

## Aguilarite from the Camoola Reef, Maratoto Valley, New Zealand

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**SUMMARY.** Aguilarite,  $\text{Ag}_4\text{SeS}$ , occurs in a hydrothermal vein deposit associated with sphalerite, chalcopyrite, galena, and native silver. Physical and chemical data agree with descriptions from Guanajuato (type locality). Differential thermal analysis of synthetic material indicates an inversion temperature of  $122 \pm 1$  °C. The mineral crystallized late in the paragenetic sequence, probably slightly above 200 °C.

THE rare sulpho-selenide of silver, agularite, has previously been proven in only two localities, Guanajuato, Mexico (Genth, 1891) and the Comstock lode, Nevada (Coats, 1936), although Ramdohr (1969) believes it is probably more common. The material described in the present investigation comes from the Camoola Reef of the Silver Queen mine, Maratoto Valley, Coromandel Peninsula (fig. 1), where, apart from trace amounts of native silver, it is the only silver mineral present. In other major reefs known within the main mine area silver occurs solely as the telluride, hessite, and assays of ore samples from these reefs fail to show other than trace amounts of selenium (Main, 1971).

*Camoola Reef.* The Camoola vein crops out over 1150 m along a general strike of  $15^\circ$  magnetic. It has a proven vertical extent of greater than 120 m with a width varying between 2 and 12 m, and a dip of  $55$  to  $86^\circ$  W.

Seven distinct stages of gangue mineralization are found in the vein, forming 2 to 3 cm bands running parallel to the walls. The associations noted are: quartz, pseudomorphous after calcite, associated with manganese oxides; finely crystalline quartz; coarsely crystalline quartz; clay minerals; vein breccia; and carbonates (calcite, siderite, and rhodochrosite) pervaded by quartz. Mineralization in the form of

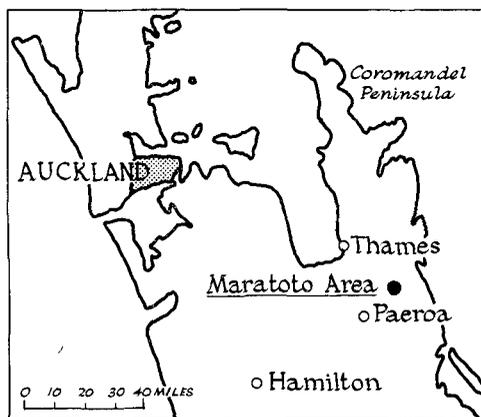


FIG. 1. Locality map showing position of mine area with respect to Coromandel Peninsula.

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sulphides and selenide is restricted to the breccia and carbonate layers. The country rock, into which the vein was emplaced as a fissure filling, is propylitized andesite of the Beeson's Island Volcanics. It is this rock that forms the breccia.

*Ore minerals.* Aguilarite occurs in the mineralized portions of the vein as clusters of anhedral crystals (0.001 mm to 1.5 mm dia.) associated with sphalerite, chalcopyrite, galena, and rare native silver and pyrite, in a quartz-carbonate matrix. The aguilarite content of the bulk ore seldom exceeds 0.05%. In a concentrate of the sulphides and selenides the approximate proportions were sphalerite:chalcopyrite:galena:aguilarite = 7:6:4:3.

The fairly transparent sphalerite occurs often as more or less rounded grains with ragged outlines (smooth within chalcopyrite areas). Chalcopyrite and galena, as well as aguilarite, form irregular mono- or poly-mineralic patches and very fine shreds disseminated through the carbonate aggregate. The simple grain boundaries with galena preclude the interpretation of aguilarite as a product of secondary enrichment. Pseudomymekitic intergrowth textures with chalcopyrite (either mineral can be host or inclusion) would indicate an essentially simultaneous growth. Occasionally fine round inclusions of native silver are observed but it cannot be proven that they represent true exsolution bodies.

*Synthesis.* In order to obtain an abundant supply of aguilarite for reference purposes, the mineral was synthesized after the method of Earley (1950). Charges of chemically pure sulphur, selenium, and silver were mixed in stoichiometric proportions and sealed in evacuated silica tubes. Complete, rapid reaction was obtained at the melting point of silver, 960 °C. Below this temperature reaction was slow and generally incomplete. The resulting, soft, malleable pellets took a reasonable polish when great care was taken. Examination in reflected light showed native silver diffused through the light grey aguilarite as reddish inclusions arranged in a rectangular pattern.

*Properties.* Physical properties of both the natural and synthetic material agree closely with those given by Dana (1944) but little data on the optical behaviour of aguilarite is available. In part this is due to its extremely soft and malleable nature which makes it difficult to polish and causes it to be scratched easily. Heavy loading causes smearing so that all structures are distorted at the surface. Even in the most carefully prepared specimens many scratches and pits mar the surface. The synthetic material took a better polish than the natural mineral but both specimens displayed similar optical behaviour.

In reflected light the mineral is light grey in colour (comparable to chalcosine) but with a distinct blue-green tinge. Reflectivity is rather low and reflection pleochroism was not observed. The natural mineral is only weakly anisotropic although the synthetic material shows distinct greys and blues. The visibility of this property depends on the quality of the polished surface and is thus better on the synthetic material. No cleavage or twinning of any sort is observed in the natural mineral, but the synthetic material shows sets of spindle-shaped twin lamellae under crossed nicols. Oil immersion lowers the reflectivity considerably, and makes aguilarite appear darker and dirty

greenish grey in direct comparison with light bluish secondary chalcosine replacing galena; anisotropism is hardly enhanced, while bireflection is still not noticeable.

The X-ray powder diffraction pattern of aguilarite is known only from the work of Earley (1950). Preliminary investigations cast some doubt on the completeness of his data, the magnitude of the relative intensities of some of the reflections, and the position of a few of these peaks. The three strongest reflections given by Earley, 4.10, 2.43, and 2.20 Å, serve to identify the mineral only where a sufficient concentration can be obtained. In the present bulk ore these lines were never observed. In a sulphide-selenide concentrate, weak lines at 2.43 and 2.20 Å appeared above the background. Even after upgrading the aguilarite content by flotation of the bulk of the accompanying chalcopyrite and sphalerite in warm saturated Clerici solution (S.G. = 4.5 to 4.8) no positive identification could be obtained from the X-ray pattern. Powder-diffraction examination of the synthetic material and a sample from Guanajuato suggest that the line which Earley records at  $2\theta = 10.85^\circ$  seldom shows an intensity of 5 as he records, and appears to be too weak for diagnostic purposes in other than pure samples. A detailed study of the system Ag-Se-S is in progress.

Aguilarite, like argentite, naumannite, and hessite, is believed to be isometric at high temperatures but inverts on cooling to an unknown system. The X-ray data of Earley do not allow for indexing on the isometric, hexagonal, or tetragonal systems. The temperature of inversion has been recorded as 133 °C but Ramdohr (1969, p. 475) queries this figure because of its coincidence with that of Ag<sub>2</sub>Se. Differential thermal analyses in air of both the synthetically prepared material and a galena-aguilarite concentrate showed a pronounced exotherm with a maximum at  $122 \pm 1$  °C. Roy, Majumdar, and Hulbe (1959) have shown the usefulness of Ag<sub>2</sub>S and Ag<sub>2</sub>Se as geological thermometers because of the insensitivity of their inversion temperatures to pressure and it is probable that aguilarite could be of similar use.

*Composition.* Microprobe examination of a single crystal was complicated by the high relief of the specimen surface. The grain appeared homogeneous and an analysis showed Ag 79.9, Se 14.4, S 6.1, total 100.4 %. The figures for silver and sulphur are close to those given by Genth (1891, 1892) for material from Guanajuato and give a formula close to the theoretical Ag<sub>4</sub>SeS. No other elements were found, though this does not rule out trace amounts of elements such as Cd, Sn, Sb, and Te, which have fairly high detection limits under the operating conditions used. Three of the analyses given by Genth show significant Cu, Fe, and Sb, although these are possibly due to impurities in the analysed samples.

*Paragenesis.* The previous records of aguilarite make no reference to its position within the paragenetic sequence. The deposition of the material of the Camoola Reef took place from hydrothermal solutions in the temperature range 200–350 °C (Main, 1971). The temperature of ore formation was closer to the lower temperature, with aguilarite forming as the last mineral in the sequence with its deposition overlapping that of chalcopyrite and galena.

It seems to be characteristic for aguilarite to avoid the siliceous parts of the ore and to concentrate in the abundant carbonate patches, especially in the form of

innumerable fine shredded particles. That in the neighbouring vein the silver mineral is hessite, not aguilarite, may be related, among other factors, to the scarcity of carbonate there.

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#### REFERENCES

- COATS (R. R.), 1936. *Amer. Min.* **21**, 532.  
DANA (J. D.), 1944. *Syst. Min.*, 7th edn, **1**, 178.  
EARLEY (J. W.), 1950. *Amer. Min.* **35**, 337.  
GENTH (F. A.), 1891. *Amer. Journ. Sci.* ser. 3, **41**, 401.  
— 1892. *Ibid.* **44**, 381.  
MAIN (J. V.), 1971. *Geology of the Maratoto-Waipahaheke area, Coromandel Peninsula, Auckland*.  
M.Sc. Thesis, University of Auckland Library.  
RAMDOHR (P.), 1969. *The Ore Minerals and their Intergrowths*. Pergamon. London.  
ROY (R.), MAJUMDAR (A. J.), and HULBE (C. W.), 1959. *Econ. Geol.* **54**, 1278.

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