

*On some Cornish Tin-stones and Tin-capels.*

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THE MINERAL ASSOCIATES OF CASSITERITE.—These are much the same in Cornwall as have been observed in other tin-producing districts, as in Saxony, Bohemia, Brittany, Finland, Spain, the Malay Peninsula,\* Banca, Blitong, Queensland, New South Wales, Tasmania, &c. In the following lists of minerals which are associated with Cassiterite in the different kinds of country-rock in Cornwall, I only refer (*a*) to those which appear to have been formed contemporaneously with the Cassiterite, and (*b*) to those which have been observed in immediate contact with it and mostly deposited upon it.

*Granite*.—Here the most usual associates as thus defined are, in the *a* class, besides the constantly occurring *quartz*, *felspar* (orthoclase, usually converted more or less completely into kaolin), *mica* (lepidolite, lepidomelane and the constantly occurring Gilbertite), and *tourmaline*; less frequently *wolfram* and *stannite*; and occasionally *topaz*, *apatite*, *Scheelite*, *fluellite*, *Favistockite*, *Churchite*, and *molybdenite*. In the *b* class we have, besides *quartz*, *mispickel*, *pyrites*, *chalcopyrite*, *smaltite*, *blende*, *bismuth*, *bismuthinite*, *hematite*, and *limonite*, with occasionally *native-copper*, *pitch-blende*, and *uranium-ochre*. The reported occurrence of *chalcolite* (Torbernite) and *autunite* at Stenna Gwynn needs confirmation.

*Elvan* (Quartz and Felspar Porphyries).—Here, in the *a* class, besides *quartz*, *felspar*, and *mica*, as in the case of the rocks of granitic districts, we have *tourmaline* still more generally associated with the Cassiterite, but often only in microscopic crystals. In the *b* class I have only met with *quartz* and *hematite* as associates.

*Killias* (clay-slate, tourmaline-schist, "knoten-schiefer," &c.).—Cassiterite occurring in these rocks is invariably associated with *quartz* and microscopic or macroscopic *tourmaline*. Other frequently associated minerals in the *b* class are, *chalcedony* (Pedandrea, East Pool, &c.), *chlorite*, *mispickel* and *pyrites*; more rarely *wolfram*, *chalcopyrite*, *smaltite*, *cobaltite*, *hematite*, *limonite*, *blende* and *chalybite*; still more rarely *pitchblende*,

\* P. Doyle, Quart. Journ. Geol. Soc. 138. May 1879.

pearlspar, *pharmacosiderite*, *uranochre*, *chalcosiderite*, *Henwoodite*, *Andreusite*, *olivenite*, *topaz*, and *apatite*.—The occurrence of *calcite* associated with *cassiterite*, which has been reported from Polgooth, seems to need confirmation.

*Hornblendic slates*.—Many so-called greenstones are really hornblendic slates, as at Botallack and Wheal Owles in St. Just, and Terras Mine, St. Stephen's. Oxide of tin is always very rare in such rocks. When it does occur its associates are *hornblende*, *actinolite*, *apatite*, *epidote*, *axinite*, *garnet*, in the *a* class; and *magnetite*, *hematite*, *chalcocite*, *chalcopyrite*, *diallogite*, *Penwithite*, *carbonate of bisnuth*, *calcite*, *Dolomite*, *olivenite*, *scorodite*, and *pharmacosiderite* in the *b* class.

*Greenstone*.—In this rock the occurrence of tin oxide is very rare, but occasional veins of it occur associated with *chlorite*, *limonite*, and other products of change.

ORIGIN OF THE VARIOUS FORMS OF TIN-OXIDE.—I venture to think that, after a due consideration of the facts stated in reference to the large number of specimens described in my first and second papers, few if any of my readers will demur to the conclusion stated on page 4, *viz.* that all the different forms of native tin-oxide described have been deposited in their present situations from stanniferous solutions; all are aqueous or humid in their origin; none are in any sense igneous deposits. The frequent occurrence of minute crystals of Cassiterite lining fissures in quartz, which is frequently full of minute fluid cavities, would be altogether inexplicable on any other supposition. I have seen well-marked veins of tin-oxide, in crystals, where the whole vein did not exceed  $\frac{1}{10,000}$ th of an inch in thickness.

A difficulty, however, may be at first felt by some chemists in receiving this conclusion, arising from the well-known great insolubility of many tin compounds, and especially of the native tin-oxide. This difficulty will probably disappear when it is remembered that, although tin-oxide in its present state is very insoluble,\* yet that some salts of tin, and notably the fluorides and chlorides (and possibly the borate) are very soluble in water.

The constant occurrence of *schorl*, *topaz*, and other minerals containing fluorine, with oxide of tin,—when it occurs in granite or porphyry, has led Von Buch, Elie de Beaumont, Daubrée, and other chemical geologists, to the conclusion that the tin has been brought into its present situation by the agency of fluorine; and Daubrée has even produced artificial crystals

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\* Recently precipitated tin-oxide is rather readily soluble in many menstrua, and I find that native tin-oxide (*cassiterite*) is very perceptibly acted upon by dilute *aqua regia*, especially when it is finely powdered.

of oxide of tin by passing vapours of perchloride of tin and of water through a heated porcelain tube. The crystals so obtained did not appreciably differ from natural crystals of *cassiterite* in physical characters, although the "forms" were different. He used the perchloride instead of the fluoride simply because it was easier to get; but there can be little doubt that similar results would have been obtained by using the fluoride.

My examination of a very large series of Cornish tin-stones—many of which have been described in the foregoing pages—has proved that not only in granite and porphyry, but also in killas, a fluorine-bearing mineral (tourmaline) is invariably present in notable proportion. Chlorine also is usually present, although only in minute proportion, more especially as a constituent of the liquid occupying the numerous fluid-cavities always observable in vein quartz. Fluor-spar is not universal, simply because lime is a somewhat rare ingredient in the Cornish metalliferous districts, but locally it is tolerably abundant.

Daubr e remarks that it is difficult to specify the actual reactions which have taken place,\* because we see only the final results of a series of changes. This is no doubt the case, but perhaps the action was not greatly different from the following:—

The granite being still at a high temperature, but a good deal fissured, and containing many shrinkage cracks, was exposed to the action of highly-heated water, or water vapour containing hydrofluoric acid, with occasionally hydrochloric acid, boracic acid, fluoride of tin, and other easily decomposable fluorides. As the fissures would naturally be more abundant near the outskirts of the several granite masses than elsewhere, the action would be greatest in these situations. The felspar would readily give up its alkali (and part of its silica also) to the acids or decomposable fluorides, being thereby reduced to the state of silicate of alumina (kaolin), while a part of the alkaline fluoride would be carried off by the waters, and another portion would be deposited as lepidolite and Gilbertite (some of the alumina being used up in forming these minerals) among the particles of kaolin. Where iron was present, if the fluids contained also boric acid the highly stable compound tourmaline would be formed, as we find it in great abundance. A somewhat similar action upon the *highly felspathic* killas near the junctions would probably result sometimes in the formation of tourmaline-schist, which pretty constantly occurs in such situations, and at other times in the production of the slaty varieties of tin-capel.

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\* M moire sur le gisement, la constitution, et l'origine des amas de minerais d' tain. *Ann. des Mines*, xx, 1841.

Briefly, we may say that fluorine is every where present in the tin-producing districts of Cornwall, as well as boron and iron.\* It seems to me, therefore, that the facts lend strong support to Daubrée's theory, and even extend its action to the killas tin-deposits. As might be expected, the stanniferous solutions have notably altered the characters of the neighbouring rocks, in some cases depositing silica throughout their substance (forming the so-called capels), in others depositing veins of crystalline or cryptocrystalline quartz; in others again carrying away a great part of the felspathic ingredients of the granite, and leaving the quartz in loose grains, so producing the "sand-lodes," such as have been described as occurring at Wheal Coates† and Great Beam Mine.‡

Still more commonly, in granite districts, the solutions have kaolinized the "country" to considerable distances from the lodes, not being able apparently to use up all the alumina in cases where the original rock contained much felspar. In all these instances the fluorine (and boron if present) appears to have become "fixed" in the form of tourmaline, Gilbertite and the other minerals mentioned above.

*The Gilbertite.* The constant and almost invariable occurrence of this greenish-yellow hydrated mica§ in the granitic "gites" of tin-oxide in Cornwall renders its composition a matter of some importance. It has been regarded as an altered (hydrated) Muscovite, but while Muscovite is one of the least alterable of minerals, it has been frequently noticed in immediate association with unaltered Muscovite. It has also been regarded as a variety of margarodite, and as an impure kaolin, but it differs essentially from both these minerals, and I am disposed to agree with Frenzel that it is a good and distinct species.

In colour it is greenish-yellow to yellowish-white; translucent to opaque; it occurs massive and also in spherical masses with radiated concentric structure; or in stellate groups; or, rarely, in six-sided tables. The hardness varies from 1 to 2.5, or perhaps 3; the specific gravity from

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\* See "The Hensbarrow Granite District, by J. H. Collins, Truro, 1878; and Foster, *Quart. Jour. Geol. Soc.* Nos. 135, 1878. See also Foster, Tin Deposits of East Wheal Lovell. *Trans. Roy. Geol. Soc. Corn.* 1875. p. 174.

† Davey, *Trans. Roy. Geol. Soc., Corn.* iv. p. 484.

‡ *The Hensbarrow Granite District*, p. 39. It is observable that these loose crystal line particles of quartz, as well as those existing in the natural China clay rock (*Carclazyte*), always have rough irregular corroded surfaces, as if they had been partially dissolved by some strong solvent.

§ Its occurrence in the tin mines of the Erzgebirge (Saxony and Bohemia) Zinnwald and Ehrenfriedersdorf is recorded by Frenzel, and noted by Dana in his Second Appendix (p. 24).

2.6 to 2.82. It feels very greasy, and this character has often led to its being mistaken for talc. When heated in a matrass it usually becomes silvery-white and opaque; it gives off water, but only at a somewhat high temperature, and this water has usually an acid reaction from the presence of fluorine. Heated before the blowpipe it fuses, if in thin splinters or plates, tinging the flame red. It is pretty readily soluble in sulphuric acid, but hardly at all affected by nitric or hydrochloric acid. The following are analyses of Cornish specimens; the first by Le Hunt, the next three by myself. Nos. 1, 2 and 3 were from Stenna Gwynn, No. 4 from St. Just. The latter had a specific gravity of 2.78, and was part of a great vein of nearly pure Gilbertite, which was, in some parts, from 10 to 14 feet wide, and which contained microscopic crystals of topaz and a little Cassiterite.

|                             | 1.           | 2.            | 3.           | 4.           |
|-----------------------------|--------------|---------------|--------------|--------------|
| Silica ... ..               | 45.15        | 45.10         | 44.90        | 48.12        |
| Alumina ... ..              | 40.11        | 36.00         | 35.80        | 34.90        |
| Ferrous Oxide ... ..        | 2.48         | 1.10          | .70          | .65          |
| Manganous Oxide ... ..      | —            | trace         | trace        | trace        |
| Lime ... ..                 | 4.17         | 1.50          | 1.60         | .31          |
| Magnesia .. ...             | 1.90         | .90           | .50          | .22          |
| Potash (with a little Soda) | —            | 11.40         | 10.40        | 9.71         |
| Lithia ... ..               | —            | traces        | traces       | trace        |
| Fluorine ... ..             |              | .54           | .72          | 1.42         |
| Water ... ..                | 4.25         | 3.70          | 4.21         | 3.21*        |
|                             | <u>98.01</u> | <u>100.24</u> | <u>98.83</u> | <u>98.54</u> |

Le Hunt's analysis is manifestly wrong, as it gives the alumina much too high and shows no alkalis. Thomson gives an analysis of Gilbertite from Stenna Gwynn, containing 9.23 per cent. of soda, but I have never found any either there or at any other locality containing more than about 1.5 per cent.

The following analyses are quoted by Dana in his Second Appendix (p. 24). 1 was a massive specimen from Ehrenfriedersdorf; 2 a similar specimen from Pobersbau; and 3 a crystallised specimen from Ehrenfriedersdorf.

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\* Of which .60 was lost at a temperature of 120° C.

|                   | 1.           | 2.            | 3.            |
|-------------------|--------------|---------------|---------------|
| Silica ... ..     | 48.96        | 48.10         | 48.10         |
| Alumina ... ..    | 30.96        | 32.30         | 31.55         |
| Ferrous Oxide ... | 2.24         | 3.30          | 3.10          |
| Lime ... ..       | 0.26         | 0.40          | 1.30          |
| Magnesia ... ..   | 1.97         | 1.12          | 1.33          |
| Potash ... ..     | 8.47         | 10.02         | 8.62          |
| Soda... ..        | 1.65         | —             | 2.14          |
| Fluorine ... ..   | 1.04         | 0.81          | 0.88          |
| Water ... ..      | 3.83         | 4.09          | 3.52          |
|                   | <u>99.38</u> | <u>100.14</u> | <u>100.54</u> |

A comparison of these analyses with those given by Dana under Muscovite, headed "Margarodite (in part)," shows that his quoted analyses Nos. 3, 6, 19, and 27, may very well be included under Gilbertite, the only material difference being that the small quantity of iron present is stated as peroxide, whereas in the Cornish Gilbertites the equally small quantity of iron is present as protoxide. It is probable, too, that the "Margarodite" from Lambhoga, analysed by Dr. Heddle, and which is associated with kaolin, should be placed here.\*

|                     | a.           | b.           | c.            | d.           | e.           |
|---------------------|--------------|--------------|---------------|--------------|--------------|
| Silica ... ..       | 47.05        | 44.60        | 46.42         | 46.75        | 50.77        |
| Alumina... ..       | 34.90        | 36.23        | 37.92         | 39.20        | 31.71        |
| Ferric Oxide ... .. | 1.50         | 1.34         | 0.46          | trace        | 1.32         |
| Manganous Oxide...  | —            | —            | —             | —            | .23          |
| Lime ... ..         | —            | 0.50         | 0.67          | 0.39         | .95          |
| Magnesia .. ..      | 1.95         | 0.37         | 0.17          | 1.02         | .79          |
| Potash ... ..       | 7.96         | 6.20         | 9.63          | 6.50         | 5.11         |
| Soda ... ..         | 4.07         | 4.10         | 1.54          | —            | .53          |
| Fluorine ... ..     | —            | trace        | —             | —            | —            |
| Water ... ..        | 1.45         | 5.26         | 4.40          | 4.90         | 7.97         |
|                     | <u>98.88</u> | <u>98.60</u> | <u>101.21</u> | <u>98.82</u> | <u>99.38</u> |

In the last of these the deficiency of protoxide bases seems to be made up by the larger quantity of water present. The alumina is certainly

\* The analyses referred to are as follows:—*a.* from Zillerthal (Dana, anal. 3); *b.* from Litchfield, Conn. (Dana, anal. 6); *c.* from Ross Hill, Iowa (Dana, anal. 19); *d.* from Unionville (Dana, anal. 27); and *e.* from Lambhoga (Heddle, anal. 1, Chapters on the Mineralogy of Scotland, The Micæ, p. 13).

somewhat low and the silica high, but perhaps there was a small admixture of free silica present in the form of quartz grains; at any rate, this is often the case with the Cornish Gilbertites, as in the specimen from St. Just, referred to above.

*The Tourmaline.*—Several analyses of the tourmaline occurring in the granite of Devon have been published, but the following (*a* and *b*) are, so far as I know, the first analyses of Cornish tourmalines. The first (*a*) is of a specimen of radiated black tourmaline from the kaolin of Little Carclaze, analysed by my pupil and friend, Mr. F. Johnson, an Associate of this Society; the second (*b*) is a specimen from the Trevisco kaolin, analysed by myself. I add the well-known analyses of Mitscherlich (*c*) Gmelin (*d*) of fine crystals of black tourmaline from Bovey Tracey for comparison.

|                          | <i>a.</i>   | <i>b.</i>    | <i>c.</i>    | <i>d.</i>    |
|--------------------------|-------------|--------------|--------------|--------------|
| Silica ... ..            | 46.12       | 43.22        | 87.00        | 85.20        |
| Alumina... ..            | 18.40       | 23.14        | 33.09        | 35.50        |
| Ferric Oxide } ... ..    | 21.90       | 20.87        | { 9.33 }     | 17.86        |
| Ferrous Oxide }          |             |              | { 6.19 }     |              |
| Manganous Oxide ... ..   | —           | .10          | —            | 0.43         |
| Magnesia ... ..          | 0.50        | 0.40         | 2.58         | 0.70         |
| Lime ... ..              | 0.40        | 0.51         | 0.50         | 0.55         |
| Soda } ... ..            | 4.50        | { 2.10       | 1.39         | 2.09         |
| Potash }                 |             | { 2.34       | 0.65         |              |
| Phosphoric Acid ... ..   | —           | traces       | .12          | —            |
| Boracic Acid ... ..      | 5.40        | 5.60         | 7.66         | 4.11         |
| Loss on ignition ... ..  | 1.50        | 1.47         | —            | —            |
| Fluorine and loss ... .. | .68         | .25          | 1.49         | 3.56         |
|                          | <hr/> 99.40 | <hr/> 100.00 | <hr/> 100.00 | <hr/> 100.00 |

It will be seen that the principal differences are in the relative proportions of silica, alumina, and iron oxides.

*Proportion of Fluorine in Tin-stones.*—Taking the proportion of oxide of tin present in a given vein in granite to average 1 per cent. of the whole vein—not an unfair estimate, the proportion of Gilbertite to be 5 per cent. of the same vein, and the fluorine in the Gilbertite at 1 per cent. of its weight, we have then for 100 parts of tin-oxide, 500 of Gilbertite, or 5 parts of fluorine. This is certainly a low number, but if we bear in mind the fact that the Gilbertite extends into the country rock far beyond the limits of the workable tin, this dis-

proportion at once vanishes, and there is seen to be fixed in the immediate neighbourhood of the Cassiterite an ample quantity of fluorine to have acted originally as the tin-carrier, and being set free to act on the felspar, &c., and to form the Gilbertite. Again, as regards the tourmaline, taking the oxide of tin, *e.g.* at Rock Hill, at  $\frac{1}{3}$  per cent. of the total weight of the rock and the tourmaline at 30 per cent., both reasonable estimates, and farther reckoning only 1 per cent. of the tourmaline as fluorine, then 100 parts of Cassiterite correspond to 60 parts of fluorine, which is far more than sufficient for the purposes of the theory.

Even in the compact tin-stones of the deep tin mines of the Camborne district the fluorine will be found to bear not a very small proportion to the tin oxide present.\*

Assuming, then (1), the former existence of such fluo-boro-chloro-stanniferous solutions, and (2) of fissures, cavities or shrinkage-cracks in which the new combinations might have a chance of taking place, we have evidently agencies quite sufficient to produce all the phenomena observed—capable of dissolving out and carrying away earthy minerals and of depositing Cassiterite and its associates in their places—either in a crystalline, cryptocrystalline, or amorphous form.†

That tin-oxide is still present in so many localities after such long periods of time have elapsed (the tin lodes being the oldest of the metaliferous deposits of Cornwall and Devon), and in spite of the subsequent circulation of mineral solutions of a different character, is manifestly due to the very fact of its permanency, *i.e.* its power of resisting the solvent action of these later solutions, which we have reason to suppose were destitute of fluorine.

With regard to the wood-tin, its frequent concentric globular or mammillary form would suggest that it was originally deposited in an amorphous form (and perhaps from a very concentrated fluid), like *limonite*, *psilomelane*, and the *calcite* of stalactites, in successive layers; these differences being due to changes in the nature or composition of the depositing solutions. The radiated structure would then be due to a further develop-

\* I found in one specimen 0·10 per cent. of fluorine, and in another 0·15 per cent. It is worthy of note that Delabeche, many years since, estimated the fluorine in the ordinary granites of Cornwall and Devon to amount to from 0·18 to 0·21 per cent.

† That the circulation of stanniferous solutions is still going on, or at least was so in geologically very recent times, is indicated by the occurrence of tin in the interior of a deer's horn (see *supra*, 2nd paper), and perhaps of that in the "alluvial faults" of Rosevear Moor.



ment of the crystallising forces, exactly as observed in stalactites of carbonate of lime or sulphate of baryta. That such was really the origin of the radiated structure is indicated by the fact that the *tin-crusts* already referred to (see 2nd paper) possess a similar structure, although we can hardly suppose that the ingot of tin was originally oxidised on its surface in this particular form.

F. Becke regards wood-tin as merely an extreme form of needle-tin. I certainly cannot agree with this, as the latter is always remarkable for its extreme transparency and the former is equally remarkable for its extreme opacity. Moreover, there are no intermediate stages known, although we do sometimes see masses of wood-tin encrusted with acicular crystals of Cassiterite, and even find these latter occupying fissures in such masses.

With regard to the pseudomorphs from Wheal Coates, it has been very truly remarked by Mr. W. Mansell Tweedy in the paper already quoted,\* that "these crystals appear to have been formed in matrices formerly filled with felspar," and "that disintegrating forces of great power have been in action in the immediate neighbourhood is evident from the extensive beds of sand and china clay which are found very near."

*Source from which the Tin has been derived.*—As to the source from which the tin was derived, whether it was brought up from some deep-seated deposit or layer in the earth's crust, or dissolved out from the surrounding rocks, as suggested by F. Sandberger† and others, further information is urgently needed on this point.

Evidence of a conclusive nature, however, will be very difficult to obtain. For, suppose the country rock originally charged pretty equally but in very minute proportion with some stanniferous compound capable of being dissolved out and re-deposited: then we might expect to find (1) that those portions of the rock immediately bounding the fissure or cavity in which the tin came to be finally deposited would be *more* highly charged than the main mass of the rock, while (2) those parts a little further removed would have *less* than the normal charge, the rock at a considerable distance from the fissures or cavities being (3) in its normal state, there being no way for the tin to make its escape. But the first modification would equally be met with if the tin arrived in the circulating channels from below, and the tin present in (2) and (3) is normally so small in quantity that it would be very difficult to find any difference; at any rate

\* *Report Roy. Inst. Corn.* 1845, p. 20.

† *Ueber das Vorkommen des Mines in Silicaten*, von F. Sandberger, *Sitzb. d. K.K. Akad. d. Wiss. Wien*, 4 Mar. 1878. See also *Zeitschr. der deutschen geol. Gesellschaft*, 1880. Stelsner combats this theory.

the most careful and minute microscopical and chemical investigations would be necessary before any conclusion could be arrived at.

There is, however, one class of facts which seems to indicate that the tin is derived from the country and not from deep-seated sources communicating with the country rock by fissures. I refer to the frequent occurrence in granitic districts of apparently isolated masses of Cassiterite. Some of these are occasionally of considerable bulk, and the idea they suggest is certainly that they have merely passed into a previously existing cavity or "vugh" from the surrounding country.

I must confess that I incline to this latter supposition, and I am glad to find that so eminent a mining geologist as Mr. J. A. Phillips, F.R.S., agrees with me.\* In either case, given a fissure filled with fluo-boro-chloro solutions at a high temperature, and a compound of tin upon which those solutions could act, and it must be admitted that the fissures would probably become filled or partly filled with crystals of Cassiterite whether the original tin-supply was situated below or around.

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\* To what extent these deposits were produced by waters rising from below, and how far they were influenced by lateral percolation, cannot be determined. The effects produced on the contents of veins by the nature of the enclosing rock, and the frequent occurrence of deposits of ore parallel with the dip of the adjoining country, would, however, lead to the conclusion that lateral infiltrations must have materially influenced the results. Phillips, Q. J. Geol. Soc. 1875, p. 342.

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