Wairauite—a new cobalt–iron mineral

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Summary. A new cobalt–iron mineral of composition close to CoFe has been found associated with awaruite (Ni_3Fe) in the Red Hills serpentinites of the Wairau Valley, South Island, New Zealand. The name wairauite, after this locality, is proposed. Electron-probe analysis of the small grains so far discovered has shown that the nickel content is very low ($0{\cdot}5 \pm 0{\cdot}1$ wt. %). Wairauite is optically very similar to awaruite but a tendency to form euhedral grains (octahedron and cube) and a slightly lower reflectivity are an aid to identification. No X-ray data are available at present, but it is suggested that the structure may correspond to that of the ordered CsCl type of the synthetic alloy of the same composition.

A NATIVE cobalt–iron alloy of constant composition and with a low nickel content has been found during the course of electron-probe analysis of grains of the nickel-iron mineral, awaruite (Ni_3Fe). The new mineral occurs in serpentinite at the western contact of Red Hills, a large ultramafic intrusion on the northern side of the Wairau Valley, South Island, New Zealand, and the name *wairauite* (pronounced WAIR$\overline{\text{AU}}$·AIT) is proposed, after this locality. Associated with it are chromite, magnetite, awaruite (Ni_3Fe), and native copper. Both awaruite and wairauite form very small grains distributed throughout the serpentinite close to the contact. They are occasionally concentrated in late serpentine veins and around the margins of serpentine pseudomorphs after olivine. Grains rarely exceed 5 μ in diameter and most are less than 2 μ, the largest found being 7 × 4 μ.

Physical and optical properties. The similarity between awaruite and wairauite at first led to the identification of the cobalt–iron alloy as awaruite. It was noted, however, that many grains were euhedral (fig. 1), with the cube and octahedron as common forms, whereas awaruite had hitherto only been observed as rounded or crenulated grains (Nickel, 1959). Electron-probe analysis showed the euhedral grains to be a cobalt-iron alloy of formula CoFe.

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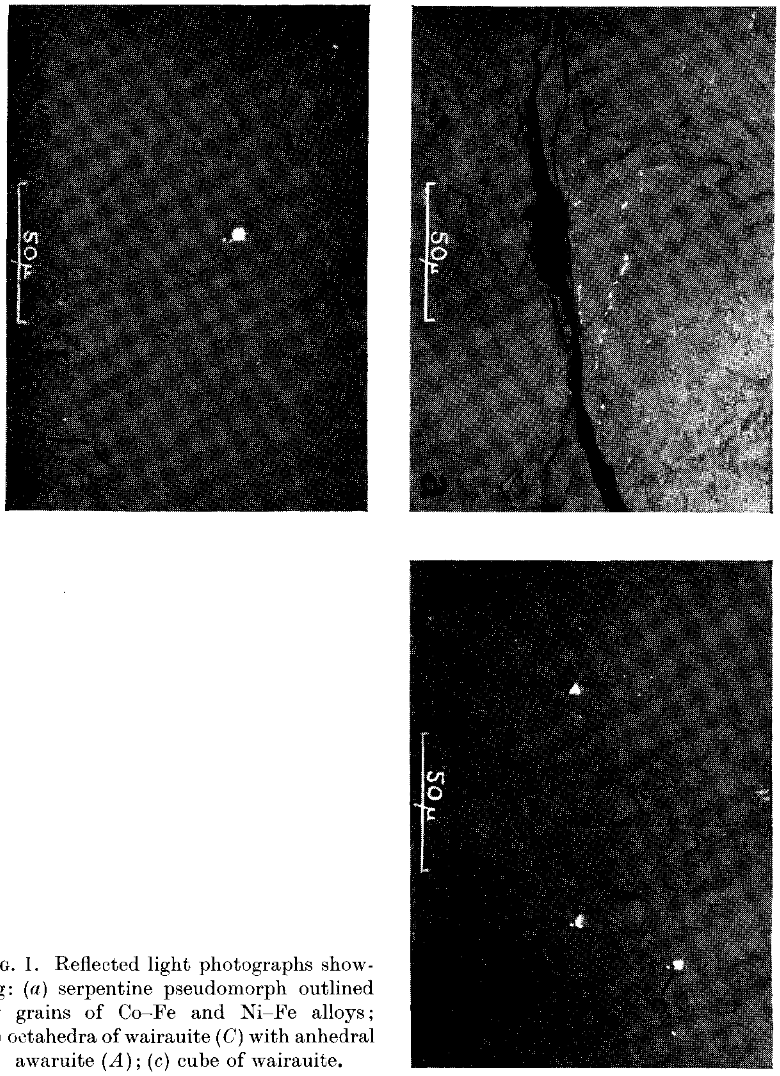

FIG. 1. Reflected light photographs showing: (*a*) serpentine pseudomorph outlined by grains of Co–Fe and Ni–Fe alloys; (*b*) octahedra of wairauite (*C*) with anhedral awaruite (*A*); (*c*) cube of wairauite.

Both minerals are easily detected in polished section at high magnification (×240) by their high reflectivity, and are white in colour. Reflectivity measurements have been made with a visual comparison microphotometer using as standard a pyrite from Brosso, which in turn had been compared with the Elba pyrite calibrated by the National

Physical Laboratory. An Ilford 'Spectrum Green' filter with a peak transmission at 5100 Å was used. Assuming the pyrite reflectivity at this wavelength to be 51 %, wairauite gave 54 % and awaruite 58 % (compared with 58·0 % for awaruite measured by photometer in white light by Folinsbee, 1949). Wairauite is isotropic.

Measurement of hardness was not possible in the grains contained in the Red Hills serpentinite. Both wairauite and awaruite, however, have a similar polishing hardness and the indentation hardness of the latter (Nickel, *op. cit.*) corresponds to about 4½. A calculation of density from the analysis obtained on the electron probe and the unit-cell dimensions of artificial alloys of the same composition gives a value of 8·23 as compared with 8·58 for awaruite. Both minerals are highly magnetic.

The euhedral form of wairauite, together with its slightly lower reflectivity, may be used to distinguish the mineral from awaruite.

Analysis. The electron-probe analysis was made on an instrument in which the electron beam is incident normally on the specimen and in which X-rays are collected at an angle of 40° to the surface. All measurements, including scanning pictures, were made with a beam-accelerating voltage of 20 kV, and pure metals were used as standards. The correction for absorption is negligible in the case of Fe-$K\alpha$ and Co-$K\alpha$ radiations. Although appreciable in the case of Ni-$K\alpha$ in the alloy, it does not affect the result in the first significant figure. Two small corrections for fluorescence effects are necessary. The first of these arises from the excitation of Fe-$K\alpha$ by Co-$K\beta$ and can be obtained approximately by adapting the formula for fluorescence enhancement (Castaing, 1951) to the case of a small grain. The second correction arises from the fact that, owing to the very small size of the mineral grains, the intensity of that part of the characteristic Co-$K\alpha$ and Fe-$K\beta$ produced by absorption of continuous radiation is smaller than it would be in a massive specimen of Co-Fe since a considerable part of the continuous radiation passes into the surrounding host mineral. This loss of intensity does not occur in the massive standards, and the concentrations of metal as recorded by the probe in the case of very small grains are consequently low. An approximate correction for this effect can be made on the basis of data published by Green (1962). It must be emphasized that both of the fluorescence corrections are subject to considerable uncertainty because the depth of the grain is unknown. The estimates have been made on the basis of a cube of 5μ side. Uncorrected and corrected measurements are listed in table I.

The analyses in table I are the result of measurements on a homo-

TABLE I. Electron-probe analysis of wairauite from Red Hills

	Measured wt. %	*Correction for excitation by* Co-$K\beta$	*Correction for loss of continuous production*	*Corrected* wt. %
Cobalt	48·3	—	+0·5	48·8±0·8
Iron	49·8	−0·5	+0·5	49·8±0·8
Nickel	0·5	—	—	0·5±0·1
Total	98·6	−0·5	+1·0	99·1

geneous grain. Some grains were found to be zoned and to consist of a core of awaruite surrounded by wairauite; scanning pictures of one such grain, taken in Fe-$K\alpha$, Co-$K\alpha$, and Ni-$K\alpha$ radiations, are shown in fig. 2. The resolution of the technique is not adequate to make reliable quantitative analyses of such small zoned grains, but semi-quantitative determinations indicate that the cobalt content of awaruite and the nickel content of wairauite are both very low.

Conditions of formation. Wairauite and awaruite are found only in the serpentinites and have never been observed in unaltered ultramafic rocks at Red Hills. The trace element analyses given in table II indicate that the formation of the Ni–Fe and Co–Fe minerals is not associated with an introduction of nickel or cobalt and that the material necessary for their formation could have come from the serpentinization of the olivine.

TABLE II. Spectrographic analyses of samples from Red Hills

	Ni (ppm)	Co (ppm)
Unaltered dunites and harzburgites	1000–4200	120–220
Serpentinite with wairauite and awaruite	1600	80
Serpentine minerals less ore minerals	1000*	45*
Olivine	2200–2800	180–220
Late-vein lizardite	50	nil

* Probably contaminated with grains of Co–Fe and Ni–Fe alloys

The presence of grains of wairauite and awaruite outlining serpentine pseudomorphs after olivine, and in the late veins of serpentine, supports the view that the formation of these minerals is closely connected with the serpentinization process. Hydrothermal experiments on the wairauite-bearing serpentinite yielded olivine above 475° C at 2000 atm during runs of 14–21 days. If wairauite and awaruite are the result of serpentinization, they appear to have formed below this temperature.

It is difficult to explain why all the nickel and cobalt did not go into the serpentine minerals on serpentinization of the ultramafic rocks, particularly as nickel- and cobalt-bearing serpentines are known. It may

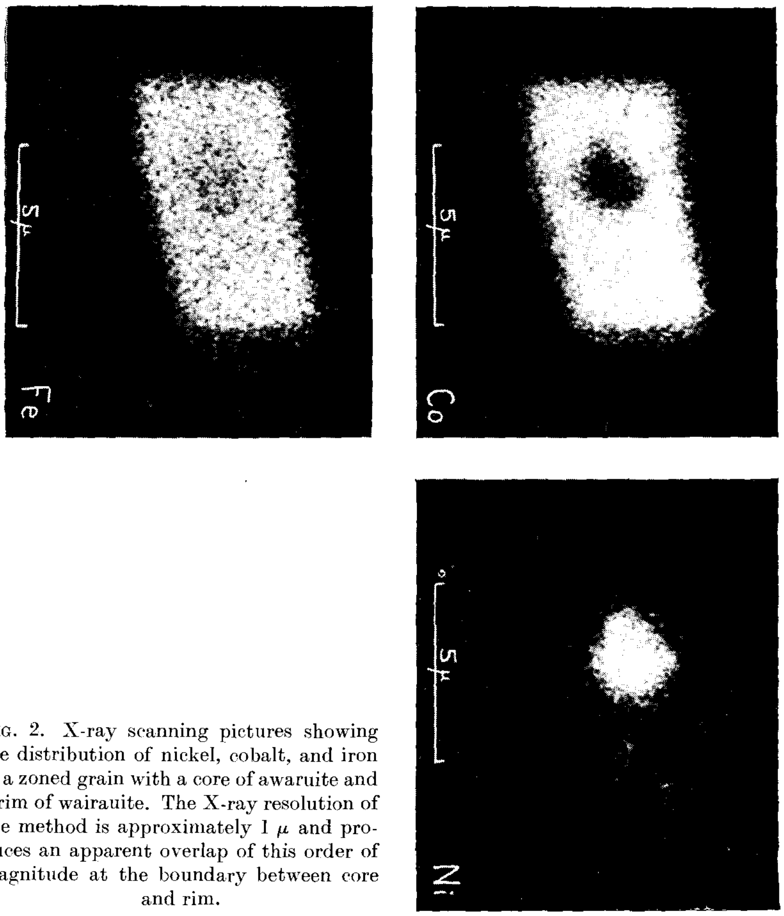

FIG. 2. X-ray scanning pictures showing the distribution of nickel, cobalt, and iron in a zoned grain with a core of awaruite and a rim of wairauite. The X-ray resolution of the method is approximately 1 μ and produces an apparent overlap of this order of magnitude at the boundary between core and rim.

be relevant that the serpentines in which the alloys are found at Red Hills are dominantly lizardite, of which available analyses (Faust, 1963) show a notable poverty of nickel and cobalt. The spectrographic analysis of a late-vein lizardite from Red Hills (see table II) shows only 50 ppm nickel and no cobalt, and it seems possible that lizardite is less able to accept nickel and cobalt into its structure than is chrysotile.

The association of Co–Fe and Ni–Fe alloys and native copper in the Red Hills serpentinites indicate strongly reducing conditions and an absence of sulphur during serpentinization.

Structure. The extremely fine grain-size of the material and the presence of two other strongly magnetic minerals, magnetite and awaruite, made it impossible to obtain sufficient pure material for X-ray powder photography and no grain large enough for a single-crystal X-ray study was found. The synthetic system Co–Fe is, however, well known and has been investigated by Ellis and Greiner (1941). They found that when alloys of composition Co_{50}–Fe_{50} are slowly cooled below a critical temperature of 700° C an ordered cubic body-centred CsCl-type structure is produced.

Ordering, indicated by the appearance of superlattice lines in X-ray powder photographs, has been observed in awaruite (Nickel, *op. cit.*), which is face-centred and of fairly constant composition Ni_{75}–Fe_{25}, suggesting that Ni occupies the face-centred sites. All grains of wairauite analysed have shown a composition close to Co_{50}–Fe_{50}, consistent with the development in the natural alloy of an ordered structure similar to that found in the synthetic system at the same composition. Conditions of slow cooling would certainly occur in such a large ultramafic mass as the Red Hills, which is 42 square miles in area. Also, the temperature of formation appears to have been below 475° C. It is suggested, therefore, that wairauite probably has a structure and unit-cell dimension similar to that of the synthetic alloy of composition Co_{50}–Fe_{50} for which Ellis and Greiner (1941) report a as approximately 2·86 Å, the lattice expanding slightly on ordering. It may be noted that in the case of awaruite, Nickel (*op. cit.*) has shown that the cell dimension is in good agreement with that of the synthetic alloy.

Although no X-ray data are available at present, it is considered that the constant composition shown by the Co–Fe alloy, together with the evidence from zoned grains, in which there is very little substitution of nickel in wairauite or cobalt in awaruite, serve to distinguish wairauite as a distinct species. The structure of the synthetic Co–Fe alloy is also distinct from that of the synthetic Ni–Fe alloys and from awaruite. There is, unfortunately, no published data on the system Co–Fe–Ni at low temperatures and the extent of substitution of cobalt and nickel in the synthetic system is therefore unknown.

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References

CASTAING (R.), 1951. Application des sondes électroniques à une méthode d'analyse ponctuelle chimique et crystallographique. Thesis, Paris: ONERA publication no. 55.

ELLIS (W. C.) and GREINER (E. S.), 1941. Trans. Amer. Soc. Metals, vol. 29, p. 415.

FAUST (G. T.), 1963. Geochimica Acta, vol. 27, p. 665.

FOLINSBEE (R. E.), 1949. Econ. Geol., vol. 44, p. 425.

GREEN (M.), 1962. The efficiency of production of characteristic X-rays. Ph.D. Thesis, Univ. of Cambridge.

NICKEL (E. H.), 1959. Canad. Min., vol. 6, p. 307.