The chemistry, reflectance, and cell size of the erlichmanite (OsS$_2$)–laurite (RuS$_2$) series

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ABSTRACT. Microprobe analyses of members of the erlichmanite–laurite series from Guma Water and Senduma, Sierra Leone and Tanah Laut, Borneo, indicate that complete solid solution is possible between OsS$_2$ and RuS$_2$ with considerable substitution of Os and Ru by Ir, Rh, and Pt. The cell size of the erlichmanite from Guma Water is $a = 5.6183 \pm 0.0003$ Å at a composition (Os$_{0.61}$Ru$_{0.30}$ Ir$_{0.06}$Rh$_{0.03}$)$_{\Sigma 0.93}$S$_2$ whilst the laurite from Senduma has a composition of (Ru$_{0.88}$Os$_{0.05}$Ir$_{0.04}$ Rh$_{0.03}$)$_{\Sigma 0.93}$S$_2$ and a cell size of $a = 5.6089 \pm 0.0005$ Å. Substitution of Os for Ru provides the predominant cause of the variation of cell size. Substitution by other elements of the platinum group appears to produce little effect on cell size and is presumably controlled by genesis rather than considerations of crystal chemistry or structure. The recorded analyses for these elements indicate a predominance of Ir over Rh for members of the series containing more than about 15 % of the laurite molecule. For the remainder of the series Rh is more important than Ir. The reflectance in air and oil of the members of the series from Sierra Leone and Borneo are presented and the microhardness of the erlichmanite from Guma Water shown to be 1854 kg/mm^2. This is the first report of laurite from Senduma, Sierra Leone.

SNETSINGER (1971) provided the first description of naturally occurring osmium disulphide which he named erlichmanite. The material he described consisted of a few grains (~ 20 μ in diameter) contained in a Pt–Fe alloy from placer deposits of MacIntosh Mine, California, and a second sample from western Ethiopia. In both localities the erlichmanite consists principally of osmium and sulphur with only minor quantities of other platinum group elements. The structure was shown to be cubic with a pyrite type space group (Pa3) by comparison with synthetic OsS$_2$ which has a cell edge of 5.6196 $\pm$

0.0003 Å (Sutarno et al., 1967) and the mineral is clearly the osmium analogue of laurite. The small grain size of this material precluded more rigorous study.

More recently Begizov et al. (1976) have described minerals of the 'erlichmanite–laurite series' in greater detail from occurrences in the Ural placer deposits and their descriptions included measurements of micro-hardness, reflectance and cell size. In addition Bowles (1981) and Cabri et al. (1981) have described erlichmanite occurring at Guma Water, Sierra Leone, and in Ethiopia respectively.

Laurite has been known since its description by Wöhler (1866) whilst Leonard et al. (1969) have more recently described its chemical and physical properties. The type locality for laurite is Pontijn, Tanah Laut, Borneo (now Kalimantan), but the previously reported analyses were incomplete. Wöhler (1866) analysed S and Ru and provided Os by difference; Bannister (1932) analysed only S and gave Ru by difference whilst Leonard et al. (1969) analysed Ru, Ir, and S, and gave Os by inference. New analyses are presented here of rounded grains of alluvial laurite from the type area obtained from the British Museum (Natural History)—reference BM 40505.

The overall mineralogy and occurrence of the platinum group minerals found as eluvial deposits at Guma Water, derived from the Jurassic Freetown Layered Gabbro, Sierra Leone, were described by Bowles (1981). The erlichmanite and laurite from Guma Water consist of large pyritohedral crystals up to 1 mm across set with hexagonal platelets of iridosmine and rutheniridosmine in nuggets of Pt–Fe alloy (Bowles, 1981). For the erlichmanite
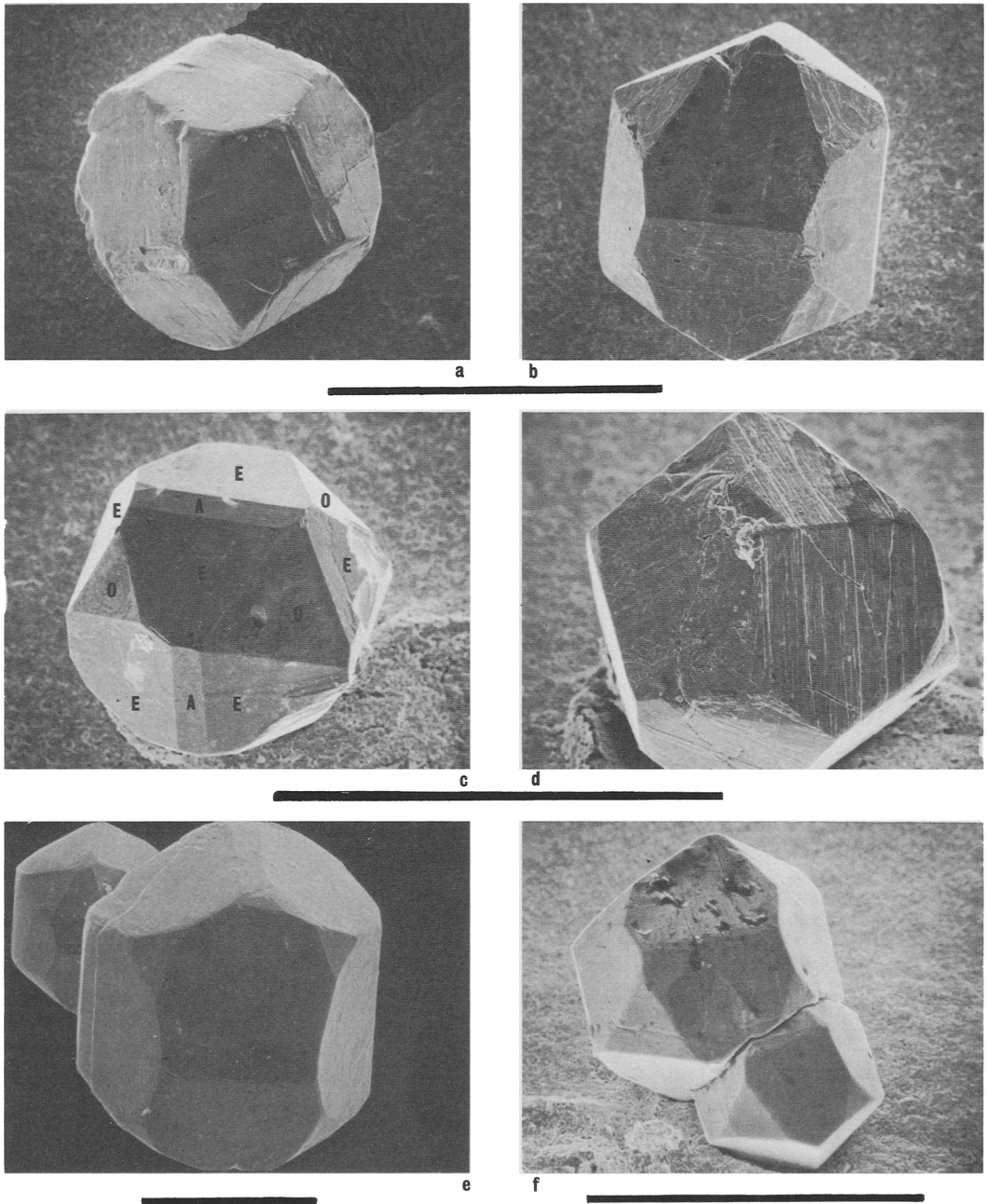
FIG. 1. (*a–f*). Well-formed pyritohedra of laurite (*c*) and erlichmanite (*a, b, d, e, f*) from Guma Water, Sierra Leone, showing the pyritohedral faces (E) and the minor octahedral (O) and cube (A) faces. The faces often show striations typical of the pyrite structural group. The examples *e* and *f* are apparently twinned with two crystals in approximately the same orientation although the structure between them (seen in *f*) seems to deny close structural association. The scale bars under *a, d,* and *f* represent 0.5 mm whilst that under *e* represents 0.1 mm.

these grains are therefore between 10 and 100 times larger than the material previously available and more suitable for morphological and X-ray studies. Among the range of alluvial and eluvial grains from this locality so far identified as erlichmanite and laurite, cubic {100}, octahedral {111}, and pentagonal dodecahedral {210} forms are observed (fig. 1).

A faint striation can be seen on many of the pentagonal dodecahedral faces similar to that commonly observed on crystals of pyrite, and occasionally a network texture is seen on the cube faces with 'pock marks' where the striations cross at right angles. These phenomena have only been observed on the minerals from Guma Water due presumably to the large size of this material and the apparently unconstrained environment in this locality during crystal growth.

Large, well-rounded crystals of laurite have also been obtained from the Senduma Chrome Mines, Sierra Leone (Dunham *et al.*, 1958). This laurite was found in alluvium in the thick laterites surrounding bodies of chromite in an Archaean greenstone belt 220 km ESE of Guma Water. There does not appear to be any connection between the two localities. This is the first mention of the occurrence of laurite at Senduma.

Electron Microprobe analysis. The compositions of the minerals described here were obtained using electron microprobe analysis and the methods and standards described by Bowles (1975). In addition, analysed iridosmine and laurite were used as standards for Os and Ru respectively. Allowance was made for the following problems of X-ray interference: Ru-$L\beta_2$ and Rh-$L\beta_1$, interfering with Pd; Cu-$K\beta$ interfering with Os and Ir-Ll interfering with Cu.

Reflectance. Reflectance measurements on the same grains used for microprobe analysis were carried out immediately after repolishing on a 1μ diamond lap for several minutes. Measurements in air were made using a $\times 10$ objective whilst for measurements in oil a $\times 8$ objective and Cargille

TABLE I. *Electron microprobe analyses of laurite and erlichmanite*

	Laurite				Erlich- manite
		Borneo		Guma Water	
	Senduma	A	B		
Pt	0.04	0.62	0.57	0.83	n.d.
Ir	4.60	13.17	7.50	6.83	4.95
Rh	1.71	0.74	0.61	2.14	1.17
Os	4.97	21.69	26.82	37.61	51.35
Ru	49.23	29.49	30.31	21.37	13.47
Cu	n.d.	n.d.	n.d.	0.01	n.d.
Fe	n.d.	0.07	n.d.	n.d.	n.d.
S	38.12	33.56	33.62	32.07	29.57
Total	98.67	99.34	99.43	100.86	100.51

Atomic proportions to 2 sulphur atoms/formula unit					
Pt	—	0.006	0.006	0.009	—
Ir	0.040	0.131	0.074	0.071	0.056
Rh	0.028	0.014	0.011	0.042	0.025
Os	0.044	0.218	0.269	0.395	0.585
Ru	0.819	0.557	0.572	0.423	0.289
Fe	—	0.002	—	—	—
Σ	0.931	0.928	0.932	0.940	0.955
S	2.0	2.0	2.0	2.0	2.0

Percentage of total platinum group metals					
Ru	87.9	60.2	61.4	45.0	30.3
Os	4.7	23.5	28.8	42.1	61.3
Ir + Pd + Rh + Pt	7.4	16.3	9.8	12.9	8.4

n.d. = not detected above a detection limit of 0.01%. Pd not detected.

D/A 58.884 oil were used; the results are presented in Table II. In all cases measurements were made on areas of perfect polish and compared with the WTiC Zeiss 140 standard at the four principal wavelengths specified by the IMA (Commission on Ore Microscopy). A line interference filter with $\Delta\lambda = 12$ nm was used. This is the first report of the reflectance in oil of analysed laurite and these data contribute to the small amount of published

TABLE II. *Reflectance (R %) in air and oil at the recommended COM wavelengths*

	In Air				In Oil			
Wavelength (nm)	470	546	589	650	470	546	589	650
Laurite								
Senduma	49.1	45.2	43.4	41.2	30.2	27.6	26.2	24.6
Borneo A	45.0	42.6	41.2	40.2	28.6	26.5	25.3	23.7
Borneo B	45.2	43.1	41.7	39.7	28.8	26.3	24.9	23.6
Erlichmanite								
Guma Water	44.6	42.5	41.5	40.1	28.6	26.5	25.5	24.1

information on the reflectance in air of erlichmanite and laurite. Allowing for differences in composition of the phases measured, the results presented here cover much the same range as those presented by other authors (Leonard *et al.*, 1969; Begizov *et al.*, 1976; Harris, 1974; Cabri, 1981; Cabri *et al.*, 1981) as shown in fig. 2. In addition Vyal'sov (1973) and Picot and Johan (1977) have reported reflectance

data on specimens of laurite for which no analyses were given.

The results obtained by Cabri *et al.* (1981) produce very smooth curves which differ from all the other measurements in showing constant reflectance (43-4 %) at low wavelengths. Results by other authors appear to indicate higher reflectance at low wavelengths (e.g. 44-50 % at 450 nm)
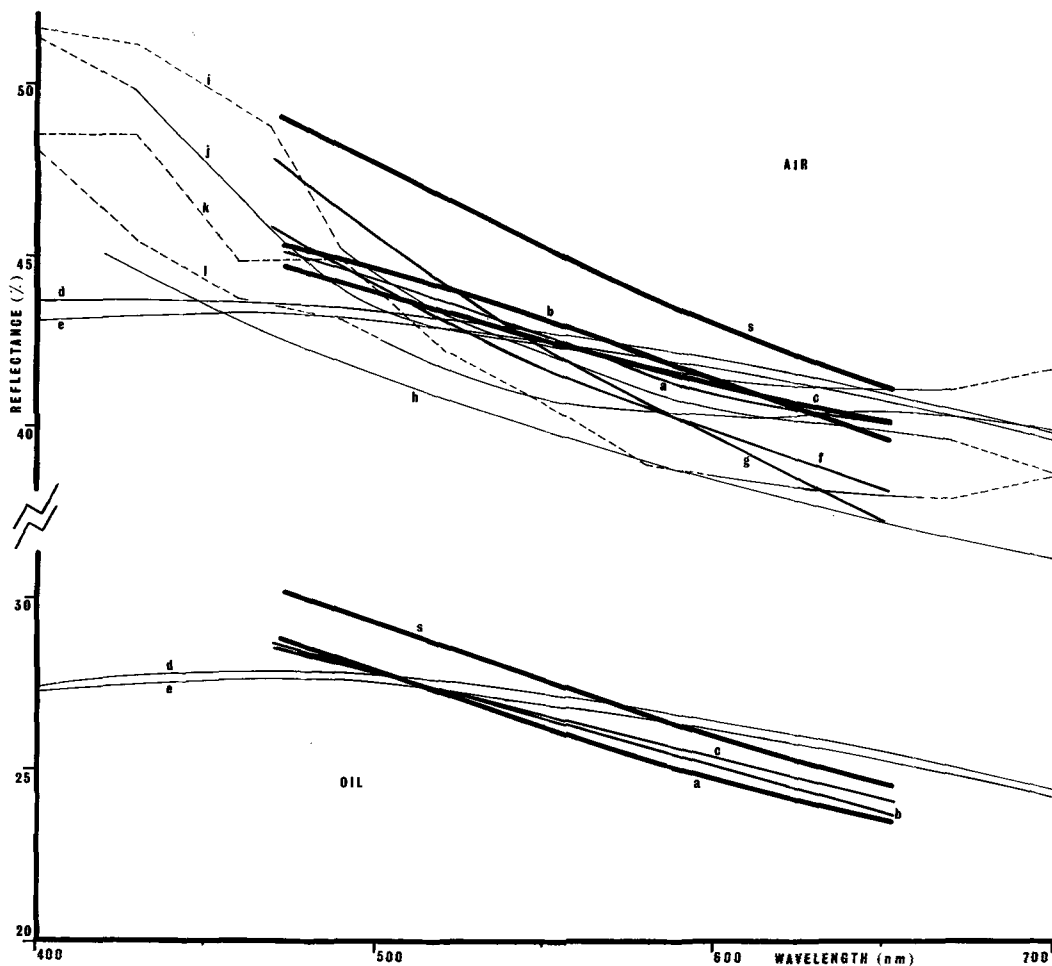

FIG. 2. Reflectance curves of members of the erlichmanite-laurite series described in this work compared with other results available in the literature. (i)-(l) are shown dashed to indicate uncertainty where drawing a smooth curve is inappropriate.

(a) Laurite, Grain A, Pontijn, Tanah Laut, Borneo. This work.

(b) Laurite, Grain B, Pontijn, Tanah Laut, Borneo. This work.

(c) Erlichmanite, Guma Water, Sierra Leone. This work.

(s) Laurite, Senduma, Sierra Leone. This work.

(d) Erlichmanite, Grain 2, Ethiopia, Cabri *et al.*, 1981.

(e) Erlichmanite, Grain 1, Ethiopia, Cabri *et al.*, 1981.

(f) Laurite, Borneo, Leonard *et al.*, 1969.

(g) Laurite, Goodnews Bay, Alaska, Leonard *et al.*, 1969.

(h) Laurite, Picot and Johan, 1977.

(i) Laurite, Clr, Ural placers, Begizov *et al.*, 1976.

(j) Erlichmanite, Cla, Begizov *et al.*, 1976.

(k) Erlichmanite, Cll, Begizov *et al.*, 1976.

(l) Irasite, Ccla, Begizov *et al.*, 1976.

although it is not possible to draw a smooth curve through the results obtained by Begizov *et al.* (1976) so that their results do not inspire confidence.

Microhardness. Following the IMA (COM) recommendations, an indentation load of 100 g was applied for 15 sec and the indentation measured at $\lambda \simeq 546$ nm. Imperfect indentations were produced because the high microhardness of these minerals gave rise to fracturing around the indentation. Consequently the four best indentations out of seven were chosen. These gave a range of microhardness from 1730 to 1950 kg/mm^2 with an average value of 1854 kg/mm^2 for the erlichmanite, which is somewhat higher than the average values of 1359–89 kg/mm^2 obtained by Begizov *et al.* (1976) on material of similar composition, although it is within the range of measurements which they obtained (1328–2012 kg/mm^2).

The values of microindentation hardness of the laurite-erlichmanite series are higher than for any other mineral and form a useful diagnostic feature.

X-ray data. The cell size of erlichmanite from Guma Water was obtained from powder photographs taken in a 114.6 mm diameter Debye-Scherrer camera using copper radiation (Cu-$K\alpha_1 = 1.54051$ Å, Cu-$K\alpha_2 = 1.54433$ Å). Photographs with sharp powder lines were obtained with well resolved α_1, α_2 doublets at the higher Bragg angles indicating well crystallized material. Values of the cell dimensions calculated from the various measured reflections were plotted against the function $\frac{1}{2}\{(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)\}$; extrapolation to zero yielded the accepted value of $a = 5.6183 \pm 0.0003$ Å. All experimental data were obtained at 20 °C. Assuming four formula units in the unit cell and the atomic proportions derived in Table I the calculated density is 8.28 g/cm^3. The grains are too small for the density to be measured. The powder diffraction data for the Guma Water erlichmanite show close agreement with those of synthetic erlichmanite (JCPDS 19-882) and also laurite (JCPDS 12-737, 19-1107) and are consistent with those of space group Pa^3 determined for the pyrite group of minerals. A value of $a = 5.6089 \pm 0.0005$ Å was obtained for the Senduma Laurite. The density of the large crystals of laurite from this locality was measured using a Berman balance to give a value of 6.43 g/cm^3 which compares well with the calculated density of 6.39 g/cm^3.

Composition and cell-size. The data presented here (Table I) and those available in the literature (Snetsinger, 1971; Begizov *et al.*, 1976; Leonard *et al.*, 1969; Harris, 1974) indicate that complete substitution between Os and Ru is possible and that up to 20 % Ir (Leonard *et al.*, 1969) may be accommodated. As much as 11 % Rh and 1.3 % Pt (Begizov *et al.*, 1976) and 0.6 % Pd (Snetsinger,

1971) are also recorded. An incomplete analysis (Kingston, 1966) suggested that as much as 5 % Pt might enter into the lattice.

In this work, the additional metals have been put together and plotted on an '$(Ir + Rh + Pd + Pt)S_2$'-RuS_2-OsS_2 triangular diagram (fig. 3). For comparison, the work of earlier authors is included on this diagram and, in addition, the measured cell size and Ir/Rh ratio are shown where this information is available.

These data reveal a distinction which can be drawn at a composition of about 15 % of the RuS_2 molecule (fig. 3). For the greater part of the series Ir is the predominant additional metal with Ir/Rh molecular ratios which vary from 1.4 to 9.6 in those instances where Rh is large enough to be reported. For the remainder of the series, Rh becomes more abundant giving Ir/Rh ratios in the range 0 to 0.47. In addition, the only palladium so far reported occurs in the specimens described by Snetsinger (1971) which lie in this part of the series. It is not clear at present if this distinction is an artefact resulting from the paucity of available analyses or if it has a mineralogical or genetic basis. The ionic radii, discussed below, appear to provide no reason to associate Ir with Ru, or Rh and Pd with Os and the data available here (fig. 3) do not point to any *continuous* minor element variation within the laurite-erlichmanite series.

The data of Sutarno *et al.* (1967) are used for the cell sizes of RuS_2 and OsS_2 and those obtained here appear to be realistic in comparison with the cell sizes of the synthetic end-member components.

Although Ir, Rh, Pd, and Pt enter into the laurite-erlichmanite lattice, there do not appear to be any clearly defined end-members involving these elements. IrS_2 (Munsen, 1968) and PdS_2 (Munsen and Kaspar, 1969) both have orthorhombic structures. $IrS_{1.9}$ with a pyrite structure has been produced ($a = 5.68$ Å) by Munsen (1968) at 60 kbar and 1500 °C, and under the same conditions he also observed the $IrS_{2.9}$ of Biltz *et al.* (1937) with the pyrite structure and a cell size of $a = 5.62$ Å. Hulliger (1964) produced, by extrapolation, a cell size of $a \simeq 5.73$ Å for what he regarded as a hypothetical RhS_2 phase, although Thomassen (1929) had previously given a cell size of $a = 5.58$ Å for RhS_2 with a pyrite structure, and Feather (1976) has reported an unnamed mineral phase with that composition. PtS_2 (Grønvold *et al.*, 1960) is hexagonal.

The influence of the ionic radii of the platinum group elements on the cell sizes of the laurite-erlichmanite series is far from clear. Metallic atom radii are available for these elements (Parthé, 1972) as are ionic radii relevant to oxide phases (e.g. Shannon and Prewitt, 1969; Whittaker and Muntus,
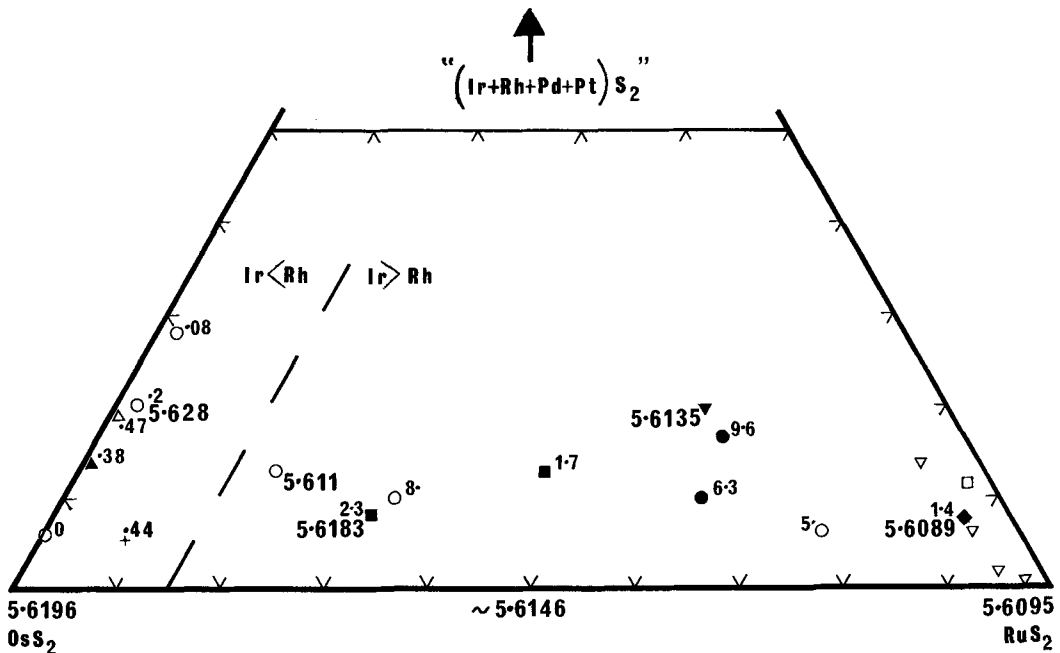
FIG. 3. Compositions of members of the erlichmanite–laurite series from this work and from the literature plotted on a '$(Ir + Rh + Pd + Pt)S_2$'–RuS_2–OsS_2 triangular diagram. Where available the measured cell size is shown in larger type and the Ir/Rh ratio is shown in smaller type. The sources of the analyses are as follows:

+ Cabri *et al.* (1981). from Birbir River, Ethiopia.
o Begizov *et al.* (1976) from the Urals.
□ Harris (1974) from Papua New Guinea.
△ Snetsinger (1971) from Ethiopia.
▲ Snetsinger (1971) from California.

▼ Leonard *et al.* (1969) from Borneo.
▽ Leonard *et al.* (1969) from Goodnews Bay, Alaska.
■ This work from Guma Water, Sierra Leone.
● This work from Tanah Laut, Borneo.
◆ This work from Senduma, Sierra Leone.

1970). Shannon (1981) has recently produced ionic radii for sulphides in a study which specifically excluded '. . . structures involving sulphur–sulphur bonds such as pyrite . . .'. Elliott (1960) studied interatomic distances in MnS_2, FeS_2, CoS_2, and NiS_2 with pyrite structure and found that variations in the sulphur–sulphur bond length approximately compensated for the changes in the metal–sulphur distance resulting in smaller changes in cell dimension that would otherwise have been expected. His explanation in terms of ligand field theory showed that the antibonding π^*3p electrons are responsible both for the variation in the sulphur–sulphur bond and the compensating variations in the metal–sulphur distance. If these conclusions can be transferred to sulphides of the platinum group elements with pyrite structure, it follows that no clear relationship between the cell size and the ionic radii of these elements is to be expected. Clearly, however, the variation from RuS_2 to OsS_2 shows a distinct change in cell size but further attempts to classify the data presented in fig. 3 are fraught with difficulty because of the disparate sources from

which the information was obtained. These data produce contradictory answers to attempts to study the association of subsidiary variations in cell size with the content of Rh, Ir, Pd, and Pt which tends to support the conclusion derived above. The only inference which can be drawn at present is that variations of the order of 0.001 to 0.006 Å on about 5.61 Å are due principally to variations between the structural determinations of different laboratories and that Ir contents up to 20 % and Rh contents up to 2 % do not effect the cell dimension sufficiently to be evident above this degree of variation. From this it follows that the distribution of the minor elements observed here, particularly Ir and Rh is probably controlled by genetic rather than structural considerations.

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