## A study of the neotocite group

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An examination has been carried out of ten specimens assigned to the group. These include metatype specimens of neotocite (Gestrikland, Sweden) and penwithite (Wheal Owles, Penwith, Cornwall) and topo-type specimens of stratopeïte (Pajsberg, Sweden), klipsteinite (Herborn, Dillenberg, Germany), and opsimose (specimen labelled klipsteinite, but from Klapperud, Dalecarlia, Sweden). The investigation arose out of the recent find of neotocite at the Geevor mine, Cornwall, close to the site of the type locality for penwithite.

In the investigation klipsteinite has been confirmed as a mixture (Fisher, 1880), the dominant mineral in the mixture giving an X-ray pattern close to birnessite. Chemical analyses, refractive indices, and specific gravity determinations are given for the remainder in the miniprint section, p. M27 (Table I). They show that the group can be represented fairly closely by the formula (Mn, Fe)SiO<sub>3</sub>.H<sub>2</sub>O, but with significant carbonate present in each sample. CO<sub>2</sub> has not generally been reported before in these minerals and the water content is lower than previous analyses, as a result of the precautions taken in drying the material before analysis (over magnesium perchlorate at room temperature).

The specimens examined are all dark brown or black in appearance (often darkening on exposure to light) with a vitreous lustre and conchoidal fracture. The group should be regarded as poorly crystalline since all the specimens gave similar Xray powder patterns with three very broad and diffuse lines around 3.5, 2.6, and 1.6 Å respectively (see Whelan and Goldich, 1961). After heating to 1000 °C all form braunite, with the exception of stratopeïte, which gave an X-ray powder pattern closer to pyroxmangite. Hausmannite or spinel were also found associated with braunite in several specimens.

The full text includes the results of differential thermal analysis and infra-red spectra from the samples.

Of the names used in the group, opsimose (Beudant, 1832) was the first recorded, but in this and the subsequent work of Bahr (1850), it was associated with material much richer in manganese. Wittingite and neotocite (Nordenskiöld, 1849) were named separately on account of the higher iron content of neotocite. Stratopeïte (Igelström, 1851) is a magnesium-bearing variety, while penwithite (Collins, 1878, 1879) was thought to have a different manganese valency state from wittingite.

In view of its current widespread usage and the fact that neotocite was originally named for an iron-bearing manganese silicate it is proposed that neotocite be defined as the group of poorly crystalline manganese silicates with formulae close to  $(Mn, Fe)SiO_3$ . H<sub>2</sub>O and Mn > Fe. With Fe > Mn the series grades into hisingerite. Limited substitution of MgO, Al<sub>2</sub>O<sub>3</sub>, and CO<sub>2</sub> should be acceptable. Finally it has been proposed that the other names be discarded. The Commission on New Minerals and Mineral Names, IMA, has approved these proposals, but came to no firm conclusion as to whether the group name should be spelt 'neotocite' or as in the original description 'neotokite'. Accordingly either are permissible.

The full paper appears in the Miniprint section, pp. M26-30.

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## Pargasite from the Eastern Ghats, Andhra Pradesh, India

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HORNBLENDES are not common in the charnockites of Kondpalli, but occur as an important constituent in the pyroxene granulites and pyroxenites of Seshadripuram hill. Analyses and optical data for two pargasites are given. (Miniprint section, p. M31.)

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# Allanite from the Kondapalli charnockites, Krishna District, Andhra Pradesh, India

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THE coarse-grained charnockites of Donabanda hill, Kondapalli, contain metamict allanite. An analysis is given, also optical data for the heated allanite, and the conditions of formation of the rocks are shortly discussed. (Miniprint section, p. M31.)

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280

# M26 A. M. Clark et al.: The neotocite group

<u>A study of the meatocite group</u> A. M. Clark, A. J. Easton, G. C. Jones Dept. of Mineralogy, British Museum (Natural History), London SW7 58D M. Mount ,Geevor Tin Nines Ltd., Cornwall

Neotocite is the name given to a series of manganese silicates close in composition to  $MnSid_3$ ,Mag, often with considerable amounts of manganese replaced by iron or by lesser amounts of calcium, magnesium, or aluminium. Structurally they are X-ray amorphous, or at best, poorly crystalline (Whelan and Goldich, 1961). The members of the group are fairly common in manganese deposits of the volcanogenic-sedimentary type (Roy, 1976) and are thought to have been formed from gelatinous siliceous subpensions deposited in cavities at low temperatures.

The investigation arose out of the recent find of such a mineral at the Geevor mine, Corrwall. This occurrence is a little over one mile NEE of Kheal Gales, the type locality for the related mineral penwithite (Collins, 1878, 1879). The mineral was first discovered at Geevor in 1967 during development of the Simms lode on the 10th level horizon. Unfortunately no specimens of this first find survive, but it was thought at the time to be a form of opal, being glassy in texture and fracture and of deep red colour which faded to dark brown several days after removal from the mine. The 'host rock' occurring within the lode structure was a dark brown iron-rich jasper with an uneven to conchoidal fracture.

Early in 1974 a similar mineral was found in a 'prospect' stope in the N-E section of the mine. This prospect was first encountered underground at 3340 ft. in 9.E.5 crosscut some 700 ft. below the surface. its outcrop having been known many years ago in the Pendeen mines as the Calartha lode. The preliminary development of this structure on the 9th level horizon had revealed an extremely complex orebody of greatly varying dip and strike, showing at least eight major mineralization phases, three of which bore cassiterite in economic quantities. It was not until stope development took place that the glassy mineral was rediscovered and specimens collected for study. The mineral showed the same properties as the 1967 find, but the host rock was more complex. being an iron-rich jasper with areas rich in mangamese minerals and dendritic native copper. A section of the lode is illustrated in Fig. 1. A second set of samples was collected in May 1974 from a pillar left after stoping. This was by far the finest exposure of this mineral, the host rock containing only a trace of manganese minerals but considerable native copper and cassiterite.



Fig. 1. The neotocite-bearing lode at the Geevor Mine

#### Nomenclature and history

A number of names have been applied to different specific occurrences of the mineral group, among which neotocite and wittingite (N. Nordenskiðld, 1849) have chronological priority. Nordenskiðld is believed to have classified wittingite and neotocite separately on account of their different iron contents. Early analyses of the two minerals (Svanberg and Igelström, 1849; Mobers, 1866; A. E. Nordenskiðld, 1863) put wittingite (from Witting); Storkyro, Finland) near MmSiO<sub>3</sub>.H<sub>2</sub>O with Fe<sub>2</sub>O<sub>3</sub> between 3 and 6%. Neotocite (from Gasböle, Ingo, Finland and Gestrikland, Sweden) was shown to be much richer in iron wittingite fram dithe graviting tail fails in an intermediate position between wittingite and the poorly crystalline hydrated iron silicate, hisingerite.

Igelström (1851) described and published the first analysis of stratopeite (from Pajsberg, Filipstad, Sweden). He believed it to be a new mineral on account of the large concentration of MgO (8%) relative to that contained in neotocite and wittingite, its iron content being intermediate between the two. Cleve and Nordenskiöld (1866) reanalysed the three varieties and assigned formulae as follows:-

| Wittingite  | (2Mn0,Mn <sub>2</sub> 0 <sub>3</sub> ) <sub>2</sub> .5Si0 <sub>2</sub> .9H <sub>2</sub> 0 |  |
|-------------|---|--|
| Neotocite   | (2R0,Fe <sub>2</sub> 0 <sub>3</sub> ) <sub>3</sub> .5510 <sub>2</sub> .7H <sub>2</sub> 0  | where $\underline{R} = Fe^{C^{+}}$ , Mn <sup>C^{+}</sup> |
| Stratopeite | (2R0,Fe <sub>2</sub> D <sub>3</sub> ) <sub>3</sub> .5Si0 <sub>2</sub> .7H <sub>2</sub> D  | where <u>R</u> = Mn <sup>2+</sup> ,Mg,Pb                 |

Collins (1878, 1879) introduced into the group a fourth name, penvithite, for a reddish brown manganese silicate from Wheal Owles. Penvith, Cornwall, associated with quartz and rhodochrosite. He justified the allocation of a new name by comparing his chemical analysis with that of the nearest member of the group, wittingite (A. E. Nordenskiöld, 1867), and concluding that manganese is present in wittingite as a sequioxide, but as a protoxide in penvithite. This claim appears rather dubious as Nordenskiöld's analysis does not make the manganese valency state in wittingite at all clear. Collins' penvithite gave an analysis close to Mn0.510<sub>2</sub>.2H<sub>2</sub>0.

Some years prior to the description of these minerals, Klaproth (1807) had published an analysis of an amorphous manganese silicate from Klapperud, Dalecarlia, Sweden, which occurred associated with rhodonite. Its composition was given as MMO 60X, S10\_225X, H\_O 13X and Beudant (1832) restated these figures, naming the mineral opsimose. Subsequently Bahr (1850) published five analyses of hydrated manganese silicates from the same locality. One of these is close to Klaproth's original analysis and is classified in Dana (1868) as opsimose, whereas the remaining four are much closer to the neotocite group, and have been entered in that section. The name klipsteinite was first used by von Kobell (1866) for a mineral from Herborn, Germany, with a similar composition to opsimose. The mineral was re-examined by Fisher (1880) who concluded that it was an intergrowth, and the validity of the species has remained in doubt ever since although the name klipsteinite is generally given in preference to opsimose.

#### Specimens examined

The investigation was undertaken to compare the mineral found at Geevor with the penwithite co-type specimens supplied to the British Museum (Natural History) by J. H. Collins. As the collection also includes topotype specimens of all the varieties mentioned previously, apart from wittingite, the opportunity was taken to include these in the study, together with a number of more recent finds of the minerals. The following specimens were examined, the names given being those under which each specimen was supplied. The same specime numbers have been used in the chemical and thermal analysis tables and figures which follow.

- <u>Neotocite</u>. Gambatesa mine, Chiavari, Liguria, Italy, BM 1968,302, consisting of brown resinous veins in quartz and manganoan calcite.
- 2. <u>Permithite</u>. Wheal Owles, Penwith, Cornwall. Five specimens from Collins are in the Collection, three having been presented by him in 1878 and two acquired much more recently with the Russell Collection. Like the Geevor mineral this material has also become much darker than originally described, now being a vitreous black colour, thin fragments appearing brown under a microscope. The specimen examined in this study (BM 52182) contains penwithite deposited on the walls of a large cavity and showing a botryoidal surface covered with a number of minute radiating spherules of a yellow-orange mineral recently identified as triploidite.
- <u>Neotocite</u>. Geevor mine, Cornwall. A number of the specimens collected in 1974 are in the Collection and two of these (BM 1974, 277 a & b) have been used in the investigation.

- <u>Penwithite</u>. Noda-Tamagawa Mine, Iwate Pref., Japan, BM 1971, 342. A dark brownish black vitreous, massive specimen. The occurrence has been described by Ito (1961).
- <u>Klipsteinite</u>. Two specimens have been examined. BM 50668 from Klapperud, Dalecarlia, Sweden, purchased in 1876 and BM 40229 from Herborn, Dillenberg, West Germany, purchased in 1866. The latter specimen showed none of the vitreous lustre associated with other members of the group.
- Penwithite. Aichi Pref., Japan, BM 1962,110. A dark brown vitreous massive specimen.
- 7. <u>Neotocite</u>. Nant manganese mine (no. 2 level), Llanfaerhys, Rhiw, Caernarvonshire. One specimen has been examined from the four collected by Sir Arthur Russell in 1911. Like the Wheal Owles penwithite, the specimens are massive, black resinous, giving dark olive-green to brown translucent fragments.
- <u>Stratopeite</u>. Pajsberg, Filipstad, Sweden. The specimen examined is BM 89836, from the Allan-Greg Collection purchased in 1860. The Allan-Greg catalogue does not reveal the source of the material, which consists of a compact deposit on reddish black hodonite.
- <u>Neotocite</u>. Erik Ers mine, Gestrikland, Sweden, BM 43219, purchased from Prof. A. D. Nordenskiöld in 1869. The specimen consists of massive black material with conchoidal fracture.

#### Chemical analysis

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Chemical analyses of the nine neotocite group specimens, together with their specific gravities and refractive indices, are given in Table I, the results being presented in order of increasing iron content. All the specimens mentioned in the previous section were included, apart from the second klipsteinite. BM 40229. The determinations were carried out using material dried at room temperature over anhydrous magnesium perchlorate.

Silica was determined after a sodium hydroxide fusion, using the reduced silicomolybdate complex; total iron on a solution in HF and  $H_{\rm SO_4}$  using the 2,2'-dipyridyl complex (Riley and Williams, 1959) and manganese as permanganate; the remaining elements were measured by atomic absorption

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spectroscopy on a separate lithium metaborate fusion dissolved in dilute nitric acid.

The total oxidation state was determined after the addition of a slight excess of solid ferrous sulphate before dissolution in an inert atmosphere (Easton, 1972), using the 2,2'-dipyridyl complex. Since only a total oxidation value was available, total iron has been calculated to  $Fe_2O_3$  since it is more likely to be stable in the presence of  $Mn^{3+}$  than ferrous iron. Since this group of minerals converts readily to braunite ( $3Mn_2O_3$ , MnSiO\_3) on heating, reduction of  $Mn^{4+}$  at comparatively low temperatures is thought unlikely to occur and total manganese has been allocated to  $Mn^{2+}$  and  $Mn^{3+}$ , applying the total oxidation values to arrive at concentrations of  $Fe_2O_3$ , MnO, and  $Mn_2O_3$ . The water and carbon dioxide determinations were made using a Perkin Elmer microanalyser (model 240) on approximately 20 mg samples.

The Geevor and Wheal Owles specimens are broadly similar in composition, both being virtually iron-free, but of the two, the Wheal Owles material shows the higher  $Mn^{2+}Mn^{2-}$  ratio and is also richer in CO<sub>2</sub>. Collins' (1879) analysis of penvithite gave similar figures, although he did not report CO<sub>2</sub>, and the water determined in the present work is much lower as a result of the precautions taken in drying the material. Neotocite from Gestrikland (BM 43219) shows by far the greatest concentration of iron, the molecular proportion being greater than that of the total manganese and the oxidation value for this specimen requires fe0 to be present in addition to Fe $_2O_3$ . Stratopetic (BM 8936) contains significantly more Fe $_2O_3$  than any of the other remaining specimens. The lowest  $SiO_2/MnO$  ratio occurs in the specimen of klipsteinite (BM 50668) which also gives the highest concentration of CO<sub>2</sub>.

Recalculation of the analyses to molecular proportions shows that, despite the amorphous nature of the minerals, the formula  $MnSin_3, H_2O$  can be applied as a reasonable approximation to the composition of the group. The chemical analyses are in good agreement with other published work apart from the generally lower  $H_2O$  values and the presence of  $CO_2$ , not widely reported in these minerals before. Specific gravities and

refractive indices (Table I) were determined for each specimen on the same sample of material and show a consistent relationship, the highest S.G. being- . found in the specimen with the highest R.I.

Since the specimens showed a marked tendency to take up moisture from the atmosphere a series of hydration experiments was carried out using a Perkin Elmer AD2 autobalance. A nickel micro-crucible containing a known weight of each mineral, together with a tare. was placed in a series of closed containers having different relative humidities at room temperature (approximately 25<sup>0</sup>C). After three or four days the samples reached constant weights. The relative humidities of the atmospheres within the container were controlled by the presence of a small beaker containing one of the following compounds in contact with its saturated aqueous solution: 0% r.h., magnesium perchlorate (solid alone); 15% r.h., lithium chloride: 35% r.h., chromic oxide; 47% r.h., potassium thiocyanate; 66% r.h., sodium nitrite; 80% r.h., ammonium chloride: 100% r.h., water. It was found necessary to make rapid weighings, since slight changes in relative humidity were sufficient to cause a change in the weights of some of the samples.

The reversible nature of the absorption and desorption of water was demonstrated on two of the samples, the Geevor and Nant mine specimens, which were cycled from 100% r.h. to 0% and back to 100%; water lost at 0% being regained

|                    |           | -            |                      |                     | -  | -                                       |          |       |       |
|--------------------|-----------|--------------|----------------------|---------------------|--|---|----------|-------|-------|
| Si0,               | 39.8      | 38.4         | 40.1                 | 41.4                | 30.0                                     | 43.8                                    | 36.6     | 39.8  | 35.7  |
| A1,03              | 1.5       | 0.4          | 1.3                  | < 0.2               | < 0.2                                    | 0.5                                     | 2.9      | < 0.1 | 0.2   |
| Mn <sub>2</sub> 03 | 5.1       | 14.1         | 7.7                  | 11.0                | 33.2                                     | 3.4                                     | -        | 1.6   | -     |
| Mn0                | 33.7      | 27.5         | 33.7                 | 25.7                | 10.4                                     | 28.6                                    | 37.2     | 24.5  | 19.1  |
| Fe <sub>2</sub> 03 | < 0.1     | 0.2          | 0.3                  | 0.4                 | 0.5                                      | 1.6                                     | 3.3      | 8.8   | 18.7  |
| FeÖ                | -         | -            | -                    | -                   | -  | -                                       | •        | -     | 9.6   |
| Ca0                | 0.2       | 0.1          | 1.3                  | 1.1                 | 0.3                                      | 0.5                                     | 2.3      | 0.4   | 1.3   |
| MgO                | 1.3       | 0.5          | 1.5                  | 4.0                 | 1.6                                      | 4.7                                     | 1.3      | 9.6   | 3.9   |
| Na <sub>2</sub> 0  | < 0.1     | 0.1          | 0.1                  | < 0.1               | < 0.1                                    | < 0.1                                   | 0.3      | 0.1   | 0.1   |
| к,ō                | < 0.1     | < 0.1        | 0.1                  | < 0.1               | < 0.1                                    | < 0.1                                   | 0.3      | 0.1   | < 0.1 |
| cō,                | 7.4       | 6.3          | 2.2                  | 4.0                 | 13.4                                     | 5.7                                     | 6.2      | 3.9   | 2.8   |
| н <sub>2</sub> ŏ*  | 10.4      | 11.8         | 11.6                 | 11.7                | 8.2                                      | 10.9                                    | 9.7      | 10.8  | 9.0   |
| Total              | 99.4      | 99.4         | 99.9                 | 99.3                | 97.6                                     | 99,7                                    | 100.1    | 99.6  | 100.4 |
|                    | Molecular | ratios based | on Si+ <u>R</u> +C+H | = 3 ( <u>R</u> = A) | 1+Mn <sup>3+</sup> +Mn <sup>2+</sup> +Fe | e <sup>3+</sup> +Fe <sup>2+</sup> +Ca+M | lg+Na+K) |       |       |
| Si                 | 0.99      | 0.94         | 0.99                 | 1.01                | 0.80                                     | 1.06                                    | 0.91     | 0.96  | 0.93  |
| R                  | 0.90      | 0.88         | 0.99                 | 0.91                | 0.99                                     | 0.87                                    | 1.07     | 1.05  | 1.19  |
| С                  | 0.25      | 0.21         | 0.07                 | 0.13                | 0.49                                     | 0.19                                    | 0.21     | 0.13  | 0.10  |
| н                  | 0.86      | 0.97         | 0.95                 | 0.95                | 0.73                                     | 0.88                                    | 0.81     | 0.87  | 0.78  |
| S.G.               | 2.08      | 2.39         | 2.41                 | 2.28                | 2.67                                     | 2.25                                    | 2.07     | 2.67  | 2.73  |
| RI                 | 1.500     | 1 548        | 1 512                | 1 512               | 1 548                                    | 1.52                                    | 1 475    | 1 568 | 1 65  |

Table I. Chemical analyses of neotocite group minerals

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 SM 1968,302. Neotocite. Gambatesa mine, Liguria, Italy.

- 2. BM 52182. Penwithite. Wheal Owles, Penwith, Cornwall.
- 3. BM 1974,277a. Neotocite. Geevor mine, Cornwall.
- BM 1971,342. Penwithite. Noda-Tamagawa mine, Japan.
   BM 50668. Klipsteinite. Klapperud, Dalecarlia, Sweden.

BM 1962,110. Penwithite. Aichi Pref., Japan.
 Russell spec. Neotocite. Nant manganese mine, Rhiw,

- Caernarvonshire (now Gwynedd).
- 8. BM 89836. Stratopeite. Pajsberg, Filipstad,
- Sweden .

# M28 Rao: Pargasite and allanite from India

at 100%. The increase in weight shown by each specimen when increasing the relative humidity from 0 - 100% is given in Table II. When the total increase in weight between 0% and 100% r.h. is plotted against the specific gravity (Fig. 2), the samples of lower specific gravity are shown to be the greater absorbers of water.

Table I1. Weight per cent increase of neotocite specimens during hydration from 0-100% r.h.  $(20^{9}C)$ 

| r.h.   | 1     | 2   | 3   | 4    | 5     | 6    | 7    | 8   | 9     |
|--------|-------|-----|-----|------|-------|------|------|-----|-------|
| 0-15%  | < 0.1 | 1.5 | 2.5 | 3.1  | < 0.1 | 0.8  | 1.4  | 1.1 | < 0.1 |
| 15-35  | 4.6   | 4.2 | 6.8 | 6.6  | 2.0   | 5.7  | 4.5  | 2.0 | 0.7   |
| 35-47  | 7.3   | 5.0 | 7.4 | 8.9  | 2.2   | 7.0  | 5.8  | 1.9 | 0.9   |
| 47-66  | 10.2  | 5.6 | 7.9 | 10.0 | 2.9   | 9.2  | 10.0 | 1.8 | 1.2   |
| 66-80  | 11.5  | 5.3 | 7.8 | 11.0 | 4.1   | 10.6 | 10.9 | 1.9 | 1.1   |
| 80-100 | 11.5  | 5.6 | 8.1 | 11.0 | 4.0   | 10.6 | 13.6 | 1.9 | 1.2   |



Fig. 2. Percentage increase in weight, during absorption of water, plotted against specific gravity, for the nine neotocite samples.

#### Thermal analysis

Each of the specimens was examined by simultaneous differential thermal analysis and thermogravimetry with 0.1-0.2 g of crushed material being heated in air at an average rate of  $6.3^{\circ}$ C per minute up to temperatures of 1000-1150°C. The DTA profiles (Fig. 3) each show an endothermic peaks at  $150^{\circ}$ C resulting from the loss of water and exothermic peaks between 280°C and 330°C. The latter peaks, apparently the result of oxidation of Mn<sup>2+</sup> to Mn<sup>3+</sup>, were not reported in the work of Ito (1961) or Whelan and Goldich (1961), although their investigations were carried out under broadly similar conditions. Specimens from the Geevor mine (3) and the Nant mine (7) show low broad peaks in this region. The reason for clear, since both have values of Mn0/Nn<sub>203</sub> typical of the whole group. Possibly the oxidation process in these samples proceeds at a slower rate, maintaining near equilibrium conditions.

The nature of this exothermic peak was examined in more detail on the Noda-Tamagawa mine specimen which showed the peak quite strongly. Separate samples of the mineral were heated to temperatures of 180°C and 350°C, either side of the peak. Chemical determinations on these samples showed that the specimen heated to the higher temperature had increased its oxygen content by 7.9%. This is in very good agreement with the calculated figure of 8.0% obtained from the full chemical analysis when  $\mathrm{An}^{24}$  is converted to  $\mathrm{Am}^{34}$  and the assumption made that at 180°C no water remains in the sample. This experiment also reinforces the assumption that mangames is present in these minerals primarily in the oxidation states  $\mathrm{Mn}^{24}$  and  $\mathrm{Mn}^{34}$ .

The DTA profiles in Fig. 3 have also been arranged in order of increasing iron content and it can be seen that for the two iron-rich specimens (3 and 9) the position of the exothermic peak shifts noticeably to higher temperatures. The thermogravimetric curves (not reproduced here) correlate with the DTA data, showing the greatest loss in weight between 100 and  $200^{\circ}$ C, during dehydration. The total weight loss over the whole heating range varied between 14 and 233 (Table 111).

Each DTA run was repeated several times, although only one from each specimen is shown in Fig. 3. In addition to the two peaks described several others are visible in individual samples, but are ascribed to sample impurities since only one of these was reproduced in separate runs. The one referred to is the endothermic peak at  $750^{\circ}C$  on the klipsteinite specimen (5). Since this mineral is low in  $SiO_2$  and rich in  $CO_3$ , comparatively large quantities of rhodochrosite are thought to form at low temperatures during the run, the peak representing its decomposition.



Fig. 3. DTA profiles for the nine neotocite specimens.

#### Infra-red spectra

The infra-red spectra (Fig. 4) were recorded using a Grubb Parsons Spectromaster infra-red spectrophotometer over the wavelength ranges 2 to 5  $\mu$  m and 5 to 25  $\mu$ m. The samples were allowed to equilibrate in air before being pressed into discs with KC1. KC1 was found to give a blank free from absorptions in the range studied, whereas KBr gave small variable peaks at around 3.0, 6.3, and 7.0  $\mu$ m even after prolonged drying.

The spectra are all similar, the major differences being due to the varying carbonate content of the samples. The carbonate peaks at 7.0, 11.45, and 14.1  $_{\rm MI}$  are clearly visible in spectrum 5 and correspond to the v3, v<sup>2</sup>, and v<sup>4</sup> modes of the (CO\_3)<sup>27</sup> ion in calcite. The carbonate peaks in spectrum 7 however, correspond more closely to those given by

# M29

the  $(\text{CO}_3)^{2^-}$  ion in rhodochrosite. All the spectra show the 6.9 to 7.0 µm carbonate absorption. Among the remaining peaks present are those due to Si-O stretch at around 9.80 µm, and Si-O bending at around 16 and 22 µm. The peaks at 2.75 and 2.95 µm are due to OH stretchring, those at around 6.2 µm to OH bending. Definite assignment of these hydroxyl peaks would require further investigation and a better understanding of the structure of these minerals; there is also the possibility of the hydrogen bonding being affected by the interaction of the samples with KC1.



Fig. 4. Infra-red spectra of the nine neotocite specimens.

#### X-ray studies

X-ray powder films, using a 6 cm. diameter camera, were made from samples of the unheated mineral from each of the British localities and on the residues from each of the thermal analysis experiments. Details of the films obtained are given in Table III, showing that each of the unheated specimens gives a similar pattern with three very broad and diffuse lines around 3.5, 2.6, and 1.6 Å respectively. These lines agree with those reported for neotocite from the Montreal mine, Wisconsin (Whelan and Goldich, 1961). The films from two separate samples of the Geevor material showed admixed hematite. Thus natural neotocite is not completely amorphous, but should be regarded as poorly crystalline. No discrete carbonate minerals were detected in any of the unheated samples so their CO<sub>2</sub> contents camot be ascribed to impurities.

For the heat-treated material the dominant product in the temperature range 1000-1100°C is shown to be brawnite. The main exception was the stratopeite specimen (BM 89836) which gave a diffuse photograph at 1090°C and a pattern resembling pyroxmangite at 1135°C. This specimen appears to behave in a fashion similar to that outlined by 1to (1961) who reported that his Noda-Tamagawa material formed braunite, which was stable up to  $1000^{\circ}C$  whereupon the appearance of rhodonite was first noticed, this being the dominant phase at 1100-1200°C. In the case of stratopeite, significant iron is present, leading to the formation  $\rho f$  pyroxmangite instead of rhodonite. The neotocite from Gestrikland (BM 43219) contains by far the greatest concentration of iron, and the phase forming at  $1000^{\circ}C$  is found to be a spinel (jacobsite or magnetite) as was found by Ito (1961) in an iron-rich specimen from Noda-Tamagawa.

| Spec.<br>no. | Max. temp.<br><sup>O</sup> C   | X-ray identification   | Wt. loss<br>%  |
|--------------|--------------------------------|--|----------------|
| 1            | unheated<br>1070               | diffuse (neotocite)<br>braunite (+ quartz)                                       | 23.05          |
| 2            | unheated<br>1050               | diffuse (neotocite)<br>braunite  |                |
| 3            | unheated<br>1005               | diffuse (neotocite + hematite)<br>braunite                                       | 16.44          |
| 4            | unheated<br>185<br>350<br>1000 | diffuse (neotocite)<br>pyroxmangite + rhodochrosite<br>rhodochrosite<br>braunite | 21.58          |
| 5            | unheated<br>1000<br>1070       | diffuse (neotocite)<br>braunite + hausmannite<br>braunite + hausmannite          | 18.95          |
| *5a          | unheated<br>1050               | birnessite +<br>braunite + hausmannite   |                |
| 6            | unheated<br>1075               | diffuse (neotocite)<br>braunite  | 21,28          |
| 7            | unheated<br>1010<br>1055       | diffuse (neotocite)<br>braunite<br>braunite                                      | 20.33          |
| 8            | unheated<br>1090<br>1135       | diffuse (neotocite)<br>diffuse<br>nr. pyroxmangite                               | 15.88<br>15.81 |
| 9            | unheated<br>980                | diffuse (neotocite)<br>spinel (jacobsite or magnetite)<br>+ braunite             |                |

\*Specimen 5a, BM 40229, klipsteinite, Herborn, Dillenberg, West Germany

It is worth noting that both the klipsteinite specimens (EM 50668 and BM 40229) contain a small amount of hausmannite in addition to braunite in the temperature range  $1000 - 1100^{\circ}$ C. This phase possibly results from the decomposition of rhodocinrosite previously mentioned. An X-ray powder photograph of the unheated Herborn klipsteinite (EM 40229) gave a pattern differing from the remainder of the neotocite group by showing a number of sharply defined lines due to the presence of several minerals, the dominant phase being birnessite. Fisher's (1880) conclusion that this skipsteinite is an intergrowth is therefore confirmed, and the material was not for this reason included in the major part of the investigation reported here.

#### Discussion

Of the names used in this mineral group, opsimose (Dalecarlia, Sweden) was the first to be documented. The analysis in the present study confirms this occurrence as low in  $\mathrm{Si0}_2$ , but with high  $\mathrm{CO}_2$  not reported in the old analyses. Its thermal properties are in good agreement with the other specimens examined. Stratopeite has been confirmed as a member of the group, but rich in MgO. In addition to the original Cornish find, penwithite is the name more recently applied to several Japanese occurrences of the mineral (Kato, 1924; Ito, 1961), but the two specimens from that country examined here are typical of the group as a whole. Penwithite was the last name to be introduced (in 1879) and there would seem, therefore, to be no justification for extending this name to the whole group.

The name neotocite, however, has been the most widely used for these silicates, additional occurrences having been described in detail by Pardee et al. (1921), Ham and Oakes (1944), Lee (1955), and Whelen and Goldich (1961). It is unfortunate therefore that the topotype material studied here furnished a manganese-iron silicate with Fe slightly greater than Mn (i.e. ferrian neotocite). Nevertheless, in view of current usage, it is proposed that neotocite be defined as the group of poorly crystalline manganese silicates with formulae close to (Mn,Fe)Si0\_3.H\_2U with Mn>Fe. Limited substitution of MgO, Al\_2O\_3, and CO\_2 should be acceptable and the other names in the group should be discarded. The Commission on New Minerals and Mineral Names, IMA, has approved these proposals, but came to no firm conclusion as to whether the group name should be spelled " neotocite" or as in the original description "neotokite". Accordingly either are permissable.

The neotocite series probably grades into hisingerite but as all reported occurrences of the latter mineral have iron substantially greater than manganese, the Gestrikland material is, for the present, included with neotocite. Whelan and Goldich (1961) have noted a similarity in the X-ray powder patterns of the two minerals, despite the broad and diffuse nature

# M30

of the lines. They draw attention to similaritids between the hisingerite patterns and those of montronite and iron-rich saponite. Lindqvist and Jansson (1962) pursued this question by examining a number of manganeserich hisingerites (including neotocites from Gestrikland and Klapperud), suggesting instead a micaceous nature for the group. The neotocite specimens and mineral fragments examined in the present study do not support this conclusion. Soklakow and Operfam (1964) on the other hand put hisingerite in a series grading into chinglusuite, an amorphous (metamict?) silicate of manganese, titanium, and sodium. There is clearly scope for examining neotocite in conjunction with end-member hisingerite and chinglusuite.

The role of iron in these minerals is possibly of some significance. Roy (1976) has pointed out that in the types of deposit in which neotocite is found, manganese and iron are precipitated from acidified sea-water when the solution is oxidized and rendered alkaline through mixture with fresh sea-water. Iron is precipitated under conditons of lower Eh and pH than manganese and, in slowly changing environments, is generally precipitated first, leaving the manganese in solution to form later separate deposits. On the other hand, rapid oxidation and increasing alkalinity results in the co-precipitation of iron and manganese. The iron content of these gel-like silicates is therefore a possible indicator of this aspect of a deposit's formation conditons.

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