

# New data for pitticite and a second occurrence of yukonite at Sterling Hill, New Jersey

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington DC 20560, USA

**ABSTRACT.** Pitticite is re-examined analytically and found to be a gel-like mineral of widely varying composition. Previously reported minor amounts of accessory elements are indeed present in pitticite. The name pitticite has validity only as a generic name for gel-like ferric iron arsenate minerals of varying composition.

Yukonite is reported from the Sterling Hill mine, Ogdensburg, New Jersey, the second occurrence. New data for yukonite suggest the name should be retained.

THE occurrence of a mineral that appeared to be yukonite from the Sterling Hill mine, Ogdensburg, New Jersey, prompted an analytical re-examination of type yukonite and a study of some substances collectively referred to as pitticite. Yukonite had been previously known only from the type locality, Tagish Lake, Yukon Territory, Canada. This second occurrence adds some measure of authenticity to the species status of yukonite.

*Analytical procedures and reliability.* The samples studied herein were chemically analysed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.15  $\mu\text{A}$ . The standards were manganite for Mn; synthetic olivenite for As; synthetic ZnO for Zn; hornblende for Fe, Al; celestine for S; fluorapatite for F; and diopside for Si, Mg, and Ca. The data were corrected using a modified version of the MAGIC-4 computer program of the Geophysical Laboratory. Water was determined for four samples using the Penfield method.

The determined data are subject to a substantial error of at least  $\pm 5\%$  of the amount present. Although this is considerably higher than the error % associated with good contemporary microprobe analyses, it is derived after consideration of a number of complex factors, which are discussed below.

It was necessary to prepare the samples in epoxy which is cured at 110°C. Subsequent to their preparation, it was noted that the gel-like samples had, for the most part, cracked and generated a crazed surface similar to that sometimes found on

amber and copal resins and attributed herein to the loss of water at very low temperatures. This is consistent with prior pitticite analyses by Koritnig (1940) and Church (1871), who noted water losses of approximately 8 to 10% at c.110°C, and also with the observations of Tyrrell and Graham who noted that yukonite (to be discussed on subsequent pages) sustained a water loss of 10.91% at 110°C. The data could not be corrected for a measured water loss by normalization of the data because, as is shown later, the samples are hygroscopic after the removal of  $\text{H}_2\text{O}^-$  (moisture). These problems are compounded by the unmeasurable effects of additional (and perhaps reversible) losses of water under the vacuum used in the carbon coating of the samples and the high vacuum attendant in the microprobe sample chamber.

Subsequent to Penfield determinations, the four samples were allowed to re-equilibrate with air at room temperature and all regained minor amounts of moisture (approximately 1% by weight). This demonstrated non-equilibrium of pitticite with respect to  $\text{H}_2\text{O}$ , together with the lack of any structural controls in this gel-like mineral, requires that the analytical data be regarded as less accurate than are normally obtained.

As a control on the accuracy of the microprobe data, several samples were submitted to neutron activation analysis and the results compared with the microprobe data presented in Table I. As expected, the error in the microprobe determinations provided higher data than that derived by neutron activation analysis. This is consistent with the loss of water in preparation procedures as noted above. The two control samples do not provide a reliable correction but indicate that the given  $\text{Fe}_2\text{O}_3$  values might be as much as 2% by weight too high, and that  $\text{As}_2\text{O}_5$  values might be less than 1% by weight too high. The error for other constituent elements is insignificant. All studied specimens are chemically homogeneous over 10  $\mu\text{m}$  sample spots. The published analyses were

TABLE I. Analyses of pitticite (nos. 1-12) and yukonite (nos. 13-18)

| Locality                             | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> <sup>9</sup> | MgO | CaO   | MnO  | ZnO | As <sub>2</sub> O <sub>5</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | H <sub>2</sub> O <sup>-</sup> | H <sub>2</sub> O <sup>+</sup> | H <sub>2</sub> O† | Total  | n     | D <sub>obs</sub> | Sample no. | Anal. no. |
|--------------------------------------|------------------|--------------------------------|---|-----|-------|------|-----|--------------------------------|-------------------------------|-----------------|-------------------------------|-------------------------------|-------------------|--------|-------|------------------|------------|-----------|
| Schwartzenberg, Germany <sup>1</sup> | —                | —                              | 34.85                                       | —   | —     | —    | —   | 26.70                          | —                             | 13.91           | 24.54                         | —                             | —                 | 100.00 | —     | —                | —          | 1         |
| Saxony, Germany <sup>2</sup>         | —                | —                              | 33.46                                       | —   | —     | 0.59 | —   | 26.06                          | —                             | 10.75           | 28.48                         | —                             | —                 | 99.34  | —     | —                | —          | 2         |
| Manhattan, Nevada <sup>3</sup>       | —                | 3.11                           | 34.01                                       | tr. | tr.   | —    | —   | 14.54                          | —                             | 17.97           | 29.64                         | —                             | —                 | 100.40 | —     | —                | 95426      | 3         |
| Cornwall, England <sup>4</sup>       | —                | —                              | 32.54                                       | —   | —     | —    | —   | 33.99                          | 1.27                          | 7.28            | 24.92                         | —                             | —                 | 100.00 | —     | —                | —          | 4         |
| Tintic District, Utah <sup>5</sup>   | 1.92             | —                              | 33.89                                       | —   | —     | —    | —   | 39.65                          | —                             | 1.14            | 18.24                         | —                             | —                 | 100.09 | —     | —                | —          | 5         |
| Freiberg, Germany                    | 0.0              | 1.0                            | 37.1  | 0.2 | 0.2   | tr.  | 0.4 | 22.0                           | 3.2                           | 14.9            | 12.07*                        | 13.53*                        | —                 | 104.6  | 1.640 | 2.40             | R5781      | 6         |
| Schwartzenberg, Germany              | 0.0              | 1.3                            | 38.2  | tr. | 0.2   | tr.  | 0.3 | 20.7                           | 3.2                           | 16.5            | —                             | —                             | 19.6              | 100.0  | 1.641 | 2.49             | 12568      | 7         |
| Schneeberg, Germany                  | 0.1              | 1.0                            | 37.7  | 0.3 | 0.2   | tr.  | 0.3 | 18.0                           | 3.2                           | 14.4            | 13.10*                        | 13.91*                        | —                 | 102.2  | 1.634 | 2.37             | 138862     | 8         |
| Manhattan, Nevada                    | 0.1              | 1.3                            | 37.4  | 0.7 | 0.1   | 0.2  | 0.3 | 13.0                           | 3.4                           | 15.0            | 12.05*                        | 13.36*                        | —                 | 96.9†  | 1.638 | 2.42             | 95426      | 9         |
| Tintic District, Utah                | 8.9              | 0.4                            | 48.5  | 0.5 | 6.7   | tr.  | 0.8 | 14.5                           | 1.6                           | 3.0             | —                             | —                             | 15.1              | 100.0  | 1.740 | 2.68             | 105192     | 10        |
| Tintic District, Utah                | 8.9              | 0.2                            | 49.2  | 0.6 | 6.7   | tr.  | 0.4 | 14.5                           | 0.9                           | 0.2             | —                             | —                             | 18.4              | 100.0  | 1.765 | 2.72             | 45248-3    | 11        |
| Cornwall, England                    | 0.0              | 0.5                            | 35.4  | 0.2 | tr.   | 0.9  | 0.4 | 30.9                           | 0.7                           | 6.1             | 12.60*                        | 12.07*                        | —                 | 99.8   | 1.664 | —                | R5780      | 12        |
| Sterling Hill, N.J.                  | 2.2              | 0.8                            | 28.8  | 0.4 | 10.4  | 2.1  | 3.3 | 32.1                           | 0.0                           | 0.2             | —                             | —                             | 19.7              | 100.0  | —     | —                | private    | 13        |
| Sterling Hill, N.J.                  | 0.6              | 1.0                            | 28.8  | 0.6 | 10.4  | 2.2  | 3.8 | 39.9                           | 0.0                           | 0.2             | —                             | —                             | 12.5              | 100.0  | —     | —                | 146880     | 14        |
| Yukon, Canada                        | 0.6              | tr.                            | 36.9  | 0.3 | 11.9  | 0.4  | 0.5 | 36.8                           | 0.9                           | 0.2             | —                             | —                             | 11.5              | 100.0  | —     | —                | R5783      | 15        |
| Yukon, Canada <sup>6</sup>           | —                | —                              | 36.6  | —   | 10.6  | —    | —   | 36.3                           | —                             | —               | 17.9                          | —                             | —                 | 101.4  | —     | —                | —          | 16        |
| Yukon, Canada <sup>7</sup>           | —                | —                              | 35.72                                       | —   | 10.00 | —    | —   | 34.06                          | —                             | —               | 20.28                         | —                             | —                 | 100.06 | —     | —                | —          | 17        |
| Yukon, Canada <sup>8</sup>           | —                | —                              | 36.81                                       | —   | 10.14 | —    | —   | 33.83                          | —                             | —               | 20.28                         | —                             | —                 | 101.06 | —     | —                | —          | 18        |

<sup>1</sup> Rammelsberg (1875) (1845).<sup>2</sup> Stromeyer (1819).<sup>3</sup> Foshag and Clinton (1927); total includes 0.72% FeO and 0.41% insol.<sup>4</sup> Church (1871).<sup>5</sup> Genth and Penfield (1890); total includes 4.08% insoluble Fe<sub>2</sub>O<sub>3</sub>, 1.17% CuO.<sup>6</sup> Pers. comm. J. L. Jambor.<sup>7</sup> Tyrrell and Graham (1913).<sup>8</sup> *Ibid.*<sup>9</sup> Calculated as Fe<sup>3+</sup> on the basis of microchemical tests.\* H<sub>2</sub>O<sup>-</sup> and H<sub>2</sub>O<sup>+</sup> determined by Penfield method.† H<sub>2</sub>O by difference.‡ Contains Fe<sup>2+</sup> and (CO<sub>3</sub>)<sup>2-</sup>.

Fluorine less than 0.3% for all analyses.

obtained using a 40 $\mu$ m beam to minimize 'boil-off' effects. Analyses nos. 1–12 are of pitticites and nos. 13–18 are of yukonites.

*Yukonite* was originally described by Tyrrell and Graham (1913) as a calcium ferric-iron arsenate hydrate from Tagish Lake in Yukon Territory, Canada, but was not found elsewhere. Yukonite similar to type material was subsequently restudied by Jambor (unpub. pers. comm. and 1966), who verified the data of Tyrrell and Graham, but found 17.9 wt% H<sub>2</sub>O instead of the 20.28 considered by Tyrrell and Graham to be more reliable than their Penfield determination of 17.57%. Because Jambor's figure was determined by DTA-TGA, it probably represents a more accurate determination, and his analysis (no. 16) in Table I is probably the best extant data for type yukonite. Jambor also measured the poor X-ray diffraction pattern of type yukonite. His complete data are (*d* in Å, intensity): 5.60 (8), 3.25 (10), 2.79 (8), 2.52 (3), 2.33 (3), 2.23 (3), 1.97 (1), 1.83 ( $\frac{1}{2}$ ), 1.76 ( $\frac{1}{2}$ ), 1.63 (4, broad), and 1.51 (2, broad).

A mineral with the same powder pattern was found among the arsenate assemblage discovered in the Sterling Hill Mine, Ogdensburg, New Jersey. The samples were reported to have been found in the 960 stope on the 340 level. The Sterling Hill material occurs in two distinct habits. One of these (analysis no. 13) is reddish-brown waxy gel-like material quite undistinguishable from pitticites. The second (analysis no. 14) is markedly different and consists of dark-brown lath-like aggregates, which are pseudomorphous after remnant parasymplesite and köttigite. This second habit occurs in intimate association with ogdensburgite, Ca<sub>3</sub>ZnFe<sub>6</sub><sup>3+</sup>(AsO<sub>4</sub>)<sub>5</sub>(OH)<sub>11</sub>·5H<sub>2</sub>O (Dunn, 1981).

Because both Sterling Hill occurrences yield identical powder patterns in excellent agreement with that of type yukonite, and have very similar compositions, they should be considered yukonite until further occurrences either validate or discredit the species. Although there is little firm evidence for the characterization of yukonite, the second occurrence, together with the nearly consistent composition (the presence of Ca and the absence of S and P), argue for the retention of yukonite as a species name.

*Pitticite* is a generic name for ill-defined Fe<sup>3+</sup> arsenate sulphate hydrate minerals. They are amorphous to X-rays for the most part. Their colour varies considerably, but most are reddish brown. Pitticite is similar to solidified gels in appearance and texture and many samples have the appearance of dried-out resins. Pitticite occurs in massive form only and no crystals have ever been found. The lustre may be vitreous, earthy, or waxy with the waxy lustre predominant at most

localities. Pitticite is formed as a secondary mineral, frequently as an oxidation product of arsenide minerals, and is usually the last mineral to form in an assemblage.

Because pitticite has been used as a group name for ill-defined gel-like substances, many compounds may have been labelled pitticite in error because of the lack of definition, and hence, no proof of identity was possible. Some prior analyses of pitticite have been included in Table I as analyses nos. 1–5 for comparison. For the purposes of this study, samples were included that either were previously published as pitticite or that fit the general composition of Fe<sup>3+</sup>-SO<sub>4</sub>-As<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O amorphous compounds.

The wide variance in composition of previously examined pitticites had precluded a chemical definition of the mineral. The seemingly insignificant amounts of minor elements were usually considered to be admixed impurities and were frequently ignored in recalculations of the analyses. The samples studied herein were analysed by electron microprobe to ascertain whether or not these small amounts of Si, Al, Ca, and P were due to mixtures of other phases or truly part of the composition of some pitticites.

Although not intended to be comprehensive, the analytical data presented in Table I clearly demonstrate that the composition of pitticite varies significantly and non-systematically. The small amounts of Si, Al, and P reported by some analysts are indeed present in some pitticites. There is no correlation among the various analyses in terms of the ratios of divalent, trivalent, and pentavalent ions and none between the ratios of cations: anions. Pitticite is indeed a catch-all substance, which can accommodate wide variations in its composition. The present use of the name pitticite as a generic term for undefined Fe<sup>3+</sup>-As<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O compounds should be retained. Sulphur, like phosphorus and calcium, is apparently non-essential for the formation of pitticite.

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EDITOR'S NOTE. The name Pittizit (anglicized to pitticite, probably by J. D. Dana, *Syst. Mineral.* 3rd edn. 1850, 453) was given by J. F. L. Hausmann (*Handb. Mineral.* 1813, **1**, 285) to a mineral from the Christbescherung mine, Freiberg, Saxony, named Eisenpecherz by D. L. G. Karsten (*Mineral. Tab.* 1808, 66 and 98), analysed by M. H. Klaproth, and more fully described by Karsten and Klaproth (*Mag. Ges. naturforsch. Freunde*, Berlin, 1808, 191); Klaproth's analysis shows 67% Fe<sub>2</sub>O<sub>3</sub>, 8% SO<sub>3</sub>, and 25% H<sub>2</sub>O.

In 1819, F. Stromeyer (*Ann. Phys. (Gilbert)*, **61**, 181) examined Eisenpecherz from several localities in Saxony and found As<sub>2</sub>O<sub>5</sub> as a major constituent of all, with varying amounts of SO<sub>3</sub>; he obtained, through C. S. Weiss, a portion of Klaproth's original specimen, and found it to be identical with his Eisenpecherz specimens (Klaproth's detailed description of his procedure suggests that his analysis was sound; probably the specimen, clearly a large one, was inhomogeneous).

Most mineralogists have followed Stromeyer in redefining Pittizit (= Eisenpecherz) as a basic iron arsenate with more or less sulphate (e.g. K. C. von Leonhard, *Handb. Oryktogn.* 1821, 364). F. S. Beudant (*Traité Mineral.* 1832, **2**, 484), however, retained Pittizit for the basic sulphate, citing both Klaproth's analysis and one of a synthetic basic iron sulphate by J. J. Berzelius (*Ann. Phys. (Gilbert)*, 1812, **40**, 294; *Afh. Fis. Kemi, Mineral.* 1818, **5**, 157) with 15.9% SO<sub>3</sub>; Beudant proposed the name sidérétine (often misspelt Sideritine) for the arsenate-sulphate, but has found few followers.

C. F. Naumann (*Elem. Mineral.* 4th edn., 1855, 254) proposed the name glockerite for material from Obergrund, Zuckmantel, analysed by Hochstetter, with 15.2% SO<sub>3</sub>, 20.7% H<sub>2</sub>O, and includes Berzelius's material here. Berzelius and J. G. Gahn (*Afh. Fis. Kemi, Mineral.* 1815, **4**, 307) noted a yellow basic iron sulphate occurring with botryogen at Fahlun, Sweden, but it was not analysed, and its identification with the synthetic material and with glockerite is speculative.

M. H. HEY