides or of cryolite on kaolin. In any such reaction no carbon dioxide would be liberated; hence we may not expect to find it very frequently in the liquid state in topazes, and when it does occur it may have been enclosed simply because it happened to be present, and not because it was a necessary product of the reaction by which the mineral was formed. At the time of its enclosure the water may have been in the vaporous state, and it is almost certain that the carbon dioxide was not liquefied, but in the condition of a highly compressed gas. That a high temperature pervaded the material at the time of its crystallisation is shown,

I think, by the fact which I have observed in some specimens, viz., that numbers of cavities, many of large size, were only half filled with a liquid which we have good reason to believe was water. The contraction of the water to one-half or less of the volume of the cavities' capacity is doubtless due either to condensation from the state of an enormously compressed vapour, or to contraction after cooling from a temperature approaching the critical point of water. In one and the same specimen of topaz I have noticed cavities containing very little, in fact a mere trace of water, and so much liquid carbon dioxide that the latter substance filled the cavities by expansion before the critical point of the substance had been reached. Let us call these cavities *a*. Side by side with these were cavities filled one third by water, one-third by carbon dioxide liquid, and the remaining space by the same substance as gas; let these be denoted by *b*. The critical point, which was the same in all the cavities, 27.5° C., shows that there is only a small amount of any incondensable gas present.

The contents of both cavities *a* and *b* must have endured the same pressure, which could not have been less than 109 atmospheres (tension of liquid CO_2 at $30.92^{\circ} = 109$ atmospheres, Andrews), and was probably very much greater. Now inasmuch as the carbon dioxide in the water cavity *b*, of which Fig. 1 is an example, is half gaseous and half liquid at the critical temperature 27.5° , and that in the cavities *a*, containing little water, is wholly liquid (in which the incondensable gas seems to dissolve, for it totally disappears when the liquid is expanded to the utmost), I conclude that the difference in the proportion of gas to liquid in *b* is due to the contraction of the water upon cooling. Any expansion of the crystal on the release of pressure it endured *in situ*, would have but slight effect on the capacities of the cavities, and may be disregarded. We do not know the rate of expansion of water at high temperatures, but between 4° C. and 100° C. it amounts to an increase of only 0.043109 in 1 volume (Kopp). The critical point of water, according to Cagniard de la Tour, is near the melting-point of zinc, or not lower than 342° C. (Daniell). No doubt the expansion of water would increase with great rapidity as the temperature approached its critical point. From these data I conclude that the temperature of the mineral at the time of formation was in all probability approaching the critical temperature of water. That the critical point was not attained I infer from there being so little water in the cavities *a*, for had such a temperature been attained, the mixture of gas and water vapour would have been uniform in composition, and a corresponding uniformity would have been noticed in the contents of the

FIG. 1.

cavities. Although in the particular specimen to which I here make reference the temperature may have been below that at which water under any pressure assumes the condition of a vapour, yet in many other cases I am led to believe the temperature to have been above this point, on account of the small quantity of liquid present, thus in the topazes from Brazil, New Holland, and from Scotland (Nos. 17, 18, and 20).

Calculations necessitating a knowledge of the expansion of water at high temperatures, and the decrease in volume of its vapour by pressure when above its critical point, as well as the reduction in volume of incondensable gases at high pressures, must at present be little more than conjectures, since these are matters concerning which we require considerable additions to our present knowledge.

II. *An Examination of Rock Sections.*

A number of sections from the following rocks were cut for me and submitted to microscopical examination in the manner already described in one of my former communications: Basalt, from Samson's Ribs, Edinburgh; from Bolam, Durham; from Madeira. Volcanic breccia from Arthur's Seat, and gabbro from Corstorphine Hills, Edinburgh. Sections of the following granites: from Aberdeen, Peterhead, Tudyvan, Cornwall, St. Leven, Cornwall, Mount Sorrel, Leicestershire, the Mourne Mountains, Ireland, and Egyptian granite. Granitic porphyry from Altenburg, Saxony; quartz porphyry from Pwllheli, North Wales; porphyry from Royelle Bay, Jersey; Schorl granite from Luchons, Pyrenees; porphyry from the Chimney Rock, Penzance; and syenite from Guernsey.

Many of these specimens, in fact, almost all granites and porphyries, contained water cavities. These were found generally in the quartz, very seldom in the schorl, and scarcely ever in the felspar crystals. In some cases the cavities were very minute, and their contents barely distinguishable with a magnifying power of 800 diameters. Carbon dioxide appeared to be present in only two of these specimens, namely, in a granite from Cornwall, and in a specimen from the Mourne Mountains, but its occurrence is somewhat doubtful, as only one cavity in each section gave evidence of its presence. A specimen of felstone from near the summit of Snowdon, kindly lent to me by Mr. J. C. Young, F.G.S., contained in the quartz crystals a number of water cavities. In one of these, to which my attention was particularly directed by Mr. Young, there appeared to be no liquid; at least no bubble was seen; in a cold room, however, a moving bubble had been noticed.

By dropping a little ether on the slide it was sufficiently cooled by evaporation to allow of the liquid being seen. By immersion in iced water and hasty removal therefrom, the critical point was taken, or

rather what was the *apparent* critical point, namely the temperature at which the bubble disappeared; this, as I have shown already, is not necessarily identical with the true critical point. At 18° C. the bubble was plainly visible, and at 18.5° C. it had disappeared. The greatest diameter of this cavity was about $\frac{1}{80.000}$ of an inch, and at 0° C. the bubble had a diameter of about $\frac{1}{10.000}$ inch. Under certain conditions the bubble was kept in constant motion, but with regard to this fact I shall have further observations to make in a separate communication. I was at considerable pains to ascertain whether this liquid simply filled the cavity by expansion, or whether it attained its critical point at 18.5° . I found it had simply expanded. Previous to my having made this examination of rock sections, I was impressed with the idea that the depths of the earth contained carbon dioxide and water in superabundance, and that the enclosure of these substances was simply a matter of accident, and not immediately connected with the reaction or reactions resulting in the formation of the minerals. I therefore expected to find carbon dioxide of constant occurrence in rocks and minerals, for since little or no special search seems to have been made for it, it was quite likely that it might be contained in cavities of minute size, such as are seen in granites, &c., and have been regarded hitherto as water. I have now a decided inclination to believe that it occurs but rarely.

III. *On Gas-bubbles denser than Water.*

I have already pointed out (on variation in the critical point of carbon dioxide in mineral cavities, *Journal of the Chem. Soc.*, 1876, vol. ii, p. 237) that by compression a gas may be rendered denser than water. I have since obtained evidence of the existence of gases in a piece of rock-crystal so condensed that these conditions may easily be induced. The gas-bubbles float on a liquid, which I have proved to be water. By exposing the crystal to a uniform rise of temperature, the water is expanded and the gas compressed to such an extent that the bubbles sink and do not rise till after the liquid has sufficiently cooled.

It is here to be remarked that experiments made upon a hot stage which warms only one side of the cavity are apt to give fallacious results, and it is necessary to make use of a microscope with a revolving stage, so that the bubble may be moved about freely. It should be of such a size as to be plainly discernible with a 2-inch objective, and sufficiently mobile to act like the bubble in a spirit-level. The sinking and rising motion is slow, like the movement of a globule of oil in water. The supposition that the temperature causes the gas-bubble and the liquid to change their relative densities is favoured by the fact that when the specimen is cooled in iced water, a much higher temperature than usual is required to produce the effect. Then again

in large deep cavities the bubbles were seen to descend so far as to be entirely out of focus, and in order to bring them into view, the object-glass was made to approach the specimen; but when on cooling the bubbles returned to their original position, the objective had to be withdrawn. I desire particularly to point out that, as I have noticed other effects due to heat which might under certain conditions cause bubbles to move towards the lower ends of their cavities, great caution was taken to eliminate all circumstances which might lead to a wrong interpretation of facts, and some thousands of experiments were made on different cavities.

FIG. 2.

An account of the method of ascertaining the temperature at which the bubbles sink here follows. A cavity of regular shape in a specimen of rock-crystal (Fig. 2) which contained carbonic acid cavities, proved an exceedingly good one to operate upon. It contained but one liquid, water, and the bubble could be seen with a 2-inch objective moving about from point to point as the microscope stage was rotated. Preliminary trials with a hot spatula

showed that in whatever position the cavity was placed the bubble always sank by rise of temperature.

The specimen was then detached from the glass and mounted between pieces of stout sheet platinum. The microscope was in a horizontal position, so that the specimen hung vertically. Mercury was heated in a platinum crucible, and the specimen, after being arranged in the focus of the instrument, and adjusted in such a manner that it could be instantly replaced, was removed and plunged into the hot mercury.

The following is a statement of the observations made in this way, and I am convinced that they may be depended on:—

Temperature.

1st Exp.	200° C.	The bubble had sunk into the lowest extremity, and was seen to return suddenly.
2nd Exp.	190	Bubble had sunk, but floated again on cooling.
3rd Exp.	180	The same.
4th Exp.	160	The same.
5th Exp.	150	The same.
6th Exp.	140	The bubble had not changed its position.
7th Exp.	145	The bubble had not moved.

Temperature.

8th Exp.	150° C.	The bubble had not moved.
9th Exp.	150	The bubble had sunk.

On this last occasion the bubble did not quite resume its original position on cooling. Hence it appears that at 150° C. the gas is denser than water. Without knowing the exact composition of the enclosed gas and the variations from Boyle's Law that it would exhibit at high pressures and at a temperature of 150° C., it is not possible to ascertain to what extent it has been compressed. It is by no means unlikely that the carbonic acid now found in the liquid state in cavities was originally floating as a dense gas forming a sort of emulsion in the silica solution before its solidification took place.

IV. *On Crystal-shaped Cavities.*

In the course of my experiments I have frequently remarked the symmetrical arrangement of cavities around the axis of the crystals in which they were contained. Thus in a beryl, the cavities took the shape of tubes lying parallel to the six faces of the prism. In a hexagonal prism of quartz the cavities were of irregular shape, but so disposed round the principal axis that they were evidently caused by enclosures of water during successive growths of the crystal. Generally speaking, the cavities themselves are irregular in form and more or less rounded; especially is this the case in crystals artificially formed; but I have observed that in certain cases the cavities are not only angular, but that they take the form of the crystals in which they are enclosed so closely, that each side of each cavity is parallel with a face of the crystal. This has been seen in quartz porphyry from Arran; in granite from the Mourne Mountains; in Aberdeen granite; in the granite from Tudyvan, Cornwall; and in quartz from Snowdon. A glance at the illustrations will at once give an accurate idea of the appearance of the cavities as we see them; of course by transmitted light. The bubble will always be noticed near the centre or towards one end of the cavity. In the Arran porphyry the quartz takes the form of the double hexagonal pyramid, and so likewise do the cavities. The best and most striking, and at the same time most numerous examples of this symmetrical formation of cavities are to be met with in a prism of rock-crystal which I have had cut into sections, both parallel with and at right angles to the principal axis.

The cavities, as seen in both sections, are shown in Figs. *a* and *b*, and it will be noticed that there are a few of a prismatic shape, but the majority are simply double pyramids. Were it not for the presence of the bubbles, it would be impossible to believe that these

were not crystals of quartz enclosed. The following is what I conceive to be the origin of these symmetrical cavities. The mineral is crystallised at a high temperature, say 150°C. , for by raising the rock-crystal to this temperature I find the water entirely fills the cavities. The high temperature has diminished the tendency to cohesion. The water exerts a resistance to compression which is comparable with that of a solid body; but unlike that of a solid body the direction of the resistance can be changed, *i.e.*, the shape of the enclosed water can be altered so as to conform to the planes of crystallisation of the mineral; consequently we have the molecules of the silica grouped around the resisting liquid, as if they were arranged round another crystal as in the formation known as *capped quartz*. To show that these crystal-shaped cavities are not of rare occurrence, at least in some specimens, I have only to refer to Fig. *c*, which gives some idea of a complete chain of them, each one of which contains a fluid and a bubble. As the best and most regular crystals are formed slowly, so are these crystal-shaped cavities apparently formed more generally where the growth of the crystal has been gradual, that is to say where cavities are of rare occurrence, slowly grown crystals being to a great extent free from cavities.

CRYSTAL-SHAPED CAVITIES.

Explanation of the Drawings.

- a.* Cavities in a transverse section of a crystal of quartz, evidently hollow six-sided pyramids. At the apex of each is seen a bubble, the liquid contents are water. The true outline of the section of the crystal is drawn in the position it was fixed in during observation. It will be noticed that the sides of the cavities are parallel to the faces of the crystal in which they are contained. $\times 250$ diameters. Sometimes as the cavities are obliquely inclined, they appear distorted, as for instance the one to the right in the drawing.
- b.* Cavities seen in a longitudinal section of the same crystal. Many of these evidently resemble the double pyramid and other modifications of crystals. $\times 250$.
- c.* A string of geometrical cavities observed in the same specimen. $\times 250$.
- d.* Cavities taking the form of the quartz crystals in porphyry from Arran. The sides are parallel to the sides of the crystal. $\times 400$.
- e.* Another crystal in the same specimen containing similar cavities. $\times 400$.

a.

c.

b.

d.

e.

f.

g.

h.

- f.* Quartz with crystal-shaped cavity in granite from the Mourne Mountains. $\times 400$.
 - g.* The same in Aberdeen granite. $\times 400$.
 - h.* Crystal-shaped cavities in quartz from Snowden. $\times 400$.
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