

STUDIES OF HEAVY DETRITAL MINERALS

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## ABSTRACT

This paper embodies the results of a detailed investigation of the heavy detrital minerals in the sands and gravels in streams, beaches, terraces etc. in a wide variety of localities in South Island, New Zealand.

Appropriate techniques using screens, bolting silk, electromagnets, and the centrifuge among other devices have been developed for this and earlier work, and some well-known techniques have been modified to suit the special conditions imposed during this investigation. The centrifuge proves superior to the ordinary separating funnel if fine-grained material is handled. Various acids prove effective as solvents for calcium carbonate. Attention has been focussed on the inadvisability of using Clerici solution under certain conditions. Heavy mineral fractionation by heavy liquids in flat-bottomed porcelain dishes, rather than in ordinary filter funnel or separating funnel, is fully described, as well as the preparation of pure mineral samples.

Detailed optical, density, and chemical studies of over 50 placer minerals are fully reported. Geological occurrence of the economically important tantalum cassiterite, gadolinite, monazite, thorite and its varieties, xenotime, scheelite, and zircon and its varieties is emphasized. Some varieties of thorite exhibit properties that are absolutely distinct from those previously recorded.

The nature and causes of the metamict state in radioactive minerals are considered in the light of modern data on crystal structure, and although this question is not fully answered the opinion is ventured that bombardment of unstable structures by alpha-particles is a vital factor. Micro-fissuring of radioactive minerals is discussed and it is concluded that the web of fracture therein may be attributed to expansion resulting from transformation to the metamict state.

An inquiry into the location and nature of the source rocks of the heavy detrital minerals concludes the report.

## ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Mr. F. T. Seelye for excellent analyses carried out with so much care and for numerous discussions on chemical problems; to Professors Adolf Pabst and F. J. Turner of the University of California and Professor D. L. Webster, Stanford University for valuable arguments and constructive criticism; to a number of gold dredging companies, Mr. Ian MacKellar, and many others for their kindness and assistance in supplying material; to Professor F. W. Tickell, Stanford University, for his painstaking editing; to Miss Louise Ricks for her accurate typing of the manuscript; and to Mr. Frank D. Banham for his help, co-operation, and advice in the fabrication of some of the special instruments used in this study.

Any acknowledgment would be incomplete without an expression of deep gratitude to my wife, May, for her encouragement and active help at all times.

The author alone is responsible for errors of fact or interpretation.

## OBJECT OF THE WORK

The investigation was begun as part of a program involving the search for radioactive minerals in territory from which they had not hitherto been reported. As the work progressed, the writer set about attempting to determine

the nature of the heavy detrital minerals in a wider range of localities with particular reference to their physical and chemical properties. To gain some idea of the ultimate source rocks of some of the more important minerals, the minor accessory constituents of a wide variety of rocks from appropriate localities were separated and studied.

#### SCOPE OF THE WORK

In the main, the work involved a detailed study of the heavy detrital minerals in beach, river, terrace, and dune deposits in a wide range of localities in South Island, New Zealand, with particular attention to material from distributive provinces in which acid plutonic rocks outcropped. Concentrates from dredges, prospectors' and gold-miners' pannings and washings, pay-streaks on beaches and along water-courses, and the products of the writer's pannings in a wide range of localities where dredges or prospectors were not active formed the basis of the investigation.

Appropriate methods were devised to examine the material, which in most instances contained a preponderance of heavy minerals, either ferromagnetic or strongly to moderately paramagnetic. At the same time, the efficacy of various laboratory methods of mineral concentration and preparation was investigated, particularly techniques for preparation of pure mineral fractions required for analytical purposes. In view of the difficulties involved and the scanty work on such problems, the diagnosis of opaque detrital minerals was considered.

Several unusual minerals were diagnosed by optical means alone, but in view of the poor optical and chemical data available for some uranium- and thorium-bearing minerals and the various rare earth compounds, all information possible on the chemical compositions of pure minerals, especially the thorites, was sought to enable an understanding of the optical data.

Although the general problem of the nature and distribution of the heavy detrital minerals throughout South Island is incomplete, the writer's departure from New Zealand will not permit his undertaking any further studies on this problem; however, the work should indicate the directions for future investigations and

it is hoped that it may serve as a guide in general geological problems, particularly on the west coast of South Island. Further, it may show geologists the value from many points of view, economically, mineralogically etc., of work of this nature.

#### PREVIOUS WORK

In New Zealand, very few special studies of the heavy mineral assemblages of beach and stream sands, gold-miners' and dredge concentrates, or incoherent rocks have been made, and only a few of these are in any detail (Finch, 1948; Hutton, 1940b; 1945a; 1945b; 1947a; 1947b; Hutton and Turner, 1936; Morgan and Gibson, 1927; Speight, 1928; N. H. Taylor, 1933; Turner, 1944; Williams, 1934; and Wylie, 1937); most of these investigations have been concerned with titaniferous ironsands on the west coast of the North Island. No thorough studies of South Island Quaternary sediments have been made although several New Zealand Geological Survey Bulletins discuss the South Island west coast blacksand beaches, chiefly on account of their gold content. In some of these publications and in numerous Annual Reports of the Dominion Laboratory, references are made, sometimes without sufficient data, to the presence of monazite, cassiterite, platinum, osmiridium, yttrotantalite etc. in auriferous placers and other deposits (Bell and Fraser, 1906; Henderson, 1917; Morgan, 1908; 1911; 1927; and Webb, 1910). Analyses of concentrates from sluicing claims, dredging companies, and other sources (material from Addison's, Westport, Dominion Analyst, 1917, p. 25), and blacksand paystreaks (for material from Charleston see Dominion Analyst, 1926, p. 21) have been recorded but these data are usually unsupported by mineralogical determinations.

#### PART 1. MINERALOGICAL TECHNIQUES

##### *Introduction*

Some of the methods employed by the writer in this and other work are recorded in detail for the use of others concerned with similar problems, but some of the methods discussed are not original, having been adapted or modified for some specific purpose. Since the various prob-

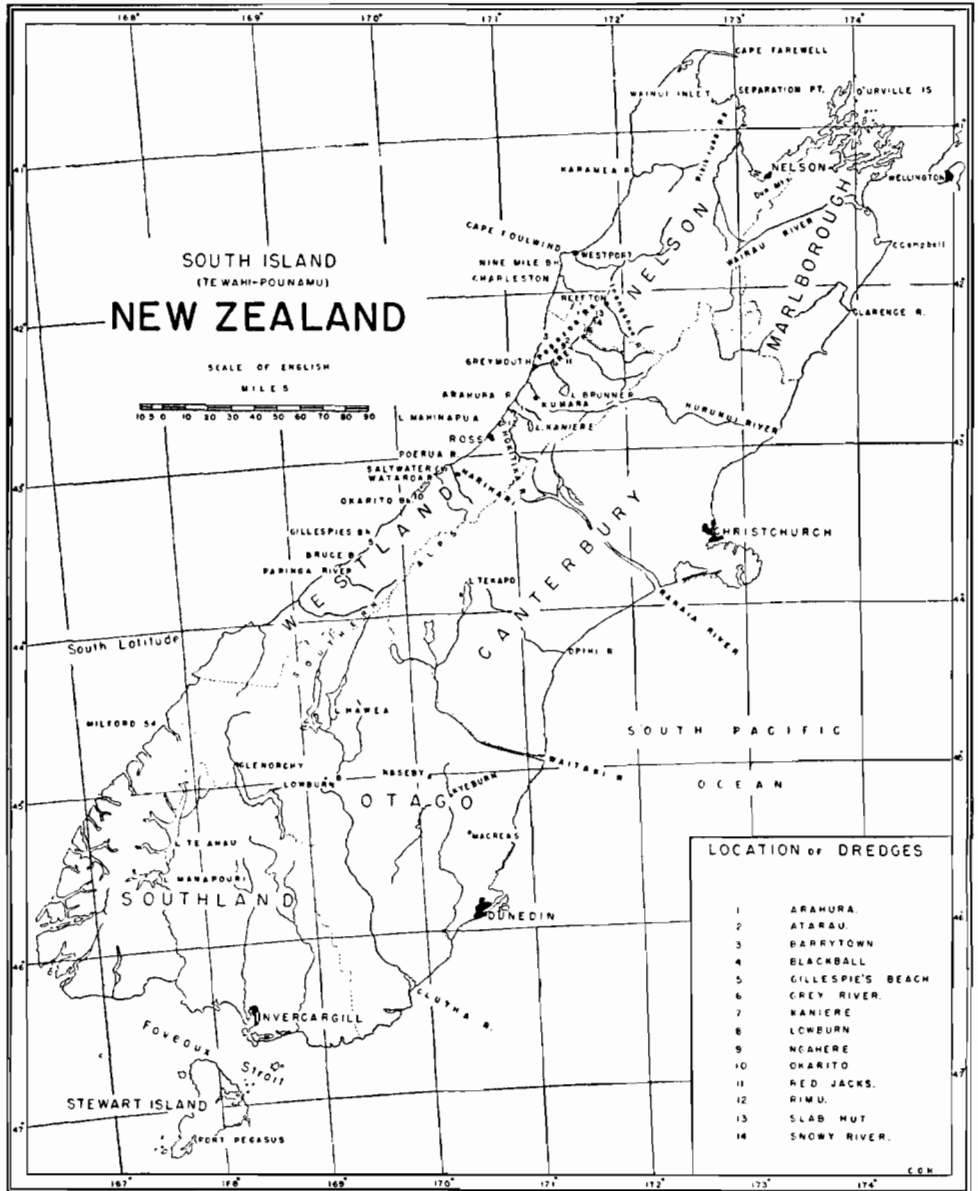


FIGURE 1—LOCALITY MAP OF SOUTH ISLAND, NEW ZEALAND

lems concerned with mineral isolation, concentration, determination, and so on differ so much, it is neither easy nor desirable to lay down definite rules for work of this nature, and therefore the experimenter must devise the most appropriate combination of manipulations for a specific task.

#### *Preparation of Original Material for Heavy Mineral Separation*

The original materials can be grouped into four main categories:

- (a). Soft, coherent but not dominantly carbonate-bearing rocks.

- (b). Hard rocks devoid of much carbonate.
- (c). Carbonate-rich rocks.
- (d). Incoherent materials.

Specimens belonging to categories (a)-(c) require complete disaggregation; for this purpose specimens weighing about 2-3 pounds have usually been found to be sufficient.

(a). A soft specimen may be completely broken down by working small fragments between the fingers; if not amenable to this treatment, it may be so after soaking or boiling in water. If a rock will not yield to these methods it should be soaked in a hot solution of sodium sulphate or ordinary photographers' hypo, until the specimen itself is thoroughly saturated. It should then be removed from the solution, placed in a suitable dish, and the salt allowed to crystallize. Expansion of the growing crystals will often reduce a coherent rock to fine composite particles more easily dealt with. Some rhyolite tuffs were thus broken down to almost completely monomineralic powders. If these methods fail, the rock should be broken into small fragments and finally rubbed down, but not ground, in a cast iron mortar with a long-handled iron-headed pestle.

(b). Hard rocks may be broken down to conveniently sized fragments in a jaw crusher or placed in a deep iron mortar and pounded with the long-handled pestle into small chips. For disaggregation of the fragments pounding them in an iron mortar may be satisfactory in the case of specimens that are semi-coherent such as sandstones and some schists, but with fresh, massive igneous rocks, quartzites, etc., disintegration may be conveniently accomplished with a special percussion steel mortar and pestle (Fig. 2). The eccentrically placed percussion point is a necessary feature of this tool since it serves to prevent wedging of the pestle in the sleeve by the powder forming from the rock chips under treatment.

It is necessary to screen the crushed material of the last two groups, but the choice of sieve openings depends very much on the grain sizes of the rocks concerned. The writer has found it convenient to screen a rock powder through sieves with openings of 4, 2, 1, 0.5, and 0.25 mm. (Wentworth grade scale) and to examine test samples from each fraction beneath a

binocular microscope for composite particles. If these are found, almost certainly in the coarser screenings, the fraction or fractions containing them are reduced further. When sizing of a disaggregated sediment is required,

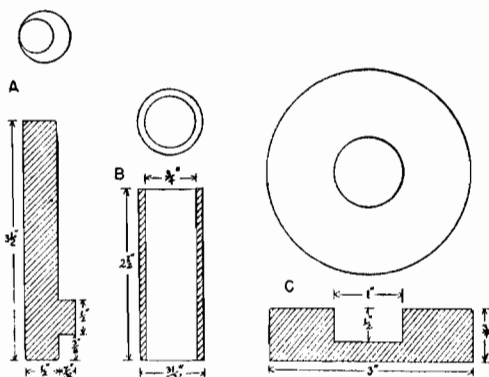


FIGURE 2.—PLAN AND SECTION OF PERCUSSION STEEL PESTLE AND MORTAR  
A. pestle; B. sleeve; C. mortar.

screens with openings 0.125 and 0.062 mm. should be added. However, if it is only proposed to investigate the minor accessories of a rock it is preferable to use bolting silk for the finer particle sizes since this is readily cleaned and contamination is less likely than with fine mesh metal screens. A nest of silk screens is used, details of which will be given later.

After disaggregation is complete, the powder must be freed from clays and dust before satisfactory sedimentation or electromagnetic fractionation can be undertaken. This may be accomplished by careful elutriation of 50 gm. portions of rock powder in a pear-shaped separatory funnel under a slow but constant up-flow of water with simultaneous collection of the overflow in a series of 1- or 2-liter capacity beakers, if ultimate study of the clay or fine fraction is desired. It is just as efficient and certainly much quicker, to pour the powder into a 1-liter beaker which is nearly filled with water making certain, at the same time, that the powder is thoroughly wetted and dispersed; with very fine powders, dampen the powder with alcohol before adding water to hasten thorough wetting. After the muddy liquid settles for about 90 seconds, 750 ml. of the

supernatant liquid are either decanted or siphoned off; this liquid is retained as before. The process is repeated until, after a 90-second settling period, the supernatant liquid no longer remains cloudy.

(c). Carbonate-rich rocks should be broken down by any suitable method, the powder so obtained washed free from clay and fines, followed by solution in acid to remove carbonates. Since it is generally held that a number of heavy minerals found in carbonate and other rocks are soluble in strong mineral acids, a number of authors have suggested the use of either citric or acetic acids instead. The present writer believes that the usual constituents of a heavy mineral assemblage are almost insoluble when treated with mineral acids of moderate concentration in the cold for short periods of approximately 20–30 minutes, and this also applies to apatite except in a very finely divided form, less than about 50 microns. A similar view expressed by R. D. Reed (1924, p. 324) appears to have been lost sight of. A greater disadvantage of the use of strong mineral acids such as HCl on detrital mineral grains than the negligible possibility of loss of essential material, is the not infrequent production of etch figures, and if these are found on grains treated in this manner they cannot readily be distinguished for natural ones. However, neither acetic nor citric acid is at all satisfactory when large quantities of carbonates are to be dissolved, owing to the limited solubilities of their salts<sup>1</sup>, particularly calcium citrate; in addition, both the calcium acetate and citrate become less soluble with temperature increase in marked contrast to the solubility of calcium chloride. Nevertheless acetic acid is useful when calcium carbonate is only a minor constituent of a sediment<sup>2</sup>. Instead about 4N HCl has been found most satisfactory in spite of possible partial

<sup>1</sup> Solubility of calcium acetate: 2.72 gms. in 100 gms. of water at 0°C. and 2.29 gms. in 100 gms. of water at 100°C.

Solubility of calcium citrate: 0.22 gms. of  $\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)$  per 100 cc. of aqueous solution saturated with  $\text{Ca}(\text{C}_6\text{H}_5\text{O}_7) \cdot 4\text{H}_2\text{O}$  at 30°C. and at 95°C. 0.183 gms. of  $\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)$  per 100 cc. of aqueous solution (Seidell, 1940, pp. 246, 255).

<sup>2</sup> Professor F. G. Tickell has suggested to the writer that trichloro-acetic acid, a strong organic acid, might prove useful for dissolving carbonates.

solution of some of the heavy mineral suite. The procedure usually is as follows: A 25 gm. portion of powdered carbonate-rock is placed in a 400 ml. capacity beaker and treated with about 150 ml. of 4N HCl, added 50 ml. at a time; normally this should be sufficient acid to dissolve all of the carbonate present. When effervescence has ceased the liquid is heated to ensure complete solution of any dolomite present. After settling of the insoluble residue, the supernatant liquid is carefully decanted through a filter, and 20 ml. of 4N HCl added to the residue to prove that solution of the carbonates has been complete. The residue is then thoroughly washed with distilled water and dried in an oven at 90°C.

Pure HCl has been suggested for solution of carbonates since commercial type acid contains  $\text{SO}_4$  ions and this would result in the contamination of the insoluble residue with calcium sulphate, presumably in the form of gypsum. Because analytically pure HCl is much too expensive for this use, commercial acid is recommended; but since a small check portion of the original powdered carbonate rock without prior acid treatment should be fractionated in bromoform of density about 2.88 to detect the presence of any acid soluble minerals other than carbonates therein, the presence of introduced gypsum can be observed. Even if the specimen should be contaminated with gypsum, and no instance of this has occurred in the writer's work, the heavy mineral fraction should be devoid of this constituent if the separation has been clean.

(d). Incoherent materials studied by the writer include a wide variety of eluvial, alluvial, littoral, and aeolian materials, and in this investigation a wide range of tailing, sludges, and panned concentrates was also examined.

Careful elutriation is often the sole requirement for preparing specimens of incoherent materials for mineral fractionation; with dredge concentrates and pannings, not even this treatment is required. However, tailings, panned concentrates as well as some sands contain a high proportion of minerals of density greater than 2.85, and it is more satisfactory to fractionate electro-magnetically each grade-size before flotation in heavy liquids.

### *Fractionation in Heavy Liquids*

Both bromoform and acetylene tetrabromide have been used but the writer favors bromoform because it has a decidedly lower viscosity, *viz.* 0.068 as compared with 0.098 poise for  $C_2H_2Br_4$ , and hence filtration and sedimentation are both quicker, a factor of some importance when a large number of specimens has to be run through. In the writer's opinion this advantage outweighs that of slightly higher density of acetylene tetrabromide for most purposes. Alcohol, acetone, or benzene ( $C_6H_6$ ) are satisfactory diluents or wash liquids and bromoform from washings is easily recovered. Both alcohol and acetone are readily removed from a mixture of either of these compounds with bromoform by washing with liberal quantities of water and drying the recovered bromoform over fused calcium chloride, whereas benzene must be removed either by fractional distillation or by fractional crystallization. If fractional distillation is employed, the entire operation should be carried out at reduced pressure (approximately 16–25 mm. of Hg) and preferably on a shaded bench, but certainly out of direct sunlight if extensive decomposition of bromoform is to be prevented. If methylene iodide is also present in this mixture it may be recovered at the same time although the percentage recovery is not as good as that for bromoform. A more convenient method of recovery, by which little decomposition need occur, is to place the benzene-bromoform mixture in a flask in a freezing mixture; since the melting point of bromoform is about 7°C. and benzene 5.5°C., bromoform will crystallize out before the benzene commences to do so. The same procedure may be adopted with bromoform-alcohol mixtures.

The method used for the actual separation of the heavy mineral fraction will depend upon the average grain-size of the original material. For grains finer than 0.125 mm. in diameter the usual separating funnel methods are unsatisfactory, and such material must be separated centrifugally (Hutton, 1943). This opinion is not in agreement with Grout's (1937) findings on the efficacy of centrifuge separations, but it is in partial support of the data presented by Tyler and Marsden (1937). Additional work on

this problem, since the publication of the author's earlier study, has shown beyond all doubt that for very fine-grained sediments both the yield of heavy minerals and the relative frequencies of the different minerals are significantly different when obtained by centrifuge methods instead of the usual funnel technique.

If the material is relatively coarse, as are most panned and dredge concentrates, fractionation is readily and accurately accomplished in a simple porcelain evaporation dish about 3–3½ inches in diameter, preferably one with vertical sides, such as a flat-bottomed Coors dish.

The dish is half filled with bromoform, or what liquid the operator wishes to use, and about 20–25 gm. of cleaned, graded, and absolutely dry material is carefully poured into the liquid. The grains floating at the surface are continuously but carefully stirred until fractionation is considered complete. Then the dish is tilted slightly and the layer of heavy grains is brushed towards the side of the dish below the lip; this operation may be assisted by tapping the bottom of the dish so that the grains roll or slide. Now wash back into the dish with bromoform from a wash-bottle the wet but mainly light grains that are adhering to the brush and carefully stir the surface layer once again, with special care not to cause convection currents strong enough to bring about redistribution of the segregated heavy grains. After 3–4 minutes, carefully skim aside a portion of the light layer and determine whether there has been further sedimentation. If not, the light fraction is recovered by decantation through a filter<sup>3</sup> and the dish and heavy fraction contained therein carefully washed with bromoform, decanting the liquid after each washing until only the heavy fraction, completely free from light grains, remains in the dish. Wash finally with alcohol, decant wash-liquid, and place the dish with the "heavies" on a hot plate at a temperature of 90°C. If it is necessary to separate additional portions of the original material a supplementary 20–25 gm. lot should be added after decantation of the first light

<sup>3</sup> Whatman's No. 4 papers have been found most suitable for this work.

fraction; washing with alcohol is carried out after the last separation has been completed.

Using an open dish is a relatively rapid way to fractionate large amounts of material and the wide surface area and absence of sloping sides or shoulders assists rapid sedimentation. Washing the heavy residue with bromoform in the dish after decantation of the bulk of the light grains provides one with a very clean fraction, uncontaminated by light grains, and final recovery of the "heavies" in the dish rather than in a filter-paper means a minimum of loss of very small and fine-grained residues. Finally, porcelain dishes are cheaper to buy and easier to clean than glass separatory funnels.

For separating heavy minerals from fine-grained materials by centrifuging methods, modified Taylor (G. L. Taylor, 1933) tubes are used. Two or four tubes are used simultaneously and each tube has a total capacity of about 110 ml. with a narrow waist dividing each tube into a small lower bulb, with a capacity of approximately 6–10 ml., and a larger upper portion. This enables a large residue to be accumulated before it is necessary to wash out the heavy fraction. Samples are usually centrifuged for from 2–5 minutes, at speeds ranging from 1500–3500 revolutions per minute.<sup>4</sup> The method is as follows: To each thimble or tube about 10–15 gm. of dry, elutriated, and graded powder is added; the tubes are then partially filled with bromoform (or other heavy liquid), and the pair or pairs of thimbles are balanced by addition of the appropriate weight of heavy liquid. After centrifuging, a cork stopper that is firmly attached to one end of a brass rod is carefully worked through the layer of light grains near the top of the thimble, and securely plugged into the waist of the tube. The light fraction may now be tipped out without any loss of heavy grains, and the tube above the stopper washed clean with bromoform; the plug is now withdrawn and the heavy fraction poured out, preferably into a small flat-bottomed dish and the tube rinsed out with bromoform. The small amount of bromoform in this is decanted through a small filter into the stock-bottle and the heavy grains washed, and recovered in the manner described earlier. If insufficient residue

<sup>4</sup>The radius of the thimble-holders is approximately 70 mm.

has been obtained the first time another portion of the original material is poured into the thimbles immediately after decantation of the light fraction, bromoform added again, the tubes balanced and then centrifuged. This process is continued until sufficient heavy residue has accumulated. The upper part of each thimble is then washed clean and the heavy grains recovered in a clean porcelain dish as detailed before. Although this process requires a considerable volume of bromoform most of it is recovered and returned through a filter to the stock-bottle and, by careful manipulation, it is possible to obtain uncontaminated residues with ease.

Similar methods are used for separation of pure mineral samples from rock powders, except that this is not usually a simple separation into two fractions. The rock powder must be carefully sized, and to ensure an absence of composite particles, grains with inclusions, and so on, it is usually necessary to reduce the rock to particles that will pass through bolting silk with a mesh of about 0.125 mm., although finer grinding may be necessary in some instances. Following this the powder should be carefully washed free of dust and dried at 110°C.<sup>5</sup> A plan of order of separation is then worked out so that the minimum number of manipulations will be necessary. As an example let us consider the case of a schist composed of albite, quartz, clinozoisite, spessartite-almandine, prochlorite, actinolite, with minor amounts of iron oxides, titanite, and apatite; a pure sample of prochlorite having a density about 2.96 is desired. In this case one might reasonably proceed as follows: Centrifuge the prepared rock powder in bromoform, portions at a time, until the lower bulbs are filled with material of density

<sup>5</sup>This temperature cannot be rigidly adhered to since some minerals must be dried at approximately room temperatures otherwise water may be lost. Among the silicates this is true for minerals of the stilpnomelane group and the zeolites. The zeolites are very sensitive to rise in temperature and the usual temperatures employed for mounting rock chips on glass slides with Canada balsam are generally sufficient to change the optical properties significantly. An excellent example of this was observed with a specimen of potassic thomsonite (Hutton, 1942, p. 181) the optical orientation of which was found to be different in crystals mounted in Canada balsam and cooked at the usual temperatures, and those that were merely immersed in refractive index liquids without prior heating.



greater than 2.88 (approximately). Clean the upper parts of the tubes above the stoppers, withdraw the stoppers, and partly fill the tubes with a methylene iodide-bromoform mixture of density 2.98. The small amount of bromoform saturating the mineral powder in the lower bulbs will reduce the overall density very slightly. Shake the tubes and thoroughly mix the mineral powder and liquid; then centrifuge. If the density of the liquid has been adjusted satisfactorily prochlorite will be floating and almost free from any of the denser grains which will have remained behind in the bottom bulbs. To each tube add two or three drops of alcohol and centrifuge once again, and repeat this process until it is evident that the prochlorite would precipitate with any further dilution. At this stage, the required mineral should be absolutely free of any of the denser minerals and in addition it should be freed from any flakes of oxidized or weathered chlorite. Insert the stoppers and decant the prochlorite concentrate into clean thimbles together with the liquid floating it. Add two or three drops of alcohol to each thimble, shake, and centrifuge, repeating this process until the chlorite sinks. Carefully check the surface of the liquid in each thimble for the presence of any grains of quartz or feldspar, and if present insert the stoppers and decant; re-centrifuge the chlorite with the same liquid once again to make doubly certain that no light minerals are occluded with the flakes of chlorite. The purity of the material so prepared may be checked by immersion in a liquid with refractive index equal to that of the chlorite and examined under high magnification. One important requirement is the careful adjustment of the density of the liquid so that the nearly purified powder sinks or rises slowly during the period of centrifuging. For example, if the density of the liquid is very much less than that of the nearly pure powder, the latter will sink rapidly and in a dense clot, and as a result will carry down with it a small but significant percentage of some lighter material. Finally, while on this subject, the author would make a plea for greater use of the centrifuge as a tool for the separation of pure mineral powders from rocks for analytical purposes. Our literature is cluttered up with analyses of impure minerals, because of the universal occurrence

of inclusions in minerals. Centrifugal separation is a very sensitive process and with reasonable manipulative skill and care the complete separation of two minerals whose density differs only by 0.01 can be readily accomplished.

#### *Sample Splitting*

The total volume of a completely disintegrated specimen is often in excess of the amount required for heavy mineral separation and therefore subdivision is necessary. Unless this is performed carefully, considerable error is likely. Sample splitting has been conveniently accomplished in the past by pouring the powder into a glass filter funnel which is mounted vertically and symmetrically over a divider. The latter is merely an inverted V-shaped piece of brass with a knife-edge ridge; the lower sides of the divider are shaped so that the partitioned powder will pour into two porcelain containers. Such a piece of equipment is easily made in the laboratory and appears to be as efficient as the Jones ore sample splitter.

Since thoroughly representative fractions of heavy mineral residues are required for permanent mounting, electromagnetic fractionation, flotation in other liquids etc., careful subdivision is of the utmost importance and one cannot condemn too heartily the common practice of taking samples with the point of a pen-knife. Heavy residues are generally small in volume, often less than 1000 grains, and consequently it is doubly important that splitting should be as accurate as possible, and the personal factor eliminated. The most satisfactory method involves the use of Otto's microsplit. A second method when a microsplit is not available, requires: a small filter funnel about an inch in diameter at the wide end, with the tube-end ground off perpendicular to the axis of the funnel, a sheet of glass 6" x 6", and a razor blade. The funnel is allowed to stand vertically with the ground-off end on the glass plate, and the heavy grains are poured into it. The funnel is tapped gently to shake down any adhering grains and then lifted vertically and slowly off the plate, allowing the grains to arrange themselves into a small cone, which may be quartered down with the razor blade by drawing each portion aside until the desired volume or num-

ber of grains is obtained. It is more accurate to use a funnel to obtain the cone than to pour the sample on to the glass directly from the container, since rolling the grains off a surface usually causes decided concentration of particular grains which may not be distributed evenly within the cone.

*Concentration of Samples Before Fractionation  
in Heavy Liquids*

*Screening.*—In a great many instances, the heavy mineral fractions of many sandstones and so-called "mudstones" are entirely limited to grade-sizes with diameters less than 0.125 mm. In such cases it is often profitable to disaggregate a larger initial sample of rock since a considerable percentage of the rock powder will consist of grade-sizes coarser than 0.125 mm. and these can be discarded. The author has made it routine practice to screen disaggregated sandstones through bolting silk of approximately 0.125 mm. mesh, split off a small fraction of the coarser material, and run a trial heavy liquid separation to make certain that it is free from heavy minerals. Satisfactory correlation of sediments has been made utilizing only the heavy fraction present in the minus 0.062 mm. material, even when a small percentage of "heavies" did occur in coarser screenings. This greatly reduces the amount of laboratory preparation.

In a recent study of the heavy mineral assemblages of some beach sands, screening was carried out in the field after it was found that the heavy fraction was almost entirely limited to grains finer than 0.25 mm.; a screen with mesh openings of 0.5 mm. served to reduce the bulk of samples as much as 70–90 per cent. The original sands were dried in the sun and weighed in specimen bags with a hand spring balance and their weight recorded on the labels attached to screened samples. These samples were further reduced in volume in the laboratory where a more careful watch could be kept for the presence of heavy grains.

*Panning.*—In view of the experiments of Smithson (1930) and Ewing (1931), considerable care should be taken if panning methods are adopted to reduce the volume of samples. However, in some specimens the percentage of

heavy minerals is so low that panning is necessary for economy of heavy liquids and time. Panning of sands in the field is often convenient to reduce the bulk of samples, and in this event, Rastall's (1923, p. 33) advice "to pan a large amount in several instalments not carrying the process too far at first, then adding together all the partial concentrates for a final panning carried out with special care" is worth while.

The reduction of soils by panning to material suitable for ultimate heavy mineral separation in the laboratory is an invaluable aid towards mapping the areal extent of a number of rock-types when a few exposures are available.

*Electromagnetic fractionation.*—Two types of electromagnets have been devised, one using A. C. and the other D. C. The former device consists of two pole-pieces made from a strip of soft iron, approximately 5" x 1" x  $\frac{3}{16}$ ", bent to a U-shape with a slight closure so that the ends of the pole pieces are about  $\frac{3}{8}$ " apart. Two bobbins are wound with 26-gauge silk-covered wire to fit each pole piece, leaving about  $\frac{3}{8}$ " of the ends of the poles uncovered; these pole pieces are attached to one end of a wooden handle about 12" long and  $\frac{3}{4}$ " in diameter. On one side of the handle, *viz.* the left side when the instrument is held with the pole pieces pointing vertically downwards, a simple make-and-break switch is attached so that slight pressure from the thumb closes the switch and release of pressure breaks the circuit. This hand electromagnet is connected by 3 or 4 feet of light twin-flex to a rheostat which provides a range of voltage; in actual practice a range of from 2–6 volts has been found most satisfactory.

This instrument is invaluable for clean, rapid separation of magnetite, titanomagnetite, pyrrhotite, odd fragments of steel etc. from samples. The sample is spread out thinly on a shallow aluminum tray, and the magnet, with the switch closed, is moved steadily over the grains at a distance from them that will just allow attraction of the ferromagnetic material but will cause the somewhat less susceptible material such as ilmenite to agitate vigorously; the attracted material is quickly carried aside and dropped in a porcelain evaporating dish by a movement of the thumb on the switch, and the process repeated until the sample is free of ferromagnetic grains. The use of alternating

current instead of direct current has three distinct advantages: the rapid agitation of the grains makes for a clean separation, and since the pole-pieces are completely de-magnetised the moment the circuit is broken, no ferromagnetic grains remain attached thereto; finally the ferromagnetic grains are not themselves magnetized in the process and hence the operator may employ them immediately for hand-picking, screening, and so on, without the difficulty of coalescence of grains.

This magnet is always used to remove magnetite and other ferromagnetic minerals from heavy residues prepared from sediments, black-sands, dredge concentrates etc. before making permanent mounts, or carrying out further electromagnetic fractionation in strong fields.

The second electromagnet uses direct current ranging from 2–12 volts, and is employed for careful fractionation of paramagnetic material. It is an improvement on the instrument designed by Ksanda (1926): (a) The adjustable pole pieces are mounted on the top of the coils, so that manipulation and illumination of the material under examination is much more readily accomplished. (b) The specimen is held in a circular aluminum tray on the underside of which is a pin that enables the tray to be held on an adjustable arm that is attached to one of the corner posts by a well-fitting ring; the height of this arm may be altered by means of the collar and thumb-screw on the post below the arm ring. (c) The post has a fine scale marked thereon to enable the tray to be set at known distances from the apices of the pole pieces.

This instrument has been found invaluable for rapidly obtaining a sufficiency of some rare constituent from a heavy mineral assemblage, for determination of optical properties, chemical tests etc. However, certain precautions must be observed if any electromagnet is to give satisfactory results, particularly when preparing pure fractions: (1) The mineral grains must be washed free from dust. (2) The material for separation should be very carefully graded or, otherwise, a disproportionate percentage of the larger grains in a particular grade-size will be attracted. (3) The mineral grains must be absolutely dry; material for fractionation should be kept in an oven at 90°C. until it is required.

(4) The differences between the susceptibilities of ferromagnetic and paramagnetic minerals are so great that before fractionation is attempted, ferromagnetic material should always be removed with the A. C. hand-magnet. (5) Material with average grain diameter of 0.040 mm. can be conveniently fractionated with the large magnet, provided the precautions listed above are observed. With decrease of grain-size, however, obtaining clean separations becomes more difficult owing to mutual adherence of the grains, due partly to adsorbed moisture. To some extent this condition may be overcome by immersing the apices of the pole pieces and the mineral preparation in the pan in either alcohol or ether. (6) It has been found that a D. C. electromagnet of the type described here retains an appreciable amount of magnetism—permanent magnetism—after the circuit is broken, thus preventing free discharge of attracted grains. This circumstance has been overcome by the use of a double-pole double-throw switch for making and breaking the circuit, wired to provide for a momentary reversal of current, after a period of magnetisation, so as to destroy residual permanent magnetism. This switch may be mounted on the bench in front of the operator or more conveniently a simple mercury switch may be mounted on the floor and worked by the foot, thus leaving both hands free for the separation.

*Cardboard method.*—The cardboard method is a useful adjunct to screening technique for the separation of micas from rock powders. In many instances some degree of concentration of mica can be achieved initially by screening a disaggregated rock powder through appropriately sized screens; careful pounding in a mortar of mica-rich portions so obtained will often reduce the sizes of fragments of brittle minerals but leave the mica plates relatively unaffected. Thus by repeated screening and pounding, samples with fairly high percentages of mica may be obtained. Subsequently the mica in these samples can be nearly completely segregated by treatment on an inclined cardboard tray, consisting of a sheet of fairly smooth cardboard such as Bristol board, about 18" x 8" with the longer edges turned up at angles of 90°, glued on a piece of thin plywood or masonite of similar size but leaving about  $\frac{1}{2}$ "

of the Bristol board unsupported at one end. The tray should be inclined at a low angle, the mica-rich powder spread out thinly near the higher end, and the tray tapped gently. As tapping is continued, the more equidimensional grains will tend to roll or move rapidly down the inclined plane whereas the flakes of mica will lag behind; by careful adjustment of the angle of tilt of the board and the vigor of tapping a high degree of concentration of mica may be obtained. In some instances it is often helpful to breathe heavily over the surface of the board before attempting to separate a powder because the film of moisture so produced seems to obstruct free movement of the mica plates.

If partial concentration of micas has not been attempted by screening as a preliminary measure, then the micaceous rock powders must be reasonably well sized if manipulation of the board is to be in any way efficient.

#### *Hand-Picking and Isolation of Grains*

A number of special instruments have been devised for assisting isolation of particular mineral grains from a sample (Howard, 1932; Calkins, 1934 *et al.*) but these have not been found to offer any advantages over the use of simple dissecting needles, fine pointed tweezers, and fine pipettes. For inspection under a binocular microscope it has been found useful to spread the sample out thinly on a smooth card, half of which is black and the other half white. Grains with diameters larger than 0.25 mm. can be removed with the tweezers; for particles of smaller size, a dissecting needle, the point of which has been dipped in a tiny spot (1.0 mm. in diameter) of clove oil or other suitable refractive index oil on a glass slide, is adequate. Grains can be conveniently collected in the hollows of black or white colored spot-test tiles. In order to remove a particle from the point of the dissecting needle and guard against its loss on account of the resilience of the needle, the point of the latter need only be dipped into a spot of clove oil or other suitable liquid on a glass slide or in one of the depressions of the tile. It is often particularly convenient to remove a grain and place it directly in refractive index liquids for immediate observation. Further, if the particle is opaque and less than 0.25

mm. in diameter it may be crushed directly on the glass slide by gently applied pressure from a small agate pestle, and at the same time the liquid serves to prevent loss of any fragments of the crushed grain. This technique was found of considerable value for rapid diagnosis of chromian spinels, hematite, martite etc. since these minerals are normally opaque except in the thinnest fragments.

If it is necessary to remove a particular grain from a mineral assemblage already mounted in oils, the tweezers will again serve for the coarser material. For fine particles, however, the required grain may be safely and conveniently removed from its associates, together with a minute amount of immersion liquid, with a tiny pipette (Lindberg, 1944) and transferred directly to a second glass slide, or alternatively placed in a drop of xylene in a hollow-ground slide to remove the immersion liquid if that should be necessary. This method is much more convenient than the use of gums, vaseline, or Canada balsam on a needle point.

#### *Bolting Silk Screens*

Bolting silk has proved to be most useful for sizing fine materials and is especially valuable for splitting up heavy mineral residues. The value of the silk lies in the fact that contamination of the residues, which are usually of small bulk, is unlikely to occur since the silk can be quickly and completely cleaned after each operation; and further with the 1" diameter screen a very small quantity of material can be graded without loss. Clothholders of different sizes have been designed to permit large or small quantities of material to be graded through one or a nest of silk screens. These holders, 2", 3", and 4" in diameter, are made from seamless brass tubes, machined at each end so that they fit one into the other with sufficient freedom to allow insertion of a thickness of bolting silk between them. If only one holder is required, a simple brass ring holds the silk tautly. For a bottom pan, suitably sized evaporating basins or simply clean, glazed paper are used.

It might be pertinent at this stage to mention that, in the preparation of microslides of fragments of pure minerals for class-work, it has been found useful to grind up the mineral con-

cerned so that it passes completely through bolting silk with approximately 200 meshes per lineal inch. The fine powder is collected in an evaporating dish, washed to remove fine material and dust, and then dried on a hot plate; the material remaining is then of convenient size for study purposes, and the entire operation can be carried through in a very short time.

#### *Diagnosis of Scheelite*

Small grains of scheelite are conveniently distinguished from heavy non-tungstenian grains of similar appearance by boiling them in aqua regia in a porcelain dish for 2–3 minutes and subsequently examining them in oblique illumination under a binocular microscope. The characteristic bright-yellow coating of  $WO_3$ , readily soluble in aqueous ammonia will have formed on any grains of scheelite.

To determine the distribution of scheelite in a large specimen of quartz an alternative method is preferable. A reasonably large surface should be roughly polished, the specimen placed in a dish together with shot-sized grains of ferrous sulphide, and concentrated HCl added. The vigorous reaction that ensues is allowed to continue for about 3–4 minutes in a fume cupboard, when the specimen is washed vigorously in running water and examined. Any scheelite present will have changed to a grayish-blue color as a result of formation of one of the lower oxides of tungsten, and will accordingly be prominently differentiated from the white or creamy colored gangue. Ferrous sulphide is much more efficacious than zinc for this test.

#### *Diagnosis of Cassiterite*

Cassiterite exhibits a wide range of color from the colorless stream tin of Potosi to the deep blood-red, pleochroic, tantalian variety of Greenbushes, W. A., Westland, N. Z. and other localities. Excluding accurate but time-consuming refractive index determinations, the most simple yet rapid way of proving whether a mineral particle is cassiterite or not, is the reduction method with zinc and HCl. If the grains are numerous and large, it is only necessary to place them in a small porcelain crucible (5 ml. in capacity) together with small shot-

sized granules of zinc and add concentrated HCl. However, for a few small (<0.25 mm.) isolated grains the same test can be accomplished without loss of material by the following method: Select a granule of zinc about 4–5 mm. in diameter and punch a depression in it having a volume of approximately 1–2 ml. Next place the zinc granule on a small watch-glass and drop the grain to be tested in the concavity; add a drop or two of concentrated HCl. After 3–4 minutes remove the grain by carefully washing it out of the cavity, dry it, and rub it in a fold of a small piece of chamois leather, smooth side inwards. The grain under test should then be examined with a binocular microscope in oblique illumination when the shiny metallic luster of tin will be obvious if the grain is cassiterite.

#### *Refractive Index Liquids*

Numerous media have been recommended (Johannsen, 1918, p. 259–265; Winchell, 1928, p. 74–76; Emmons, 1929, p. 482–483; Holmes, 1930, p. 119–122; Ford, 1932, p. 236; Rogers, 1937, p. 154; Krumbein and Pettijohn, 1938, p. 381–384; Milner, 1940, p. 182–183; Twenhofel and Tyler, 1941, p. 166–167; Switzer, 1944, p. 389; Wahlstrom, 1945, p. 44–45; *et al.*) for refractive index determinations by the immersion method, and a number of authors have simply adopted the list arranged by Larsen and Berman (1934, p. 12). However, so many of the liquids suggested have high viscosities which make careful matching more tedious than it need be. The writer has found that the following liquids serve very satisfactorily for making up sets of refractive index liquids: 2 (butoxy-ethoxy) ethanol (1.43), 1-bromonaphthalene (1.658), methylene iodide (1.74), and methylene iodide saturated with sulphur and tetra-iodoethylene<sup>6</sup> (1.81). The mixtures of the first two compounds are clear, almost colorless, and have low volatility and viscosity. For media of higher refractive index West's (1936) liquids should be added and the entire series from 1.43–2.06 made up in steps of 0.01.

<sup>6</sup> The author would like to point out that in his paper on the determination of xenotime (Hutton, 1947a, pp. 143–4) tetra-iodo-acetylene should be read as tetra-iodo-ethylene.

### *Use of Clerici Solution*

The value of Clerici solution for determination of mineral densities and as a high-gravity liquid for mineral separation is well enough known (Vassar, 1925; Jahns, 1939) to require elaboration here, but a note of warning concerning the use of this liquid in some instances needs to be sounded. Pehrman (1935, p. 54-55) has found that the density of ordinary gypsum increased fairly rapidly when immersed in Clerici solution of high density due, presumably, to the formation of thallium sulphate, and that after an immersion period of 42 hours the density of the mineral was in excess of 4. Holzner (1933) and Gruner (1935, p. 704) have shown that minerals of the stilpnomelane group and glauconite will take thallium into their structures when treated with solutions of thallium salts; and further Gruner (1935) has observed that the density of glauconite increased from 2.81-3.02 after being boiled in thallium nitrate for 4 hours. Admittedly this was most drastic treatment and not comparable to the conditions to which a mineral would be subjected under ordinary circumstances, but significant alterations in the densities of minerals may occur within the time required to match the density of Clerici solution with that of a mineral grain, or particularly the time spent separating a pure sample of a mineral from a rock powder. For example, a fragment of chabazite weighing 8.6 mgm. had its density of 2.11, as determined with the Berman balance, increased to 2.21 after 35 minutes in Clerici solution.<sup>7</sup> Further, a tendency for the density of montmorillonite to increase during centrifugal separation in Clerici solution has been noticed by the writer. Therefore it cannot be held that Clerici solution is entirely "stable and inert toward all water-insoluble minerals at ordinary temperatures" (Jahns, 1939, p. 117), and it is deemed advisable to avoid using Clerici solution in work involving minerals showing base exchange properties.<sup>8</sup> This will mean no hardship since such

<sup>7</sup> Zeolites with very high thallium content have been prepared by Hey and described by him in a number of papers (1932, etc.) but their nature has little bearing on the subject in hand since they were prepared by drastic dry fusion methods.

<sup>8</sup> A similar objection may be raised to the use of Thoulet's solution (a potassium mercuric iodide and also known as Sonstadt's solution) since Hille-

minerals generally have densities less than 3.2 and hence methylene iodide-bromoform and bromoform-acetone mixtures may be substituted for Clerici solution with no inconvenience.

Clerici solution is an expensive material to use, and on those occasions when a liquid of lower density will suffice, it has been found convenient to use the cheaper thallium formate alone, for at a temperature of approximately 30°C. a saturated solution of this salt has a density of approximately 3.60-3.65. Since the solubility of the formate increases very rapidly with the rise of temperature (Sullivan, 1927, p. 21, fig. 10) it is possible to use formate solutions for separations at much higher densities if the operations are carried out in some type of simple calorimeter.

### *Preparation of Black Sands, Dredge, and Panned Concentrates for Mineralogical Investigation*

These samples have high percentages of heavy minerals, sometimes as high as 95 per cent, but rarely less than 40 per cent; for this reason the methods adopted differ considerably from those used for the examination of heavy residues from normal sandstones, siltstones etc. Since no two samples are ever quite alike, some variation of the procedure is often necessary. A brief preliminary examination with hand-lens and microscope, and perhaps some screening, should always be made in order to devise the best procedure.

1. A portion of the original sample, about 75-100 gms., is weighed and washed. If the mineral grains are heavily coated with iron oxide as is often the case with dune-sands, black sands from deep leads, and dredge concentrates,<sup>9</sup> the iron

brand (1913, p. 439) observed that during use of this liquid for the separation of tyuyamunite (a type of calcium-bearing carnotite) most of the calcium therein was replaced by potassium with profound changes in the optic axial angle. And further Walker (1922, p. 101) found that gmelinite with 0.69 per cent  $K_2O$  and 10.08 per cent  $Na_2O$  when suspended in Sonstadt's solution for 20 minutes underwent a profound chemical and physical change; an analysis of this zeolite after such treatment showed 14.86 per cent  $K_2O$  and only 1.20 per cent  $Na_2O$ . Similar results were obtained with okenite.

<sup>9</sup> Fragments of steel from buckets, screens, jigs, etc. often contaminate dredge concentrates and, unless the latter are dried efficiently and quickly before samples are bagged, the minerals therein may be found later to be extensively coated with rust.

stain should be removed before screening, and for this the ammonium sulphide method of Drosdoff and Truog (1935) is most convenient, because little or no solution of any of the constituent minerals will occur.

2. The sample is screened through a nest of wire sieves with openings of 4, 2, 1, and 0.5 mm. in diameter; any material finer than 0.5 mm. is best split up with bolting silk screens, although standard wire screens are also used.

3. Each grade-size is weighed after which ferro-magnetic minerals are removed with the A. C. hand-magnet.

4. The ferro-magnetic fraction of each grade-size is weighed.

5. Each fraction of para-magnetic and non-magnetic minerals is separated in bromoform by the open dish method; generally the quantities of minerals with densities  $<2.85$  are small and the different grade-sizes of these are placed in tubes, labelled, and reserved for later study if that is required.

6. The minerals<sup>10</sup> retained on screen numbers<sup>11</sup> 5 and 10 are hand-sorted, and for this purpose spot-test tiles with 12-16 hollows are very useful in which to collect the different varieties. Sorting according to color has been found most profitable, although subdivision of this coarse material of the basis of density or magnetic susceptibility is sometimes more helpful.

7. For many samples it is advisable to fractionate further a representative portion of each of the +18, +35, +60, +120, +230, and -230 grade-sizes into fractions with densities  $<3.85$  and  $>3.85$  using Clerici solution.

8. Each of the fractions prepared in the sixth step are now split into paramagnetic and non-magnetic portions; often it is useful to split up the paramagnetic assemblages into samples of different magnetic susceptibility.

9. Precise identification of the minerals in the assemblages of the different fractions is now undertaken.

10. Permanent mounts in both hyrax, aroclor 4465, and Canada balsam are made of all samples of the three finest grades but it is generally of little use to make micro-preparations

of coarser materials; these should be preserved in small glass tubes for future reference.

#### *Grain Counting and Determination of Mineral Frequencies*

The relative proportions of the different heavy detrital minerals were determined by counting carefully sized preparations. The latter precaution is most necessary since, if ungraded material is used and the range of grain-sizes is considerable, the sizes of these grains must certainly be taken into account (Stuart, 1927). To enable counting to be carried out quickly and yet in a representative manner a mechanical stage was mounted on the microscope; the stage was racked slowly from left to right and only those grains that touched the intersection of the cross-hairs were counted. At the end of the lateral run the stage was racked an appropriate distance upwards or downwards as the case warranted, and another lateral run was commenced, this time from right to left. If the grains to be counted are fairly large, *viz.* -60 +120, it is expedient to count all the grains as they touch the vertical cross-hair during the lateral runs. In every example studied at least 250 grains were counted, and usually 400 were dealt with in this manner. The latter number appeared to be quite adequate since several counts at different times of the same preparation did not show a maximum variation in excess of 5 per cent for the more plentiful constituents. Counting of an additional number of grains uses up a great deal of time and does not contribute importantly to greater accuracy as Dryden's (1931) curves clearly show.

There is no general agreement as to method of representing mineral frequencies. In the past the writer has employed straight percentages of the total number of grains counted, or represented the minerals present as predominant (p), abundant (a), fairly abundant (fa), minor (m), or rare (r). Actual percentages of minerals are not readily compared in some instances, and the inherent difficulties of sampling one's material does not warrant the accuracy implied by strict percentages. The second method of designating the proportions present by names has considerable use in those cases where large

<sup>10</sup> Hereafter the minerals discussed are those with densities  $> 2.85$ .

<sup>11</sup> U. S. sieve series.

grains are being counted or where, owing to the percentage of opaque constituents, identification of some grains or crystals is open to doubt. The use of names alone without any specification of approximate percentage range makes interpretation by other workers difficult. For instance, what one observer might consider to be a fairly abundant constituent another might believe to be abundant or even predominant. Unfortunately, several schemes involving the use of symbols are in use, such as those suggested by Watts (Milner, 1940, p. 457), Salmojraghi (Boswell, 1923, p. 226) and others, and assessment of these different terms for correlative purposes is not often completely satisfactory.

Therefore, in order to represent the relative abundance of the different minerals present in the three finest grade-sizes, for in these fractions fairly accurate and complete mineral identification was possible, the method used by the geologists of the Burmah and Assam Oil Companies is employed (Evans, Hayman, and Majeed, 1934, p. 39 *et seq.*) in this study. This system overcomes "the difficulties of plotting a truly logarithmic scale by adopting a series of frequency numbers most of which are in geometric progression. This scale is straight forward down to frequency of 3, but for the lower numbers is slightly artificial" (p. 40-41). Their scale is as follows:

Frequency	Approximate percentage
8+	90-100 per cent.
8	75-89
8-	60-74
7+	45-59
7	35-44
7-	28-34
6+	23-27
6	18-22
6-	14-17
5	7-13
4	4-6
3	2-3
2	1-2
1	$\frac{1}{2}$ -1
1*	1 grain only

This system makes comparison between samples simpler, and the minor irregularities in counting due to the personal factor, misidenti-

fication of odd minerals, and so on, were reduced in importance; it also has the decided advantage of "weighting" the smaller percentages, and any important differences in the frequencies of minor or uncommon minerals are accentuated.

For grade-sizes of 60-mesh or coarser the following system has been used:

p	= predominant (> 60 per cent)
a	= abundant (20-59 per cent)
fa	= fairly abundant (5-19 per cent)
m	= minor constituent (< 4 per cent)
r	= rare.

#### GRAIN-SIZE OF THE DREDGE CONCENTRATES, BLACKSANDS, ETC.

In general, the mineral assemblages of the dredge concentrates were more complex than the blacksand paystreaks found on open beaches. In some respects this was due to the rarity or absence in most samples from the beaches of material with grain-size finer than 230-mesh; in about 70 per cent of such samples, grains with diameters less than 125 microns were almost absent. In dredge concentrates, on the other hand, material finer than 120-mesh often represented a large proportion of a total sample. This explains, for instance, why uranorthite and biaxial  $\text{ThSiO}_4$  are only very rare constituents of most of the black sands of the beaches between Bruce Bay in the south and Saltwater Creek further to the north; the size fraction in which the greater proportion of these minerals are to be found, -120 +230 mesh, is generally absent from such concentrations, but has been carried offshore to where finer particles can settle. Also the conditions for concentration of minerals on beaches is vastly different from those obtaining on the jigs and tables of a dredge, since the latter are adjusted to the optimum position for retention of high-density materials such as gold.

The black sand paystreaks found along the western coast beaches of South Island generally have rather simple assemblages and contain opaque minerals (chiefly ilmenite) and garnet as the dominant constituents, if some contaminating quartz and feldspars are neglected; they usually show little likelihood of any economic value except for the gold that may be



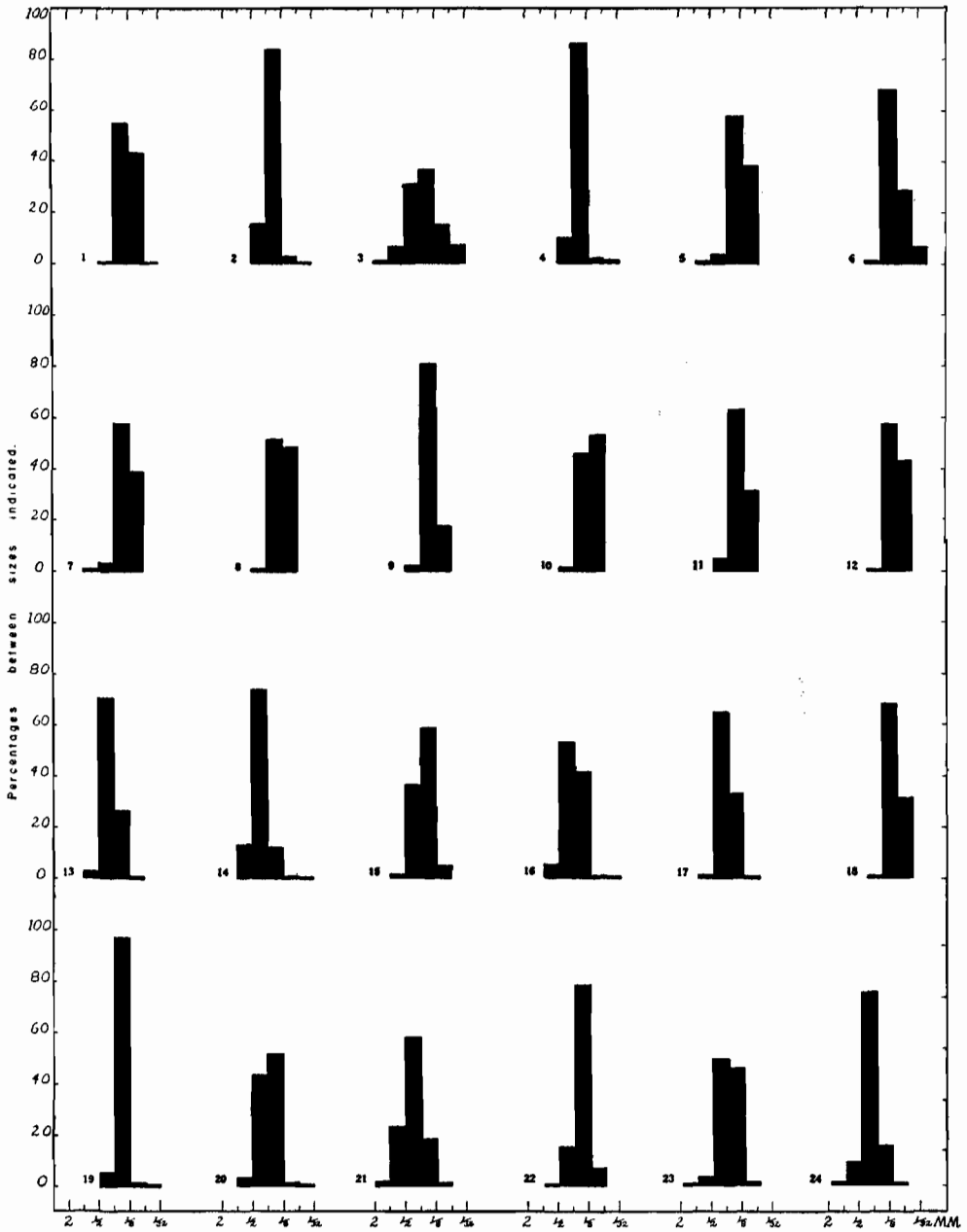


FIGURE. 3—HISTOGRAMS OF WESTLAND AND SOUTHWEST NELSON BEACH SANDS

1. Blacksand, 1½ miles north of Cape Foulwind; 2. Grey sand, 1½ miles north of Cape Foulwind; 3. Mouth of Fox River; 4. Dune sand, Bruce Bay; 5. 1 mile north of Cape Foulwind; 6. Wainui Inlet; 7. West of Charleston Hotel; 8. Karamea Beach; 9. 1 mile south of Buller River mouth; 10. Tauranga Bay, ¼ mile south of Cape Foulwind; 11. North end of Nine Mile Beach; 12. Nine Mile Beach, south of Westport; 13. 200 yards north of Five Mile Bluff, Okarito; 14. Five Mile Beach, Okarito; 15. 13 miles north of Greymouth; 16. Ross; 17. 14 miles north of Greymouth; 18. 15 miles north of Barrytown; 19. Paystreak, 14 feet below surface, Gillespie's Beach; 20. 3 miles south of Poerua River; 21. Gillespie's Beach; 22. Hunt's Beach; 23. Bruce Bay; 24. Center of Three Mile Beach, Okarito.

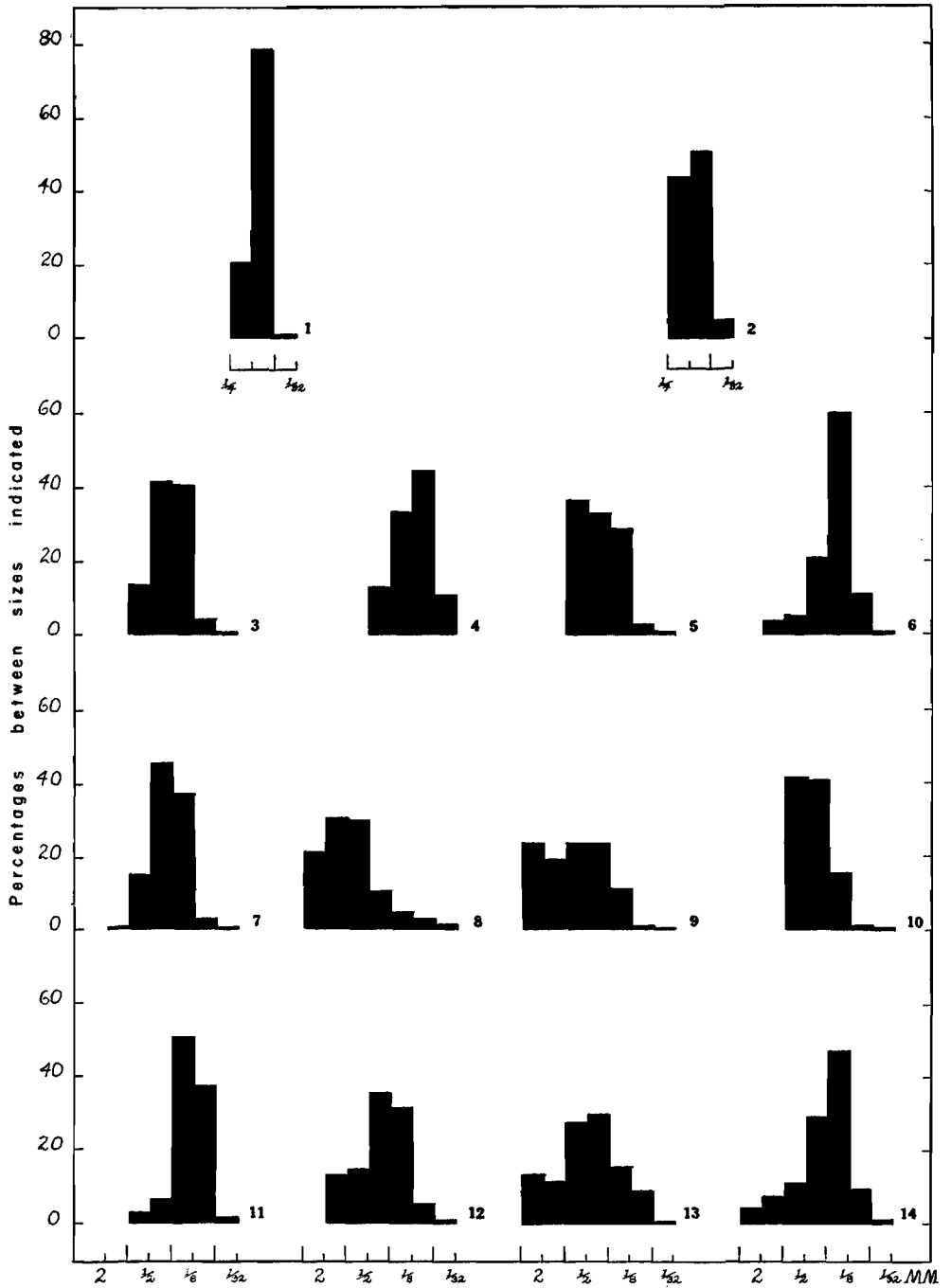


FIGURE 4—HISTOGRAMS OF DREDGE CONCENTRATES

1. Barrytown; 2. Atarau; 3. Kaniere; 4. Okarito; 5. Lowburn; 6. Ngahere; 7. Red Jacks; 8. Blackball; 9. Rimu; 10. Arahura; 11. Gillespie's Beach; 12. Snowy River; 13. Grey River; 14. Slab Hut.

contained in them. However, the beach sands, dune and terrace materials of the central to southern Westland coastal strip contain interbedded with the mineralogically simple black-sand lenses or paystreaks, the finer-grained silts in which thorites are usually found. Having determined that most minerals of any value were restricted for the most part to the finer grades, size analysis was a rapid means of determining the possible economic value of a beach sand. Size analyses of samples of some of these sediments are illustrated in Figure 3, and it will be observed that most of these sands are well graded since the bulk of the particles are restricted to either one or two size fractions.

The grading of particular dredge concentrates varied to some extent from time to time but the range in any individual case was not excessive. Therefore, for the sake of comparison with the beach sands, grading analyses of at least three samples taken at different times from a number of dredges have been averaged and the results presented in histograms (Fig. 4).

In some instances magnetite and other ferromagnetic material had been removed from samples of dredge concentrates before they were made available for this work but where such material was present when collected or sent to the writer, it was removed electromagnetically before size analyses were made.

## PART 2. MINERALOGY

The chemical and physical properties of all the minerals in the concentrates, sands, and gravels collected by, or made available to the writer have been determined as completely as possible, and the outcome is detailed in this section of the work. A few grains which defied satisfactory diagnosis, since they are never more than rarities, are listed as unknowns without any qualifications. The occurrences of the mineral species, with their frequencies are set out in Table 19, but every sample studied has not been listed here. For example, of over 30 concentrates available from the Arahura River, three analyses that appeared fairly representative have been listed. Occasionally the averaged analyses of four or five concentrates, obtained from a dredge or sluicing claim over a period of time are listed. Other properties such as solu-

bility, stability, and alteration have been discussed when needed and a few of the minerals which have somewhat unusual properties have been discussed in some detail.

**ACTINOLITE:** Actinolitic amphiboles have been recorded in concentrates of two dredges, Lowburn Ferry, near Cromwell in Central Otago, and Snowy River, in Southwest Nelson, and from pannings of the sands and gravels of Hokitika River and Kyeburn Stream and its tributaries. Actinolite is most abundant in Lowburn material but does not make up more than 2 per cent and 1 per cent of the -230 and -120 +230 grades respectively; it occurs in short, prismatic crystals with weak but distinct pleochroism: X = very pale yellowish-green; Y = green; Z = bluish-green. The beta refractive index was determined as  $1.648 \pm 0.003$ , with  $\gamma \wedge c = 17-19^\circ$ , and  $2V$  approximately  $60^\circ$ . The amphibole is therefore comparable to the variety frequent in the green schists of Western and Central Otago (Turner, 1933; Hutton, 1940a, p. 43), and is an actinolitic member of the actinolite-glaucophane series as defined by Kunitz (1930). Similar properties were recorded for Hokitika River material. Occasional acicular amphibole fragments, present in -230 mesh fractions of Bruce Bay beach sand concentrates, differed somewhat from the actinolite just described. Here the Z-vibration direction is blue to mauve, the birefringence is lower, about 0.014, and a slight dispersion is evident. The amphibole is similar in some respects to crossite from Coronet Peak (Hutton, 1938b, p. 210-211) but differs from that mineral in that the axial plane is parallel to (010). This Bruce Bay mineral is believed to be an aluminous member of Kunitz (1930) glaucophane-riebeckite series.

**ANATASE:** Anatase (Pl. 2, fig. 33) is a rare constituent of a beach sand (Wainui Islet) as simple pyramidal forms with prominent development of basal plane  $c$  (001). Striations are well developed parallel to the prism-pyramid join. The color is yellow to yellowish-brown with only faintly perceptible dichroism; tiny clouds of fine dust-like material, presumably magnetite or ilmenite, were the only inclusions noted.

**ANDALUSITE:** Andalusite was recognized only in the finest fraction (-230 mesh) of Snowy

River material. It formed irregularly terminated, prismatic, unaltered grains, devoid of inclusions and with distinctive pale-pink to pale-green pleochroism. The refractive index

$\beta$  was found to be 1.634 and 1.636 for two fragments.

APATITE: Although apatite is present in most of the samples examined, the percentage in

PLATE 1.—TYPICAL FRAGMENTS AND CRYSTALS OF ZIRCON AND HYACINTH

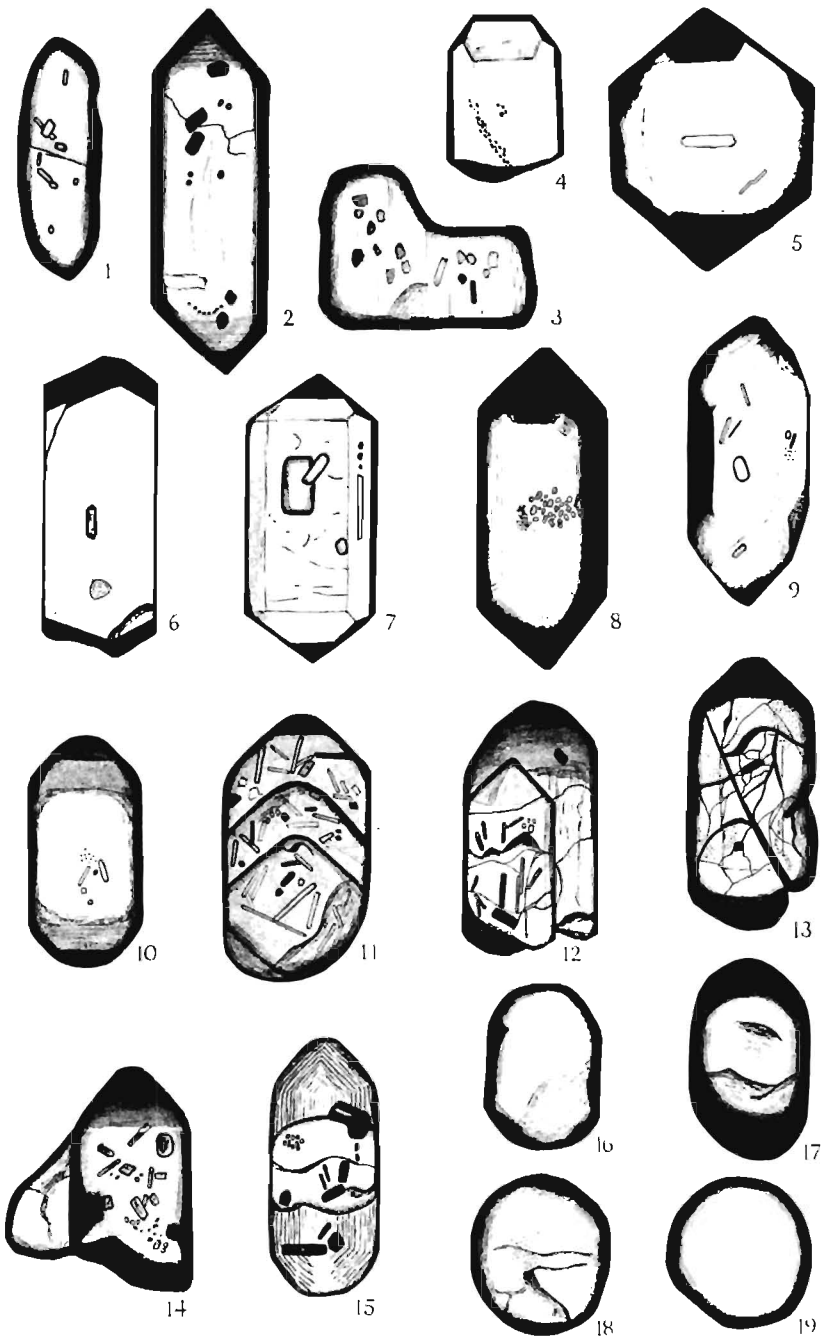
Figure

1. Zircon, showing moderate degree of rounding. Barrytown.  $\times 90$ .
2. Zircon, with simple development of first order prisms and pyramids. Gillespie's Beach.  $\times 125$ .
3. Zircon, probably a crystal broken in a rather unusual manner and subsequently subjected to considerable abrasion. Kaniere.  $\times 105$ .
4. Zircon showing development of (110) and (100) prisms, with (111) pyramids. The (001) face developed here is unusual. Atarau.  $\times 200$ .
5. Zircon with (110), (100), (111), and (101). Short stumpy habit uncommon. Recent beach sand, Wainui Inlet.  $\times 105$ .
6. Zircon, common type. Barrytown.  $\times 140$ .
7. Zircon, simple type, not common. Barrytown.  $\times 105$ .
8. Zircon with development of (110), (100), (111), and (311). Okarito.  $\times 105$ .
9. Zircon, common type. Barrytown.  $\times 115$ .
10. Zircon, purple variety of characteristic simple habit. Ngahere.  $\times 65$ .
11. Zircon, purple variety with zonary structure. Ngahere.  $\times 65$ . Mounted in hyrax.
12. Zircon, purple variety including a second sharply euhedra crystal of purple zircon. Atarau.  $\times 105$ .
13. Simple crystal of purple zircon with faint zoning and showing very extensive fissuring. Ngahere.  $\times 75$ .
14. Simple purple zircon with outgrowth of similar color. Ngahere.  $\times 43$ .
15. Purple variety of zircon with delicately developed zonary structure, and a nucleus of intensely abraded purple zircon. Atarau.  $\times 75$ . Mounted in hyrax.
16. Well rounded purple zircon, devoid of inclusions and without zoning. Ngahere.  $\times 80$ .
17. Well rounded purple zircon. Ngahere.  $\times 80$ .
18. Purple zircon, well rounded. Ngahere.  $\times 80$ .
19. Extremely well rounded purple zircon. Ngahere.  $\times 80$ .

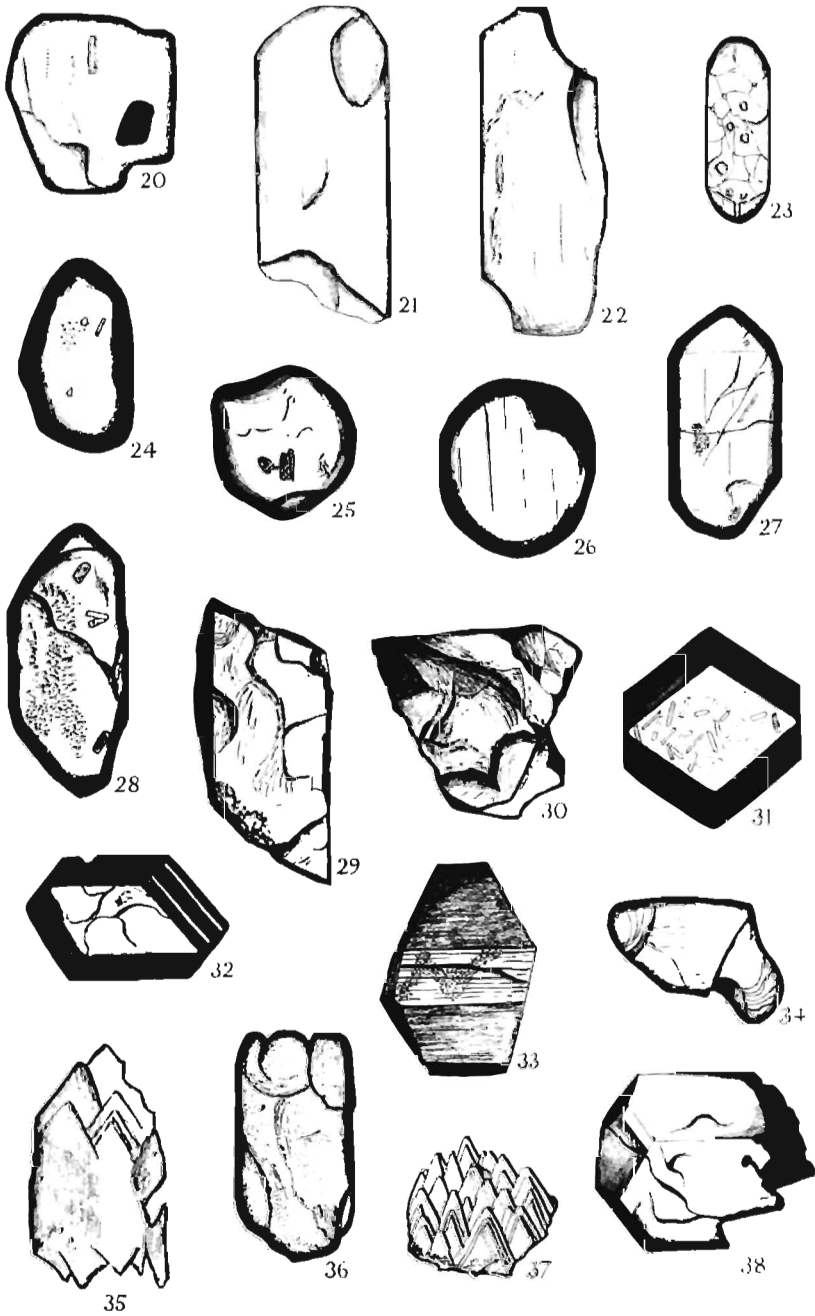
PLATE 2.—TYPICAL HEAVY DETRITAL MINERALS

Figure

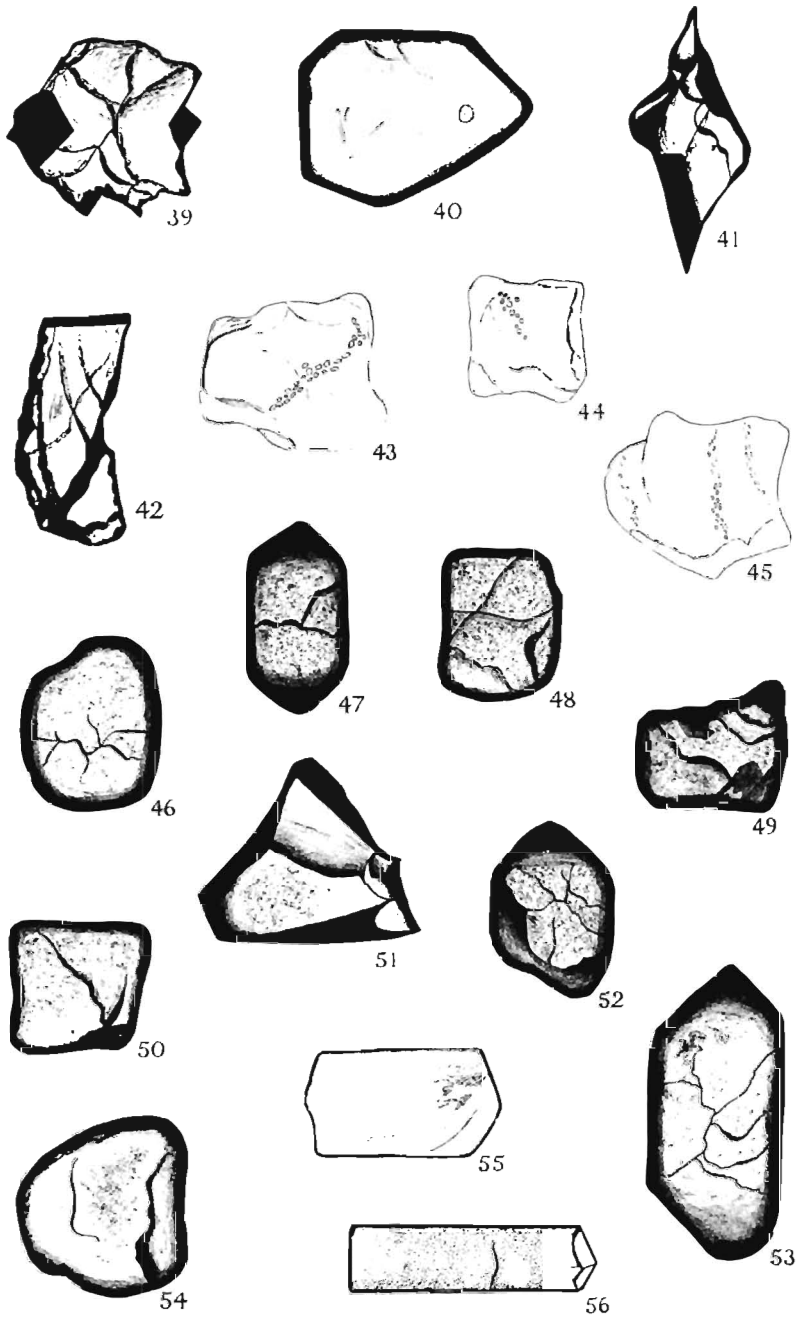
20. Apatite, Arahura.  $\times 120$ .
21. Apatite, simple crystal and little worn. Arahura.  $\times 145$ .
22. Apatite. Arahura.  $\times 145$ .
23. Idioblastic ferrous epidote with characteristic system of fractures. Lowburn.  $\times 50$ .
24. Worn grain of almost colorless monazite. Barrytown.  $\times 180$ .
25. Monazite. Barrytown.  $\times 180$ .
26. Well rounded monazite. Barrytown.  $\times 125$ .
27. Euhedral tablet of monazite parallel to (100) showing poor development of (010) cleavages. Barrytown.  $\times 125$ .
28. Monazite, similar to fig. 27. Atarau.  $\times 75$ .
29. Cassiterite. Barrytown.  $\times 105$ .
30. Cassiterite. Barrytown.  $\times 105$ .
31. Sharply euhedral spessartite. Lowburn.  $\times 85$ .
32. Almandine. Arahura.  $\times 125$ .
33. Yellowish-brown anatase. Recent beach sand, Wainui Inlet.  $\times 125$ .
34. Somewhat worn grain of cinnabar, showing perfect cleavage. Barrytown.  $\times 105$ .
35. Scheelite. Barrytown.  $\times 105$ .
36. Scheelite. Barrytown.  $\times 105$ .
37. Fragment of scheelite. Barrytown.  $\times 145$ .
38. Euhedral titanite. Recent beach sand, Wainui Inlet.  $\times 40$ .



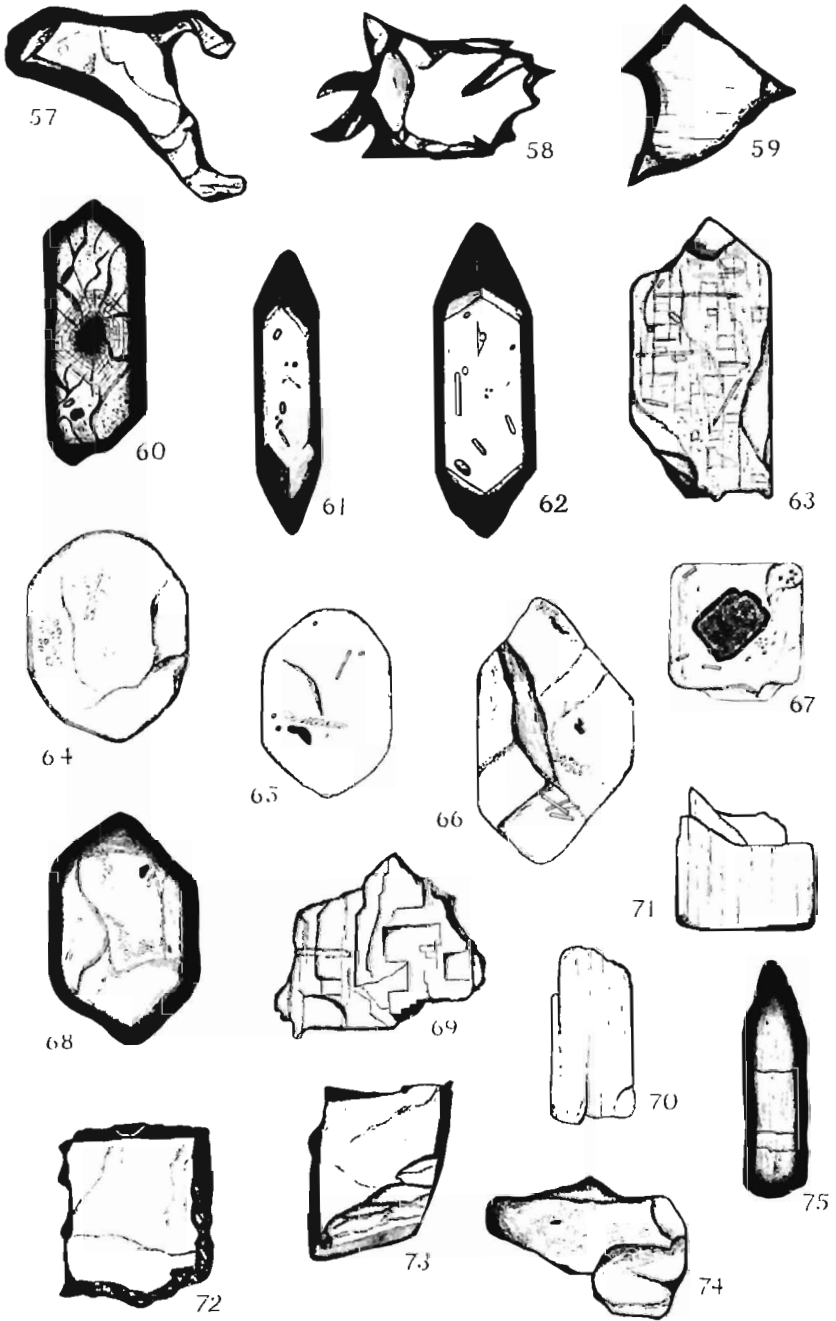
TYPICAL HEAVY DETRITAL MINERALS



TYPICAL FRAGMENTS AND CRYSTALS OF ZIRCON AND HYACINTH



TYPICAL HEAVY DETRITAL MINERALS



TYPICAL HEAVY DETRITAL MINERALS



the different assemblages is never high except in beach sands from the Ligar Bay—Separation Point area in north-west Nelson. It usually occurs as slightly worn, uni-terminated, rather stumpy, prismatic crystals (Pl. 2, figs. 21–22), although well worn or irregularly shaped anhedral (Pl. 2, fig. 20) are usually present, and dominant in some cases. The grains of apatite

## PLATE 3.—TYPICAL HEAVY DETRITAL MINERALS

## Figure

39. Titanite. Wainui Inlet.  $\times 30$ .
40. Titanite. Wainui Inlet.  $\times 150$ .
41. Titanite. Wainui Inlet.  $\times 60$ .
42. Titanite. Wainui Inlet.  $\times 35$ .
43. Topaz. Okarito.  $\times 235$ .
44. Topaz. Okarito.  $\times 165$ .
45. Topaz. Okarito.  $\times 135$ .
46. Worn grain of uranothorite. Gillespie's Beach.  $\times 80$ .
47. Uranothorite, showing simple development of (110) and (111). Gillespie's Beach.  $\times 90$ .
48. Uranothorite, common rectangular type. Gillespie's Beach.  $\times 70$ .
49. Uranothorite. Gillespie's Beach.  $\times 60$ .
50. Uranothorite, common rectangular type. Gillespie's Beach.  $\times 60$ .
51. Uranothorite. Gillespie's Beach.  $\times 75$ .
52. Uranothorite. Harihari.  $\times 60$ .
53. Sharply euhedral grain of uranothorite. Harihari.  $\times 115$ .
54. Uranothorite. Harihari.  $\times 75$ .
55. Tourmaline, clear type. Barrytown.  $\times 180$ .
56. Tourmaline, typical "schist" type. Lowburn.  $\times 40$ .

## PLATE 4.—TYPICAL HEAVY DETRITAL MINERALS

## Figure

57. Strongly etched garnet. Rimu Dredge.  $\times 105$ .
58. Strongly etched garnet. Snowy River Dredge.  $\times 125$ .
59. Sub-euhedral table of  $\beta$ -zoisite, oriented  $\perp$  to Bxa, and showing (010) cleavage. Grey River Dredge.  $\times 195$ .
60. Hyacinth, showing fine zonary structure surrounding a nucleus of opaque material. Slab Hut Dredge.  $\times 175$ .
61. Colorless zircon showing prominent development of steep pyramid (331) and very fine zonary banding. Snowy River Dredge.  $\times 100$ .
62. Colorless euhedral zircon showing development of steep pyramid (331). Snowy River Dredge.  $\times 100$ .
63. Hypersthene with pale brown inclusions (schiller-structure). Snowy River Dredge.  $\times 215$ .
64. Moderately rounded euhedron of xenotime; embedding material is hyrax ( $n = 1.70$  approx.). Snowy River Dredge.  $\times 215$ .
65. Same description as figure 64.
66. Same description as figure 64.
67. Slightly worn grain of xenotime oriented with Z perpendicular to the plate; such grains give centered uniaxial interference figures. Mounting medium is hyrax. Large inclusions of brown unidentified mineral with high refractive index. Snowy River Dredge.  $\times 110$ .
68. Slightly worn grain of xenotime mounted in Canada balsam. Snowy River Dredge.  $\times 215$ .
69. Irregularly terminated bladed crystal of kyanite. Red Jacks Dredge.  $\times 180$ .
70. Slender, flattened prism of sillimanite. Rimu Dredge.  $\times 140$ .
71. Stumpy prism of sillimanite. Snowy River Dredge.  $\times 140$ .
72. Colorless (001) cleavage fragment of monazite showing traces of cleavages parallel to (100) and (010). Blackball Creek Dredge.  $\times 240$ .
73. Same description as figure 72.
74. Irregular grain of staurolite with marked conchoidal fracture. Blackball Creek Dredge.  $\times 105$ .
75. Deep red prismatic grain of rutile with rounded terminations. Blackball Creek Dredge.  $\times 105$ .

are usually colorless and water-clear with a complete absence of dichroism. Inclusions are not distinctive but magnetite, titanite, and zircon have been recognized; strings of minute cavities have been observed in some grains, with swarms of indeterminate needles, oriented parallel to the *c* crystallographic axis, in others. In the Ligar Bay beach sands apatite is such an important constituent that it was possible to study it in greater detail than in other occurrences. In this material the apatite occurs in stout prismatic crystals with a ratio breadth: length of approximately 1:2 in the finer grade-sizes; in the coarser screenings, viz. -60 +120, because of considerable wave action, the crystals are more equant, with subhedral to anhedral forms predominating. In the finer grades, apatite crystals are usually terminated at both ends by basal plane and a combination of pyramids. An imperfect cleavage, parallel to (0001) can be observed in most grains, and usually the shape of fractured grains has been determined by this incipient cleavage direction. Inclusions are fairly common and more interesting in this material; the following details have been noted: (1). Tiny grains of what seem to be sharp euhedra of apatite. (2). Lines of brown needle-like bodies, arranged in bands, both bands and needles oriented parallel to the *c* crystallographic axis. (3). Patches or clouds of dust-like unidentifiable material that gives the grains a smoky aspect when viewed under low magnification. (4). As in (2) above, but whereas the needles are arranged parallel to the *c* axis the bands are perpendicular thereto. (5). Rows of tiny globules, possibly gas filled, perpendicular to the *c* direction. Measurements of refractive indices for a number of crystals from the Ligar Bay area showed a range as follows: E = 1.633-1.635 ± 0.001; O = 1.638 - 1.640; O - E = 0.005. The mineral therefore appears to be a normal fluorapatite; microchemical tests showing only a trace of chlorine and an absence of hydroxyl support this conclusion. Further qualitative chemical tests (following the method of Watson, 1935, p. 28) proved that silica was present in crystals devoid of inclusions, but the location of the silicon in the structure has not been determined. It is sufficient to state at this stage that replacement of P<sup>5+</sup> by Si<sup>4+</sup> would require a balancing substitution to occur else-

where in the structure, which could be effected with replacement of Ca<sup>2+</sup> by Y<sup>3+</sup> as Wickman (1943, p. 387-8) has suggested. Extensive substitutions of this nature are known as in the mineral britholite (Hägele and Machatschki, 1939) and its isomorph, the yttrium silicate apatite, abukumalite (Hata, 1938a). It would be interesting to determine whether the distinct range of hardness found in different specimens of apatite can be correlated with the CaP ⇌ YSi substitution, since a hardness of 6 has been reported for abukumalite.

**BARITE:** Very rare, slightly abraded cleavage fragments of barite recognized among the finest fraction of concentrates from Grey River dredge are colorless and devoid of inclusions, the  $\beta$  vibration direction of the refractive index ellipsoid was determined as 1.635-1.637. They appear to be basal sections, their shape determined chiefly by cleavage parallel to 001.

**BIOTITE:** As expected of a relatively low-density and flaky mineral, biotite is a minor accessory, although it occurs in many of the samples studied. By way of contrast, heavy residues from a great many Tertiary sediments from Westland localities are exceedingly rich in brown mica. Red-brown plates with strong to intense pleochroism and small optic axial angle are most frequent. The mica may be very pale brown (Ligar Bay) or greenish-brown (Arahura River); in the latter some of the mica is oxidized in part to reddish-brown plates, and the mineral appears to become uniaxial or very nearly so.

**CASSITERITE:** Cassiterite, though recognized in every Westland and Nelson dredging examined, is no more than a mineralogical curiosity except in Ngahere material where it makes up approximately 13 per cent of the -60 +120 screening, and Blackball samples. Generally it occurs in conchoidally fractured anhedral or pronounced irregular form. Grains similar to those illustrated (Pl. 2, figs. 29-30) are typical; rarely traces of crystal faces were observed and twinned crystals are rare.

Most cassiterites are deep red to reddish-brown; pale to colorless examples are much less common. The strongly colored varieties exhibit intense dichroism quite comparable to that characteristic of members of the tapiolite-mossite series. In the preliminary stages of the

study the exact nature of the mineral was in some doubt. Dichroism in most examples followed the scheme: O = pale greenish-yellow. E = deep reddish-brown (blood-red in some instances). Absorption: E > O.

Although a uniaxial positive character was general, biaxial interference figures with small optic axial angles (approximately  $10^\circ$ ) were found, the sign, however, remaining positive. The biaxial character of cassiterites that do not show strain effects is not easy to explain, but Gotman's (1939, p. 472) assumption that such anomalies are connected with the development of zonary structures is not supported. Although zoning was observed in a few cases, some unzoned crystals are biaxial.

Refractive index determinations by the immersion method on several varieties of cassiterite gave results as follows:<sup>12</sup>

Clear red	=	1.996
Semi-opaque red	=	1.994
Deep red-brown	=	$\begin{cases} 1.998 \\ 2.001 \\ 2.008 \end{cases}$
Zoned cassiterite:		
Red central zone	=	1.997
Pale brown peripheral zone	=	1.993

These values accurate to  $\pm 0.003$ , compare with those generally recorded (Milner, 1940, p. 259; Winchell, 1933, p. 52), although the refractive index of the ordinary ray in one deep red-brown variety is slightly higher than in normal cassiterite.

Density determinations gave a range of 6.72–6.91. A distinctly blotchy effect characterizes much of the material examined; this feature has been commented upon by other writers (Milner, 1940, p. 259).

The intensity of absorption in these cassiterites distinguishes them from those previously described from New Zealand. The cassiterite from the eluvial deposits of the Tin Range, southern Stewart Island (Williams, 1934, p. 352) is opaque or pale amber in thin splinters, an observation confirmed by the writer's examination of several specimens of cassiterite from this and other localities in the vicinity of Port Pegasus. Cassiterite from pegmatites in

Doubtful Sound area is colorless (Turner, 1937b, p. 242–243), although some (Hutton and Turner, 1936, p. 259) in Tertiary sandstones from the Lake Manapouri area was deep red-brown but dichroism was not distinctive. However Rastall (1919, p. 272) has recognized cassiterite with red to grayish-brown dichroism in heavy residues from the Lower Greensand of Eastern England, whereas Scrivenor (1919, p. 123–124) recorded cassiterite from Siam with an intense dichroism, E = deep red, O = green, which he believed was due to the presence of titanium, although the analysis showed only 0.17 per cent of  $\text{TiO}_2$  to be present. Groves (1932, p. 210) has described very pale or nearly colorless cassiterite with deep blood-red zones, also unzoned varieties with intense dichroism, brownish-green to deep blood-red (1932, p. 207), and has found blood-red cassiterite in the detritus from the Dartmoor granites (1931, p. 74). Among the minerals of the Center Strafford pegmatite, Switzer (1938, p. 817) found cassiterite with colorless to dark reddish-brown dichroism, and Stheeman (1932, p. 144) noted a pink tint in zonal cassiterite from Uganda.

The intensity of absorption of some of the Westland cassiterite and its physical similarity to tapiolite suggested the presence of tantalum; certainly the ionic radii of tantalum ( $\text{Ta}^{5+} = 0.68 \text{ \AA.}$ ) and tin ( $\text{Sn}^{4+} = 0.74 \text{ \AA.}$ ) are close enough to allow some substitution without any rupture of the structure. With this in view, a portion of the concentrates from Ngahere Dredge was treated by screening and electromagnetic methods and in a sample containing a high percentage of cassiterite and somewhat contaminated with zircon, Mr. Seelye found 2.3 per cent of  $\text{Ta}_2\text{O}_5$ <sup>13</sup>; thus tantalum cassiterite (ainalite of A. E. Nordenskiöld or tantalocassiterite of Schoeller, 1937, p. 31) would appear to be an appropriate term for the red Westland cassiterite. Tantalum in cassiterite<sup>14</sup>

<sup>13</sup> The absence of niobium may be unusual since, although niobium is found in the second and tantalum in the third long periods, their ionic dimensions are almost identical as a result of the lanthanide contraction, and their presence together in cassiterite might be expected.

<sup>14</sup> While this work was in manuscript form, Liebenberg (1946) has shown that the dichroism of cassiterites from S. W. Africa and S. Rhodesia is due to small quantities of tantalum and niobium in solid solution.

<sup>12</sup> The values for  $N_o$  only were determined as accurately as possible;  $N_e$  was not found but is in excess of 2.07 in the grains employed.

is probably far more common than it appears to be; Headden (1906, p. 167), Simpson (1910, p. 310), Schaller (1912), p. 18–22), and others have observed it, although analyses report not more than about 5 per cent of  $Ta_2O_5$ <sup>15</sup>, whereas the extent of the replacement of tantalum by tin in tapiolite, mossaite, or tantalite-columbite appears to be about 2.5 per cent<sup>16</sup>. Schaller (1912, p. 22) was of the opinion that miscibility of cassiterite and tapiolite was complete, but from a structural point of view there does not appear to be room for extensive substitution because some other ion, probably a trivalent one such as  $Fe^{3+}$  would have to be introduced into the lattice for compensatory purposes.<sup>17</sup> Laboratory experiments by Quensel (1941) have suggested that cassiterite may take up about 25 per cent of tapiolite into solid solution, but whether the compounds so formed are stable or metastable only at ordinary temperatures is not explained. On the other hand, Edwards (1940), finding that cassiterite with 3.86 per cent of  $Ta_2O_5$  from Greenbushes, Western Australia, contained inclusions of tantalite, concluded that at high temperatures cassiterite and tapiolite (and perhaps mossaite) are isomorphous but that exsolution of the greater proportion of one component occurs at ordinary temperatures. No analyses, together with evidence of homogeneity, are available, at least to the present writer, to show the existence of complete ionic substitution between cassiterite and tapiolite, and a recent re-investigation of a number of old specimens of ainalite and ixiolite by Åmark (1941) has proved that they are mixtures of cassiterite and columbite or tapiolite and not truly homogeneous min-

erals; in addition the X-ray studies of Brandt (1943) have clearly proved that a tin-bearing manganese tantalate from Varutrask, Sweden, is merely a mixture of cassiterite and columbite.

Polished sections of Westland cassiterites containing 2.3 per cent of  $Ta_2O_5$  showed no indication of inhomogeneity resulting from exsolution and it must be assumed, then, that the tantalum is in solid solution. This and the data supplied by Edwards clearly suggest that the limit of solid solution of tantalum in cassiterite lies somewhere between 2.3 and 3.86 per cent of  $Ta_2O_5$ .

**CHLORITE:** Chlorite group minerals are entirely restricted to the finer grade-sizes of the samples studied, and they belong to the prochlorite group as defined by Orce! (1927, p. 341); they compare closely with chlorites in the metamorphic rocks of Western Otago (Hutton, 1940a). For isolated flakes the following data were determined:

*Lowburn Dredge*  
 $\beta = 1.633-1.635; \pm 0.002$   
(in four samples)

*Elongation.* = Z  
*Dispersion.* =  $\rho > \nu$   
*Anomalous tints:* Purple to blue.

*Arahura Dredge*  
 $\beta = 1.615-1.620; \pm 0.002$   
(three samples)

*Elongation* = X  
*Dispersion* =  $\rho < \nu$   
*Anomalous tints:* brown.

The chlorites were typically pale grass-green and the pleochroism was faint but distinct in all cases. In occasional flakes some oxidation had occurred, resulting in (a) a change of color from green to greenish-brown or brown, and (b) a distinct rise in the refractive indices and birefringence (Winchell, 1936, p. 644–645). One oxidized chlorite gave the following data:  $\alpha = 1.637$ ;  $\gamma = 1.654$ ;  $\gamma - \alpha = 0.017$ . This change in chlorites results in a product not unlike some members of the stilpnomelane group of minerals, but most of the chlorites may be readily distinguished by their lower refraction (Hutton, 1938a, p. 187), weaker absorption, and absence of brittleness; members of the stilpnomelane group are always optically negative.

**CHLORITOID:** The only fragments of chloritoid

<sup>15</sup> 2.34%  $Ta_2O_5$  in cassiterite from Kara-su, Turkestan Range, Fioletova, 1940; 4.64%  $Ta_2O_5$  in cassiterite from Niriella, Ceylon, Palache *et al.*, 1944, p. 576; 3.26%  $Ta_2O_5$  and 0.04%  $Nb_2O_5$  in cassiterite from Kimito, S. W. Finland, Pehrman, 1945. (Whether these cassiterites are homogeneous is unknown.)

<sup>16</sup> 1.26%  $SnO_2$  in tapiolite from Skogböle (Schaller, 1912, p. 19); 0.53%  $SnO_2$  in tapiolite from Finland (Pehrman, 1932); apparently in traces only in tapiolite from Belgian Congo (Buttgenbach, 1933); Sn is absent in tapiolite from Cresciana (Casasopra, 1938); 2.16%  $SnO_2$  in tantalite from Brazil, (De Almeida *et al.*, 1944, p. 218).

<sup>17</sup> The electrical balance of the lattice could also be maintained by simultaneous addition of  $Sc^{3+}$  (Rankama, 1948, p. 29).

recognized during this investigation were found in the -35 +60 fraction of one of the concentrates from Snowy River dredge. The mineral was sieved with inclusions of quartz, sodic plagioclase, and magnetite, and a value of 1.721 was found for the beta direction of the refractive index ellipsoid; a distinctive pleochroism follows the scheme: X = pale bluish-green; Y = greyish-blue; Z = pale green;  $Y \geq X > Z$ . The birefringence was low, certainly not in excess of 0.01, and strong zoning was apparent. These properties are almost identical with those of chloritoid observed by the writer in slates in the Anatoki Valley, northwest Nelson.

**ALUMINIAN CHROMITE:** Aluminian chromite is the only member of the spinel group, excluding magnetite, of any importance in the samples studied. It is well represented among some of the coarser screenings, ranging up to 21 per cent in one sample (Blackball dredge), but is rare in finer fractions. Chromite particles range from sharply euhedral octahedra to well-rounded forms in the coarse grade-sizes; fragments with pronounced conchoidal fracture are usual in the finest screenings. The mineral is quite opaque except in the thinnest flakes, but observed in oblique illumination, the worn chromite grains had a strikingly smooth, brilliant, jet-black appearance, and if broken, a very pronounced conchoidal fracture; occasionally octahedra were noted with well developed natural etch marks in the form of deep triangular pits (Ngahere dredge) on the octahedron faces. Comparable etch-pits were produced artificially but with difficulty on chromite octahedra by treatment with perchloric acid (Frankel, 1940, p. 198-199), and treatment of the mineral grains for 5 minutes in molten potassium pyrosulphate had a similar effect. These properties, quite distinct from those shown by the associated opaque constituents, permitted reasonably accurate estimation of the quantities of this constituent. Confirmation of the identity of each grain was obtained by removing the particles on the point of a needle or by means of fine-pointed forceps, crushing them finely in clove oil directly on a glass slide if possible, and examining the powder in transmitted light. A yellowish-brown color is characteristic and in no instance were reddish tints observed.

Sufficient octahedra, or portions thereof, were separated from Slab Hut dredge concentrates in which they are particularly plentiful, by hand-picking beneath a binocular microscope, and quantitatively analyzed (Table 1).

The determination of ferrous oxide in refractory minerals is extremely difficult; several methods were tried by Mr. Seelye but none were entirely satisfactory, although Seil's<sup>20</sup> method gave the best results; however some preliminary experiments with Rowledge's (1934) sodium metafluoborate method gave promising results. Therefore before calculation of the structural formulae, correction of the FeO:Fe<sub>2</sub>O<sub>3</sub> ratio was made in order to satisfy the requirements of the spinel formula. Except for the small percentage of SiO<sub>2</sub> in analyses C and E, the type of ionic substitution is quite usual. SiO<sub>2</sub> has been ignored in these calculations because the writer has no definite information as to whether it is present as a mechanically mixed impurity or in solid solution in the spinellids. Careful microscopic examination of the purified and powdered minerals did not reveal any adhering serpentine, talc, or chlorite, and the writer would suggest that the silicon was in solid solution. Silica is not uncommonly recorded in analyses of members of the spinel family, and although it is not always certain that the analysed material was pure, silica has been recorded in very carefully purified spinel by Vincent (Tilley, 1938, p. 83), and strength is added to the suggestion of solid solution by the work of Rankin and Merwin (1918, p. 307) who found that synthetic spinel with about 5 per cent of SiO<sub>2</sub> appeared to be homogeneous.

For comparison with other chromites, the compositions of the New Zealand minerals may be expressed as end-members per unit cell.

*Viz.*

	B	D	F
Spinel	3.63	4.14	4.13
Magnesiochromite	1.69	1.55	1.66
Ferrochromite	2.01	1.95	1.73
Magnetite	0.67	0.36	0.48

Stevens (1944, p. 31) has conveniently classified the chromium-bearing spinels into six main groups by means of a ternary diagram, and if the analyses of the New Zealand chromites are

<sup>20</sup> J. Ind. Eng. Chem. Anal. Ed. 15 (1943), p. 189,

TABLE 1.—ANALYSES AND PHYSICAL PROPERTIES OF ALUMINIAN CHROMITES

	A	B	C	D	E	F	G	H
Cr <sub>2</sub> O <sub>3</sub> .....	36.37	38.29	43.46	43.67	42.80	43.45	35.5	46.16
Al <sub>2</sub> O <sub>3</sub> .....	24.72	26.03	24.60	24.72	23.65	24.01	26.2	10.89
Fe <sub>2</sub> O <sub>3</sub> .....	—	7.45	1.58	4.07	3.78	5.26	7.9	2.78
FeO.....	20.47	13.36	13.54	11.36	12.12	10.90	12.4	20.48
MgO.....	14.12	14.87	15.87	15.93	15.84	16.08	15.2	11.04
TiO <sub>2</sub> .....	1.54	—	0.34	—	0.46	—	0.3	—
SnO <sub>2</sub> .....	2.24	—	—	—	—	—	—	—
MnO.....	trace	—	0.24	0.25	0.17	0.18	0.1	0.26
SiO <sub>2</sub> .....	—	—	0.38	—	0.40	—	0.2	5.76
H <sub>2</sub> O.....	—	—	—	—	—	—	—	2.21
CaO.....	—	—	0.23	—	0.20	—	0.1	—
CoO.....	—	—	—	—	0.12	0.12	—	—
NiO.....	—	—	—	—	0.04	—	—	—
	99.46	100.00	100.24	100.00	99.58	100.00	99.2	99.58
n <sup>18</sup> .....	1.972	—	1.970	—	1.970	—	—	—
D. 20° C.....	4.67	—	4.67	—	4.66	—	—	—

A. Spinel from Slab Hut Dredge concentrate, 20 chs. 15° from Trig. S. T., Mawheriti S. D. Owing the small amount of the sample available and its extremely refractory nature, ratio FeO:Fe<sub>2</sub>O<sub>3</sub> was not determined; total is therefore reported as FeO. Analyst: F. T. Seelye.

B. Recalculation of analysis A to agree with spinel formula after exclusion of ilmenite and cassiterite.  
 C. Aluminian chromite separated from mesh-serpentinite, Cerberus Peak, Livingstone Range. Analyst: F. T. Seelye.

D. Recalculation of analysis C to agree with spinel formula; SiO<sub>2</sub>, CaO, and TiO<sub>2</sub> neglected.

E. Aluminian chromite separated from mesh-serpentinite, Hapuka Point, D'Urville Island. Analyst: F. T. Seelye.

F. Recalculation of analysis E to agree with spinel formula; TiO<sub>2</sub>, SiO<sub>2</sub>, CaO and NiO neglected.

G. Chromite from Silver Lease Mine, Oregon, analysis no. 25; 1.3 per cent H<sub>2</sub>O + is included in the total. Analyst; R. E. Stevens (Stevens, 1944, p. 11).

H. "Beresovskite"<sup>19</sup>, Jimblebah, Western Australia. Analyst: H. Bowley (Bowley, 1940, pp. 203).

Assuming that the spinel structure has a unit cell of 8 (RO·R<sub>2</sub>O<sub>3</sub>) (Bragg, 1937, p. 98), analyses B, D, and F have been recalculated to give the figures in Table 2.

<sup>18</sup> ± 0.003.

<sup>19</sup> Simpson (1920, p. 105) called this chromian spinel, beresofite, a name reserved earlier for chromate of lead. Bowley (1940) has added to the confusion by renaming the spinel "beresovskite", which is quite unnecessary and should be abandoned. Similarly it might be noted that Barsanov (1941) needlessly called chromian magnetite, ishkulite, and listed an analysis in which the RO:R<sub>2</sub>O<sub>3</sub> ratio is so low that it does not even approximately satisfy the spinel formula. This indiscriminate naming of minerals is to be condemned.

TABLE 2.—STRUCTURAL FORMULAE OF NEW ZEALAND ALUMINIAN CHROMITES (B, D, and F, Table I)

	Wt. per cent	No. of metal atoms
B		
Cr <sub>2</sub> O <sub>3</sub> .....	38.29	7.27
Al <sub>2</sub> O <sub>3</sub> .....	26.03	7.38
Fe <sub>2</sub> O <sub>3</sub> .....	7.45	1.35
FeO.....	13.36	2.68
MgO.....	14.87	5.32

TABLE 2—(Continued)

	Wt. per cent	No. of metal atoms
D		
Cr <sub>2</sub> O <sub>3</sub> .....	43.67	8.29
Al <sub>2</sub> O <sub>3</sub> .....	24.72	6.99
Fe <sub>2</sub> O <sub>3</sub> .....	4.07	0.72
FeO.....	11.36	2.26
MgO.....	15.93	5.69
MnO.....	0.25	0.05
F		
Cr <sub>2</sub> O <sub>3</sub> .....	43.45	8.26
Al <sub>2</sub> O <sub>3</sub> .....	24.01	6.79
Fe <sub>2</sub> O <sub>3</sub> .....	5.26	0.95
FeO.....	10.90	2.18
MgO.....	16.08	5.79
MnO.....	0.18	0.02
CoO.....	0.12	0.01

plotted on this figure, they fall just within the field of aluminian chromite and very close to the boundary of chromian spinel.

The figures for alumina and magnesia appear surprisingly high at first sight, but nevertheless they accord with analyses listed by Stevens and support the view that true chromite ( $\text{FeO Cr}_2\text{O}_3$ ) or ferrochromite is of very limited occurrence (Fisher, 1929). On the other hand, it is clear that very extensive ionic substitution is usual in these minerals. To determine whether the composition of the aluminian chromite in the concentrates is characteristic of that in New Zealand peridotites and serpentinites, two samples of pure chromite were separated from ultrabasic rocks from widely separated localities. These analyses (Table 1, columns C and E) are closely comparable with analysis A. So far as the writer is aware, only one other complete analysis of a New Zealand chromite has been made, with a mineral separated from dunite (Peterson, 1869, p. 138); this analysis shows a higher percentage of  $\text{Cr}_2\text{O}_3$  (56.54 per cent) than any in Table 1 but is too inaccurate to consider further since total iron is quoted as FeO; also the RO group is in excess of  $\text{R}_2\text{O}_3$ , which suggests that some of the iron is in a trivalent state. If the analysis is recalculated to allow for this, the already excessive summation of 101.22 would be increased.

A high percentage of alumina appears to be general in chromian spinels from ultrabasic rocks; Tatarinov and Krasnovsky (1940) have found that alumina averages about 20 per cent in over 60 chromites from harzburgites from localities in the Urals. Further, van der Walt (1942) has drawn attention to similar characteristics for 50 examples of chromites from the Western Bushveld Complex, and Stevens (1944) illustrates similar features for chromites from the North and South American Continents.

Since Bowen (1928, p. 279-281) put forward his views on the origin of chromite and the possibility of considerable variability of composition, little work has been carried out to follow up these ideas. Recently, however, van der Walt's excellent study has shown that the composition of the spinel reflects the composition of the magma from which it separated, and Meniaylov's (1946, p. 352) statement that "chromite has separated out before chrom-spinellid and magnetite" from a complex of

basic and ultrabasic rocks certainly suggests control of composition by differentiation. Thayer (1946) has shown very clearly that the composition of chromites and their host rocks may be correlated, and the aluminous nature of the New Zealand aluminian spinels (analyses C and E, Table 1) obtained from mesh-serpentinites of the dunite type with associated plagioclase-bearing ultrabasic and basic rocks supports this.

**CINNABAR:** An exceedingly rare constituent of the finest screening of one sample only (Barrytown), cinnabar occurs in tablet-like fragments with a perfect cleavage (Pl. 2, fig. 34). The very bright-red color is distinctive but no dichroism was noticeable. When heated alone the mineral volatilized but when heated with sodium carbonate, globules of mercury were obtained, confirming the initial optical diagnosis.

**CLINOZOISITE:** Iron-poor or iron-free members of the epidote group occur in the majority of the samples studied, limited, with few exceptions, to the finer-grade sizes. Relative frequency counts clearly show that members of this mineral group are of minor importance in the different assemblages of dredge concentrates since they do not exceed 8 per cent of any sieve fraction. In most instances, clinzoisite occurs in subhedral, rather equidimensional grains, although short, stout, prismatic euhedra are well represented in occasional examples (Lowburn). The mineral is colorless with a low birefringence and blue-grey or slate-grey anomalous interference tints; for two crystals the following optical properties were recorded:

$$\begin{aligned}\beta &= 1.728; 2V = 87^\circ; \rho < \nu \\ \beta &= 1.723; 2V = 83^\circ; \rho < \nu\end{aligned}$$

According to Winchell's tables (1933, p. 313), these properties indicate approximately 3 per cent of  $\text{Fe}_2\text{O}_3$  in the crystals concerned. Generally clinzoisite grains are free from inclusions but in some examples, particularly those from Lowburn dredge concentrates, dense clouds of iron-ore dust usually render the grains semi-opaque (Hutton, 1940a, p. 36); this feature of the clinzoisitic members of the epidote group is in marked contrast to the normally inclusion-free condition of the iron-rich members.

**CORUNDUM:** In colorless or parti-colored anhedral, corundum was a rare constituent of three concentrates (Barrytown, Blackball, and

Gillespie's Beach); quite frequently these grains appear to orient themselves in the mounting media so as to give a centered interference figure, which suggests the occurrence of plates, the shapes of which are determined mainly by the basal parting. A biaxial, negative interference figure with an optic axial angle of 10–20° was not unusual, and a determination of the refractive index for the ordinary ray gave  $1.769 \pm 0.002$  for one grain.

**EPIDOTE:** Epidote has the same general distribution as clinozoisite but in individual samples is a much more important member of the mineral assemblage; in Lowburn and Atarau concentrates it rises to 27 and 10 per cent respectively of the finest screenings (–230 grade-size), and 34 and 23 per cent respectively of the –120 +230 grade-size. In coarser fractions, however, the epidote group makes up only a few per cent of any particular screening, except in the case of samples from Lowburn dredge. Epidote occurs either as highly irregular grains with a general aspect suggesting composite particles, made up of sub-rounded individuals, or as broken fragments showing some tendency to prismatic habit. Typically the mineral is greenish-yellow with a weak but distinct pleochroism and high birefringence giving characteristic high-order interference colors. Inclusions are less frequent than in clinozoisite, but not rare; iron-ore in dust-like state of subdivision or as large particles, grains of quartz and albite, flakes of chlorite and needles of rutile have been identified. In a few grains (Barrytown), zonary structures were found, in which clinozoisite or iron-poor epidote formed cores with the peripheral zones richer in iron.

**GADOLINITE:** Occasional well-rounded grains of the beryllium yttrium silicate, gadolinite, were recognized in a coarse fraction (–35 +60 mesh) of concentrates from Barrytown dredge<sup>21</sup>. The anhedral are shining-black with vitreous luster and exhibit pronounced conchoidal fracture. Hardness is approximately 6–7 and density  $4.25 \pm 0.03$ . In thin fragments, the mineral is deep bottle-green, and numerous, minute, opaque particles, not diagnosed, have been seen.

<sup>21</sup> There were fewer than 25 grains in the entire mineral assemblage in the –35 +60 fraction of Barrytown material, and therefore, the individual constituents are not listed in Table 19.

The mineral is quite isotropic, that is completely altered to the metamict state, and has a refractive index of  $1.783 \pm 0.002$ , comparable to the determination of  $1.781 \pm 0.002$  made by the writer for metamict gadolinite from Broddbo, Norway, and Ytterby, Sweden but rather higher than the figure of 1.776 (approximately) found by Mountain (1931) for metamict gadolinite from Onseepkans and Bokspuit, Cape Province. Incidentally the density of the South African material was also distinctly lower than that of the Barrytown example, 4.085, suggesting a greater degree of hydration in the South African mineral. When fragments of gadolinite were brought to dull-red heat, the metamict condition was destroyed and a state of anisotropy resulted. At the same time the color changed to pale brown, and the refractive index rose to approximately 1.80 for the fast direction in the crystal, and a birefringence of 0.015 was measured. However, this transformation did not appear to be accompanied by any sudden emission of light (Levy, 1915, p. 35–36; Faessler, 1942). Hofmann and Zerban (Levy, 1915) have stated that this glowing will take place suddenly at 430°C., whereas Faessler observed that this change occurred suddenly at 800°C. but more slowly at lower temperatures, *viz.* 590°C. Heating of the Westland gadolinite was carried out over a range of temperatures but although the metamict condition was destroyed, a sudden luminescence or glowing was not observed at any stage.

Although ignition to fairly high temperatures will cause metamict gadolinite to return to a condition of anisotropy, it does not necessarily restore the refractive indices to the values that would have been found for the unaltered mineral since the divalent iron is almost wholly oxidized by the heating process, causing a distinct change in color and an increase in the birefringence above that found in the original unoxidized mineral.

In order to verify the determination of gadolinite, Mr. Seelye was asked to check for the presence of beryllium and rare earths in a few grains submitted to him; he supported the writer's identification and reported that "beryllium was identified in the sample by means of the Kolthoff Curcumin reaction after separating rare earths as fluorides, and any excess of



aluminum and iron by means of sodium fluoride. The presence of beryllium was further confirmed by the quinalizarin test."

**GARNET:** Recognized in every concentrate examined to date and often the predominating constituent in coarse grade-sizes, garnet is rarely of much importance in the finest screenings (Rimu dredge is an exception). The form of the mineral ranges from sharply euhedral crystals to sub-rounded or worn grains, characteristic of the coarser grades, to the sharply angular fragments with marked conchoidal fractures most frequent in the finest screenings. The morphology is always very simple. The rhombic dodecahedron (Pl. 2, figs. 31, 32) is by far the most usual form developed, whereas the trapezohedron is distinctly uncommon; combinations of these forms occur but the former is almost always predominant. In a few examples (Slab Hut), well marked striations oriented parallel to the shorter diagonals suggests oscillatory combination of the dodecahedron and the tetrahexahedron. Although no statistical counts were made, the outstanding predominance of the dodecahedron over the trapezohedral form and the correspondence of composition to almandine with ranging amounts of spessartite in solid solution in all cases except one (a nearly pure spessartite) shows an anomaly in the Donnay-Harker (1937, p. 460-461) law for the crystal morphology of garnet that the trapezohedron should predominate over any other form since the planes bounding this form are parallel to the net planes with the greatest reticular densities (or the smallest mesh areas). However, Pabst (1943, p. 234) has recorded evidence that among 90 almandine garnets studied, the dodecahedron (the form ranking second in importance, according to Donnay and Harker) has slight predominance over the trapezohedron (leucitohedron). For the nearly pure spessartite only the rhombic dodecahedron was observed, in accordance with the writer's observations for similar garnets in the Central and Western Otago schists. Further, a cursory examination of the almandine-rich gneisses from the Southland Fiord country only rarely found any form other than the simple dodecahedron. Thus the marked predominance of the dodecahedron in almandine and spessartites in a number of New Zealand localities seems clear.

In some of the concentrates are occasional garnet fragments of extremely irregular outline (Pl. 4, figs. 57-58) which suggests that they may have been subjected to the action of solvents, but the forms are quite distinct from the authigenic etch patterns found by Bramlette (1929) on garnets from Venezuela, or the pitting and etching observed by Wilgus (1933, p. 86) in garnets from the Dresbach sandstone of western Wisconsin. That garnet may be readily dissolved by natural solvents under some conditions is not universally accepted. Smithson (1942, p. 33-4) believes that garnet in sediments may and does dissolve by means of solvents working along the cleavage planes of that mineral; Edelman and Douglas (1934) concur in this, but believe that the process is rare and that the absence of garnet is more likely to mean absence from the sediments when they were being deposited. L. and C. Dryden (1946) list garnet as even less stable in sediments than hornblende, but Condit (1912) expressed the opinion that garnet was one of the most stable constituents of the mineral assemblages in sedimentary rocks. The extreme angularity and deep re-entrants so well developed in many of the garnets from Snowy River and Rimu could scarcely have survived even the slightest abrasion or transportation; the writer therefore believes that these grains are merely remnants produced by actual solution of much larger grains in the loose, water-filled gravels. Solution with ultimate disappearance of garnet from loose, saturated sediments may possibly be more important than generally considered; clearly this condition need not apply only to older sediments.

A distinct though not wide range of colors was noted in garnets from most of the localities studied, from pale pink, through red to brownish-red; since this range of color would likely be connected with a range of chemical composition, refractive index and density, determinations were made for more than 30 samples from widely separated localities (Table 3). They show a range of 1.795-1.825 for refractive index and 3.94-4.20 for density, Lowburn garnet excepted in both. Thus the pale-pink to pink tints appear to generally characterize garnets with refractive indices usually less than 1.806 and densities that do not exceed 4.01. The deeper red or brownish-red garnets usually have dis-

TABLE 3.—PHYSICAL PROPERTIES OF GARNETS

Specimen	Color	R. I.	Density
Grey River dredge	red	1.825	4.20
“ “	pink	1.795	4.01
“ “	pink	1.798	3.95
“ “	red	1.800	4.08
“ “	pink	1.795	3.98
“ “	red	1.795	4.02
Snowy River dredge	brownish-red	1.815	4.12
“ “	brownish-red	1.815	4.10
“ “	brownish-red	1.813	4.10
“ “	pink	1.803	3.98
Slab Hut dredge	red	1.809	4.04
“ “	red	1.805	4.10
“ “	brownish-red	1.805	4.09
Beachsand, 1 ml. from South end, Bruce Bay	pink	1.806	3.98
“ “	pink	1.805	3.94
“ “	red	1.798	4.00
Concentrate from stream, 1 ml. N. of Lake Paringa.	red	1.795	4.12
“ “	pink	1.803	3.98
“ “	brownish-red	1.800	4.12
Kaniere dredge	brownish-red	1.820	4.19
Lowburn dredge	pink	1.783	3.90

TABLE 4.—ANALYSIS OF ALMANDINE FROM SLAB HUT CONCENTRATES

SiO <sub>2</sub> .....	36.89	Mode:	
Al <sub>2</sub> O <sub>3</sub> .....	20.92	Gr.....	2.7
FeO.....	29.82	Sp.....	21.75
Fe <sub>2</sub> O <sub>4</sub> .....	nil	Py.....	6.0
MnO.....	9.26	Al.....	69.55
MgO.....	1.82	RO:Al <sub>2</sub> O <sub>3</sub> :SiO <sub>2</sub> =	
CaO.....	1.06	2.97:1.00:2.99	
TiO <sub>2</sub> .....	0.06		
Na <sub>2</sub> O.....	0.05		
K <sub>2</sub> O.....	0.04		
H <sub>2</sub> O at 105°C....	0.15		
	100.07		

tinctly higher densities and refractive indices. Qualitative chemical tests on 10 of the garnets listed in Table 3, showed plentiful manganese. Therefore, these garnets would seem to be chiefly spessartite-almandine with small percentages of pyrope, and less grossularite in

solid solution (Winchell, 1933, p. 176). As the garnet in the Lowburn concentrates probably contains in excess of 50 per cent of the spessartite molecule (Hutton, 1940a, p. 24), and is derived from the Chlorite Zone Otago schists,

TABLE 5.—RECALCULATION OF ANALYSIS OF GARNET ON THE BASIS OF 12 OXYGEN ATOMS TO THE UNIT CELL

	Wt. per cent	No. of metal atoms	Arrangement in groups	Ideal composition
SiO <sub>2</sub> .....	36.89	3.00	3.00	3
Al <sub>2</sub> O <sub>3</sub> .....	20.92	2.00	2.00	2
FeO.....	29.82	2.03		
MgO.....	1.82	0.22	} 2.98	3
CaO.....	1.06	0.09		
MnO.....	9.26	0.64		

Formula:  $[\text{Fe}_{2.03}\text{Mg}_{0.22}\text{Ca}_{0.09}\text{Mn}_{0.64}]\text{Al}_2\text{Si}_2\text{O}_{12}$ .

it is distinct from the other garnets studied here from Westland and Nelson Provinces. In order to determine the chemical nature of the garnets more accurately, a complete analysis (Table 4) was obtained of garnet separated in the pure state from Slab Hut concentrates by electromagnetic and flotation methods. For this material the constants were:

Observed:  $n = 1.815-1.818$   
 D. 21°C. = 4.18-4.20  
 Calculated (Ford, 1915):  
 $n = 1.812$   
 D = 4.17

If recalculated on the basis of 12 oxygen atoms to the unit cell and the small percentages of alkalis and titanium are neglected (Table 5), this analysis nearly completely agrees with the structural formula without the necessity of grouping any aluminum with the four-fold coordinated ions, as Alderman (1935) found necessary for a number of almandines from Botallack. Although Fleischer (1937, p. 752) was not able to disprove Alderman's explanation of anomalies in the RO:R<sub>2</sub>O<sub>3</sub>:RO<sub>2</sub> ratio in some garnets, he believed that this position was much more likely due to the difficulties of determining the percentage of ferrous oxide. While fully aware of this very considerable difficulty that besets the determination of ferrous iron in refractory minerals, it is quite clear that in a first-class analysis

of an almandine showing negligible or no ferric iron, the ferrous determination must have been correct. Yet Pabst (1938, p. 101) published an analysis of an almandine with only 0.24 per cent of  $\text{Fe}_2\text{O}_3$  but with a  $\text{RO}:\text{R}_2\text{O}_3:\text{SiO}_2$  ratio of 2.82:1:2.87; if this analysis is recalculated on the basis of 12 atoms of oxygen it is only necessary to transfer the almost negligible quantity of 0.02 atoms of aluminum from six-fold co-ordination to four-fold co-ordination in order to bring the silicon group to the theoretical figure of 3. On the other hand there is still a marked discrepancy between theoretical and actual values that cannot be allowed for by appropriate ionic substitution. Similar conditions apply in the case of Pabst's (1943) Fort Wrangell almandine. In both instances, neither ionic substitution nor incorrect ferrous iron determination can explain the anomalies in the oxide ratios. In an almandine from Botallack (Alderman, 1935, p. 46) that is  $\text{Fe}_2\text{O}_3$ -free, correspondence with the theoretical formula results when the appropriate ionic substitutions are assumed; this, however, is not the case of some almandines with small amounts of  $\text{Fe}_2\text{O}_3$  quoted by Alderman, and the RO group remains too low in spite of a transfer of  $\text{Fe}^{3+}$  to this group.

Zoning is not infrequently developed in spessartite-almandine, but is not often noticeable unless the particles are immersed in a medium with a refractive index of about 1.80. Two distinct developments were found. The more usual variety exhibited numerous concentric bands, in most cases probably less than 1 or 2 microns wide. No distinction in color was apparent but very prominent Becke lines separated from these zones on racking the microscope tube up or down. In the second form, the central portions of the garnet crystals were red or brownish-red, but the intensity of absorption decreased without abrupt change towards the margins where a pale pink color predominated. The refringence of the different zones could be determined in only one case: Central zone =  $1.795 \pm 0.003$ ; median zone = 1.806; peripheral zone = 1.795.

Garnet free from inclusions is uncommon and they are usually arranged haphazardly with only an occasional specimen showing evidence that distribution of the inclusions has been

influenced by the zony development (Atarau Dredge); in some crystals inclusions were more densely aggregated in the central areas. Although the inclusions could not always be identified definitely, epidote, clouds of iron oxides or manganiferous dust, magnetite, titanite, quartz, and feldspar were diagnosed. Very deep staining by iron is common.

**GOLD:** Since samples from dredges had gone through a process of amalgamation, gold was absent except in concentrates from Ngahere and Gillespie's Beach dredges. In Ngahere material gold particles were completely coated with ferric oxides and had to be treated with warm concentrated HCl for identification. Apparently this protective coating of oxide inhibited complete amalgamation, and as a result, valuable amounts of gold were rejected with the tailings. In the Gillespie's Beach dredge, the concentrates may have been imperfectly handled since the gold therein was quite free from any protective coating that would have prevented amalgamation. Gold was found in a number of beach sands and river pannings, and ranged from flattened grains or "slugs" 9 mm. long down to fine flour that passed a 230-mesh U. S. screen. The finest particles are usually skeletal in form but fliform, granular, and flakelike shapes were often found. The metal was readily diagnosed by its distinctive color beneath a binocular microscope in oblique illumination, the ease with which a flake or particle may be pricked and hence picked up on a needle point, and its reaction towards a globule of mercury.

Particles of gold from Ngahere dredge showed a density range of 17.02-18.07.

**HEMATITE:** In the main hematite is restricted to the coarser fractions of concentrates from Ngahere, Blackball, and Red Jacks, although it is an occasional constituent of a number of grade sizes of a number of other concentrates. Pseudomorphs after pyrite in the form of pyritohedra, striated cubes, and fragments of these are most often found; rolled grains are not infrequent. Very occasionally, notably from Atarau and Slab Hut dredges, thin plates of hematite were found in which the basal plane was dominant but prisms and pyramids exceedingly poorly developed; the density of such crystals ranged from 5.20-5.24. Hematite is dull brown to shining grey in reflected light,

and is opaque except in the thinnest flakes. A considerable number of grains were tested by removing them on a needle point, crushing them directly on a glass slide in refractive index liquids, and then inspecting the powder obtained therefrom in transmitted plane polarized light. These very thin particles were deep brownish-red but not sensibly dichroic. The refractive index was decidedly in excess of 2.08.

Although the writer was unable to obtain any interference figures or to determine the value of the optic axial angle owing to minuteness of particles, the determination of high density and the knowledge that the refractive index is very much in excess of 2.08 for any orientation appears to rule out any possibility of the mineral being lepidocrocite, whereas the high density and absence of dispersion should remove goethite from the list of possible minerals. Therefore, the recognition of these grains as hematite appears to be reasonably well founded.

**HORNBLENDE:** Few specimens, such as black sands from the western side of Wainui Inlet, north west Nelson, and concentrates from the Kanieri dredge and Arahura River, were found to contain hornblende in excess of 2 per cent. Generally, the amphiboles occur in elongated cleavage plates with ragged ends (Wainui Inlet), in rolled and rounded or angular grains. A green to blue-green type and a rare red-brown barkevicitic variety were noted. In two examples of the former type the following optical properties were found:

*Wainui Inlet, north-west Nelson*

- X = greenish-yellow.  
 Y = olive-green.  
 Z = deep bluish-green; almost opaque in thick fragments.  
 Absorption: strong with  $Z > Y > X$ .  
 $\alpha = 1.646$ .  
 $\gamma = 1.668$ .  
 $\gamma - \alpha = 0.022$ .  
 $Z \wedge c = 20^{\circ}-22^{\circ}$ .

*Arahura Dredge, Westland*

Pleochroism: similar to the preceding variety, but the refractive indices differ slightly with the  $\gamma$  value showing a range of 1.670-1.683.

The brown varieties usually show strong pleochroism with a range of intensities, the absorption for the Z vibration direction being intense for barkevicitic types.

The hornblende grains from the Wainui Inlet-Ligar Bay sands are completely unaltered but preliminary alteration to chlorite has occurred in some instances (Okarito and Atarau). Inclusions are infrequent but apatite, epidote, opaque minerals, either in clouds of dust-like particles, rods or grains, quartz and feldspars, titanite, and zircon have been definitely diagnosed.

**HYPERSTHENE:** Hypersthene (Pl. 4, fig. 63) appears to be limited to the finest screenings of one sample only (Snowy River). It occurs in prismatic grains with somewhat ragged terminations and a pale but distinct pleochroism was evident according to the scheme: X = brown to brownish-pink; Z = pale green. Numerous inclusions take the form of (1) minute dark-brown needles that occur in patches and (2) numerous more or less rectangular brown inclusions similar to those figured by Hutton and Turner (1936, Pl. 23, figs. 8, 9). The patches have not been definitely identified but they may be thin plates of rutile lying within and oriented by the planes of the prismatic cleavages. One determination of the refractive index for the Z-vibration direction in hypersthene gave 1.705, which corresponds to approximately 38 per cent of the molecule  $\text{FeSiO}_3$  (Henry, 1935, p. 223). In all cases the mineral was moderately paramagnetic and could therefore be concentrated by magnetic fractionation.

**KYANITE:** Kyanite, in relatively few samples and nowhere a constituent of any importance, occurred as rather regularly shaped grains, tabular parallel to (100) and showing two cleavages intersecting at  $90^{\circ}$  (Pl. 4, fig. 69). An extinction angle of  $30^{\circ}$  between Z and the 010 cleavage was obtained on this plate, together with a more or less centered biaxial interference figure. Minute inclusions lying parallel to (001) were present in some cases (Red Jacks dredge).

**LEUCOXENE:** The few rounded grains of leucoxene recognized were always restricted to the finest grade-sizes. The mineral is translucent, pale yellow to amber, with a white porcelain-like appearance in oblique illumination. The refractive index of this constituent, for the grains investigated, was slightly in excess of 2.07, and the birefringence was fairly high. Experiments with a few isolated grains proved that they were anhydrous, lime-free, and very

high in  $\text{TiO}_2$ . These data are not comparable to those determined by Edwards (1942, p. 273-274) for leucoxene from some Victorian bauxites that he was able to separate pure in quantities sufficient for analysis, since his material contained water and was isotropic.

It would seem likely, then, particularly in view of the X-ray investigations by Tyler and Marsden (1938), Coil (1933), and others, that much so-called leucoxene seems to be merely one modification of titanium dioxide and not titanite as so often assumed. Further, material described as leucoxene appears to be either highly birefringent or isotropic. The isotropic, hydrated, titanium oxides should perhaps be included in the term doelterite, and the term leucoxene restricted to micro-crystalline, anhydrous, highly birefringent titanium dioxide, whether in the form of anatase or not.

**MONAZITE:** The cerium phosphate, monazite, occurs in all samples examined except those from Central Otago and the beaches of Wainui Inlet. The mineral characteristically occurs in slightly abraded, egg-shaped grains, and in most instances it is concentrated in the -60 +120 and -120 +230 grade-sizes, although often a minor constituent of coarser screenings. Broken fragments are rare. These rounded grains do not give easily recognizable interference figures and are interpreted to be abraded (100) tablets; the (001) cleavage is rarely seen but in some instances a longitudinal cleavage is developed parallel to the clinopinacoid (Pl. 2, figs. 26-28). In rare cases (Pl. 4, figs. 72-73), rectangular-shaped grains show a nearly centered interference figure and a birefringence of about 0.002; such grains appear to be basal cleavage plates, with rectangular form determined by the pinacoidal cleavages.

Although slightly less susceptible than the associated spessartite-almandine garnet and ilmenite, monazite is decidedly paramagnetic, and this allows ready concentration of the phosphate from samples. For instance with a Frantz Separator set at a slope of  $15^\circ$  and a tilt of  $8^\circ$ , practically all of the monazite is attracted at a current of 0.40 amps. A very faint yellow color in the mineral is noticeable only in the coarser screenings, or in electromagnetically concentrated fractions; the color corresponds approximately with Colonial Buff 21'd (Ridg-

way, 1912). In grains less than 62 microns in diameter the mineral appears to lack color in the usual mounting media, Canada balsam or clove oil.

Refractive index determinations for a number of samples gave the following averages, with none of the measurements differing by more than 0.003:  $\alpha = 1.787 \pm 0.003$ ;  $\beta = 1.789$ ;  $\gamma = 1.839$ ;  $\gamma - \alpha = 0.052$ . One sample (Ngahere dredge) gave the following data:  $\alpha = 1.791 \pm 0.003$ ;  $\beta = 1.792$ ;  $\gamma = 1.844$ ;  $\gamma - \alpha = 0.053$ ; optical axial angle determinations gave a range of  $12^\circ$ - $14^\circ$ .

Many of the monazite grains contained inclusions but all could not be diagnosed with certainty. The following minerals were found as inclusions: stumpy euhedra of colorless zircon (Grey River, Atarau), granules and dust-like clouds of opaque ores (Blackball), rutile (Snowy River), and red-brown stains (Slab Hut). However, the majority of crystals were devoid of inclusions, and in this respect they are like those described from the Dartmoor area by Brammell (1928, p. 29-30).

The possibility of confusion in diagnosing monazite when such constituents as xenotime, titanite, bāstnasite, and yellow zircon are present (Hutton, 1947a) will be considered more fully when discussing xenotime.

The refractive indices of the New Zealand monazites are as low as any recorded for that mineral but their optical properties compare to those for a thorium-free specimen from Bolivia (Gordon, 1939, p. 7), and for monazite with 0.2 per cent of  $\text{ThO}_2$  from Katanga (Thoreau, Breckpot, and Vaes, 1936). However, the New Zealand monazites contain over 5 per cent of  $\text{ThO}_2$  and 1.23 per cent of  $\text{U}_3\text{O}_8$  in one instance. Analyses of New Zealand monazites, compared with several others (Table 6), show the presence of 5.48 per cent of the oxides of tantalum and niobium in monazite from Westland. It should be stressed, however, that the sample analysed contained approximately 10 per cent of tantalian-cassiterite, but since this mineral contained only 2.3 per cent of  $\text{Ta}_2\text{O}_5$ , and no other tantalum-bearing mineral was present, the tantalum must be present in the monazite structurally. This is substantiated by the analyst's report that "when the original sample was treated with boiling concentrated  $\text{H}_2\text{SO}_4$  alone,

the rare earths and phosphorus pentoxide of the decomposed monazite were rendered almost completely soluble and could be removed by filtration, the filtrate containing only a very small amount of the total tin of the sample".

vaal, and Madagascar, but the  $Ta_2O_5$  recorded therein does not exceed 1.10 per cent. If tantalum is, as appears, a replacement ion in monazite its location in the structure is now a question.

TABLE 6.—ANALYSES OF MONAZITE

	A	B	C	D	E	F	G	H	I
$Ce_2O_3$ .....	19.00	22.95	27.30	28.43	30.72	33.06	25.82	22.63	21.08
$La_2O_3$ etc.....	23.42	28.28	30.00	31.17	30.02	30.21	30.62	34.63	31.27
$Y_2O_3$ etc.....	3.54	4.28	2.24	2.32	2.74	0.14	2.03	4.66	3.53
$ThO_2$ .....	4.40	5.32	5.28	5.47	5.00	5.03	9.60	7.32	11.08
$U_2O_5$ .....	1.02	1.23	nil	—	—	—	—	0.32	0.42 (UO <sub>2</sub> )
(Ta,Nb) <sub>2</sub> O <sub>5</sub> .....	4.54	5.48	—	—	—	—	—	—	—
SnO <sub>2</sub> (insol.).....	9.50	—	—	—	—	—	—	—	—
SiO <sub>2</sub> .....	2.04	2.46	1.72	1.18	1.20	1.22	1.85	1.54	2.98
TiO <sub>2</sub> .....	1.76	—	0.40	—	—	—	—	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	4.62	2.88	1.26	0.93	3.00	2.21	1.01	0.08	0.66
P <sub>2</sub> O <sub>5</sub> .....	22.46	27.12	27.50	28.57	26.29	26.70	27.07	27.89	27.52
ZrSiO <sub>4</sub> (insol.).....	1.08	—	—	—	—	—	—	—	—
H <sub>2</sub> O - (105°).....	0.22	—	—	—	—	—	0.35	0.06	0.56
H <sub>2</sub> O + (105°).....	—	—	—	—	—	—	—	0.34	
Undetermined.....	2.40	—	—	—	—	—	0.18	—	—
CaO.....	—	—	0.79	0.82	0.15	0.90	0.91	0.35	0.52
ZrO <sub>2</sub> .....	—	—	1.13	—	—	—	—	—	—
Al <sub>2</sub> O <sub>3</sub> .....	—	—	1.62	1.03	0.35	0.44	0.15	0.10	0.80
ZnO.....	—	—	0.50	—	—	—	—	—	—
MgO.....	—	—	0.08	0.08	—	0.21	0.03	0.02	0.27
MnO.....	—	—	trace	—	—	—	0.08	nil	—
Loss on ignition.....	—	—	—	—	0.25	0.59	—	—	—
PbO.....	—	—	—	—	—	trace	0.58	0.33	—
	100.00	100.00	99.82	100.00	99.72	100.71	100.28	100.27	100.69
Sp. Gr. 20° C.....	—	5.26	—	5.23	—	5.26	5.18	5.270	5.17

A. Monazite from Ngahere Dredge concentrate, containing approximately 15 per cent of zircon, tantalian cassiterite, and ilmenite. Analyst: F. T. Seelye.

B. Analysis of pure monazite after elimination of impurities by calculation.

C. Monazite from Mudtown, Pegasus District, Stewart Island, containing approximately 6 per cent of gahnite, zircon, and ilmenite-titanhematite. Total iron (FeO + Fe<sub>2</sub>O<sub>3</sub>) is expressed as Fe<sub>2</sub>O<sub>3</sub>. Analyst: F. T. Seelye.

D. Analysis of monazite C, after elimination of ilmenite-titanhematite, zircon, and gahnite by calculation.

E. Monazite from Ekole, Northern Nigeria (Johnstone, 1914, p. 57, table 6, analysis I).

F. Monazite from Moolyella (Simpson, 1912).

G. Monazite from Dillingø, Norway (*see* Hintze, 1923, p. 368, analysis IX).

H. Monazite from Dickens Township, Nipissing District, Ontario (Ellsworth, 1932b, p. 26).

I. Monazite from Ishikawa, Iwaki Province, Japan (Shibata and Kimura, 1923a, p. 14-15).

Therefore, 5.48 per cent of (Ta,Nb)<sub>2</sub>O<sub>5</sub> cannot have been obtained by simple solution of the cassiterite. Tantalum in monazite is not unknown, and Hintze (1923) records analyses of tantalian monazite<sup>22</sup> from Australia, Trans-

Since only a small percentage of the tantalum ion occurs, two possibilities present themselves:

(a) Tantalum occurs in four-fold co-ordination replacing phosphorus in the P-O tetrahedra,

or (b) Tantalum replaces ions in the six-co-ordinated groups. This possibility is favored chiefly because:

<sup>22</sup> As distinct from analyses of monazite sands which may include tapiolite, tantalite, tantalian cassiterite, fergusonite, etc.

(1) The Ta-O radius ratio lies within the limits for six-fold coordination although that value is not far removed from the minimum figure when either four- or six-fold co-ordination would be possible.

(2) The writer is not aware of any structures in which Ta<sup>5+</sup> occurs in four-fold co-ordination.

Tantalum is in six-fold co-ordination in the compounds NaTaO<sub>3</sub> and KTaO<sub>3</sub> (Rankama, 1944, p. 49) which have the perovskite structure and also in columbite-tantalite (Sturdivant, 1930, p. 88); but in the compound K<sub>2</sub>TaF<sub>7</sub>, Ta<sup>5+</sup> is in seven-fold co-ordination (Hoard, 1939, p. 61). However, it must be remembered that any substitution of rare earth ions by tantalum must be very limited in view of the discrepancy of ion sizes.

Substitution of rare earths by quintavalent tantalum and tetravalent thorium involves an upset in electrical neutrality unless there is compensatory exchange elsewhere in the molecule. Significant in this respect is the presence of a moderate percentage of silica in most analyses of pure monazites, although in some instances, such as a specimen from Huron Claim, Manitoba, Canada (Hecht and Kroupa, 1936, p. 98), this oxide may be as high as 8.5 per cent<sup>23</sup>. The monazites from New Zealand show no indication of silica as inclusions of quartz or silicates, or as an alteration product as Ellsworth (1932b, p. 25-26) found. Considerable substitution of phosphorus by silicon can result from the similarity of the radius ratio of silicon and oxygen and of phosphorus and oxygen shown so clearly in the mineral ellestadite (McConnell, 1937). Such ionic replacement will cause an upset in electrostatic balance and, in the writer's opinion, electrical neutrality may be restored, at least in monazite, by substitution of thorium (Th<sup>4+</sup> 1.10), and tantalum (Ta<sup>5+</sup> 0.65) for cerium (Ce<sup>3+</sup> 1.18), yttrium (Y<sup>3+</sup> 1.06), and lanthanum (La<sup>3+</sup> 1.22).

The monazite analysed by Hecht and Kroupa contained 8.5 per cent SiO<sub>2</sub> and 14.42 per cent ThO<sub>2</sub>, whereas the thorium-free monazite from Bolivia (Gordon, 1939) contained only 0.27 per cent of SiO<sub>2</sub>. However, an increase of thorium or of uranium in monazite is not always paralleled by simultaneous increase in the content of

silicon (G-I, Table 6). It is not clear how 11.08 per cent of ThO<sub>2</sub>, for example, is compensated, certainly it is not by substitution of silicon for phosphorus; this leads one to suspect inclusions

TABLE 7.—RECALCULATION OF ANALYSES OF MONAZITE

	Wt. per cent	Metal atoms
<i>Analysis B</i>		
Ce <sub>2</sub> O <sub>3</sub> .....	22.95	1.294
La <sub>2</sub> O <sub>3</sub> .....	28.28	1.606
Y <sub>2</sub> O <sub>3</sub> .....	4.28	0.350
ThO <sub>2</sub> .....	5.32	0.186
U <sub>3</sub> O <sub>8</sub> .....	1.23	0.032
Fe <sub>2</sub> O <sub>3</sub> .....	2.88	0.334
Ta <sub>2</sub> O <sub>5</sub> .....	5.48	0.229
SiO <sub>2</sub> .....	2.46	0.379
P <sub>2</sub> O <sub>5</sub> .....	27.12	3.536
		4.031
		3.915
<i>Analysis B (without Fe<sub>2</sub>O<sub>3</sub> and recalculated to 100 per cent)</i>		
Ce <sub>2</sub> O <sub>3</sub> .....	23.63	1.333
La <sub>2</sub> O <sub>3</sub> .....	29.13	1.655
YO <sub>3</sub> .....	4.40	0.360
ThO <sub>2</sub> .....	5.47	0.192
U <sub>3</sub> O <sub>8</sub> .....	1.27	0.051
Ta <sub>2</sub> O <sub>5</sub> .....	5.64	0.236
SiO <sub>2</sub> .....	2.53	0.391
P <sub>2</sub> O <sub>5</sub> .....	27.93	3.644
		3.827
		4.035
<i>Analysis D</i>		
Ce <sub>2</sub> O <sub>3</sub> .....	28.43	1.616
La <sub>2</sub> O <sub>3</sub> .....	31.17	1.705
Y <sub>2</sub> O <sub>3</sub> .....	2.32	0.191
ThO <sub>2</sub> .....	5.47	0.193
Fe <sub>2</sub> O <sub>3</sub> .....	0.93	0.108
CaO.....	0.82	0.131
Al <sub>2</sub> O <sub>3</sub> .....	1.03	0.186
MgO.....	0.08	0.018
SiO <sub>2</sub> .....	1.18	0.184
P <sub>2</sub> O <sub>5</sub> .....	28.57	3.755
		4.148
		3.939

of thorium-bearing minerals such as thorianite within the crystals of these monazites.

Analyses of both New Zealand monazites have been recalculated on the basis of 16 oxygens to the unit cell (Parrish, 1939) and set out in Table 7. Silicon has been grouped with phosphorus and it is particularly evident that without including 0.379 and 0.184 atoms of silicon in analyses B and D the four-coordinated groups would be distinctly less than the struc-

<sup>23</sup> The high summation of their analysis, 101.14 appears to result from calculation of cerium and rare earths as CeO<sub>2</sub> etc.

tural value required. On the other hand, the ferric oxide in monazite analysis B, 2.88 per cent, is believed to occur structurally and not result from chemical solution of inclusions of ferrous minerals. This contention is supported by the second calculation of analysis B from which ferric oxide was excluded and the value for the six-coordinated group is distinctly less than 4. In analysis D, the small percentages of CaO, Al<sub>2</sub>O<sub>3</sub>, and MgO were included with the main constituents.

**OLIVINE:** A beach concentrate recently sent the writer from Bruce Bay, South Westland, the analysis of which is not listed in Table 19, differed from other samples from that locality because olivine was found in the -35 +60 size fraction. This mineral occurred in chipped, clear bottle-green unaltered fragments with pronounced conchoidal fracture. The color was most obvious when the particles were studied in oblique illumination with the binocular microscope, but the crushed fragments were colorless in transmitted light. Olivine is completely devoid of iron oxide inclusions but nevertheless was concentrated in the more paramagnetic fractions along with monazite. Refractive indices determined for a number of grains showed the following range:  $\alpha = 1.670 - 1.678$ ;  $\gamma = 1.704 - 1.712$ .

**OPAQUE MINERALS:** The opacity of a number of the minerals has rendered diagnosis difficult; it should be noted, however, that two of these minerals, martite and wolframite, are translucent but only in exceedingly thin plates or splinters, such as are produced when individual grains are pulverized.

Several grains belonging to this group, but not satisfactorily identified, owing chiefly to rarity of material, are not discussed. However, a few grains found in the -35 +60 mesh fraction of concentrates from Blackball Dredge and classified as "unidentified" (Table 19) gave strong reactions for Fe, Mn, and Ta; these data in conjunction with relative insolubility in strong acids, marked cleavage, and high density, 7.2-7.4, suggest the possibility of a member of the columbite-tantalite series, close to the tantalum end of the series.

Minerals definitely identified are: ilmenite, magnetite, martite, wolframite, ilmenite-titanhematite intergrowths, chalcopyrite, pyrite, marcasite, lead, arsenopyrite, pyrrhotite. A

few grains with properties that render them distinct from these listed could not be definitely identified, but they do not exceed 0.5 per cent in any one sample, or fraction of a sample.

Identification of minerals that are opaque to light even at diameters of approximately 50 microns is no easy matter. It is admitted that such material may be embedded in cement, polished, and then diagnosed in vertical illumination by its reflectivity, reaction to chemical solutions, and so on, and this method has been used in a few instances, but unfortunately from a practical point of view, when an investigator is dealing with hundreds of samples, each of which may be fractionated into twelve or more parts, the labor involved in the work of mounting and polishing is wholly excessive and is unwarranted if the percentage of such material appears to be non-economic. But to identify the opaque constituents with the aid of binocular microscope and oblique illumination alone proved to be most useful<sup>24</sup>.

*Ilmenite and magnetite* are ubiquitous in the paystreaks of beach sands and rivers, and in artificially produced concentrates alike, and in almost every sample ilmenite predominated over magnetite. In a number of dredge concentrates and stream-pannings, however, a higher percentage of magnetite was present than in any of the naturally concentrated beach sands except one, a buried pay-streak at Gillespie's Beach that contained 67 per cent. The higher concentration of magnetite in dredge concentrates is of interest and it should be remembered that dredges' jigs and tables are set as near the optimum positions as possible to allow retention of gold with a density of about 19. Since it is decidedly more dense than ilmenite (density *ca.* 4.79) magnetite (density *ca.* 5.175) might be expected to be retained to a somewhat greater extent. Generally speaking, grading analyses of sands, pannings etc. indicated that the frequency of these two constituents, and also other opaque minerals, increased with increase of grain-size; the opaque minerals, chiefly ilmenite and magnetite, were the predominant con-

<sup>24</sup> A finely crushed opaque powder, e.g. pyrite, can often be diagnosed more easily in oblique illumination, if it is covered with clove oil which makes the color of the pyrite more obvious. The properties of some minerals when viewed by vertical illumination are more easily recognized when the surface is covered with a thin film of clove oil, especially if that surface is not very well prepared.



stituents in the -35 +60 screening of about half of the dredge concentrates investigated.

The very marked predominance of ilmenite over magnetite is of some importance since it had been believed that with the establishment

alone. One of the better methods of distinguishing between them is to pass the particles through a weak magnetic field. Magnetite is attracted and ilmenite remains behind. If the field strength is then increased slightly opaque

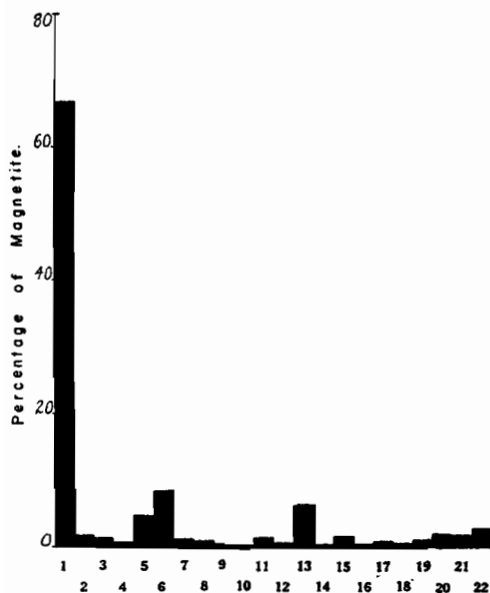


FIGURE 5.—MAGNETITE IN WESTLAND AND SOUTH-WEST NELSON BEACH SANDS

1. 14 feet below surface, Gillespie's Beach; 2. 3 miles south of Poerua River; 3. South end of Hunt's Beach; 4. Bruce Bay; 5. Center of Three Mile Beach, Okarito; 6. 200 yards north of Five Mile Bluff; 7. Five Mile Beach, Okarito; 8. Ross; 9. 13 miles north of Greymouth; 10. 14 miles north of Greymouth; 11. 15 miles north of Barrytown; 12. West of Charleston Hotel; 13. Karamea Beach; 14. One mile south, mouth of Buller River; 15. Tauranga Bay; 16. North end of Nine Mile Beach; 17. Nine Mile Beach, south of Westport; 18. 1 mile north of Cape Foulwind; 19. Greysand, 1½ miles north of Cape Foulwind; 20. Mouth of Fox River; 21. Blacksand, 1½ miles north of Cape Foulwind; 22. Dune sand, Bruce Bay.

of a steel industry in New Zealand, the West Coast blacksands could be utilized to augment the Parapara limonite and hematite ores (Mason, 1945). With one exception, a blacksand layer 14 feet below the present level of Gillespie's Beach, not one sand contains magnetite in economic quantities (Fig. 5).

Both ilmenite and magnetite occur as rolled, well-rounded grains, angular fragments with conchoidal fracture, and as euhedra. In many instances anhedral grains of the two minerals could not be differentiated by visual means

TABLE 8.—ANALYSES OF OPAQUE MINERAL FRACTIONS FROM NGAHERE DREDGE CONCENTRATES

	A	B	C	D
SiO <sub>2</sub> .....	4.05	3.59	0.7	1.4
TiO <sub>2</sub> .....	42.44	20.31	6.8	1.6
FeO.....	37.18	21.98	29.6	30.0
MnO.....	1.68	0.5	1.1	0.3
MgO.....	0.56	—	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	8.17	48.15	60.4	63.4
Al <sub>2</sub> O <sub>3</sub> .....	3.15	3.47	0.9	1.2
Cr <sub>2</sub> O <sub>3</sub> .....	0.45	—	—	—
V <sub>2</sub> O <sub>5</sub> .....	0.016	—	—	—
H <sub>2</sub> O —.....	0.54	0.78	0.3	0.3
Zircon & insol....	1.90	0.92	0.4	2.4
	100.13	99.70	100.2	100.6
D. 25°C.....	4.61	—	—	—

A. Least susceptible fraction consisting of nearly pure ilmenite; solution in acids difficult. Analyst: F. T. Seelye.

B. Moderately magnetic fraction, consisting of martitized magnetite and ilmenite. Analyst: C. Osborne Hutton.

C. Strongly susceptible fraction composed chiefly of titanomagnetite. Analyst: C. Osborne Hutton.

D. Most susceptible fraction; chromite removed by hand-picking. Mainly magnetite. Analyst: C. Osborne Hutton.

grains with a distinct range of magnetic susceptibility can be attracted before pure ilmenite is removed. To determine how far variation in titanium content accounted for this range, analyses were made (Table 8), in some instances partial only, of four fractions; no attempt was made to separate out different opaque minerals but translucent minerals were removed as far as possible, chiefly by hand-picking.

Crystal form has been rarely preserved in beach sands but is more often found in the river concentrates, and served at times to distinguish between the two minerals. Ilmenite usually had squat tabular crystals produced by development of prominent basal plane and rhombohedrons, but ranged to grains with remnants of basal planes and rhombohedrons

and most commonly of all, anhedral grains with hackly fracture. A considerable number of anhedral grains tended to be either prismatic or distinctly platy. Magnetite showed the same wide diversity of grain-shape, but, when euhedral, octahedral crystals were more frequent than octahedrons modified by dodecahedral faces; cubes modified by octahedron faces were noted but rarely.

Since magnetite grains began their sedimentary evolution as octahedra it is perhaps to be expected that abrasion of such crystals would lead to the development of anhedral grains with a greater degree of sphericity than ilmenite. This distinction is quite marked in the river concentrates but is much less so in the beach sands. A conchoidal fracture and a shining metallic luster were much more noticeable in magnetite than in ilmenite (Milner, 1940; Raeburn and Milner, 1927), and although a number of writers have stated that ilmenite has a steel-grey luster with a distinct purple sheen or iridescence, this property was observed just as often in magnetite.

A number of grains of magnetite showed a distinctive set of parallel striations but these could not be diagnosed further. In addition to the purple iridescence, magnetite alone exhibited a red-brown coating of oxide, and in river sands in particular this feature provided quick identification.

While discrimination between ilmenite and magnetite by mere inspection is usually difficult and often impossible, careful observation for degree of luster, well-developed conchoidal fracture, striations, red-brown oxide coating, and form in euhedra is often of considerable assistance. Of course final testing beneath a binocular microscope in oblique illumination with a fine magnetized needle should assist accurate diagnosis. Unfortunately this method is quite inadequate at times; for example octahedra of partially martitized magnetite recognized in a number of sands have in some cases magnetic susceptibility approximately equal to that of ilmenite.

*Martite*, found in a number of sands and concentrates, reached its greatest abundance in the -35 +60 screening of the concentrates from Lowburn Dredge. It ranged from well-rounded or fragmental anhedral to octahedrons and dodecahedrons or combinations of these. In the

latter, striations parallel to the junctions of the octahedron-dodecahedron faces were developed. Distorted cube forms and pentagonal dodecahedrons were found, and in the majority of cases the faces of the cubes were strongly striated so as to produce a pyritohedral symmetry.

In oblique illumination, martite was iron-black with a splendid metallic luster in most cases although occasionally dull. Each particle was tested for magnetic susceptibility, removed on a needle point crushed on a glass slide in a liquid of refractive index 2.07, and then inspected in transmitted light with the polarizing microscope. When the refractive index of the crushed powder, which was deep red-brown in transmitted light, was greatly in excess of that of the liquid, it was assumed that the material was hematite and not goethite. The martite appears to be pseudomorphous after magnetite or pyrite.

The pseudomorphs after pyrite must be distinguished from the equally abundant pseudomorphs of similar form that when crushed give yellowish-brown powder composed of cryptocrystalline and amorphous material; these are diagnosed as limonite (used *sensu lato*) pseudomorphous after pyrite.

Roughly prismatic and angular grains of *wolframite* were usually readily recognized beneath the binocular microscope by the presence of perfect cleavage, together with the pronounced and brilliant reflection of light from the cleavage planes. The particles are opaque and, by reflected light, iron-black. If, however, a grain is crushed, the fragments must be washed free from fine dust, otherwise the particles appear to be a deep red-brown in reflected light. In transmitted light, very thin flakes of the mineral were deep red-brown with only faint pleochroism according to the scheme: X = deep red-brown; Z = deeper red-brown to opaque in thicker flakes. The refractive index in every instance was distinctly greater than 2.07. The pleochroism suggests that the wolframite has a composition close to that of ferberite. This was checked by making colorimetric determinations of the manganese content using small fragments of the mineral; the values ranged between 3.2-4.3 per cent of MnO, and according to Hess and Schaller (1914), would indicate ferberite rather than hubnerite. Incidentally the compo-

sition of Westland wolframite appears to compare closely with wolframite from Port Pegasus, Stewart Island (Williams, 1934, p. 353), and found to contain 19.6 per cent of FeO and 3.9 per cent of MnO in one instance.

Wolframite was found to be relatively insoluble in hot concentrated hydrochloric acid and repeated evaporations of the finely powdered mineral in boiling aqua regia were needed to produce any sign of the canary-yellow oxide  $WO_3$ .

Associated with wolframite in a number of Westland sands and with the wolframite-gahnite-cassiterite-monazite assemblage at Port Pegasus is a mineral that is superficially comparable to wolframite in many ways (Table 9). In reflected light these mineral grains showed what appeared to be good cleavage, are dark brown to black, and very thin flakes have a similar appearance to wolframite. The mineral has approximately the same hardness as wolframite and a dark red-brown streak, but a density of approximately 4.8. The magnetic susceptibility of the mineral was about equal to that of wolframite. Interpretation of the analysis (Table 9) was obscure until a polished section made of a few grains from the -18 + 35 screening of Blackball dredge and Mudtown concentrates proved that the material under investigation was of a composite nature and probably an intergrowth of ilmenite and hematite. A recalculation of analysis of the Mudtown material on the assumption that the hematite is titanhematite containing in solid solution the maximum allowable 10 per cent of  $TiO_2$  (Ramdohr, 1926, p. 357), and the ilmenite is saturated at 6 per cent of  $Fe_2O_3$  (Edwards, 1938, p. 42), gives a mode of approximately 46 per cent of titanhematite and 54 per cent of ilmenite with no excess of oxides; the small percentage of the pyrophanite molecule was included in ilmenite rather than with titanhematite. In similar ilmenite-titanhematite intergrowths, Edwards (1938, p. 46) mentions the development of pronounced lamellar twinning; although this feature was not present in the polished section of the New Zealand minerals, the pronounced striations so clear in reflected light may well have been this and not cleavage as supposed.

It is believed that much so-called arizonite (Palmer, 1909; Wadia, 1943, p. 10) and also minerals similar to that described by Mackin-

tosh (1885, p. 342-3) are probably of this nature.

Ragged anhedral grains believed to be *chalcopyrite* have been observed as rare constituents of the coarser fractions of Ngahere dredge con-

TABLE 9.—ANALYSIS OF ILMENITE-TITANHEMATITE INTERGROWTH FROM MUDTOWN, STEWART ISLAND (Analyst: F. T. Seelye)

$Fe_2O_3$ .....	45.48
FeO.....	20.28
$TiO_2$ .....	30.50
$Al_2O_3$ .....	1.00
MnO.....	1.49
MgO.....	0.21
CaO.....	nt. fd.
$SiO_2$ .....	0.52
$H_2O$ at 105°C. ....	0.21
	99.69

centrates. The mineral was quite opaque even in the thinnest flakes and the finest powder but in oblique illumination has a bright brassy yellow color. Green and greenish-blue staining of this material was very rarely seen, but a brown limonitic coating was more prominent. The mineral is readily soluble in hot concentrated nitric acid.

*Pyrite* was found in most samples from the dredges but in few beach sands; and in the latter category an important sample was collected just north of the Waitakere River mouth in the Nelson Provincial District. In most examples the percentage of pyrite in the mineral assemblages of the various screened fractions increased with increase of grain-size, and in one instance, the -10 + 18 fraction from Ngahere Dredge, pyrite was predominant.

In the finest grades, pyrite ordinarily occurred in anhedral and splintery fragments and in a few instances (-230 fraction, Snowy River) as globular or concretionary particles; in one sample dendritic forms were common (Blackball dredge). Between these forms and the euhedra so characteristic of the coarser fractions of many samples, there is every gradation.

In the coarser fractions, cubes, perfect, distorted, or striated, pentagonal dodecahedrons (pyritohedrons), and combinations of these were

the most usual forms. Rarely cubes modified by slight development of octahedron faces were found. Pentagonal dodecahedrons with lineage structures (Buerger, 1932, p. 181) were not uncommon.

When the mineral is quite fresh and unaltered, it has a characteristic pale brass-yellow color but in many examples this was obscured by the brown tarnish of oxidation. Such crystals when crushed were frequently found to be completely pseudomorphed by limonitic material or hematite, but however complete the alteration, the detection of parallel striations, which result from oscillatory combination of (100) and (120), was usually sufficient evidence of pyrite, or a pseudomorph thereof. Anhedra of pyrite are sometimes difficult to distinguish from similar particles of chalcopyrite by mere inspection but two tests were usually sufficient: (a) approximation of hardness by crushing, and (b) addition of ammonium hydroxide to the nitric acid solution of the mineral gives a deep blue coloration if the mineral is chalcopyrite;  $\text{Fe}(\text{OH})_3$  is of course precipitated in both cases.

No *marcasite* was diagnosed with certainty and the problem of distinguishing between it and pyrite when they occur in grains devoid of any crystal faces deserves some comment. Bannister (1932, p. 180) has pointed out that most text-books base description of the color of *marcasite* and pyrite on tarnished specimens; in freshly polished specimens, *marcasite* is tin-white and pyrite is pale brass-yellow. In addition, *marcasite* is strongly anisotropic but pyrite is isotropic or exhibits only very faint polarization colors. Solution of the powdered mineral in hot concentrated nitric acid, suggested by many writers (Ford, 1932, p. 438) is not a reliable method of distinguishing between the two minerals. In doubtful cases, polished sections should be made and the color of the mineral and its effect on polarized light determined. These observations should suffice for accurate diagnosis, but there is a minimum limit to the grain-size that may be satisfactorily tested in this way.

*Lead*, though absent from the beach sands, is a constituent of a number of dredge concentrates, and it was limited to mineral assemblages coarser than 250 microns. In a sample from Blackball Dredge, lead made up 8 per cent of the -35 + 60 fraction. The metal was invari-

ably found as spherical pellets dulled by thin gray-white surface coatings. Freshly cut surfaces had a high reflectivity and the material was completely and readily soluble in warm dilute nitric acid.

There is every reason to believe that the lead in the different samples has been derived initially from shot-gun cartridges, the result of sportsmen's activities within the immediate drainage area, and that it is not native lead. The metal never occurred as slugs or aggregates but appeared to be limited to particles within a narrow range of size. Arsenic is present in each of the particles tested, and generally about 0.2 per cent of arsenic is added to lead during the manufacture of shot for hardening purposes. So far as the writer is aware arsenic is not a contaminant of native lead.

The presence of *arsenopyrite* was confirmed in one specimen only, where it was found to occur as rare subhedra with striated prisms and a steel grey color when observed in oblique illumination.

*Pyrrhotite* is another sulphide that is restricted to dredge concentrates in its distribution, and, when present in an assemblage, only occasional particles were found. The mineral occurs as irregularly shaped anhedra and less commonly as spherical aggregates that seem to be composed of finely divided pyrrhotite cemented with a clay-like matrix. The following properties taken together are considered to be diagnostic: (1) Reddish-yellow to bronze color in oblique illumination; (2) Strongly ferromagnetic; (3) Soluble in warm hydrochloric acid with evolution of hydrogen sulphide; (4) Some grains were determined by means of the dimethylglyoxime test to be nickeliferous.

**ORTHITE:** Although the cerium epidote is not an uncommon constituent of the granites and schists in the areas from which the sands studied were originally derived, orthite was a very rare constituent of those sands and appears to be limited to Snowy River, Gillespie's Beach, Arahura, and Wainui Inlet material. Orthite occurred as slightly chipped, prismatic crystals, transparent, deep brown and distinctly pleochroic; the mineral has a birefringence of about 0.020 with  $\beta = 1.730 \pm 0.003$ , for Wainui Inlet material.

The author is of the opinion that some of the semi-opaque, brown-colored, anhedra grains

found in a number of preparations and not satisfactorily diagnosed might well be orthite. Since that mineral is often found in various stages of metamictization and a number of other radioactive minerals have similar physical properties, recognition is often difficult, if not impossible, unless sufficient material can be separated for chemical tests.

**RUTILE:** Rutile has been observed in most of the finer fractions of dredge concentrates but is generally absent from beach sands; on occasions the mineral has been found in screened fractions coarser than 35 mesh, *viz.* Slab Hut. Stumpy, prismatic, subhedral grains with rounded extremities are usual (Pl. 4, fig. 75), with broken euhedra and well abraded spherical grains not uncommon. In those grains showing a minimum of abrasion, longitudinal striations parallel to the prism edge were often seen, although occasionally striations oblique to the elongation were observed. Genuiculated fragments are rare.

Color is typically reddish-brown with a poor dichroism as follows: O = yellow to golden-yellow; E = red-brown; E > O. Rutile from Barrytown dredge was similar except that the ordinary ray has a distinct greenish-yellow tint. A foxy-red color for this mineral was very rarely observed.

Some rutile crystals of one sample (Slab Hut) were separated for determination of density and values ranging from 4.24–4.26 were found with the Berman balance. These data indicate that such rutile crystals, which incidently are comparable with those in other samples, are pure  $TiO_2$ , or that the ions that may substitute for Ti, *viz.* Fe, Ta, and Cb, are present in traces only.

In oblique illumination, rutile is readily distinguished from the associated minerals by its prismatic habit, brown color, and resinous luster; however, it is difficult to discriminate thus between broken or anhedral grains of rutile with pronounced sub-conchoidal fracture, and lighter-colored cassiterite fragments. Distinction may be made between such grains by removing them on a needle point, crushing them in oils, and examining the powder by transmitted light.

**SHEELITE:** Scheelite is a characteristic detrital mineral in many of the concentrates from Southern Westland and particularly noteworthy

in samples from: Five Mile Beach, Gillespie's Beach, Harihari, Saltwater Creek, and Bruce Bay. From other localities in northern Westland, southern Nelson etc., scheelite was either rare or absent altogether. In the southern Westland occurrences, scheelite is most abundant in the -60 + 120 screenings but is almost restricted to these and finer material.

Scheelite occurs most frequently as equidimensional anhedral, which in oblique illumination often exhibited bright reflections from octahedral and possibly basal cleavage faces. Occasionally, however, extraordinarily beautiful sets of pyramidal faces were developed (Pl. 2, fig. 37), as many as 45 complete pyramids having been counted on a grain measuring approximately 90 microns in diameter. From the position of the cleavage faces, the pyramidal faces were interpreted as  $p$  (111) forms, but no tripyramidal forms were obvious. In those crystals in which pyramidal forms were well developed, the apices of the crystals were almost invariably truncated by a small plane (Pl. 2, fig. 37); it is not clear whether this is an expression of basal cleavage or represents a poor development of  $c$  (001), but the latter possibility is favored.

The removal of the apices of the pyramidal crystals might naturally be ascribed to damage during transportation but for the regularity and evenness of the development. Between these and the anhedral fragments are grains (Pl. 2, figs. 35–36) showing every gradation in the perfection of form.

Since the optical properties of scheelite are so similar to those of a uranium-free thorium silicate, tentatively called thorite, found associated with the tungstate, and since preliminary examinations failed to differentiate between them, the physical properties of both minerals have been determined with care. To enable this to be accomplished satisfactorily about 2 grams of scheelite-thorite concentrates were prepared from original material by screening and removal of magnetically susceptible material<sup>25</sup>; after splitting, convenient quantities were mounted in Canada balsam and hyrax. The following properties were determined for scheelite: Uni-

<sup>25</sup> The southern Westland uranium-free thorite may be removed from a mixture with scheelite but only in an intense magnetic field; with the Frantz Isodynamic separator, fractionation was made at 1.4 amps., cross slope 10°, and longitudinal slope 15°.

axial and optically positive;  $O = 1.919 \pm 0.001$ ;  $E = 1.935$ ;  $E - O = 0.016$ ; no dispersion;  $D_{20^\circ\text{C}} = 6.03 \pm 0.02$ .

The mineral is very pale yellow-white and, in oblique illumination, a sub-vitreous luster is characteristic. Apart from its optical properties,

TABLE 10.—ANALYSES OF RUTHENIAN  
SISERSKITE

	A	B
Os.....	49	41.9
Ir.....	35	34.8
Ru.....	10	11.8
Rh.....	2.5	0.1
Pt.....	trace	8.1
Fe.....	—	2.3
Undetermined.....	3.5	—
	100.0	99.0
D. $23^\circ\text{C}$ .....	19.6	—

A. Kaniere River Dredge, Westland, New Zealand.

B. Nevyansk, Ural Mountains, Russia. Analysis no. 4, table 3, Swjaginzeff, 1932, p. 182.

scheelite may be readily distinguished from the optically similar thorite by the yellow  $\text{WO}_3$  that is formed on its grains when boiled in aqua regia for 3-4 minutes; further, in ultraviolet light of wave-length approximately  $2540 \text{ \AA}$ ., scheelite gives a characteristic blue fluorescence whereas thorite emits a faint dull white with a pink tinge.

**SILLIMANITE:** Sillimanite has been recognized in the concentrates from Snowy River and Rimu Dredges. In both instances the mineral was found to be restricted to screenings coarser than 230- and finer than 120-mesh and only occasional grains were found in either sample.

In both occurrences, sillimanite took the form of short, stout, colorless prisms with pronounced cross-fracture (Pl. 4, figs. 70-71); the crystals are devoid of inclusions, have parallel extinction and positive elongation. Determination of optic axial angle in one crystal by universal stage methods gave a value of  $25^\circ \pm 3^\circ$ .

**SISERSKITE:** A ruthenian variety of siserskite was not identified in any of the samples examined by the writer but it is listed here, since several large oval plates or slugs weighing 2.7 gms. in all were recovered on one occasion

during a wash-up of the final concentrates from Kaniere Dredge by the dredge-master. One of these plates has been analysed by Mr. F. T. Seelye (Table 10, analysis A).

The analyst further reports: "Palladium was not detected and platinum if present is probably in very small amount." In a thorough search of the literature available to the writer an analysis of siserskite from the Ural Region listed by Swjaginzeff (1932, p. 182) was the closest approximation found (Table 10, analysis B). In most analyses of iridosmine discussed by Swjaginzeff, platinum is present, with one analysis showing as much as 13 per cent of that metal. Platinum, however, is present in all analyses of siserskite, except one (1932, p. 174, analysis no. 9), an old analysis which may not be quite trustworthy. The lack of platinum in the New Zealand material is, therefore, somewhat unusual.

The metal has a dull silvery-grey luster and steel-grey to white color in oblique lighting. Even in naturally rolled and worn grains, a distinct cleavage is evident. It is relatively hard and cannot be pricked and picked up with a needle point. This property, together with siserskite's insolubility in aqua regia and distinct cleavage, constitute useful criteria for distinguishing this alloy from platinum.

The name siserskite is used here in its original sense, since in the New Zealand material  $\text{Os} > \text{Ir}$  (Palache *et al.*, 1944, p. 113).

**SPINEL:** A ferroan variety of spinel is an occasional constituent of the finest grade-size of material from Red Jacks dredge concentrates, occurring as dull-green fragments with pronounced conchoidal fracture that are translucent when finely crushed. The mineral is isotropic, devoid of inclusions but intersected by numerous cracks; it is moderately paramagnetic and has a refractive index of  $1.782 \pm 0.002$  and a density determination gave  $3.74 \pm 0.01$ .

The writer would like to stress the fact that before material from this dredge was studied, a few fragments of gadolinite had been identified from Barrytown material, and when the granules of spinel were found, it was by no means obvious at first that it was green spinel, due to the optical similarity of gadolinite and ferroan spinel. However, the densities of the two minerals are sufficient to allow differentiation,

and more noteworthy still, upon heating, spinel will remain isotropic whereas gadolinite becomes strongly anisotropic since its metamict condition is destroyed. Further confirmation was obtained by microchemical tests for the presence of magnesium. These details are stressed because it has been observed that, in California, students would often quickly dismiss an isotropic green detrital mineral as chrome garnet simply because that mineral has been diagnosed in the heavy mineral assemblages of sediments from that State, when instead they were dealing with green spinels. Thus green isotropic grains should be identified with some care, but usually refractive index data are sufficient to lead to correct identification. Minerals such as yttrialite and gadolinite, which are usually found in a metamict state and have properties similar to those of green spinels, cannot be recognized by inspection alone.

**STAUROLITE:** Only rare anhedral grains of staurolite were found in the -230 fraction of the concentrates from Blackball Dredge (Pl. 4, fig. 74). Since this mineral has not previously been recorded from New Zealand, the grains were isolated and all the data possible were determined for them, as follows:

$$\alpha = 1.744 \pm 0.003$$

$$\gamma = 1.755$$

$$\gamma - \alpha = 0.011$$

Biaxial and optically positive.

2V = large, probably in excess of 75°.

Pleochroism is weak according to the scheme:

X = colorless to very pale yellow.

Z = pale yellow.

Z > X

The mineral exhibited no cleavage, but had a pronounced conchoidal fracture and numerous sinuous lines of minute opaque inclusions that are believed to be carbonaceous material.

**THORITE:** Several varieties of thorite have been noted in specimens from a wide variety of localities, but they were never more than mineralogical curiosities except in the central and southern Westland region. In concentrates from Harihari, Saltwater Creek, Gillespie's Beach, Okarito, and Bruce Bay areas, a biaxial thorium silicate, hereafter called thorite, and uranothorite sometimes ranked as the most important minerals present after removal of iron ores. Since three distinct varieties of thorite

have been found each will be discussed separately.

*Uranothorite* is particularly abundant in the -120 + 230 mesh fractions of samples from Harihari, and this material is more or less typical of all other occurrences. It (Pl. 3, figs. 46-54) occurs in well worn and rounded grains to strictly euhedral crystals of simple habit in which the only forms developed are *m* (110), and *p* (111); occasionally poorly developed basal planes were observed (Goldschmidt, 1923, vol. 8, table 80, fig. 4). Splinters and fragments with marked conchoidal fractures were not uncommon. Generally the mineral grains were quite translucent but in a number of cases they were rendered semi-opaque by dense aggregates and liberal dustings of unidentifiable alteration products. In many instances, crystals of uranothorite exhibited curiously anastomosing systems of cracks with no orderly arrangement, although occasionally they appeared to originate in the center of a crystal and to radiate outwards. In some crystals, the central areas were somewhat darker than the remaining portions, and still less frequently, contained dark or opaque inclusions. Not uncommonly the walls of these cracks were stained with brown films, possibly limonitic, and in rare instances these spaces were filled with opaque dust-like particles determined as magnetite. Whether the limonitic stains are the result of alteration of uranothorite is not clear, but the strings of magnetite dust would certainly seem to have been so derived. These irregular networks of cracks have often been observed in radioactive minerals (Brögger, 1890, p. 123-126, in thorite and orangite; Ellsworth, 1927a, p. 367, in euxenite; Hess and Wells, 1930, p. 19-20, in samarskite.); and, further, in many instances have been found to radiate outwards from the actual mineral grains into the surrounding matrix of crystals<sup>26</sup>.

There is considerable variation in color and it is difficult to match them exactly with the

<sup>26</sup> Hidden, 1905, p. 423 (surrounding cyrtolite); Landes, 1932, p. 386 (surrounding allanite and fergusonite); Spence, 1930, p. 480; Richmond, 1937, p. 293 (surrounding orangite and allanite); Walker and Parsons, 1923a, p. 17 (surrounding ellsworthite, zircon, fluocerite, and allanite); Ellsworth, 1924, p. 12cI-14cI (surrounding zircon, cyrtolite, allanite, hatchettolite, columbite); Henrich, 1948, p. 68 (surrounding euxenite); Shannon, 1926, p. 36-37 (surrounding hatchettolite).

Ridgway standards (Ridgway, 1912). However, they range from drab, dirty brown (c.f. Ridgway's Isabella Color, 19" i) to olive-yellow (c.f. Ridgway's 23" olive yellow). In a few crystals the color is closer to Ridgway's deep chrysolite green (27"), and these are usually quite translucent and free from dusty alteration products. By and large, the more translucent the crystals the more decidedly green their color.

Uranothorite is distinctly dichroic, but the primary colors depend upon the degree of alteration of the mineral. The clear, translucent crystals show the most pronounced dichroism as follows: X = pale lime green (c.f., lime green 25"); Z = Cource green, 25", i.; Z > X.

For the analysed material the following range of refractive indices was measured:  $\alpha = 1.818-1.825 \pm 0.003$ ,  $\gamma = 1.839-1.840$ ,  $\gamma-\alpha = 0.015-0.021$ . For separate grains the lowest value found for  $\alpha$  was 1.815, whereas the highest figure for  $\gamma$  was 1.850. For a considerable number of crystals the actual determination of  $\alpha$  and  $\gamma$  was impossible, or rendered exceedingly difficult, owing to an apparent recrystallization of uranothorite to give radiate aggregates of flake-like individuals, though still retaining the simple tetragonal prismatic habit and outline. These aggregates, oriented in all possible directions, give such crystals anomalous optical character since, during a 360° rotation of the microscope stage, total extinction was never completely obtained. For clear green homogeneous uranothorite, uniaxial and optically positive interference figures were obtained.

Owing to the high density of uranothorite, flotation methods were impractical for determination of this property. Measurements were made with the Berman balance, but since the grain diameters did not exceed about 0.2 mm., it was not possible to employ single grains or to differentiate between altered and fresh material. Using approximately 8 mgm. portions of pure uranothorite, several determinations gave an average value of  $6.7 \pm 0.05$ . A similar figure was obtained using a micropyknometer.

The mineral was moderately paramagnetic but with a susceptibility decidedly less than that of monazite, and as a result uranothorite was fairly easily fractionated from its associated

minerals<sup>27</sup>. A nearly pure sample of uranothorite prepared by the writer and analysed by Mr. F. T. Seelye (Table 11, analysis A) shows that the mineral is a true uranium-bearing thorite, which is decidedly low in water-content in comparison with uranothorites from other localities. This particular feature is reflected in the high density and anisotropic state of the Westland mineral and is in marked contrast to the thorite from MacDonald Mine (analysis C), which has a much lower density and is completely metamict. The dominant green of Westland uranothorite is also distinctive since most thorites, whether they contain uranium or not, are red or brown.

A *uranium-free thorite*\* has a similar general distribution to that of the uranothorite but it is somewhat more abundant. In marked contrast to the associated uranothorite, thorite is colorless to palest yellow; appears to be almost completely non-magnetic, contains no uranium and is almost always anhedral; an approach to subhedralism was rarely observed in any preparation and the grains generally were highly irregular in outline and exhibited a pronounced conchoidal fracture. In addition to uranothorite, thorite is associated with a small percentage of scheelite in the southern Westland material and due to the striking similarity of its optical properties to those of scheelite, it was not recognized at first. However, when the almost non-magnetic fraction, thorite-scheelite-zircon was inspected in ultraviolet radiation of wavelength of approximately 2540 Å., scheelite appeared intensely blue, zircon, gold, whereas uranium-free thorite fluoresced with a faint dull white with a pinkish tinge. If this fraction is treated with aqua regia, washed, dried and then examined under a binocular microscope, scheelite may be readily distinguished from thorite by the distinctive coating of yellow oxide formed on the tungstate.

The following optical properties have been

<sup>27</sup> After removal of more susceptible material uranothorite was attracted in the Frantz separator with a current of 0.9-1.1 amps., cross-slope of 10, and a longitudinal slope of 15.

\* A monoclinic symmetry has been demonstrated for the uranium-free thorium silicate described herein by recent work (Hutton and Pabst).



TABLE 11.—ANALYSES OF URANTHORITE

	A	B	C	D	E
PbO.....	—	0.40	1.32	1.67	—
Pb.....	0.47	—	—	—	—
UO <sub>2</sub> .....	11.5	—	7.67	—	—
UO <sub>3</sub> .....	—	9.96	9.46	9.78	7.70
ThO <sub>2</sub> .....	62.6	52.07	46.33	50.06	64.56
Ce <sub>2</sub> O <sub>3</sub> .....	—	—	0.08	1.39	—
CeO <sub>2</sub> .....	1.1	—	—	—	—
Y <sub>2</sub> O <sub>3</sub> .....	—	—	0.36	—	—
FeO.....	—	—	0.43	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	2.3	4.01	0.75	7.60	0.78
FeS <sub>2</sub> .....	—	—	trace	—	—
MnO.....	—	—	0.07	trace	—
Al <sub>2</sub> O <sub>3</sub> .....	—	0.33	0.13	—	—
CaO.....	0.3	2.34	4.38	1.99	0.95
MgO.....	0.3	0.04	<0.01	0.28	—
SiO <sub>2</sub> .....	19.5	19.38	19.56	17.04	13.00
H <sub>2</sub> O —.....	0.25	} 11.31	3.57	} 9.46	5.30
H <sub>2</sub> O +.....	1.68		5.67		5.74
Insol.....	—	—	0.15	—	—
	100.0	99.95	99.94	100.13*	98.03
Sp. Gr. 25° C.....	6.25 ± 0.05	4.126	4.414	4.38	—
U.....	10.14	—	14.63	—	—
Th.....	55.02	—	40.72	—	—
Pb.....	0.47	—	1.22	—	—
Pb.....	0.0157†	—	0.04	—	—
(U + 0.36Th).....					

A. Uranthorite from Gillespie's Beach, Southern Westland; analysis recalculated to 100%, after eliminating zircon, scheelite, ilmenite, and 1.83% of undetermined material. Analyst: F. T. Seelye.

B. Uranthorite from Lake Champlain; total includes alkalis 0.11% (see Dana, 1892, p. 488, analysis no. 5).

C. Uranthorite, MacDonald Mine, Hybla, Ontario (Ellsworth, 1927b, p. 370).

D. Uranthorite from Arendal, Southern Norway (see Brögger, 1890, p. 121, anal. no. 7).

E. Orangite from basin of Sahavary River, Madagascar (Turner, 1928, p. 76, table 2, analysis no. 16).

\* Total includes 0.86% of P<sub>2</sub>O<sub>5</sub> and uranium is quoted as U<sub>2</sub>O<sub>3</sub>.

† This factor multiplied by 7600 gives the age in millions of years as 119. This age determination, which is a minimum figure only since the mineral was not found *in situ*, is equivalent to the lower part of the Cretaceous Period.

determined for this constituent:

Refractive indices:

$$\alpha = 1.898 \pm 0.003$$

$$\beta = 1.900 \text{ (by calculation)}$$

$$\gamma = 1.922$$

$$\gamma - \alpha = 0.024$$

Dispersion: moderate with  $\rho < \nu$ .

$$2V = 25^\circ \pm 2^\circ$$

D. at 20°C. =  $7.1 \pm 0.1$  (using approximately 40 mgm. of material).

In a statistical analysis of grains of uranium-free thorite mounted in Canada balsam, 7 per

cent of the grains had similar orientation, since such grains exhibited low double refraction and gave interference figures in which the positive acute bisectrix lay just outside the edge of the field of view. Since these grains were anhedral, this orientation suggests cleavage, perhaps parallel to a flat pyramid or basal plane.

A small sample of the present mineral was separated in the pure state by the writer and analysed by Mr. Seelye; only 7 mgm. of material were available for analysis and hence only thorium, uranium, silica, and water determined;

the remainder, determined by difference, was reported to consist of rare earths and  $\text{Fe}_2\text{O}_3$ . For a second pure sample, the writer determined the iron, reported in the ferric state, to be 1.2 per cent, rare earths 2.6 per cent, traces only of manganese and phosphorus, and an

TABLE 12.—ANALYSIS OF URANIUM-FREE THORITE, GILLESPIE'S BEACH

$\text{ThO}_2$ .....	76.6
$\text{UO}_2$ .....	nil
$\text{SiO}_2$ .....	19.7
$\text{Fe}_2\text{O}_3$ .....	1.2
$\text{CaO}$ .....	nil
$\text{MgO}$ .....	nil
$\text{MnO}$ .....	trace
$\text{P}_2\text{O}_5$ .....	trace
$\text{Ce}_2\text{O}_3$ etc.....	2.6
$\text{H}_2\text{O}$ (total).....	nil
	100.1

absence of calcium and magnesium. Both uranium and water are absent (Table 12). The chemical composition and the optical and physical properties of the south Westland thorite are quite distinct from those recorded for thorite from numerous other occurrences, and it might be profitable to list the most distinctive features now. These are as follows:

(1) The mineral is colorless. The writer can find no record of colorless thorite; brown, black, or orange-yellow, as in the variety orangite, is usual.

(2) A relatively high birefringence, *viz.* 0.024, is unusual; the mineral is usually reported to be isotropic, and when anisotropic, a birefringence in excess of 0.01 does not appear to be found (Winchell, 1933, p. 185). Brögger (1890, p. 123-124), in thin sections of altered thorite and orangite, has observed what he believed to be strongly birefringent remnants of unaltered thorium silicate, but he did not give exact figures; and Lacroix (1922, p. 243) has listed thorite from Madagascar as uniaxial and positive, but usually isotropic.

(3) The mineral is anhydrous whereas all analyses of thorites listed by Hintze (1915, p. 1675) show a high percentage of water; 18 analyses showed a range from 6.14-12.05 per cent.

(4) The density, determined with approximately 40 mgm. of fine-grained material is  $7.1 \pm 0.1$  at  $20^\circ\text{C}$ ., greatly exceeding the values previously recorded for thorite. Brögger (1890, p. 120) has stated that the specific gravity of thorite has a range of 4.4-4.8, whereas orangite may range from 5.19-5.40; Dana (1892, p. 481), quoting Chydenius, lists a range of 4.888-5.205 for orangite, and, incidently, a value as low as 4.126 for uranothorite.

(5) The mineral does not gelatinize upon treatment with a variety of concentrated acids. (*See* Murata, 1943, p. 552.)

(6) The mineral is characteristically biaxial, whereas thorite is stated to be uniaxial, as it should certainly be on account of its symmetry.

These properties suggest that this  $\text{ThSiO}_4$  is quite distinct from normal tetragonal thorite and that it is some other crystalline modification of  $\text{ThSiO}_4$ . If this is so the mineral should not be called thorite and a new name is required, but the writer is loathe to introduce such a name until further information can be obtained. The lower densities and refractive indices and isotropic character of previously recorded thorites have, in the writer's opinion, resulted solely from hydration of thorite due to metamictization; further, there is no sound basis for assuming that the variety orangite should have a higher density than thorite itself. Several variable factors may affect the physical properties of thorite and its variety orangite, two of the most important being (1) the degree of metamictization, and consequently the extent of hydration, and (2) the extent of substitution by other ions, chiefly uranium and iron.

Doelter's statement (1918, p. 230) makes it clear that he believed that water-content and percentage of uranium in thorites were directly proportional. The few analyses listed by him appear to support that conclusion as do analyses of ferriuranthorite from Vernadsky Mine, Sludianka (Kalinin, 1945, p. 202), and hydrothorite from Wodgina, Western Australia (Simpson, 1928), but the uranothorite from south Westland contains a high percentage of uranium but a low water content. Another decided exception is a ferriferous thorite from northern Kirghizia in which Starik, Kravchenko, and Melikova (1941) found only 0.41 per cent  $\text{U}_2\text{O}_8$  and 5.64 per cent of water. Since

in thorite, uranium replaces thorium, and it is believed that this substitution does not upset valency relationships, there is little reason to assume a sympathetic relationship between uranium and water content.

A *phosphorus-bearing thorite* occurs as occasional grains in concentrates from Red Jacks, Blackball, and Snowy River dredges, and a sufficient quantity for close study was available only from the two latter sources. In Blackball material, phosphorian thorite was found in the -230 fraction as anhedral with marked conchoidal fracture. The mineral is pale yellow and non-dichroic, uniaxial and positive. The refractive indices and birefringence were determined to be as follows:  $\alpha = 1.78$ ,  $\gamma = 1.79$ ,  $\gamma - \alpha = 0.01$ . Dispersion, cleavage, and twinning were not seen. In Snowy River dredge concentrates, thorite was restricted to one large grain in screenings coarser than 35-mesh. This fragment was well worn, pale yellow with a density of 6.0. When powdered the mineral was almost completely soluble in concentrated nitric acid. It is quite isotropic and a refractive index of  $n = 1.87 \pm 0.01$  was found. Although a very small quantity of this thorite was available a partial analysis (Table 13) shows the presence of 4 per cent of  $P_2O_5$ . Careful microscopic examination of the powdered mineral left no doubt that it was quite homogeneous and not a mechanical mixture or aggregate of two or more constituents. Chemically the mineral is similar to auerlite (Table 13, B and C) in which considerable substitution of  $(SiO_4)^{4-}$  groups by  $(PO_4)^{3-}$  is believed to have occurred. Such replacement is not uncommon and has been clearly shown to occur in orthite-nagatelite (Machatschki, 1931), griphite (McConnell, 1942), zircon (Hata, 1938b), and garnet (Mason and Berggren, 1941). Indeed, a theoretical consideration of ionic sizes and radius ratios would allow prediction of such an interchange since the Si-O distance of 1.62 Å., is exceedingly close to the P-O distance in a structure such as xenotime, 1.64 Å. Simultaneous compensation for the electrical neutrality could be accomplished for phosphorian thorite by replacement of  $Th^{4+}$  by  $Fe^{3+}$  or  $Al^{3+}$ , or, in agreement with the composition of the New Zealand phosphorian thorite, by the trivalent rare earths,  $Ce^{3+}$ ,  $Y^{3+}$ , etc. Although substitution of phosphorus for silicon is even more extensive in

auerlite, analyses B and C, compensatory replacements do not appear to be adequate. However this disagreement may be more apparent than real since both B and C are old analyses,

TABLE 13.—ANALYSES OF PHOSPHORIAN THORITES

	A	B	C
ThO <sub>2</sub> .....	74	72.16	70.13
SiO <sub>2</sub> .....	16	6.84	7.64
P <sub>2</sub> O <sub>5</sub> .....	4	8.58	7.46
TiO <sub>2</sub> .....	1	—	—
Rare earths.....	3	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	0.2	1.78	1.38
Al <sub>2</sub> O <sub>3</sub> .....	nil	—	1.10
CaO.....	nil	—	0.49
MgO.....	nil	—	0.29
H <sub>2</sub> O.....	2	10.64	11.21
	100.2	100.00	99.70

A. Phosphorian thorite from Snowy River. U, Zr, and V absent. Determination of rare earths, iron, and water by C. Osborne Hutton, remainder by F. T. Seelye.

B. and C. Analyses of so-called auerlite from North Carolina. *Vide* Doelter, 1918, p. 234.

and in analysis B the thorium figure was obtained by difference only, presumably on the supposition that the constituents actually determined would be the only others present. In view of the hypothesis that extensive substitution of rare earths and phosphorus for thorium and silicon respectively occurs in thorites, it is questionable whether the name auerlite need be retained for a mineral that is merely a member of an ionic substitution series. The same argument certainly applies to hydrothorite (Simpson, 1928a, p. 464-465; 1928b) which appears to be only a metamict thorite containing a little more water than usual and some substitution by phosphorus, CaO, and rare earths as in auerlite.

Considering the full extent to which such substitution could occur in thorite, some of the relevant facts are: (1) The similarity of the dimensions of the interionic distances P-O and Si-O. (2) The comparable sizes of the ionic radii of  $Th^{4+}$  and  $Y^{3+}$ , 0.95 Å (Zachariasen's value for 6-fold coordination) and 1.06 Å.

With complete replacement of  $Th^{4+}$  and  $Si^{4+}$  by  $Y^{3+}$  and  $P^{5+}$  respectively, it is clear that we

have the mineral xenotime,  $YPO_4$ , and clearly the phosphorian thorite described herein appears to be an intermediate member of an isomorphous series thorite-xenotime. Whether this isomorphous replacement is unlimited or restricted within narrow limits is not known at present and an answer to this question must await further work. From a structural point of view, complete substitution should be possible. However, many of the analyses of xenotime listed (Doelter, 1918; Hintze, 1922) show appreciable but limited quantities of silica. A number of these determinations are old or incomplete but, in the best of these, appreciable silica parallels the incoming of a noteworthy amount of thorium or uranium, or both. More recently Hata (1938b) has published a more than usually complete analysis of pure xenotime in which he found 4.32 per cent  $SiO_2$ , and 2.47 per cent  $ThO_2$ , and incidently, 1.90 per cent  $ZrO_2$  also. Substitution of phosphorus by silicon is not necessarily the only interchange that may occur in xenotime, for undoubtedly as in hussakite (Kraus and Reitingner, 1901), some substitution of  $(PO_4)^{3-}$  by  $(SO_4)^{2-}$  groups is possible, apparently compensated for by some interchange of calcium for yttrium earths. Replacement of  $(SiO_4)^{4-}$  by  $(PO_4)^{3-}$  does occur in thorites, but its extent must await further study. Since this interchangeability is possible, it will be of interest to know whether  $(AsO_4)^{3-}$  groups are also present in some thorites; most noteworthy in this respect is the listing by Starik *et al.* (1941) of 0.51 per cent  $As_2O_5$  in ferrithorite. Actually arsenic was probably never looked for in the analysis of thorites; almost certainly neither was phosphorus in older work.

**TITANITE:** Titanite is a constituent of most of the dredge concentrates but in no instance makes up more than 3 per cent of any particular fraction of a sample. However, pay-streaks of titanite were found in many of the beach sands east of Tarakohe Inlet, in northwest Nelson, and in some of these titanite constitutes up to 50 per cent of the sand and is associated chiefly with zircon, apatite, ilmenite, and magnetite.

In the dredge concentrates, titanite is usually limited to the finer grade-sizes and exhibits a range of color from pale yellow to light brown. In most samples anhedral grains were found, with spindle-shaped and double-wedge-shaped crystals less common. In the north-west Nelson

beach sands, however, sharply euhedral titanite crystals are abundant (Pl. 2, fig. 38; Pl. 3, figs. 39-42). They are fairly simple in form and the dominant habit exhibits a combination of  $l$  (112),  $c$  (001), and  $x$  (102) with the latter form usually predominant; actually, the crystals are very similar in appearance and general habit to those described and figured by Webb (1939, p. 345). As a result of this habit, crystals tend to orient themselves with the flat dome in the plane of the microscope stage when immersed in oils, and, since the positive acute bisectrix  $Z$  is nearly normal to that plane, crystals showing good centered interference figures with characteristic dispersion are usually readily obtained. Cleavage, probably parallel to the unit prism, was observed in fractured crystals. Titanite from this area is pale yellow or very nearly colorless in grains with diameters less than 62 microns.

In the  $-35 + 60$  fraction of a beach concentrate recently sent the writer from Bruce Bay, South Westland, crystals of titanite of unusual appearance were found with the following properties:

(1) The crystals are black, euhedral, and exhibited the simple "envelope" habit.

(2) In transmitted light the crystals are slightly translucent at the edges but the dull-black opaque appearance in oblique illumination is clearly due to dense clouds of dustlike particles.

(3) The magnetic susceptibility of the crystals is no greater than the associated but perfectly clear, inclusion-free titanites.

(4) Chemical tests showed only traces of  $Fe^{2+}$  and  $Mn^{2+}$ , in addition to the usual constituents of titanite.

(5) After crystals were heated at dull-red heat for 2-3 minutes, they became more translucent.

In view of the absence of any increase in magnetic susceptibility above that usually found in titanite, the rarity of  $Fe^{2+}$ , and the tendency for the opacity to clear up on heating, it is believed that the inclusions are carbonaceous, rather than an iron oxide dust.

The following optical properties for titanite from Wainui Inlet, northwest Nelson were determined in sodium light:  $\alpha = 1.912 \pm 0.003$ ;  $\beta = 1.917$ ;  $\gamma = 2.08$ ;  $\gamma - \alpha = 0.168$ ;  $2V = 36^\circ \pm 2^\circ$ . Pleochroism, faint but more distinct in

crystals with diameters greater than 0.25 mm., followed the scheme: X = pale golden-yellow; Z = slightly deeper golden-yellow; Z > X. The density, determined by centrifuging the powdered mineral in Clerici solution, was  $3.54 \pm 0.02$ .

Zachariasen's (1930) work on the crystal structure of titanite has shown quite clearly that the sum of the valencies of the bonds going to the three differently positioned oxygen atoms is not in good agreement with Pauling's second rule as understood for ionic crystals, but that there could be better agreement if one of these oxygen positions is replaced by hydroxyl; in a footnote Zachariasen suggests that fluorine might possibly replace hydroxyl in some titanites (1930, p. 15). Two other investigators, Bellanca (1942) and Morgante (1943) have also suggested the presence of the group (O, OH, F) in titanite; Bellanca merely included such a group in his suggested formula, whereas Morgante actually determined the presence of (OH) analytically. In this connection it is interesting to observe that Strunz (1937, p. 10-12) believed that titanite and tilasite were isotopic, tilasite having one atom of fluorine and the formula  $[(AsO_4)F] MgCa$ . In view of these conclusions, and Sahama's (1946) later determinations, a pure sample of northwest Nelson titanite was prepared for analysis by fractionating the graded sand electromagnetically<sup>28</sup>, and subsequently centrifuging the powdered mineral in Clerici solution; both hydroxyl and fluorine ions were particularly looked for. In addition, since crystals of this particular titanite produced radiographic imprints on a photographic plate, the presence of both thorium and uranium were looked for. The analysis (Table 14, anal. A) shows 0.67 per cent of fluorine whereas the loss on ignition amounted to 0.93 per cent. Unfortunately, determination of structural water by this method is not reliable since Sahama (1946, p. 103-104) has shown conclusively that an indefinite quantity of fluorine could be lost. The total quantity of rare earths amounts to the relatively high figure of 1.06 per cent, not sufficiently high to warrant classifying the

<sup>28</sup> North-west Nelson titanite is slightly paramagnetic and therefore it was possible to use electromagnetic means for concentration. Saporte and Canal (1948, p. 21) list titanite as having a lower magnetic susceptibility than zircon, but this is not generally the case.

mineral as ytrotitanite or keilhauite. On the other hand since both alumina and ferric oxide are high, the northwest Nelson titanite would best be classified as the variety grothite (Doel-

TABLE 14.—ANALYSES OF TITANITE

	A	B	C
SiO <sub>2</sub> .....	30.35	30.32	30.48
TiO <sub>2</sub> .....	35.44	33.70	38.00
CaO.....	26.46	28.40	27.32
Fe <sub>2</sub> O <sub>3</sub> .....	2.50	nil	nil
Al <sub>2</sub> O <sub>3</sub> .....	2.15	4.44	0.05
MnO.....	0.25	0.01	0.08
MgO.....	0.10	0.16	nil
K <sub>2</sub> O.....	0.02	nil	nil
SrO.....	nt.fd.	0.005	0.29
ThO <sub>2</sub> .....	0.28	nt.dt.	nt.dt.
Ce <sub>2</sub> O <sub>3</sub> .....	0.03	0.30	0.26
La <sub>2</sub> O <sub>3</sub> group.....	0.85		
Y <sub>2</sub> O <sub>3</sub> group.....	0.18		
F.....	0.67	1.40	0.68
Loss on ignition.....	0.93	0.54	0.61
H <sub>2</sub> O at 105°C.....	0.17	0.18	0.12
	100.38	100.61	100.63
O for F.....	0.28	0.59	0.29
	100.10	100.02	100.34

A. Titanite from Wainui Inlet, N. W. Nelson. Analyst: F. T. Seelye.

B. Grothite from Parainem, Finland. Analysts: Th. G. Sahama *et al.* N. B. total includes Nb<sub>2</sub>O<sub>5</sub> 0.69, Ta<sub>2</sub>O<sub>5</sub> 0.03, V<sub>2</sub>O<sub>5</sub> 0.09, Cr<sub>2</sub>O<sub>3</sub> 0.02, FeO 0.20, ZrO<sub>2</sub> 0.06, BaO 0.003, Na<sub>2</sub>O 0.16. (Sahama, 1946, p. 94, anal. No. 3).

C. Titanite from Kola Peninsula, Russia. Analysts: Th. G. Sahama *et al.* N. B. total includes Nb<sub>2</sub>O<sub>5</sub> 1.52, Ta<sub>2</sub>O<sub>5</sub> 0.02, V<sub>2</sub>O<sub>5</sub> 0.005, FeO 0.10, ZrO<sub>2</sub> 0.05, BaO 0.006, Na<sub>2</sub>O 1.05. (Sahama, 1946, anal. No. 5).

ter, 1918, p. 61-62). Uranium was absent but the 0.28 per cent of ThO<sub>2</sub> found explains the radioactivity of the mineral. The occurrence of radioactivity in titanite is not uncommon, as Larsen and Keevil (1942, p. 209) and other workers have already shown, and some degree of radioactivity can be expected since the Ca, U and Th ions are not greatly dissimilar in size. A richly uranoan or thorian titanite is not to be expected structurally.

Zachariasen (1930, p. 15) gives the formula of titanite as CaTiSiO<sub>6</sub> but admits that, since most analyses show water to be present, presumably as (OH), a formula such as ABSiO<sub>4</sub>X,

in which X represents either O or (OH) or both, would seem more appropriate. Morgante (1943), Sahama (1946, p. 106), and Jaffe<sup>29</sup> (1947, p. 641) all suggest a formula almost identical to

TABLE 15.—RECALCULATION OF ANALYSIS OF NORTH-WEST NELSON TITANITE

	No. of (O-OH,F)	No. of metal atoms	
SiO <sub>2</sub> . . . . .	1.0116	3.94	} 4.00
Al <sub>2</sub> O <sub>3</sub> . . . . .	0.0633	0.33 { 0.06 0.27	
TiO <sub>2</sub> . . . . .	0.8872	3.45	} 3.98
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.0468	0.24	
MgO . . . . .	0.0025	0.02	
CaO . . . . .	0.4725	3.68	} 3.77
La <sub>2</sub> O <sub>3</sub> . . . . .	0.0078	0.04	
Y <sub>2</sub> O <sub>3</sub> . . . . .	0.0027	0.01	} 1.07
MnO . . . . .	0.0035	0.03	
ThO <sub>2</sub> . . . . .	0.0036	0.01	
F . . . . .	0.0352	0.27	
(OH) . . . . .	0.0516	0.80	

Formula: (Ca, La, Yt, Mn, Th)<sub>3.77</sub>(Ti, Al, Fe, Mg)<sub>3.98</sub> [(SiAl)<sub>4</sub>O<sub>19</sub>] (OHF)<sub>1.07</sub>

Zachariassen's alternative, and Morgante expressed his understanding of the possible substitutions as follows:

Formula:  $ABSi_4X$  where

$A = Ca$  and cations with radii 0.67–1.35 Å.

$B = Ti$  and cations with radii 0.57–0.67 Å.

and  $X = O, OH, F$ .

The analysis of Nelson titanite has been recalculated (Table 15) on the basis of 20 oxygen atoms to the unit cell and the figure obtained for "loss on ignition" has been interpreted here as structural water, although this figure may not be absolutely reliable. Calcium is replaced to some extent by rare earths, manganese, and thorium, and the valency upset resulting from these substitutions is made good with replacements of titanium by aluminum, trivalent iron, and magnesium. To make up the silicon group to the theoretical figure of 4, a small quantity of aluminum, such as 0.06, is considered to have coordination number 4; this is to be expected because of its radius ratio with oxygen

<sup>29</sup> Presumably Jaffe's use of two molecules of silicon in the formulae given on p. 641 is merely a typographic error.

of 0.41 (Pauling, 1948, p. 382). This substitution leaves the titanium group negligibly deficient, but the figure for the calcium group containing large ions is very much lower than the value required structurally. On the other hand the (O, OH) group, in spite of the method of determination, is high compared to the figures given by Sahama (1946, p. 96–97), and accordingly this Nelson grothite seems to show a greater degree of replacement of the O<sub>1</sub> positions by (OH) and F than is to be seen in other modern analyses available.

Thus the following formula expresses the mutual substitutions found in Nelson grothite: (Ca, La, Y, Mn, Th)<sub>3.7</sub>(Ti, Al, Fe<sup>'''</sup>, Mg)<sub>3.9</sub>(SiAl)<sub>4</sub>(O, OH, F)<sub>20</sub>.

**TOPAZ:** Topaz was recognized in sands from Okarito, Grey River, Gillespie's Beach, and Kanieri River dredges but it did not exceed 1 per cent of any of the fractions therefrom. The mineral was found as colorless, glassy, water-clear grains of tabular or platy habit due to the dominance of the (001) cleavage; a roughly square-shaped outline was not uncommon, otherwise fragments were irregular with prominent conchoidal fracture (Pl. 3, figs. 43–45). Strings of minute, colorless globular inclusions of very much lower refractive index than topaz, but otherwise unknown character, were present in occasional crystals.

The following physical properties were determined for topaz from Okarito:  $\alpha = 1.623 \pm 0.002$ ;  $\beta = 1.626$ ;  $\gamma = 1.632$ ;  $\gamma - \alpha = 0.009$ ;  $2V = 50^\circ \pm 2^\circ$ ;  $D = 3.52 \pm 0.02$ .

These data suggest that the Okarito topaz has a relatively low fluorine content (Penfield and Minor, 1894, p. 393) but with less hydroxyl than the low-fluorine topaz described by Pardee *et al.* (1937, p. 1064).

**TOURMALINE:** It was surprising to find tourmaline represented sparsely among the mineral assemblages studied here, since many of them were derived from distributive provinces in which granites are abundant. In no instance did tourmaline exceed 2 per cent of any fraction and in many only an occasional grain was found; the mineral was absent altogether from some dredge concentrates and most beach sands, although there was a tendency for it to be a more important constituent of panned concentrates.

Where present, tourmaline was restricted in the main to the finer fractions. The most common mode of occurrence was as slender to short stumpy prismatic crystals that frequently showed terminal forms at one end only; in many crystals there were distinctive cross-fractures, otherwise in irregular fragments with subconchoidal fractures. Normally the characteristic dichroism with maximum absorption perpendicular to the length of the prismatic crystals is an important diagnostic feature but care must be used in this connection. In several assemblages tourmaline fragments were found with slender prismatic form but with the elongation parallel to the Z vibration direction; therefore, these fragments showed maximum absorption parallel to the major axis. Such forms may readily be developed in the first place from stout prismatic crystals of tourmaline by the appropriate fracturing of those crystals along closely spaced planes of basal parting. This point is stressed here because cursory examinations of preparations containing such fragments might result in confusion of this mineral with some of the blue sodic amphiboles of low extinction angle. Perhaps it would be pertinent to stress a further point at this stage, *viz.* that fragments with shapes mainly determined by closely spaced (001) fractures may be tabular in that direction and therefore show a preferred orientation in the mounting media. Such fragments are isotropic but no confusion in their identification need arise if reasonable care is taken in determination.

The tourmalines found in the various sands showed a wide range of color, and dichroic schemes of the most characteristic of these are tabulated below in Table 16. Those detailed in Table 16 are not necessarily restricted to the localities mentioned except in a few instances, such as the green tourmaline in Kaniere material and the black variety in the beach sands of Wainui Inlet.

Fine dust-like clouds of opaque iron oxides are frequently included within the brown, brownish-purple and smoky-grey varieties which in this respect closely resemble the typical "schist" tourmalines described by Hutton and Turner (1936, p. 264, 268). In some sands, particularly those of Lowburn, in Central Otago, multi-colored tourmalines predominate in which one extremity is colored differently,

often a deep brown, from the remainder of the crystal, which is commonly purple or purplish-brown (Pl. 3, figs. 55-56). Most of the tourmalines found in the material used in this investigation appear to belong to the dravite-

TABLE 16.—DICHROIC SCHEMES OF TOURMALINE

Locality	E	O
Barrytown	pale yellow	deep brown
Barrytown	colorless	brownish-green
Barrytown	pale yellow	deep purplish-brown
Arahura	pale pink	deep purple
Kaniere	colorless	green
Kaniere	pale yellow	greenish-brown
Lowburn	colorless or nearly so	brown, blue, or smoky grey
Wainui Inlet	brown	black

schorlite series with the refractive index for the ordinary ray showing a range of 1.639-1.664, but the varieties in which pink or green tints predominate may possibly lie closer to the schorlite-elbaite solution series. Further work on the tourmalines in these sands is in progress.

**XENOTIME:** The yttrium phosphate, xenotime (Pl. 4, figs. 64-68), has a similar distribution to that of monazite in the samples investigated in this study, but the former mineral was very much less plentiful. Its mode of occurrence, physical and chemical properties have been described in an earlier paper (Hutton, 1947a) and need not be repeated here. However, further determinative work has found the following range of refractive indices: O = 1.720-1.724 ± 0.003; E = 1.820-1.828; E - O = 0.101-0.107. These refractive indices are distinctly higher than any hitherto recorded for xenotime so far as the writer is aware, and since, owing to the rarity of the material, quantitative chemical data are not available, these optical properties cannot be correlated therewith. However, because isolated crystals of xenotime from the Grey River area have been shown to affect an alpha-ray plate, they must contain either thorium or uranium or both and the high values for the refractive indices can reasonably be attributed to the presence of either or both of these ions. Although the exact composition of the xenotime described here is unknown, it is pertinent to point out that any replacement of

yttrium by uranium or thorium must be accompanied by complementary substitution of phosphorus by an ion of lower valency, most likely silicon. Replacement of  $(\text{PO}_4)^{3-}$  by  $(\text{SiO}_4)^{4-}$  is unlikely to affect the refractive indices of the mineral to any significant degree, and since the ions of phosphorus and silicon have similar radii, the substitution should not cause significant density changes. Therefore, determination of refractive indices and density would probably give a close estimation of the cumulative percentages of uranium and thorium in xenotime.

Xenotime can be distinguished from yellow zircon, monazite, or titanite relatively simply by optical means alone (Hutton, 1947a) but bastnäsite, a fluocarbonate of the cerium metals may be confused with xenotime. Both minerals have such similar optical properties that diagnosis on that basis alone would be doubtful. Geijer (1920, p. 11) gave  $O = 1.7225$  and  $E' = 1.8242$  for bastnäsite from Bastnäs, and Glass and Smalley (1945, p. 609) record almost identical figures for material from Belgian Congo; for other occurrences, the refractive indices were found to be very slightly but not significantly lower. Distinction on the basis of density is no more helpful; although Winchell (1933, p. 85) lists the density of bastnäsite as 5.0, distinctly higher than that usually recorded for xenotime, Silberminz (1929) has determined the density of analysed bastnäsite from Kyshtymk District to be 4.746. While working with powdered bastnäsite from Gallinas Mountains, Lincoln County, New Mexico, the writer found that in the absence of analyses or spectrographic data, the presence of a perfect cleavage and its solubility with effervescence in warm HCl acid conveniently served to distinguish it from xenotime. The latter test worked satisfactorily with -230-mesh material, and particularly so if the grains are warmed on a glass slide before a drop of acid is added with a fine dropper.

**ZIRCON:** The mineral zircon is ubiquitous in all specimens containing material of average grain-size less than 0.25 mm. It usually reaches its highest frequency in the -230-mesh screenings, but in almost all instances the frequency declines so rapidly in the coarser grade-sizes that the mineral may almost fail in a number of samples in -60 +120 screenings; it is generally absent from the coarsest grade-sizes.

Ordinary colorless normal zircon (Pl. 1, figs. 1-9) and the pale-pink to deep-purple variety, hyacinth (Pl. 1, figs. 10-19; Pl. 4, fig. 60), have widespread distribution.

The term "*normal*"-zircon is used here in the sense employed by Anderson (1941) to distinguish normal zircon of high density, refractive index, and birefringence from malacon or "*low*"-zircon. The term "*normal*"-zircon is considered synonymous with "*high*"-zircon employed by Smith (1940, p. 280). Stevanovic (1903, p. 247-252) was probably first to suggest subdivision of the zircon group on the basis of density, optical properties, and their reaction to heating. He divided zircon into three categories: (1) zircon of density about 4, (2) zircon of density about 4.7, and (3) zircon of density between those of (1) and (2). Stevanovic reported that on heating, low-density zircon exhibited no change in properties but that the refractive indices of zircon of intermediate density did change. These varieties of zircon have been called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -zircons (Spencer, 1904, p. 47-48; Smith, 1940, p. 280; Wadia and Fernando, 1944, p. 36-7; compare, however, Schlossmacher, 1932, p. 562). Chudoba and Stackelberg (1936, p. 243), following this general classification, showed that both  $\alpha$ - and  $\gamma$ -zircons would change into  $\beta$ - or "*high*"-zircon after heating to 1450°C. for 6-hour periods.

Every gradation from sharply euhedral crystals exhibiting a considerable variety of forms and habit, through slightly abraded crystals to well-worn anhedral devoid of any crystal faces were found in most samples. In addition to these, irregularly shaped fragments, flakes, or splinters with pronounced conchoidal fracture are not uncommon. Generally speaking, however, a higher percentage of unworn euhedra were to be found in the finest grade sizes, whereas zircon attained a greater degree of rounding as the grain-size became progressively coarser; when zircon was present in fractions with average grain size greater than 0.5 mm. the particles were predominantly anhedral. Among the coarsest material from one sample of concentrates from Slab Hut dredge, -18 +35 mesh, a few almost perfectly polished anhedral of zircon were obtained. These grains showed no remnants of crystal faces, were slightly flattened and ellipsoidal in outline with the major and minor axes approximately 0.85



mm. x 0.50 mm. In the three particles examined, the major axis was not parallel to the vertical crystallographic axis, obliquity being about 12°, 16°, and 21°. Since it is difficult to visualize the process whereby unbroken crystals of zircon would be abraded and polished naturally into forms having directions of elongation other than those parallel to the *c* axis, one can only assume that these grains represent the final product of abrasion of splinters of zircon crystals of considerably greater size than any so far found in any West Coast sands studied. These grains of zircon were water-clear, very faint yellow, and of gem quality.

The most usual habit found in normal zircon showed a development of second-order prisms *a*(100) terminated by first-order pyramids *p*(111) with or without third-order pyramidal faces; *m*(110) is usually present but rarely dominant (Pl. 1, figs. 8-9). Less often, second-order prisms are terminated by three orders of pyramids. Very occasionally a combination of *m*(110) and *p*(111) only was found (Pl. 1, fig. 2) but in general crystals with this simple habit are very rare in any of the New Zealand occurrences known to the writer, except in the case of hyacinth described later; however, this habit appears to be fairly common in localities elsewhere (the Dartmoor Granites, Brammall and Harwood, 1923, p. 27) although not found for zircons from Falmouth Granite in Cornwall by Ghosh (1928, p. 333). Crystals are often considerably distorted so that a crystal with *a*(100) well developed and *m*(110) poorly developed may be terminated by large first-order and small second-order pyramids at one extremity, whereas at the other end of the crystal the degree of development of these pyramidal faces is reversed, and at the same time a small basal plane is sometimes present. The basal plane *c*(001), however, is uncommon. In sands from Snowy River, a small percentage of a zircon of distinctive habit was noted. It differed from those previously described on account of the predominance of steep pyramids, probably *u*(331); and whereas the ratio length to breadth in zircons from other localities was usually approximately 2:1, the distinctive Snowy River zircons had a ratio of approximately 3:1, and occasionally 4:1 (Pl. 4, figs. 61-62). Except in Snowy River sands, and the rare crystals in material from Grey River and Slab Hut dredges,

this particular habit was not found in any other material studied.

Inclusions are frequent and varied, and only slight success resulted from attempts to separate and determine them. Selective solution of finely crushed zircon in warm hydrofluoric and sulphuric acids generally failed because the inclusions were also soluble in acid, and separation of foreign particles from finely crushed zircon centrifugally was not satisfactory in every instance because it was only convenient to use Clerici solution and zircon as well as most of the impurities had greater density than the liquid, that is 4.2. However the following inclusions have been noted:

(1) Spherical and sausage-shaped cavities, some probably gas-filled, though in rare instances globules of fluid partially filled the internal cavities.

(2) Magnetite and ilmenite.

(3) Euhedral zircon.

(4) Pale-yellow to nearly colorless monazite and xenotime; these were often seen in zircons obtained from Grey River sands.

(5) Slender, acicular, colorless crystals with refractive index close to 1.65 and relatively insoluble in acids; possibly mullite but not proven.

(6) Dark-brown, prismatic grains of rutile.

(7) Reddish-brown, isotropic grains of cubic or tetragonal aspect soluble in hydrofluoric and sulphuric acids, the solution of which gave reactions for tantalum and niobium; they might be any one of a number of brown tantalum minerals such as samarskite, euxenite, polycrase, pyrochlore, fergusonite, yttrotantalite in the metamict state. Their nature was not verified, owing to insufficient material.

(8) Clouds or stringers of fine black dust.

(9) Subhedral particles of pale-brown, poorly dichroic cassiterite.

(10) Short, stumpy prisms of brownish tourmaline.

Any orderly arrangement or preferred orientation of inclusions was most unusual, although the presumably gas-filled cavities are in some instances elongated parallel to the vertical crystallographic axis.

In some of the samples studied, the constituents have been stained by iron solutions so that the zircons have a distinctly yellow color. The ferruginous stain was very evenly deposited on the crystal surfaces and was not removed by the abrasive action of panning or shaking on concentrating tables. With a hand lens, and in

some instances even when immersed in oils and examined under the microscope, these yellow-stained zircons had the appearance of monazite; and it should be stressed that this coloration has misled some previous workers to believe that they were dealing with monazite-bearing sands. Actually, such stains are readily removed

Refractive indices of a number of typical normal zircons were measured in order to observe whether metamictization had occurred to any extent. However, these figures (Table 17) do not suggest any significant alteration or isotropization, and the range of values obtained lie within the limits listed by Winchell (1933,

TABLE 17.—REFRACTIVE INDICES AND SPECIFIC GRAVITY OF SOME NEW ZEALAND ZIRCONS

	Naseby	Lowburn	Ngahere	Arahura
O.....	1.935-1.938	1.935-1.939	1.923-1.927	1.934
E.....	1.978-1.982	1.979-1.984	1.982-1.984	1.989
E-O.....	0.042-0.047	0.043-0.048	0.055-0.059	0.055
D.....	4.64-4.67	4.65-4.67	4.62-4.68	4.65

by treating the material concerned with warm 1:1 hydrochloric acid for 5 or 10 minutes, and then washing carefully with copious warm water to which a few drops of hydrochloric acid has been added.

Zoning has been observed in a few cases (Ngahere and Kaniere dredges) but it is generally uncommon in normal zircon; it consisted of numerous exceedingly fine, almost thread-like concentric bands in a number of crystals; these zones, which alternated with the host zircon, seemed more prominent nearer the periphery than towards the center. Generally the fine zonary banding could only be observed when the vertical crystallographic axis of a zoned crystal was placed parallel to the vibration direction of the lower nicol. In this position the refractive index of the fine bands was found to be appreciably less than the appropriate refractive index of the adjoining zircon. When, however, such a crystal was rotated through 90° so that the vertical crystallographic axis was perpendicular to the plane of polarized light, little or no zoning was apparent. It would seem then that, as the zircon crystals grew, some oscillation of the composition of the supplying fluid must have occurred, resulting in abrupt changes in the composition of the crystallizing zircon such that the refractive index for the ordinary ray was similar in all zones but the refractive index for the extraordinary ray showed a distinct range of values.

Twinned crystals of zircon (Kaniere River) exhibited the usual knee-shaped forms resulting from twinning about (101).

p. 184) for that mineral, though distinctly higher in a few instances than the values determined by Morgan and Auer (1941, p. 308). No chemical analyses of normal zircon have been made, but numerous tests with a Geiger-Muller counter indicate an exceedingly low percentage of uranium or thorium or both. For instance, whereas 1 per cent of  $U_3O_8$  gives ionisation current of 16,800 amperes  $\times 10^{18}$ /sq. cms., Naseby zircon gave a value of 8 and Lowburn zircon only 7.

Very rare crystals of green, *phosphorian zircon* were isolated from the -120+230 mesh screening of one of the concentrates from Snowy River. The morphological development of these crystals differed in no important detail from those of normal zircon just described, but the refractive indices and density are decidedly lower, as follows: O = 1.921; E = 1.975; E - O = 0.054; D. = 4.56; Color: = Ridgway's Rivage green, 31' Y - G. These properties suggest comparison with olive-green beccarite from Ceylon, except that the New Zealand mineral is uniaxial. This green zircon has no greater degree of radioactivity than the colorless varieties referred to and its magnetic susceptibility is similar. Although insufficient material was available for quantitative analysis, some qualitative tests showed that, in addition to zirconium and silica, both phosphorus and rare earths were present, but no hydroxyl. Thus, although the refractive indices and density are slightly lower than those recorded for normal zircon, the absence of hydroxyl suggests that the mineral was not altered in any degree to a

metamict condition. On the other hand, the presence of phosphorus and rare earths suggests some diadochic substitution of silicon and zirconium. As previously seen, ionic substitution of silicon by phosphorus is found in a number of minerals on account of similar ionic size and suitable radius ratio and, in that case, the upset in electrical neutrality can be met by substitution elsewhere in the structure. Thus in this instance, from the evidence obtained by qualitative determinations alone, we assume a replacement such as  $\text{Si Zr} \rightleftharpoons \text{P R}$ , where  $\text{R} = \text{Y, Ce, La}$  etc. Several instances of green and brown zircon containing rare earths, with or without phosphorus, have been found by other investigators and a summary of the appropriate data might be relevant here. Naegite from Naegi, Mino Province, Japan (Shibata and Kimura, 1923b, p. 3-5) contained 6.68 per cent of rare earths in addition to thorium and uranium, but no phosphorus appears to have been found therein, whereas a very similar mineral, hagatalite from Hagata, Iyo Province (Kimura, 1925, p. 82-84) contained 13.1 per cent of rare earths, and again with uranium and thorium but apparently no phosphorus. However, oyamalite, also from Iyo Province, has been shown (Kimura, 1925, p. 84-85) to contain 7.6 per cent of  $\text{P}_2\text{O}_5$  in addition to 17.7 per cent of rare earths. Still later Kimura and Hironaka (1936) and Hata (1938b, p. 620-622) described as yamagutilite zircon that obviously did not differ in any essential detail from the oyamalite variety of zircon; in those specimens of yamagutilite rare earths amounted to 15.89 and 10.93 per cent and  $\text{P}_2\text{O}_5$  to 4.23 and 5.30 per cent respectively. All of these varieties are probably metamict, for they contain notable percentages of water. While substitution of silicon by phosphorus and zirconium by rare earths is quite understandable, the presence of a considerable percentage of rare earths without some compensatory replacement of other ions as in naegite and hagatalite requires closer study. Two possibilities are: (1) The minerals may be impure and the rare earths contained in inclusions of samarskite, fergusonite etc. (niobium and tantalum are listed in both analyses, and in addition both minerals are associated with fergusonite in pegmatites). (2) Phosphorus may be present but not recognized.

Whatever the answer, the separate names

oyamalite and yamagutilite are unnecessary since these minerals are obviously varieties of zircon and following Schaller (1930) could be termed phosphorian zircons. On the basis of the author's qualitative determinations and by comparison with these Japanese minerals, the Snowy River material is termed phosphorian zircon.

The term *hyacinth* is used here to denote pink, purple, or reddish zircon as distinct from isotropic malacon of relatively low refractive indices and density. It was a constituent of every dredge sample studied although most abundant in material from the Grey River; it is found in most size fractions.

Although no quantitative chemical determinations have been made, the Geiger-Muller counter indicated that the hyacinths are distinctly more radioactive than were the colorless normal zircons; an average reading of 45 for hyacinth as compared with 7 for colorless zircon. Both were unattracted by a magnetic field of high intensity when free from inclusions.

The hyacinth showed a distinct range from very pale pink through pink to a deep purple and, in occasional crystals, purplish-brown. Crystals are generally clear and transparent, although a number were somewhat turbid on account of aggregates of dust-like inclusions or networks of cracks. The color is best seen when the crystals are immersed in liquid with refractive index close to that of the mineral itself; ordinarily the very high refractive index of hyacinth causes excessive internal reflection when examined in the usual mounting media. Distinction between colorless zircon and pale hyacinth is most pronounced, however, when the mineral assemblage containing them is mounted on a white card, or better a vitrosil plate, and viewed in oblique illumination beneath a binocular microscope. Hyacinth differs from colorless zircon also as follows:

(1) The average grain-size is greater. Comparing the colorless zircon-hyacinth ratios in the -230 and -60 +120 mesh screenings, the frequency of zircon relative to hyacinth is found to decrease with increase in grain size.

(2) Whereas colorless zircon has been shown to exhibit a range of grain shapes, from strictly euhedral crystals to abraded and moderately rounded forms, euhedra were much more frequently found; instead, euhedra of hyacinth are

rare (Pl. 1, fig. 10) and the mineral is more frequently found as well rounded often nearly spherical grains (Pl. 1, figs. 18–19).

(3) In grains that exhibited little or no abrasive effects (Pl. 1, fig. 10), the habit of the crystals was almost always simple; a combination of  $m(110)$  and  $p(111)$ , with occasionally a development of  $u(331)$ , was most usual.

(4) Zonary structures are common (Pl. 1, figs. 11, 12, 15).

(5) A curious system of radiating or anastomosing cracks was seen in a number of hyacinth crystals (Pl. 1, fig. 13); nothing comparable has been found in colorless zircon.

(6) Outgrowths, as distinct from zonary structures, of purple zircon on hyacinth (Pl. 1, fig. 14), are rare; secondary outgrowths have not been observed in colorless zircon.

It is not necessary to enlarge upon the characteristics mentioned under (1)–(3) above, but the remaining observations require some elaboration. A number of distinct zonary patterns are apparent from a glance at Plate 1, but in many examples the very fine concentric banding (Pl. 1, fig. 15) like that described for colorless zircon, is distinct and clear when the vertical crystallographic axis is parallel to the plane of polarized light but is usually invisible or nearly so when the microscope stage is rotated through 90°. Actually it is similar to the type of zoning figured by Bruce and Jewitt (1936, p. 202, text-fig. 5, nos. 20, 23) in colored zircons from some Canadian Precambrian granites, and described by Brammall (1928, p. 28) in purple zircons from Dartmoor. Other zonary structures are:

(1) A unilateral arrangement in which purple zircon appears to have had two wide and successive layers of similar material added, but at one end only (Pl. 1, fig. 11); in some instances only one such zone was present.

(2) Later crystallization of hyacinth partially surrounding earlier but sharply euhedral purple zircon (Pl. 1, fig. 12).

(3) Occasional grains consisting of a later development of hyacinth around well rounded hyacinth and in optical continuity therewith; the later-formed zircon itself may sometimes exhibit very fine concentric zonary development (Pl. 1, fig. 15).

(4) And finally, and probably most common of all, crystals with deeply colored nuclear or

central areas that show either an abrupt or a gradational transition towards paler peripheral zones (Pl. 1, fig. 13). In many examples the dark central portions of such crystals are turbid, as if charged with clouds of exceedingly fine dust-like particles. One crystal that may be included in this category was found to have a central zone of low birefringence in comparison with the peripheral portion of the grain; this suggests a transition of the central zone towards a malacon-like material. No crystals were found to contain true isotropic malacon, however.

The systems of irregular cracks developed within a number of hyacinth crystals are quite distinctive and in the majority of examples seem to originate at, or radiate away from, central dark-brown or opaque inclusions. In this respect these zircons are very similar to those described by Robertson (1923, p. 493) from alluvial material of western Togoland. Further, the irregular micro-fissuring is comparable in most respects to that development in the uranothorite crystals and, as pointed out earlier, such characteristics are frequently found in or associated with radioactive minerals.

Secondary outgrowths upon hyacinth were only occasionally found in the several hundred preparations. In the best example (Pl. 1, fig. 14) pale-purple hyacinth, verified as zircon by refractive index determinations, has grown on one of the prism faces of a broken but otherwise euhedral hyacinth so that the vertical crystallographic axis of the sub-individual is normal to the direction of that axis in the host crystal; the secondary purple zircon is clear, unzoned, free from inclusions, and has slightly higher refractive indices than those of the host. These data are as follows:

	<i>Host grain</i>	<i>Outgrowth of zircon</i>
O =	1.921	1.929
E =	1.969	1.978

In a number of examples refractive index determinations proved that the outgrowth material was zircon. Therefore, at least for the material from the Grey River, Brammall's suggestion (Smithson, 1941, p. 104) that the secondary material might be some rare earth mineral isomorphous with zircon is not substantiated. Outgrowths of secondary zircon on well-rounded grains lacking any remnants of crystal faces always have the same orientation relative

to the host material. These outgrowths of zircon on zircon are in most respects comparable to the examples described and figured by Grout and Thiel (Tyler *et al.*, 1940, Pl. 2, fig. 1; also p. 1491), but they do not reproduce the perfection of development of the forms described (Butterfield, 1936) from the Millstone Grit of Yorkshire, or (Smithson, 1937, 1941) for material from mid-Jurassic sediments of Yorkshire. These examples are, perhaps, more comparable still to the outgrowths on purple zircon recently described by Bond (1948, p. 36–38) from the Lower Wankie Sandstone of Southern Rhodesia.

A wide range of hyacinth crystals selected for determination of optical properties lay within narrow limits:  $O = 1.920 - 1.929$ ;  $E = 1.967 - 1.981$ ;  $E - O = 0.040 - 0.054$ . These values are distinctly higher than those recorded by Tyler and Marsden (Tyler *et al.*, 1940, p. 1441) for hyacinth, and partly covers the ranges of refractive index defined by Morgan and Auer (1941) for hyacinth and normal zircon.

Measurements of the optical constants for different zones of zoned hyacinth crystals were generally unsatisfactory, but for one crystal, which has a dark-purple central zone surrounded by a paler border and had been fractured normal to the  $c$  axis, refractive indices, for both sub-individuals, are as follows:

<i>Inner zone</i>		<i>Margin</i>
O =	1.908	1.927
E =	1.930	1.976
E - O =	0.022	0.049

The refractive indices for both zones, except for that of the extraordinary ray of the outer zone, conform to the limits set by Morgan and Auer (1941, p. 308) for hyacinth, and, on account of the relatively low birefringence, the composition of the central portion of the crystal must be approaching that of malacon.

From mere inspection and evaluation by the Becke bright-line test, the central portions of the hyacinth crystals frequently appear to have lower refractive indices than the marginal zones. Actually this is contrary to the findings of Tyler and Marsden (Tyler *et al.*, 1940, p. 1442) since their experience showed hyacinth zoned externally by malacon but never malacon surrounded by hyacinth.

All of the inclusion-free hyacinth crystals tested have more or less normal densities that

show a range of 4.60–4.62. Hyacinth crystals enclosed a variety of inclusions and, the number of inclusion-free crystals is generally greater than for colorless zircon. These inclusions are similar to those already found in colorless zircon except that xenotime, mullite (?), and cassiterite have not been recognized. Tantalum- and (or) niobium-bearing minerals were more often detected in hyacinth crystals, and particularly in those crystals exhibiting excessive micro-fissuring.

The general properties of the hyacinth found in New Zealand sands are quite comparable to those found by Tyler *et al.* (1940) in the Precambrian rocks of the Lake Superior region and the mineral described so clearly by Mackie (1925 a, b) that was derived initially from the Lewisian Gneiss of northern Scotland. To make quite certain that this comparison was valid, the heavy mineral fraction was separated from a brown Torridonian sandstone that the author had collected some years ago from an outcrop just south of Loch Maree in Ross-shire, Scotland, and shown by Mackie to contain plentiful hyacinth. In these hyacinths were found all the features of zoning, micro-fissuring, and rounding to be seen in the New Zealand material and distinction between them was impossible.

The difference in the degree of rounding of both normal zircon and hyacinth has already been commented upon and a method to give some measure to this characteristic without actual determination of roundness or sphericity was sought. It should be remembered at this point that the heavy mineral residues studied were obtained either by sporadic pannings or from dredge concentrates from river silts and gravels, the latter derived in the first place from extensive and heterogeneous distributive provinces and not from specifically located rocks. Therefore, methods involving a high degree of preciseness would provide data of little or no actual value and would take unwarranted time. The methods of both Trowbridge and Mortimore (1925) and Tickell (1947, p. 6) were used at first but later discarded in favor of a simplification of Allen's (1944, p. 72) scheme whereby a factor known as the zircon abrasion index is determined. The zircon abrasion index equals the percentage of euhedra among the zircons,

and to facilitate determination of this characteristic, zircon concentrates were prepared from each specimen by running the latter through the strongest magnetic field obtainable, after suit-

TABLE 18.—ZIRCON ABRASION INDEX FOR TWO SIZE FRACTIONS

Sample	Normal Hyazircon. cinth. < 62 microns	Normal Hyazircon. cinth. 62-125 microns
Slab Hut 1.....	25 9	18 8
Slab Hut 2.....	23 10	19 7
Grey River 1.....	18 16	14 9
Grey River 2.....	19 18	15 8
Grey River 3.....	20 17	14 9
Snowy River 1.....	17 11	22 10
Snowy River 2.....	19 11	23 9
Atarau.....	14 7	15 6
Ngahere 1.....	17 9	11 7
Ngahere 2.....	16 10	12 7
Gillespie's Beach.....	25 *	15 *
Okarito.....	26 *	16 *
Naseby.....	20 *	* *
Kyeburn.....	22 *	19 *
Lowburn Ferry.....	20 *	17 *
Ligar Bay.....	30 *	25 *
Kaniere River.....	13 *	16 *
Arahura River.....	15 *	16 *
Barrytown.....	14 *	7 *
Rimu.....	17 *	15 *
Red Jacks.....	17 *	11 *

\* = Insufficient grains to enable an accurate count to be made.

ably sizing the material by screening and removing all ferromagnetic grains. Such concentrates often contained other practically non-magnetic minerals such as apatite, cassiterite, scheelite, gold, uranium-free thorium silicate etc., but the percentages of these minerals were usually too small to interfere with the work. A portion of the material thus concentrated was mounted in hyrax and the grains counted according to the methods already detailed. Crystals exhibiting any sign of abrasion were not counted as euhedra, and in most instances at least 400 grains were counted; however, any preparation with less than 100 grains was not considered to give a significant figure. These  $Z_{ai}$  factors also clearly show (Table 18) that there is a distinct tendency for larger crystals

to become rounded to a greater degree than smaller crystals of the same mineral. However, this can only be considered a generalization in this instance since there are a number of obvious divergences. In the zircons from Snowy River, an increase in the factor  $Z_{ai}$  with increase in grain-size is due primarily to an influx of larger colorless zircons of distinctive habit, a detail already commented upon. Similar circumstances may account for some of the anomalies found in other analyses. However, determination of the factor  $Z_{ai}$  can have only limited value when applied to minerals in concentrates obtained from Recent and heterogeneous river gravels since such specimens do not represent *en masse* results of careful sorting and fractionation. However, more detailed work is being carried out to evaluate the real usefulness of the abrasion index factor for material from Recent gravels such as Grey River and its tributaries.

**ZOISITE:** Zoisite has been found in a number of samples and is usually associated with the material of finer grain-size. It occurs as subhedral to anhedral grains that are either colorless or very pale yellow with distinct but weak pleochroism. Occasional semi-opaque grains with inclusions of dust-like particles of iron oxides, together with the somewhat ferrous nature of the minerals themselves, made it possible to segregate them electromagnetically. A perfect cleavage, presumably (010), was noted (Pl. 4, fig. 59), and a majority of the crystals are tabular parallel to (100); as a result, there is a tendency for such crystals to orient themselves in mounting media so that the acute bisectrix is normal to the glass slide. A characteristic strong dispersion of the optic axes, with  $\rho > v$ , produces strongly anomalous interference tints when viewed between crossed nicols. A range of  $33^{\circ}$ – $38^{\circ} \pm 2^{\circ}$  was found for optical axial angles in ten grains, in which the optic axial plane was perpendicular to the cleavage; a positive optic sign was determined. Such properties agree closely with those listed by Winchell (1933, p. 311) for  $\beta$ -zoisite and are almost identical to those found for zoisite in heavy mineral assemblages of certain eastern Otago Tertiary and Cretaceous sediments (Hutton and Turner, 1936, p. 269).

In the finest size-fractions of some of Grey





River concentrates, a second distinct type of zoisite was observed. Morphologically similar to the variety just described, it exhibited distinctive optical properties. The grains were clear and colorless, there was strong dispersion of the optic axes with  $\rho > v$ , but  $2V$  was too small to observe separation of the isogyres in white light. For  $2V_{Na}$  an angle of  $8^\circ \pm 2^\circ$  was obtained with the optic axial plane perpendicular to the cleavage (010); in blue light, however, the mineral appeared to be uniaxial. By virtue of the type of dispersion and position of the principal plane, this mineral is also  $\beta$ -zoisite with the tenor of iron less than that in the  $\beta$ -zoisite described above. In composition and optical properties, the zoisite with the small optic axial angle is almost at the transition point  $\beta$ -zoisite  $\rightarrow$   $\alpha$ -zoisite.

#### NATURE AND CAUSE OF THE METAMICT STATE

The term metamict was introduced by W. C. Brögger to denote the phenomenon of isotropy or the glassy-amorphous condition sometimes found in zircon and in other normally anisotropic minerals. This state is now generally understood to involve in minerals of appropriate composition the production of a condition of complete structural isotropy in otherwise crystalline compounds; at the same time a general decrease in density and refractive indices usually becomes apparent, and a considerable degree of hydration is also to be expected. This physico-chemical transformation or metamictization takes place only in minerals containing radio-active elements but not necessarily in all of these; notable in the latter category are monazite, thortveitite<sup>30</sup>, titanite, and possibly xenotime. A number of unsatisfactory hypotheses have been advanced to explain the mechanism of the process (Mügge, 1922; Goldschmidt, 1924; Vegard 1927), but Ellsworth (1925; 1932a) has put forward a more acceptable theory involving autoxidation, applicable particularly to uraninites but which may be extended to all minerals originally containing uranous oxide. According to this hypothesis, the disintegration of both uranium and thorium atoms gives rise, in addition to helium and

appropriate atoms of the uranium and thorium disintegration series, to two oxygen atoms that immediately oxidize neighbouring uranous ions to the uranic state, and hence according to Ellsworth (1925, p. 138) "all minerals containing  $UO_2$  automatically and irresistibly oxidize themselves at a rate depending on the rate of uranium and thorium disintegration". Tomkeieff (1946, p. 700-701), points out that if autoxidation were the only cause of a disrupted crystal lattice, a very clear correlation between the amount of lead and uranic oxide should be evident from analyses of uraninites. To evaluate this statement Tomkeieff has plotted  $PbO$  against the relative proportions of  $UO_2$  and  $UO_3$  for 52 analyses of uraninites; he found there is a wide scatter of points, but when the analyses are averaged into three groups on the basis of lead content a progressive increase of  $UO_3$  with increase of  $PbO$  is apparent, and, the curve of these averages is approximately parallel to the curve that may be deduced theoretically. This would certainly appear to substantiate Ellsworth's hypothesis, so far as uranous-bearing minerals are concerned, and as Tomkeieff puts it "autoxidation may be a very real factor in transformation of uranous into uranic oxide". As contributing factors to the ultimate results of the autoxidation process, Ellsworth suggests that competition for oxygen between later members of the uranium and thorium disintegration series, and also the force of recoil of a radioactive atom ejecting an alpha-particle must inevitably tend to produce disruption of structure. The force of recoil is a factor of considerable magnitude. Since the alpha-particle has a mass of 4 and the uranium atom a mass of 238, the latter will have approximately a sixtieth of the energy of disintegration, probably in excess of that necessary to break the chemical bonding and allow the daughter atom to project itself some distance through the crystal lattice and there take up the configuration demanded by its chemical nature.

There is little doubt that the metamictization of radioactive minerals must be due ultimately to the presence of uranium and (or) thorium ions therein, and most illustrative in this connection is the work of Stackelberg and Rottenbach (1940, p. 207-8), who found that a thin plate of zircon when subjected to a radioactive

<sup>30</sup> One specimen was found to contain only 0.09 per cent  $ThO_2$  (Marble and Glass, 1942, p. 697).



source for a period of 4 months broke down completely. And the data of Morgan and Auer (1941, p. 307) show that the birefringence of zircon is approximately inversely proportional to the measure of radioactivity for that mineral. However, the presence of radioactive elements in a mineral is not the sole condition for isotropization. If it were such minerals as xenotime, monazite, thorianite, and titanite should sometimes be found in a metamict condition. Thus some instability in the structure of the minerals may also be necessary. In his investigation of the metamict state Faessler (1942) considered that the transformation was probably due to alpha-radiation from radioactive ions, but that such transformations are more likely in minerals with complicated ion substitutions than in chemically simple compounds, which would probably be more stable. Although this may be the case for a number of radioactive minerals this is definitely not valid for zircon, chemically a relatively simple compound, while such minerals as monazite, xenotime, titanite, in which considerable substitution is generally evident, appear to be quite stable and are never, so far as the writer is aware, found in a metamict condition. Thus Faessler's supposition is not entirely acceptable.

Both Machatschki (1941, p. 38-39) and Tomkeiff (1946, p. 702) have offered hypotheses that may partially explain the phenomenon of metamictization in particular instances on the basis of structural instability. Machatschki considered particularly the structural relations in zircon and pointed out that the zirconium-oxygen distances are irregular, that is four oxygen atoms at 2.05 Å. and four at 2.41 Å. Let us examine the structural relationships in zircon, thorite, and xenotime in order to determine, if possible, whether structural instability is a necessary prerequisite for a change to a metamict state. The irregular distribution of the oxygens around the  $Zr^{4+}$  ions would appear to be an unstable arrangement, since the configuration of maximum stability would have the anions as close as possible to the central cation (Pauling, 1933, p. 1896); and theoretically the zirconium-oxygen distance should be approximately 2.27 Å. when corrected for eight-fold co-ordination and assuming a factor of 10 for the Born exponent since the former ion probably has krypton configuration. Further the

radius ratio of the  $Zr^{4+}$  ion with  $O^{2-}$  is 0.62 using univalent ionic radii, a figure usually considered too low for eight-fold co-ordination. However, with this value,  $Zr^{4+}$  may be considered to occupy a transitional position since co-ordinations of six ( $CaZrO_3$ , zirconiferous pyroxenes), seven (ammonium zirconium heptafluoride), and eight (zircon and baddeleyite, the latter with a deformed fluorite structure) are all known. And since, in a completely metamict zircon, zirconium is found in the form of baddeleyite<sup>31</sup>, a co-ordination number of eight may be the most stable configuration for that ion, and this arrangement, therefore, appears to be set up in zircon under the impetus of alpha-ray bombardment.

In the xenotime lattice, on the other hand, the observed inter-ionic distances between  $Y^{3+}$  and  $O^{2-}$  are very nearly identical, 2.23 Å. and 2.24 Å. (Vegard, 1927, p. 511) but nevertheless they are distinctly less than the corrected sum of the appropriate crystal radii, 2.41 Å. Naturally it is difficult to calculate the exact value of the equilibrium inter-ionic distances, since all the pertinent factors are not known, but because of the discrepancy between observed and calculated values, the  $Y^{3+}-O^{2-}$  bonding may be partly co-valent, in this instance at least. The ratio of the univalent radii is 0.68, not a transitional value (Pauling, 1927, p. 785) but one that would readily allow at least a square antiprism co-ordination. Therefore, on the basis of radius ratio and anion-cation distances alone, the structure of xenotime would appear to be more stable than that of zircon, and because of this stability apparently, xenotime does not become metamict.

Except for the thorites from southern Westland described earlier in this paper and one other obscure instance<sup>32</sup>, the author has found

<sup>31</sup> The following compositions for completely metamict zircon have been observed by X-ray diffraction methods:  $ZrO_2$  and tridymite, Borowsky and Blochin, 1936; microcrystalline cubic  $ZrO_2$  and amorphous  $SiO_2$ , Chudoba, 1937a; amorphous  $ZrO_2$  and amorphous  $SiO_2$ , Chudoba, 1937b; monoclinic  $ZrO_2$  and amorphous  $SiO_2$ , Stott and Hilliard, 1946.

<sup>32</sup> Professor Adolf Pabst has pointed out to the writer that Boldyrev *et al.* (1938, p. 87-8) have published a thorite pattern and from it calculated the mineral's cell dimensions, *viz.*  $a = 6.315$  Å;  $c = 5.667$  Å. Obviously these workers have used anisotropic (= metamict) material for their X-ray study, but unfortunately they have not listed any other of its physical properties.

no record of that mineral in a completely unaltered condition; Brögger (1890, p. 124) referred to optically uniaxial, positive material, but this was in the form of minute relicts within highly altered thorite. Therefore, except for Boldyrev's material only metamict varieties of thorite were available for X-ray diffraction studies (Vegard<sup>33</sup>, 1916, p. 93) and, accordingly, no structural data are available. However, from a theoretical standpoint, since ThSiO<sub>4</sub> appears to crystallize in the same way as zircon, one might reasonably assume that the former mineral consists of silicon and oxygen tetrahedrally arranged and Th<sup>4+</sup> ions surrounded by eight O<sup>2-</sup> ions; the Th<sup>4+</sup>-O<sup>2-</sup> equilibrium distance can only be assumed from the sizes of the appropriate ions. On the basis of Zachariasen's (1948, p. 1104) computations, the Th<sup>4+</sup> ion has a radius of 0.95 Å., which differs unimportantly from that of Y<sup>3+</sup>, whereas the radius ratio with oxygen of 0.67 should permit fairly stable antiprism configuration of the Th<sup>4+</sup> ion.

Hence, there appears to be little structural reason why thorite should be so readily altered and a thorian-xenotime apparently stable; we must wait until the actual structural relationships have been determined.

Tomkeieff's (1946, p. 702) theory to explain the phenomenon of metamictization was applied specifically to the break-down of uraninite, that is for the change U<sup>4+</sup>→U<sup>6+</sup>; he contended that this increase in the valency state was bound to decrease the ionic radius of the ion concerned. While such argument is correct in a general sense, the writer believes that Tomkeieff's assumption of the lowest possible radius ratio value of 0.225 for U<sup>6+</sup> is unwarranted. There is no necessity to point out that within a range of 0.225-0.414 a tetrahedral configuration is the stable one, and in fact in some instances, the figure of 0.414 is not necessarily a maximum one; for example the Ge<sup>4+</sup>-O<sup>2-</sup> ratio is 0.43, yet the former element may be tetrahedrally co-ordinated as in GeCl<sub>4</sub> (Wells, 1947, p. 282). Of course the Ge<sup>4+</sup> ion has a transitional value since GeO<sub>2</sub> is dimorphous occurring in both four-fold and six-fold co-ordinations, sim-

ilar to quartz and rutile structures respectively. Therefore, Tomkeieff's figure of 0.30 Å. for the size of the U<sup>6+</sup> ion is most doubtful, since the size of that ion might range anywhere from 0.31 Å. to 0.60 Å., but probably is closer to the higher figure, when the radius of the O<sup>2-</sup> ion is taken to be 1.40 Å. and not the value 1.32 Å. used by Tomkeieff. Nevertheless, the volume change involved in the oxidation of U<sup>4+</sup>→U<sup>6+</sup> is considerable, that is, at least a change from 0.95 Å. to 0.60 Å., and from this point of view alone Tomkeieff's speculation would seem to be valid.

Finally, it is not clear in some cases whether the presence of uranium in a thorium-bearing mineral is a prerequisite for a radical transformation in the structure of an otherwise stable mineral. For instance the completely unaltered thorium silicate from southern Westland is uranium-free, but apparently this is not a common condition (Rutherford, 1906, p. 177); however, in this particular case the biaxiality of the mineral leads one to conclude that it is not tetragonal but has a lower symmetry that might be the stable one for thorium silicate. The presence or absence of uranium cannot possibly be the sole requirement since the uranothorite from southern Westland with 11.5 per cent of UO<sub>2</sub> shows only slight alteration and monazite may contain considerable uranium and yet is never found metamict. It is the writer's opinion that this can only mean that a monoclinic symmetry is the stable one for cerium phosphate; one is inclined to speculate on the possibility of the occurrence in nature of cerium phosphate with an unstable tetragonal symmetry. Alternatively are these southern Westland thorites not old enough for the transformation to a metamict state to have taken place in spite of an age determination of approximately 119 × 10<sup>6</sup> years for one of them? Certainly the metamict minerals of southern Norway and some Canadian areas are Precambrian, but this question will have to await an answer.

#### ORIGIN OF MICRO-FISSURES IN RADIOACTIVE MINERALS

The curious arrangement or network of cracks, such as occurs both in uranothorite and hyacinth is by no means uncommon, and

<sup>33</sup> Vegard states that although several very fine crystals were tested not one of them gave any X-ray pattern at all. Thus the lattice must be completely broken down.

has been described by numerous investigators. However, such features appear to be restricted to radioactive minerals or at least have their origin therein, because from them the anastomosing systems of cracks radiate out into surrounding quartz, feldspar, mica, or other associated minerals. Landes (1932, p. 390) cites one instance where fissures radiate out 4 or 5 feet from the radioactive minerals concerned, and follows Hess and Wells (1930) in believing that the actual primary growth of the minerals, as a result of the increase in volume, shatters the enclosing but earlier crystallized minerals. In an early paper Ellsworth (1922, p. 58) stated

“Another very characteristic indication of radioactive minerals is the presence of small cracks or fractures in the rock radiating from the mineral in all directions. These radiating fractures occur in feldspar, quartz, or mica surrounding radioactive minerals and are apparently caused by pressure which the mineral has exerted outwardly, due possibly to increase of volume resulting from internal radioactive changes.”

Later, however, for a particular case he (Ellsworth, 1927a, p. 367) believed that the fracturing of radioactive minerals and enclosing matrix alike was the result of “the internal strains set up by autoxidation”, but did not amplify this further. Walker and Parsons (1923b, p. 27–28) stated that shattering resulted from either (1) expansion of the inclusion, or (2) contraction of the host. They considered that expansion may result from oxidation and hydration, although they were careful to point out that such chemical changes did not always result in volume increase. On the other hand, where two minerals cooled from the same temperature and the coefficient of expansion of the host was greater than that for the included mineral, Walker and Parsons believed that the host would be very likely shattered while the inclusion might remain undamaged.

Without doubt the shattered or fractured condition of radioactive minerals and their environment results from expansion of the radioactive minerals concerned, but if growth or different physical properties are the cause, shattering should be found just as frequently about non-radioactive minerals; this does not appear to be the case. Therefore, in the writer's opinion, such fissuring may be attributed to expansion of the minerals concerned as a result of the transformation of radioactive min-

erals into the metamict state, whether complete or not. This physico-chemical change almost invariably appears to involve a notable decrease in density of the original minerals, and this is accompanied *pari passu* by considerable hydration and volume increase. Marked degradation of the crystal lattices also develops as a result of these changes as is clearly shown by Vegard (1916, p. 65) in the case of thorite and by Stott and Hilliard (1946), Chudoba (1937a, 1937b), and Bauer (1939) for zircon.

Acting singly or together upon anisotropic material, and the term anisotropic is used here in the widest sense, such changes could produce tensional and compressional forces competent to cause rupture of the minerals concerned; or if the radioactive material were present as inclusions within other minerals, the fissures would almost certainly extend outwards into the host minerals, or even beyond these into the surrounding matrix of adjoining crystals. Conditions of this nature could very well have produced the characteristics seen in the hyacinth crystals described, for in one example the central part of a hyacinth crystal clearly showed alteration towards a metamict state. Further, the detection of tantalum and (or) niobium in inclusions in zircon suggests the presence of minerals that are notoriously unstable and almost invariably found in a metamict condition.

Another condition frequently associated with radioactive minerals although naturally not observed in this study, is the red color, seen particularly in feldspars, of the minerals in close proximity to radioactive ones. Ellsworth (1922, p. 57) considered this feature an infallible guide to the presence of radioactive minerals but, although a pink coloration adjoining radioactive minerals is frequently found in pegmatites and similar rocks, the writer does not agree that it is always found. For example the orthites of the granites of Pomona Island (Turner, 1937a, p. 88–89) and in the pegmatites of Wilmot Pass (Turner, 1937b, p. 243) in Fiordland, the titanites in the north-west Nelson granites, and the monazite and xenotime in migmatites of the Charleston-Fox River area, do not appear to have produced a red color in the adjoining feldspars. It is perhaps significant that none of these minerals is altered to any extent, whereas the red coloration seems to be developed when

the uranium or thorium-bearing minerals are metamict or in a condition approaching that state. Therefore, it is suggested that the red coloration may be developed in the following manner: The transformation of a radioactive mineral to the metamict state will result in fracturing of the mineral and the micro-fissures may in some instances extend into the surrounding matrix. These fractures will provide a ready means for solutions to circulate and facilitate further break-down of the metamict mineral with subsequent removal or dispersion of decomposition products. Most uranium- or thorium-bearing minerals contain iron, and the oxidation of this constituent in particular would produce a zone of coloration surrounding the radioactive mineral. It may be significant that distinctively colored zones surrounding radioactive minerals appear to be developed in pegmatites etc. that are geologically old; that is, sufficient time has elapsed for transformation to a metamict state to be brought about.

#### DISTRIBUTIVE PROVINANCES

The investigation of over 400 samples of beach and dune sands, artificial and natural concentrates from alluvial and eluvial sands and gravels, has enabled the writer to obtain a generalized picture of the nature and distribution of heavy minerals in several areas of the South Island, and particularly in Westland. It is freely admitted that this study is incomplete, but it should point out some of the problems pertaining to the nature and distribution of heavy detrital minerals in a region of very great interest and the highest complexity. The actual source of many of the minerals described is unknown in some instances, owing chiefly to the absence of detailed petrographic and mineralogical studies in mountainous and often almost inaccessible country. In spite of this, however, some of the facts will at least assist further prospecting for rare earth and other valuable minerals, and provide information as to the nature of the minor accessory constituents in a wide range of local rocks that may assist in general stratigraphic problems.

In a very general sense, Westland and south-western Nelson Provincial areas can be divided into three distributive provinces in which distinctive detrital mineral assemblages occur.

These are:

(1). The southern to central Westland area extending from Bruce Bay northwards to about Saltwater Creek and Harahari in which a zircon-scheelite-thorite-uranothorite assemblage is characteristic.

(2). The Ross-Lake Mahinapua-Kokatahi-Arahura area with extensions north towards near Kumara, characterized by a relatively simple zircon-garnet-epidote (clinzoisite)-hornblende assemblage.

(3). The Grey River basin and the Cape Foulwind-Westport coastal plain in southern Nelson which is characterised principally by a zircon-hyacinth-monazite-xenotime-tantalum cassiterite assemblage.

Although the mineral assemblages of southern to central Westland are relatively simple they contain three unusual minerals, scheelite and two varieties of thorium silicate, which taken together with the tourmaline, topaz, and kyanite<sup>34</sup> present seem to have been derived in the first instance from the belt of granitic and metamorphic rocks that make up the western flanks of the Alpine Chain and occur as inliers on the morainic-covered coastal area. The abundant garnet is spessartite-almadine of average refractive index 1.791, and is quite comparable optically and chemically with the garnets so common in pegmatitic dykes and sills that outcrop here and there from the Mahitahi and Paringa rivers southwards. The pegmatites in this vicinity are generally the simple quartz-feldspar-mica type and quite distinct from those that normally carry rare earth and radioactive minerals, or other pneumatolytic-hydrothermal phases.

Uranothorite occurs largely as euhedra of approximately the same order of grain-size as the associated zircon crystals, which definitely suggests that in its original habitat the mineral was widely disseminated, and its occurrence today is not the result of the break-down of economically important segregations or concentrations of large crystals in the source rocks. On the other hand, the uranium-free biaxial thorium silicate invariably in the form of fragments and quite devoid of original crystal faces, must have originated by the break-down of crystals decidedly larger than the fragments

<sup>34</sup> Boulders of muscovite-kyanite schists are not uncommon in the alluvium of Paringa River.

now found, but this does not necessarily indicate that economically valuable segregations of thorite may exist at the source; in fact, the complete absence of even occasional fragments of thorite among the coarse material indicates that any large and valuable concentrations of this mineral are unlikely to be found.

Scheelite which occurs in payable veins in the Otago schists, principally at Glenorchy and Macraes, situated some 140 miles southeast and 160 miles south from the central Westland area, is a common detrital mineral in the sands of Central Otago streams. An extension of these Otago-type schists is to be found along the western side of the Southern Alps, immediately east of the central Westland area, and therefore, the detrital scheelite found here very probably has its source in such rocks.

Black titanite was found in a beach concentrate from Bruce Bay in the central to southern Westland area. In this sample, composite fragments coarser than 18-mesh consisted chiefly of fine-grained carbonaceous schist that almost certainly belongs to the Chlorite Zone. When isolated, crushed, and centrifuged in bromoform these schist fragments gave a heavy residue of "schist"-type tourmaline (Hutton and Turner, 1936, p. 264, 268; Hutton, 1940, p. 36, 63) and euhedral titanite crystals; the latter match those found in the finer size-fractions of the beach concentrate. There seems little doubt that this variety of titanite has come from either the Chlorite Zone schists that outcrop along the western flanks of the Southern Alps to the east and south of Bruce Bay, or the schistose Greenland Series that outcrop immediately south of this locality.

Dunites, harzburgites, and other olivine-rich rocks outcrop in a narrow, 40-mile long belt on the western slopes of the Olivine Range, some 60-70 miles southwest of Bruce Bay. Most of the detritus from these rocks reaches the coast by way of the Gorge, Cascade, and Jackson rivers, and the olivine in an isolated sample from Bruce Bay probably comes from these sources, possibly added to by a very small but indefinite amount through contributions from basaltic and other basic volcanic material associated with mid-Tertiary marine sediments (Henderson, 1917, p. 106) that outcrop along the coast southwards from the mouth of the

Paringa River. Although both chromite and awaruite are found in the peridotites of the Olivine Range neither of these minerals was recognized in the mineral assemblage of this olivine-bearing concentrate.

The central Westland mineral assemblage has been found in numerous localities in the wide belt of fluvio-glacial sands and gravels that make up the sloping ridges and coastal plain fronting the main range. This alluvium has been re-worked time and again by the sea, and the heavy mineral assemblages concentrated therefrom have been buried to form fossil placers as the coast line advanced seawards. At the present day, particularly under storm conditions, the heavy mineral assemblages in the coastal dunes may be further concentrated to produce pay streaks and black sands on the beaches that are, at irregular intervals, valuable sources of gold.

The second area, characterized by the distinctive mineral assemblage zircon-garnet-epidote (clinozoisite)-hornblende with marked predominance of the last two minerals in a number of instances, suggests a metamorphic source. Undoubtedly however, the Tuhua granites have contributed a good deal of the hornblende, epidote, and clinozoisite since these intrusives have been much affected by cataclasis with the development of considerable epidotization of the plagioclase, alteration of amphiboles to chlorite, epidote, and zoisite, and production of semi-opaque titanite from opaque iron ores; the granite outcropping near the headwaters of the South Branch of Humbug Creek ( $1\frac{1}{4}$  miles N.N.E. of Frazer Peak) in Totara Survey District, Mikonui Subdivision, is typical in this respect. The occasional crystals of uranothorite, topaz, and cassiterite present in the sands and gravels of this area may possibly have the same source as the epidote, zoisite, hornblende, etc., but more probably have been transported northwards from the Bruce Bay-Gillespie's Beach area by along-shore currents and incorporated with the more locally derived material during deposition of the fluvio-glacial debris that makes up the coastal plain. Although biotite is very poorly represented in the samples studied, it is not as rare a constituent as it would appear since both muscovite and biotite are generally abundant throughout the sands and gravels of this area. The low density and flaky

nature of biotite tend to prevent it from being concentrated either on the gold-saving tables of dredges or in the gold pan. The paucity of tourmaline might appear somewhat unusual since some of the detrital material has been derived from granites. However, work on the Tuhua granites shows that this mineral is not commonly developed; notable exceptions in this respect are outcrops at the northern end of the intrusion in the vicinity of Te Kinga Peak and Hohonu Ridge, just south of Lake Brunner, and isolated and strictly local occurrences in Totara Survey District, Mikonui Subdivision.

The Grey River-Mawheraiti River basin and the triangular coastal plain lying south and east of Cape Foulwind are characterized by a third and distinctive assemblage of zircon-hyacinth-monazite-xenotime-tantalum cassiterite; concentrates from Atarau dredge, although they distinctly show the general characteristics of the Grey River area, are heavily contaminated with material from a different source than that which provided the bulk of the gravels and sands of the Grey River and Cape Foulwind areas. However, tracing the various detrital minerals to their real source is exceedingly difficult owing to an absence of any detailed knowledge of the mineralogy of the granites, schists, and gneisses that make up the main masses of the Paparoa Range west of the Grey and Mawheraiti Rivers, and the Victoria Range to the east thereof.

The dominant heavy detrital minerals in the sediments of the two areas have almost certainly been derived initially from granitic and gneissic rocks and the associated pneumatolytic-hydrothermal phases; these sources are most probably the rocks of the Paparoa Range and, before extensive capture of the head-waters of the important eastern tributaries of the Grey and Mawheraiti Rivers, the intrusives of the Victoria Range lying to the east. The distribution of these index minerals is by no means limited entirely to the Quaternary gravels of the two areas in northern Westland and southern Nelson but have been found in a wide range of rocks<sup>35</sup>. Clearly therefore, the source rocks have been providing a supply of such minerals for a considerable period. In an attempt to determine the actual source rocks of these minerals a wide, but far from complete, range of

granites, gneisses, and schists from this region were examined, but monazite, xenotime, and cassiterite were not found in the schists and granites, except in rare cases when occasional crystals of the first two minerals were represented. A few rare grains of dusky brownish zircons also found in these rocks differed from hyacinth proper in color and crystal habit. However, the gneisses, particularly those outcropping along the coast south of Charleston and the mouth of the Nile River and those occurring as boulders in the upper reaches of the Otututu River, were of considerable interest. The minor accessory minerals from four gneisses collected at intervals along the coast south of Charleston averaged 4.7 per cent by weight, and the following percentages of the different constituents were found: zircon 33, apatite 37, monazite 26, xenotime 3, opaques 1; no hyacinth or cassiterite were present, however, in any of these assemblages. In similar gneisses from other outcrops in these two general localities, occasional grains of garnet, epidote, zoisite, tourmaline, and topaz were observed in addition to the characteristic minerals mentioned. Almost certainly these or similar gneisses, which are widely distributed throughout southern Nelson, must have been the main source of supply of the monazite and xenotime found in the Quaternary gravels, although undoubtedly these minerals have been incorporated in other rocks younger than the gneisses (the Trias-Jura rocks of the Hurunui River to mention only one instance) and the decomposition and degradation of these must also in their turn have provided some portion of the material supplied to the Recent and sub-Recent gravels. No indication of the initial source of cassiterite or the origin of hyacinth has been found, but in all probability, cassiterite came from the neighbouring granites and associated pegmatites. In this connection the hypotheses of Borovick and Gotman (1937, p. 352-353) and Boldyreva (1939, p. 421) that cassiterite from pegmatite veins contains enhanced quantities of tanta-

<sup>35</sup> The distinctive heavy mineral assemblage zircon-hyacinth-monazite-xenotime-cassiterite is the dominant one in conglomeratic rocks of Trias-Jura age outcropping in the Hurunui River area, Mandamus Survey District, about 75 miles E.S.E. of Grey River; also in Tertiary cementstones and conglomerates in Lankey Gully, Reefton Survey District.

lum<sup>36</sup> and niobium, suggest that the pegmatites rather than the massive granites or their more attenuated phases may be primary source rocks for Westland cassiterite.

It was pointed out earlier that hyacinth crystals exhibited a far greater degree of rounding than the associated colorless zircon; in fact grains of hyacinth that are almost spherical are not uncommon. At first sight the rounding of hyacinth would be attributed to abrasion, many times repeated, during a long and complex history since the liberation of the mineral grains from their ultimate source, but, in this connection, it should be remembered that other workers have noted that zircon, and particularly hyacinth, are often distinctly rounded and sometimes ovoid, although still in the host rock, and they need not show sharply euhedral forms (Armstrong, 1922, p. 395; Frankel, 1943, p. 77-78; Warner, 1945, p. 95). In this work crystals of hyacinth have not so far been found in their original source rocks, although some of the dusky-brown zircons in some samples of Paparoa granite did not show the perfection of form exhibited by associated colorless zircons.

In other localities, the original source rocks of hyacinth appear to be Precambrian (Scotland, Mackie, 1925b; North America, Bruce and Jewitt, 1936; Report on Accessory Minerals in Crystalline Rocks, 1935; Tyler *et al.*, 1940; Australia, Carroll, 1939, 1941, 1944; Higgins and Carroll, 1940; Madagascar, Lacroix, 1922). On this basis it is quite unsafe to suggest an initial source of Precambrian age for the hyacinth found in these southern Nelson and Westland sediments, if only because Precambrian rocks have not yet been recognized in New Zealand. Nevertheless, this possibility must be borne in mind.

Another mineral of some consequence occurring in the sands and gravels of this area is aluminian chromite, and it reaches its greatest abundance in the coarser fractions of concentrates from Blackball and Red Jacks dredges. The presence of chromite in this general area was noted by Morgan (1911, p. 91) who com-

mented upon its relative importance in concentrates from Montgomery's Terrace Sluicing Claim. The immediate source of this mineral is not known, but outcrops of peridotites, serpentinites, and their metamorphosed equivalents, antigorite and talc schists, are not uncommon along the western slopes of the Southern Alps, and doubtless the mineral has been brought down the westward-flowing tributaries of the Grey and Mawheraiti Rivers. The relative abundance of aluminian chromite in samples from the immediate vicinity of Ngahere suggests that the Pohaturoha (or Big Grey) River, now beheaded by the Inanguahua River, may have been the vehicle for much of this material.

The mineral assemblages in samples from Atarau dredge are somewhat distinct from the type usual in the Grey River basin in that epidote and clinozoisite are generally as plentiful as zircon. This suggests that the immediate source of a considerable amount of the sands and gravels treated by this dredge is the Aorere greywackes, argillites, and schists of the southern end of the Paparoa Range.

The mineral assemblages in a number of concentrates from Barrytown dredge are typical of most of the paystreaks obtained from numerous Westland beaches from north to south. Barrytown material in particular contains such minerals as scheelite and uranotorite, and thus shows the influence of the northward-flowing off-shore current which has brought along the coast a small percentage of those constituents characteristic of the central Westland province, whereas the occurrence of monazite, xenotime, and tantalum cassiterite indicates a mingling of material typical of the northern Westland-southern Nelson region.

The paystreaks and black sands that have accumulated on beaches between Wainui Inlet and Separation Point in northwestern Nelson, of which the sample from Wainui Inlet is typical, have been derived from the Pikikiruna Range-Separation Point granites, that outcrop along these shores; the heavy detritals are especially interesting on account of the high percentage of titanite therein. Actually, the quantity of titanite in these granites is in excess of that found in normal granitic rocks, and the prominence of this mineral suggests contamination. Field examina-

<sup>36</sup> The possible occurrence of tantalite in Blackball Dredge concentrates (p. 670 of this work) and sluicing claim concentrates from Addison's, Westport (Dom. Lab. 50th. Rept., 1917, p. 25) should be noted in this connection.

tion of the relationships of the granites and closely associated marbles and quartzites leaves no doubt that much of these sediments has been metasomatized and otherwise assimilated by the granites at the time of their emplacement to produce a range of amphibolites and grossularite-bearing rocks of basic appearance. In many of these titanite is a prominent constituent. Even in those granites that appear to be removed some distance from obviously metasomatized derivatives, titanite may be clearly seen in hand specimens. Apatite is also plentifully represented among the detrital minerals concentrated on the north-west Nelson beaches; this feature may be correlated with the relative abundance of apatite in some of the metasomatized and contact-altered marbles.<sup>37</sup> Tourmaline is uncommon in Wainui Inlet and neighbouring sands in spite of the fact that the mineral is not rare in the Pikikiruna Range intrusives. A blue tourmaline<sup>38</sup>, a member of the dravite-schorlite series, that occurs at Page's Saddle is typical, although clear-yellow elbaite varieties have been found in these granites.

The mineral assemblages obtained from the alluvial sands and gravels of Central Otago are those to be expected in material derived from a region of low-grade dynamothermally metamorphosed graywackes, except for, in the Naseby-St. Bathans-Kyebrun area in particular, the quantity and nature of the detrital zircon. In the samples studied, zircon is clear, colorless, and almost invariably sharply euhedral, and since the schists are generally the metamorphosed derivatives of graywackes and similar quartzo-feldspathic sandstones, one might expect some degree of rounding in the zircons, or at least 5 or 10 per cent of fractured crystals. Such characteristics are only found in isolated crystals and cannot be considered more than a rare occurrence. Added to this is

<sup>37</sup> Bands and lenses of metasomatized marble are well developed in many places along the Pikikiruna Range, and in a typical exposure at Rameka Creek, on the western slopes of the range, approximately 10 miles south-west from Separation Point, crystals of apatite up to 5 mm. in diameter are not uncommon. Similarly near the headwaters of Brooklyn Stream, near Riwaka on the eastern side of the range, apatite is also found. A careful study of such rocks might reveal apatite-bearing material of economic value.

<sup>38</sup> E = 1.632 ± 0.002; O = 1.659; O - E = 0.027; dichroism: deep indigo blue (O) to colorless (E).

the relative abundance of zircon in the schists in the vicinity of Naseby and St. Bathans and, consequently, in the auriferous placer deposits derived therefrom. Zircon has usually been considered a very insoluble, stable mineral, and not of that group of minerals, chiefly silicates, that may be carried in solutions and ichors forming the vanguard of a regional intrusion of granitic material. The work of Goldschmidt (1919, p. 280-1), von Eckermann (1922, p. 375), Gillson (1925, p. 190), and Franco and Loewenstein (1948, p. 150) have shown beyond much doubt that zircon or zirconiferous material may be transported pneumatolytically. Concentration of zircon within limestone, but outside actual granite contacts in the Mansjö Mountain area described by von Eckermann, can have no other explanation. Therefore, to account for the plentiful, yet sharply euhedral zircon in localized areas of the Otago schists, the writer suggests that at least some of it has been introduced into the schists and, together with tourmaline (Hutton, 1939, 1940), represents one phase of emplacement of subjacent acid intrusives that was part of the general conditions culminating in dynamothermal metamorphism of the rocks of the Otago area.

Although granitic rocks do not come to the surface anywhere in the Otago Central area, there can be little doubt of their presence at lower levels in view of the wide and often plentiful distribution of tourmaline throughout the schists. And, further, the mineral assemblages in Tertiary sediments of Eastern Otago can only have been derived from rocks of the Otago schist type that have been locally metasomatized by granitic intrusions; this association of rocks is clearly shown by the occurrence in the heavy mineral assemblages prepared from some of these sediments of such minerals as kyanite and andalusite (Hutton and Turner, 1936) and corundum and spinel (in auriferous gravels at Adam's Flat, near Milton).

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MANUSCRIPT RECEIVED BY THE SECRETARY OF THE SOCIETY, MARCH 18, 1949.

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