

Unusual nickel and copper to noble-metal ratios from the Råna Layered Intrusion, northern Norway

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Rocks from the Råna Layered Intrusion usually have low concentrations of noble metals but have normal Ni and Cu concentrations. Consequently the rocks have higher Cu/Ir, Ni/Ir, Cu/Pd and Ni/Pd ratios than extrusive rocks from the literature. If a small amount of sulphide was removed from the magma prior to its emplacement at Råna the magma would be depleted in noble metals relative to Ni and Cu, and rocks forming from it would have high Ni and Cu to noble-metal ratios.

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The recent boom in the exploration for new platinum deposits has produced numerous Os, Ir, Ru, Rh, Pt, Pd and Au (hereafter referred to as noble metals) analyses. Exploration programs rarely find platinum deposits, but the noble-metal analyses that are gathered can be useful in providing information on the geochemical cycle of these elements in different geological environments. This information can be used in developing models as predicative tools for exploration (e.g. Keays et al. 1982; Naldrett et al. 1984).

Rocks from the Råna Layered Intrusion of northern Norway have exceptionally low Ir, Pt, Pd and Au contents relative to their Ni and Cu contents. This paper will: (a) Document the Ni, Cu and noble-metal concentrations of the Råna Layered Intrusion; and (b) consider how the combined effects of partial melting, sulphide segregation and silicate crystallization could have produced rocks with such unusual compositions.

Geological setting

The Råna Layered Intrusion lies 20 km southwest of the town of Narvik in northern Norway (inset on Fig. 1). The intrusion belongs to the class of layered mafic intrusions intimately associated with orogenesis, e.g. the 'Younger' Gabbros of NE Scotland, La Perouse in Alaska, and the Caledonide gabbros of Maine. It intruded graywackes and pelites of the Narvik Group after the first and second phases of Caledonide

deformation in the area (Boyd in prep.) at a depth equivalent to 2–3 kb, and was subsequently deformed and metamorphosed along with its country rocks at 6–10 kb and 600–700°C (Barnes 1986). Together with the host rocks the intrusion was tectonically emplaced into its present position during the Scandian phase (400 Ma.) of the Caledonian Orogeny as part of the tectonic unit termed the Upper Allochthon (Boyd in prep.).

Mineral and whole-rock analyses suggest that the parental magma of the intrusion was a high-Mg tholeiite, which was slightly enriched in the highly incompatible elements such as Cs, Rb, K, Ba, Hf, Zr and LREE relative to moderately incompatible elements such as Sc, Y and HREE ($La/La_N = 2.5$) (Barnes 1986 and Boyd in prep.).

The exact tectonic setting of the Råna intrusion is unclear, but on the basis of the clinopyroxene analyses and using Leterrier's et al. (1982) discrimination diagrams, the intrusion formed in 'a distension zone' (Barnes 1986). This includes ocean ridges, both in major oceans and back-arc basins, ocean islands and passive continental margins. The spinel analyses indicate affinities with abyssal tholeiites (Barnes 1986). The fact that the Råna intrusion formed at a depth equivalent to 2–3 kb in graywackes suggests that it did not form at an ocean ridge or an ocean island in a major ocean. Possibly it formed at an ocean ridge in a back-arc basin that was choked with sediment, or at a passive continental margin.

The intrusion may be divided into three zones (Boyd in prep; Barnes 1986); a lower ultramafic

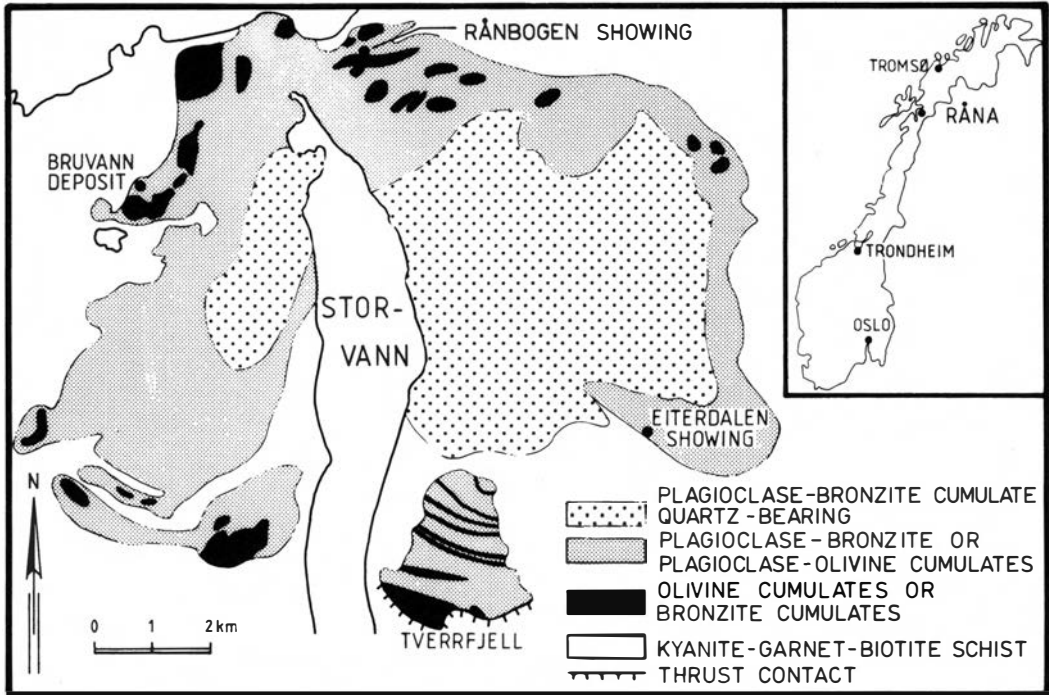


Fig. 1. Simplified geological map of the Råna Layered Intrusion; modified after Boyd & Mathiesen (1979) to show the locations of Eiterdalen, Rånbogen and Tverrfjell.

zone of olivine and bronzite cumulates, a middle mafic zone of plagioclase-olivine and plagioclase-bronzite cumulates, and an upper quartz-bearing zone of plagioclase-bronzite cumulates with interstitial quartz. Rocks from four localities at Råna-Bruvann, Eiterdalen, Rånbogen, and Tverrfjell (Fig. 1) have been analysed for the noble metals, Ni, Cu and Co. Rocks from Rånbogen and Bruvann are in the ultramafic zone and consist of olivine and bronzite cumulates containing sulphides. Bruvann is Norway's largest nickel deposit, and the results for this locality are presented separately (Boyd & Mathiesen 1979; Boyd et al. in press). The rocks from Eiterdalen come from the contact between mafic zone and the country rocks and are metagabbros containing sulphides. The rocks from Tverrfjell come from three traverses across the upper portion of the ultramafic zone and most of the mafic zone.

Analytical methods

Ni, Cu and S were determined by XRF, on pressed-powder pellets, by Midlands Earth

Sciences Associates of the U.K. The noble metals were determined by instrumental neutron activation (INAA) after preconcentration of the noble metals into a nickle sulphide bead; the Tverrfjell samples were analyzed at the University of Toronto, by the author; the other samples were analyzed at Becquerel Laboratories of Toronto. Co was determined by INAA at Becquerel Laboratories of Toronto. Table 1 lists estimates of the precision and accuracy of the analyses.

Results

The Ni, Cu, Co, S and Au contents of these rocks are greater than the detection levels. The distribution of these elements is log-normal; therefore, in addition to the arithmetic means and the ranges, the geometric means, which may be more representative, are presented in Table 2. Ru and Rh are present at less than detection level in all the rocks and will not be discussed further. Some samples from each locality have Os, Ir, Pt and Pd contents at levels less than detection level. Therefore, the mean for each element cannot

Table 1. Precision and accuracy of analyses.

XRF MESA	NGU std n = 4	1 sigma	Accepted value ¹	NIM-D	Accepted value ²	BCR1	Accepted value ²
Cu	52.5	1.5	53.4	12	10	16	20
Ni	51	1.9	51.9	2064	2050	11	10
S	38	5.4	—	103	200?	367	400
INAA Becquerel							
Co	27.9		25				
INAA UNIVERSITY OF TORONTO							
	SARM-7 n = 4	1 Sigma	Accepted Value ³				
Os ppb	73	17	63				
Ir	69	3	74				
Ru	423	20	430				
Rh	253	40	240				
Pt	4093	358	3740				
Pd	1495	68	1530				
Au	356	17	310				

¹ NGU's accepted value (Faye pers. comm. 1985).

² Govindaraju (1984).

³ Steele et al. (1975).

Table 2. Average chalcophile and siderophile element content of rocks from the Råna layered intrusion.

	Tverrfjell n = 115			Rånbogen n = 7		
	Geometric mean	Arithmetic mean	Range	Geometric mean	Arithmetic mean	Range
Ni ppm	350	443	36–1615	1800	4557	600–19,900
Cu	90	110	3–320	450	730	138–2383
Co	60	73	22–154	240	485	140–1910
S	1000	1441	0–6959	23,000	86,300	3504–405,816
Os* ppb	<2	<2	—	3	4	<3–12
Ir*	0.05	0.06	<0.01–0.35	0.8	1	<0.3–5
Ru	<10	<10	<10	<10	<10	—
Rh	<1	<1	<1	<1	<1	—
Pt*	5	6	<2–46	9	9.3	<7–15
Pd*	8	10	<20	6	7.6	<5–20
Au	5	7.3	1–35	4.5	6.4	1.7–21
Eiterdalen n = 7						
	Geometric mean	Arithmetic mean	Range			
Ni ppm	2500	3447	340–7730			
Cu	900	961	11–3846			
Co	250	337	75–716			
S	40,000	64,600	413–163,488			
Os* ppb	<3	<3	—			
Ir*	0.6	0.7	<0.3–1.4			
Ru	<10	<10	—			
Rh	<1	<1	—			
Pt*	8	9.4	<7–19			
Pd*	8	9.4	<5–22			
Au	4	5.6	1.7–14			

* Some samples contained Os, Ir, Pt and Pd at less than detection levels; therefore the means for these elements were estimated using log-probability graph paper. Bury (1975) p. 279 eq. 8.8.

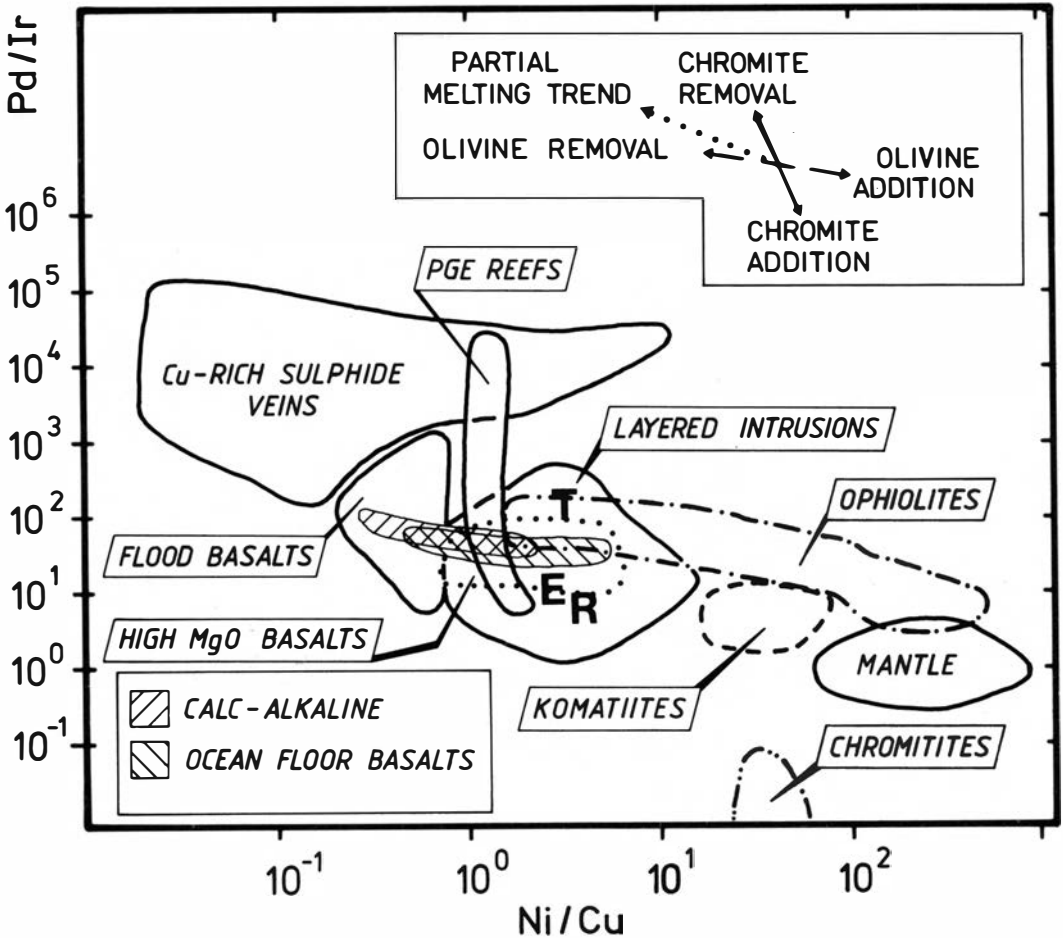


Fig. 2. The fields of Ni/Cu vs Pd/Ir for various rocks from the sources listed in the appendix. R = mean of the Rånbogen samples, E = mean of the Eiterdalen samples, T = mean of the Tverrfjell samples. Note that the mean of the Eiterdalen and Tverrfjell samples falls within the field of high-MgO basalts, which is consistent with the development of these rocks from a high-MgO tholeiite as suggested by their whole-rock chemistry. The Rånbogen samples fall on the olivine and chromite enriched field, which is consistent with the fact that these rocks are olivine and pyroxene cumulates with minor chromite.

be calculated directly. Fortunately the geometric mean may be estimated by means of log-probability paper and the arithmetic mean calculated from well-established statistical formulas (Bury 1975: 279 eq. 8.8). This technique was used for estimating the geometric and arithmetic means for Os, Ir, Pt and Pd at each locality.

The Råna rocks contain sulphides; because sulphides usually contain high concentrations of noble metals, it is common practice to recalculate noble-metal, Ni and Cu values to 100% sulphides (e.g. Naldrett 1981). However, it should be remembered that recalculation to 100% sulphides involves a number of assumptions which are not

necessarily valid for all rock types. Firstly, it assumes that all the noble elements partitioned into a Cu-Fe-Ni sulphide liquid containing 36-38% sulphur in the igneous phase of the rock's history and secondly, that since then the S, Ni, Cu and noble-metal contents of the rock have not been disturbed. This may be true in sulphide-rich rocks under certain metamorphic conditions. In sulphide-poor rocks, however, Rh, Pt and Pd may occur as compounds of As, Sb, Se, Hg and S, while Os, Ir and Au are often found in metallic form. The noble metals may not have partitioned into a Cu-Fe-Ni sulphide liquid. Furthermore, during sea-floor alteration and subsequent meta-

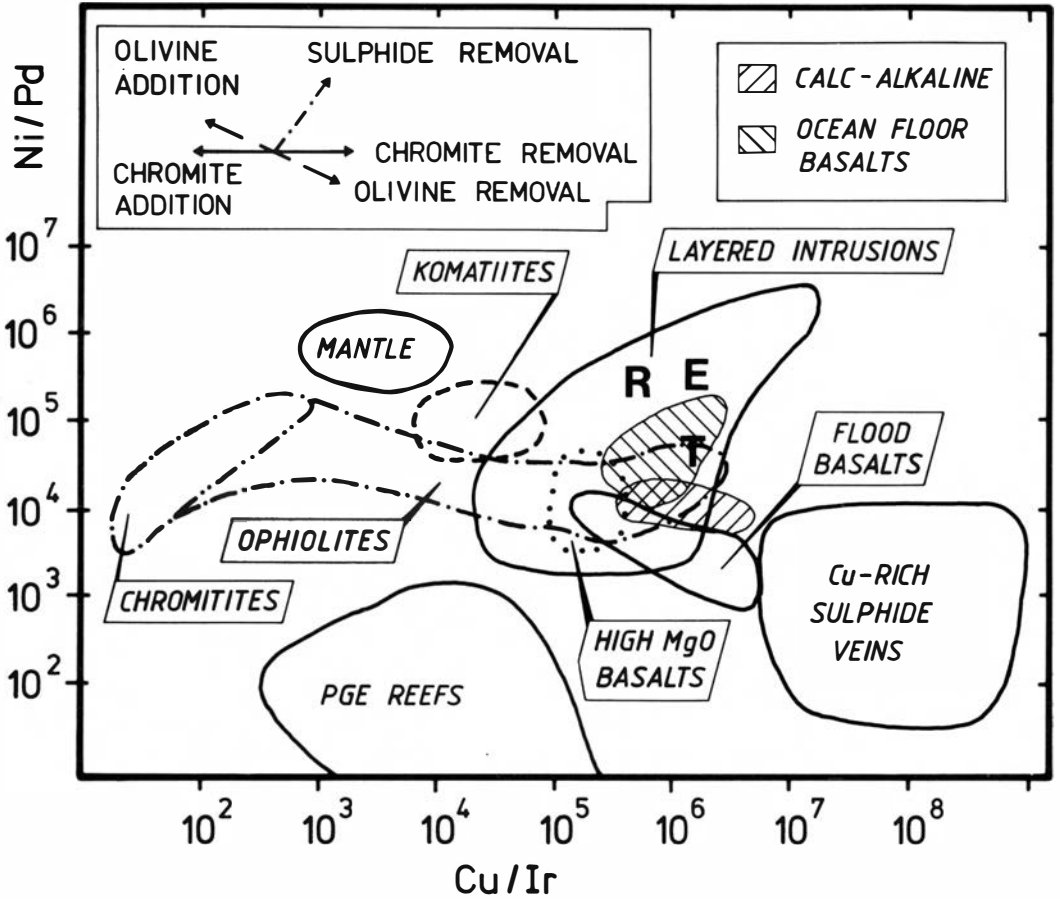


Fig. 3. Cu/Ir vs Ni/Pd for various rocks from the sources listed in the appendix. R = mean of the Rånåsen samples, E = mean of the Eiterdalen samples, T = mean of the Tverrfjell samples. Note that all the Rånåsen rocks have high Cu/Ir and Ni/Pd ratios relative to extrusive rocks, which suggests that sulphides were removed from the magma prior to the formation of these rocks.

morphism sulphur may be mobile and hence either be enriched or depleted relative to its igneous values. In order to avoid the potential errors inherent in recalculating to 100% sulphides, this work will consider Ni, Cu, Co and the noble metals in terms of whole-rock values and ratios. The reader is referred to Boyd et al. (in press) for a study which considers the Bruvann sulphide deposit at Rånåsen, in terms of 100% sulphides for the sulphide normalized approach to treating noble-metal data.

The Ni/Cu ratios for the three Rånåsen localities vary from 3.5 to 6.5, which is lower than those found in primitive rocks such as komatiites, higher than the Ni/Cu ratio found in evolved rocks such as flood basalts, and similar to Ni/Cu ratios found in high-MgO basalts. Compare the positions of

the Rånåsen rocks (R, E and T) with the other rock types in Fig. 2 (the sources for the fields outlined in Figs. 2 and 3 are listed in the appendix and the rationale behind the diagrams is outlined in Barnes et al. submitted). The similarity in Ni/Cu ratio between high-MgO basalts and the Rånåsen rocks is consistent with the whole-rock and mineral geochemistry, which suggests that the Rånåsen magma was high-MgO tholeiite.

The Pd/Ir ratio of the Rånåsen samples is lower than the Pd/Ir ratio of the Eiterdalen samples, which in turn is lower than the Pd/Ir ratio of the Tverrfjell samples (Table 2). The Eiterdalen and Tverrfjell samples have Ni/Cu and Pd/Ir ratios similar to high-MgO basalts and consequently on a plot of Pd/Ir versus Ni/Cu plot in the high-MgO basalt field (E and T in Fig. 2).

The Rånbogen samples have similar Ni/Cu ratios to high-MgO basalts but lower Pd/Ir ratios; therefore, on the Pd/Ir versus Ni/Cu plot, the Rånbogen samples plot below the high-MgO basalts, but still within the field of layered intrusions.

The differences in the composition of the rocks from the three localities may be explained by olivine and chromite crystallization. Both chromite and olivine tend to concentrate Ir over Pd and Ni over Cu. Therefore, the accumulation of chromite and olivine in a rock tends to displace the cumulate towards low Pd/Ir ratios and high Ni/Cu ratios and the fractionated liquid towards high Pd/Ir ratios and low Ni/Cu ratios, as illustrated on Fig. 2 and discussed elsewhere (Barnes et al. sub). Furthermore, the position of the Rånbogen samples in Fig. 2 suggests that these rocks are enriched in olivine and possibly chromite relative to the high-MgO tholeiite from which the rocks are formed, which is consistent with the petrographic observations that these rocks are olivine and bronzite cumulates with minor chromite. The relative position of the Tverrfjell and Eiterdalen samples suggests either that the liquid from which the Tverrfjell samples formed had fractionated chromite and/or olivine prior to the formation of the Tverrfjell rocks, or that the Eiterdalen rocks are enriched in olivine and chromite relative to the Tverrfjell samples. The Eiterdalen rocks consist of plagioclase, hornblende and sulphides and do not appear to be enriched in olivine and chromite. Therefore the difference in Pd/Ir ratio between the Eiterdalen and Tverrfjell rocks is attributed to olivine and chromite fractionation prior to formation of the Tverrfjell rocks.

The Råna rocks have much higher Ni/Pd and Cu/Ir ratios than high-MgO basalts or any other extrusive rock (Fig. 3). The rocks are cumulates, some of which contain olivine and chromite. The Ni and Cu to noble-metal ratios could have been modified by olivine and chromite fractionation. But, as can be seen in Fig. 3, no combination of olivine and chromite fractionation from a common magma type could produce rocks with Ni/Pd and Cu/Ir ratios similar to those observed at Rånabogen and Eiterdalen. Some other process has therefore occurred. Because these rocks contain appreciable amounts of sulphides and sulphides are known to concentrate both noble metals Ni and Cu, the most obvious process to investigate is sulphide accumulation. The partition coefficient of Ni and Cu between silicate

and sulphide liquid is lower than that of the noble metals and thus when sulphides segregate from a magma the sulphides tend to have lower Ni and Cu to noble-metal ratios than the melt from which they segregated. Consequently any rock enriched in these sulphides will have lower Ni/Pd and Cu/Ir ratios than the melt from which it formed. However, the decrease in Ni/Pd and Cu/Ir ratios in the sulphides is also dependent on the amount of sulphides that segregate (i.e. the R-factor) as discussed by Keays & Campbell (1981) for Cu and Pd and Campbell & Barnes (1984) for Ni and Pt. If a small amount of sulphides segregate the Ni/Pd and Cu/Ir ratios in the sulphides are lower than that of the melt, but if a large amount of sulphides segregates the Ni/Pd and Cu/Ir ratios of the sulphides approach that of the melt. In any event the Ni/Pd and Cu/Ir ratios of the sulphides never exceed those of the melt from which they formed because the partition coefficient of Ni and Cu into sulphides is lower than that of noble metals into sulphides. Thus, sulphide accumulation lowers the Ni/Pd and Cu/Ir ratios of the rocks in which they accumulate. Since the Råna rocks have higher Ni/Pd and Cu/Ir ratios than their proposed parent magma (high-MgO tholeiite) sulphide accumulation or variations in the amount of sulphide that accumulate (i.e. variations in the R-factor) will not account for the high Ni/Pd and Cu/Ir ratios in the Råna rocks.

Since sulphide accumulation lowers the Ni/Pd and Cu/Ir ratios, sulphide removal from a silicate liquid should raise the Ni/Pd and Cu/Ir ratios of the silicate liquid (Campbell & Barnes 1984 make a similar point for Ni/Pt). Thus the high Ni/Pd and Cu/Ir ratios observed in the Råna rocks suggest that prior to the emplacement of the magma at Råna sulphides segregated and were removed from the silicate liquid. These sulphides depleted the magma in noble metals relative to Ni and Cu. The depleted magma was emplaced at Råna and from it the Råna rocks developed.

The idea that sulphides have been removed from the Råna magma prior to emplacement is supported by the low Ni content of the olivines from the intrusion (Fig. 4). Many of the olivines are depleted in Ni relative to 'normal layered intrusions' as defined by Fleet et al. (1977). The removal of sulphides from the Råna magma prior to its emplacement would have depleted the magma in Ni, and consequently olivines that formed from this magma would be Ni depleted.

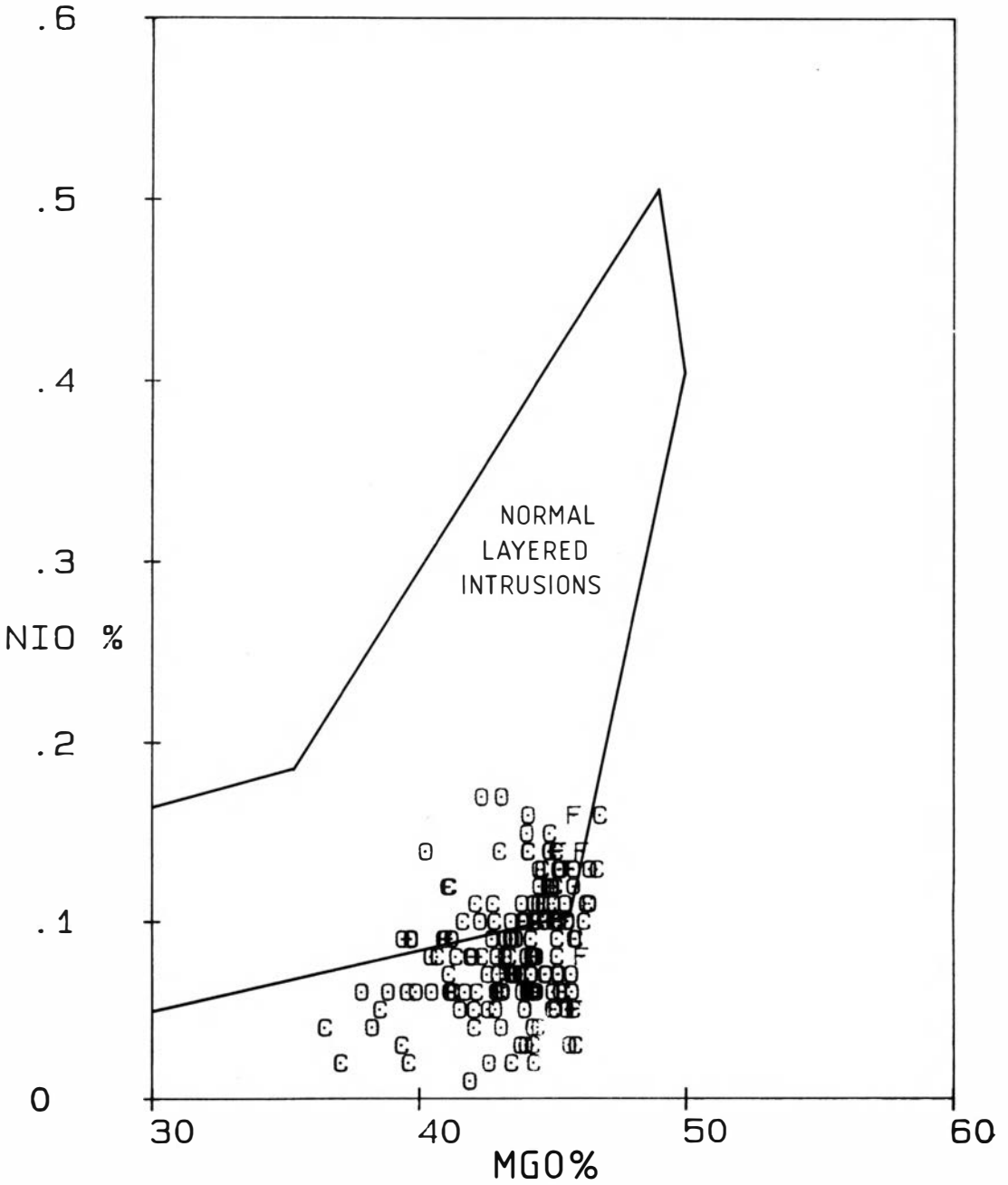


Fig. 4. MgO versus NiO for the Tverrfjell olivines. O = oikocryst, C = olivines in coronas, F = free olivines. Most of the Tverrfjell olivines are depleted in NiO relative to the field of normal layered intrusions as defined by Fleet *et al.* (1977), which suggests that sulphides segregated from the magma prior to the development of these olivines.

Numerical modelling

On the basis of the comparison of the Ni/Cu and Pd/Ir ratios with rocks from the literature the Råna rocks appear to have formed from a high-MgO tholeiite, and on the basis of the Ni/Pd and Cu/Ir ratios some sulphides appear to have been removed from the magma prior to its emplacement at Råna. The variations in the Ni and Cu to noble-metal ratios between the three localities may be explained by olivine and chromite fractionation. In the following section these ideas will be tested by attempting to numerically model the processes involved. However, because many of the parameters in the equations used below are poorly constrained, the model outlined is just one possible solution. The purpose of the modelling is to illustrate the trends in the Ni and Cu to noble-metal ratios during partial melting, crystal fractionation and sulphide segregation.

The present Ni and Cu to noble-metal ratios of the rocks is the product of all the previous processes that led to the formation of the rocks. The minimum number of processes that can be considered would be: partial melting of the mantle, followed by intrusion of the resulting magma into the crust (during this process the composition of the initial magma may have changed due to crystal fractionation), and finally the formation of a cumulate and crystallization. The effect of each of these processes is examined below.

Partial melting

The concentration of an element in a melt assuming batch partial melting is governed by the equation

$$C_1 = C_0 / (F + \bar{D} - F\bar{D}) \quad (1)$$

C_1 = concentration of the element in the liquid

C_0 = concentration in the source

F = the weight fraction of the solid that has melted

\bar{D} = the bulk partition coefficient between the restite and liquid = $\sum_{i=1}^n X_i D_i$, where X_i = the weight fraction of each mineral present in the residue, D_i = the partition coefficient between the mineral and the melt.

The only minerals that will remain Cu and Pd during partial melting of the mantle would be sulphides. At the temperatures achieved during

partial melting of the mantle (greater than 1100°C), Cu-Fe-Ni or Pd sulphides would melt. So it could be argued that all the Cu and Pd from the mantle could be release to the melt, and the partial melting equation reduced to $C_1 = C_0/F$, i.e. magmas from low degrees of partial melting, such as alkali basalts, should contain the highest concentrations of Cu and Pd. However, alkali basalts do not contain the highest Pd and Cu values (Barnes et al. 1985). This could be because, although all of the sulphides melt, not all the sulphur can dissolve in the silicate magma. Hence there is a sulphide liquid present in the residuum which will act as a host for the chalcophile elements and have the same effect as a residual mineral. In order to solve the partial melting equation, the amount of sulphide liquid left in the residuum must be decided. This is governed by the equation:

$$X_s = (C_0 - (S \times F)) \times 2.7 / (1 - F) \quad (2)$$

X_s = the weight percentage sulphides remaining
 S = the solubility of the sulphur in the magma,
 2.7 converts the concentration of S to sulphide, assuming 37% sulphur in the sulphides.

In this work S concentration in the mantle is assumed to be 0.035%E (Sun 1982), and the solubility of sulphur in the magma 0.155% (the mid point between the extremes listed by Wendlandt (1982)). A plot of the degree of partial melting versus the weight percentage sulphides in the residue based on equation 2 and these assumptions is shown in Fig. 5. Equation 2 assumes that the solubility of sulphur is constant over a range of degrees of partial melting, which it is probably not. However, in the absence of any data to guide us this equation serves as a first approximation. On the basis of a solubility of sulphur of 0.155% at least 23% partial melting is required for all the sulphides in the mantle to dissolve (Fig. 5). This calculation is consistent with a similar one presented by Morgan (1986). (If the minimum and maximum sulphur solubilities listed by Wendlandt (1982) are used, 70% and 14% partial melting respectively is required for all the sulphides in the mantle to be dissolved.) For the present calculation at greater than 23% partial melting when $D = 0$ the concentration of Cu or Pd (and by analogy, Rh, Pt and Au) in the liquid = $1/F$, i.e. there is a steady decrease in Cu and Pd as the degree of partial melting increases (Fig. 6A), but the ratio of Cu/Pd remains constant (Fig. 6B).

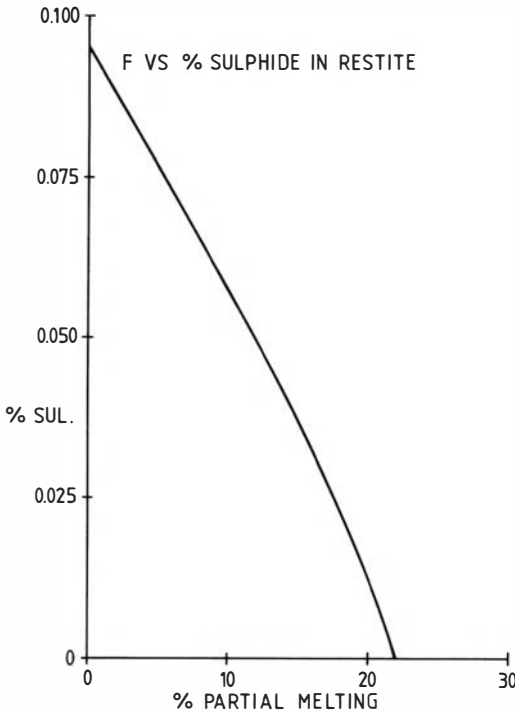


Fig. 5. Degree of partial melting vs the % sulphides in the restite. Assuming 350 ppm sulphur in the mantle (Sun 1982) and a sulphur solubility of 1550 ppm in the melt (mid-point of solubilities given by Wendlandt (1982)), 23% partial melting is required before all the sulphides are released.

At less than 23% partial melting the situation is more complex because the concentrations of Cu and Pd in the melt are proportional to both $1/F$ and $1/D$ (eq. 1). A partition coefficient of 1000 for noble metals between silicate liquid and sulphides has been assumed for the present calculation. Estimates for the partition coefficient of noble metals between silicate liquid and sulphide vary from 100 (Ross & Keays 1979) to 100,000 (Campbell & Barnes 1984). A partition coefficient of 1000 has been used in this work because, if higher values are used, practically no noble metals are released to the magma as long as any sulphides remained in the mantle. In other words, magmas formed from less than 23% partial melting of the mantle, such as continental flood basalts, should contain <0.1 ppb Pd, which is contrary to the observation that they contain 5–10 ppb Pd (Barnes et al. 1985). Naldrett & Barnes (1987) present various partial melting models using higher partition coefficients. As F increases the concentration of Cu and Pd in the melt decreases

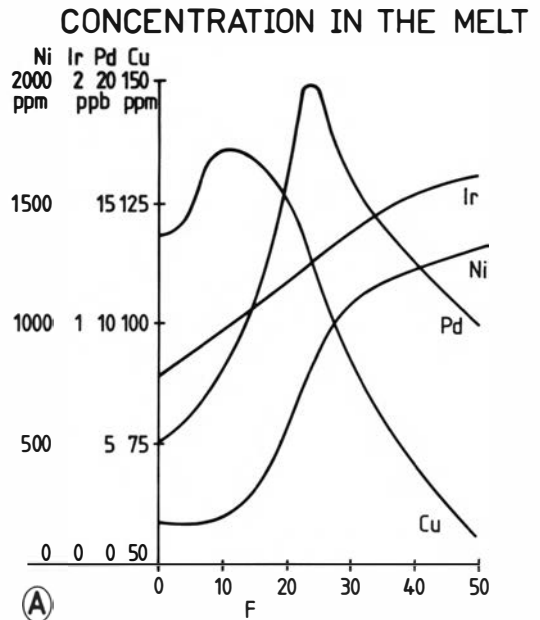


Fig. 6A. Plot of concentration of Ni, Ir, Pd, Cu in the melt vs degree of partial melting. Cu and Pd are principally held in sulphides and hence are released to the melt as the sulphides dissolve, after all the sulphides have dissolved these elements are diluted by further partial melting by the volume effect. Ni and Ir in contrast are compatible with the residue and hence their concentrations increase with the degree of partial melting.

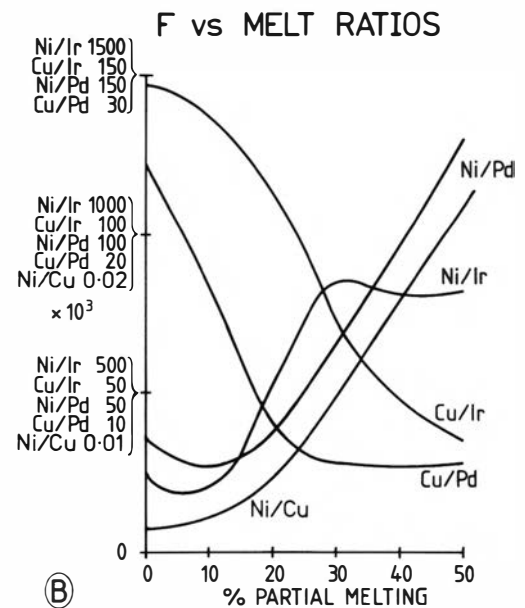


Fig. 6B. Plot of variations in Cu/Pd, Cu/Ir, Ni/Pd and Ni/Ir ratio with the degree of partial melting. Cu/noble element ratios are highest at low degrees of partial melting, in contrast Ni/noble element ratios are highest at high degrees of partial melting.

due to dilution, but as F increases the bulk D decreases because more and more sulphides dissolve in the melt. In the case of Pd the large partition coefficient of Pd into sulphides dominates the equation and the amount of Pd in the melt increases until all the sulphides have dissolved at 23% partial melting. However, in the case of Cu, with its smaller partition coefficient into sulphides, the fall in $1/D$ is offset by the rise in the $1/F$ term, such that Cu has peak values at about 10% partial melting (Fig. 6A).

The situation for Ni and Ir is more complex because, although these elements do have high partition coefficients into sulphides, they are also compatible with other phases in the residue. Ni is compatible with olivine and because olivine is a major portion of the residue during partial melting of the mantle, most of the bulk D for Ni between restite and magma is from olivine. Therefore the amount of Ni rises as the degree of partial melting increases as more and more olivine dissolves in the melt (Table 3 and Fig. 6A).

Empirical observation indicates that Ir concentrations are highest in magmas formed from high degrees of partial melting, such as komatiites, and lower in magmas formed from lower degrees of partial melting, e.g. flood basalts (Crocket 1981). Thus, during partial melting Ir behaves in a compatible fashion. At this time it is not known with which residual mineral Ir is compatible (see Barnes et al. 1985 for a further discussion of this point). For the modelling in this work a bulk D of 5 for Ir into the silicate residue has been used because this value yields similar to those observed in natural rocks (see Naldrett & Barnes 1987 for alternative models).

As a consequence of the different behavior of the elements during partial melting (Fig. 6B). Cu/Pd and Cu/Ir ratios fall rapidly from 1% to 23% partial melting (at which point all of the sulphides are dissolved). After this the Cu/Pd ratio remains constant and is the same as that of the mantle (5.6×10^3), since all the Cu and Pd has been release. The Cu/Ir ratio continues to fall, however, because Ir is still being released to the melt. The Ni/Pd ratio increases very slowly as the degree of partial melting increases from 1% to 23% melting, because both Ni and Pd are continually being released from the sulphides to the melt; however, once all the sulphides have dissolved, the Ni/Pd ratio increases rapidly because the Pd concentrations decrease while the Ni concentrations increase as Ni is release to the melt. The Ni/Cu ratios exhibit a similar trend to the Ni/Pd ratio. High Cu/noble-metal ratios are found at low degrees of partial melting, but high Ni/noble-metal ratios are found at high degrees of partial melting. At Råna the rocks have both high-Cu and high-Ni/noble-metal ratios. So partial melting by itself cannot account for the high Cu and Ni to noble-metal ratios observed at Råna.

Whole-rock geochemistry and mineral analysis suggest that the magma from which Råna formed was a MgO-rich tholeiite containing 12–18% MgO (Barnes 1986; Boyd, in prep.): the concentrations of base metals and noble elements and their ratios in such a magma should be similar to those observed in high-MgO basalt, i.e. Cu/Pd = 8×10^3 , Cu/Ir = 111×10^3 , Ni/Pd = 39×10^3 , Ni/Ir = 54×10^3 . Taking the assumptions outlined above, these Ni and Cu to noble-metal ratios may be obtained at around 20%

Table 3. Parameters used for the partial melting modelling.

Degree %	Residue sul ol wt %		Minerals sil	Partition coefficients*													
				Sulphides				Olivine				Other silicates					
				Ni	Cu	Co	PGE	Ni	Cu	Co	Pd	Ir	Ni	Cu	Co	Pd	Ir
1	70	0.0913	30	250	250	50	1000	16.8	0	1	0	5	0	0	1	0	5
5	70	0.077	30	250	250	50	1000	16.8	0	1	0	5	0	0	1	0	5
10	70	0.058	30	200	200	50	1000	11.6	0	1	0	5	0	0	1	0	5
15	70	0.037	30	150	150	50	1000	7.5	0	1	0	5	0	0	1	0	5
20	70	0.0083	30	100	100	50	1000	5.4	0	1	0	5	0	0	1	0	5
25	70	—	30					3	0	1	0	5	0	0	1	0	5

* Naldrett & Duke (1980); except Ir into olivine (see text for discussion).

partial melting of a fertile mantle (Table 3). The Råna rocks have base- to noble-element ratios one to two orders of magnitude higher than these.

Cumulate processes

The rocks at Råna are cumulates containing sulphides. The simplest assumption is that if partial melting alone cannot account for the Ni and Cu to noble-metal ratios of the Råna rocks, then partial melting followed by cumulate development and crystallization may account for the composition of the rocks. Therefore the effect of the cumulate process on the Ni and Cu to noble-metal ratios must be considered. In this work Rayleigh fractionation rather than batch segregation will be used to model the cumulate process, because batch segregation has been dealt with exhaustively in the form of the 'R-factor' in various publications (e.g. Keays & Campbell 1981). In any event, both batch segregation and Rayleigh fractionation will produce the same trends although with different absolute values for the composition of the cumulate. The concentration of an element in the *average cumulate* during Rayleigh fractionation is governed by the equation:

$$C_c = C_1 (1 - F^{\bar{D}}) / (1 - F) \quad (3)$$

C_c = concentration of the element in the cumulate

C_1 = concentration of the element in the liquid

F = the weight fraction liquid remaining

$\bar{D} = \sum_{i=1}^n X_i D_i$ as in equation 1.

From this equation it can be seen that the concentration of an element in the cumulate is controlled both by the degree of crystallization ($1 - F$) (i.e. how much of the magma has crystallized) and by \bar{D} , the bulk partition coefficient between the magma and the cumulate. Noble metals and Ni and Cu have extremely high partition coefficients from silicate magma into sulphides, so D is strongly influenced by how much sulphide is present in the cumulate. Further, the partition coefficients for the noble metals into sulphides are much greater than that of Ni and Cu. Consequently the Ni and Cu to noble-metal ratios of the cumulate changes depending on the percentage sulphides present in the cumulate. Fig. 7 shows the *change* in Ni and Cu to noble-metal ratios for

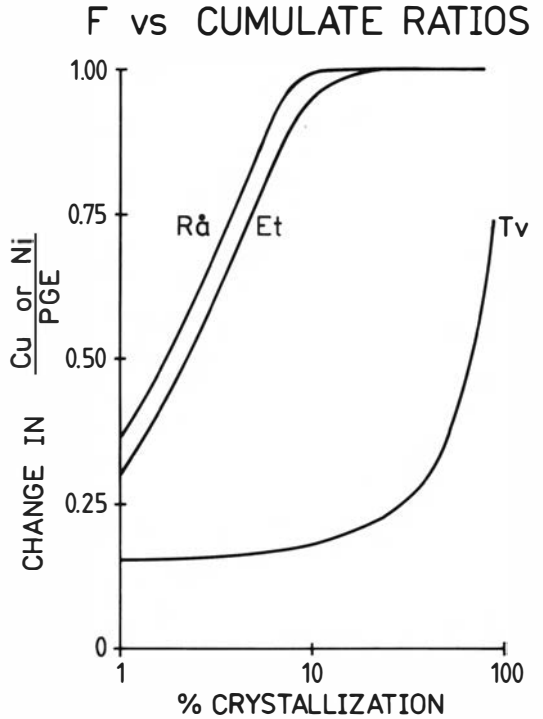


Fig. 7. Plot of variations in (Cu or Ni)/noble-element ratios in the cumulates with the degree of crystallization of the melt. Tv = curve, assuming 0.39% sulphides in the cumulate, the amount present in the average Tverrfjell sample, Et = curve assuming 17% sulphides in the cumulate, the amount present in the average Eiterdalen sample, Rå = curve assuming 23% sulphides in the cumulate as there is in the average Rånbogen sample.

the *average cumulate* with degree of crystallization assuming 23%, 17.5% and 0.39% sulphides in the cumulate (these are the percentages of sulphides present in average Rånbogen, Eiterdalen and Tverrfjell samples respectively). Note that although at two of the localities in the cumulates contain large amounts of sulphide, the Rayleigh model does *not* require that the liquid segregates these sulphides from equal volumes of magma and cumulate. Consider for instance the Rånbogen locality, which contains 23% sulphides. If it is assumed that sulphide saturation takes place when the magma contains 0.26% sulphur (maximum estimate of sulphur solubility listed by Wendlandt 1982), then approximately 0.70% sulphide liquid may form within the magma. This sulphide might then accumulate at various places in the magma chamber, in structural traps or by gravity settling, to form a rock

containing more than 0.7% sulphide. The presence of the rock containing 23% sulphides requires only that the volume of magma from which the sulphide was collected be at least 33 times the volume of the present cumulate (23/0.7), i.e. that 97% of the magma has not crystallized. Fig. 7 indicates that the change in Ni and Cu to noble-metal ratios increases rapidly from 1% to 10% crystallization and then levels out at approximately 0.95 for the two localities that contain large percentages of sulphides. In contrast the change in Ni and Cu to noble-metal ratios is fairly constant from 1% to 10% crystallization at about 0.2 and then increased rapidly to 0.74 at 90% crystallization for the low percentage of sulphides present at Tverrfjell.

If only partial melting and cumulate processes have affected the Ni and Cu to noble-metal ratios (nc/nm) at Råna, then

$$\text{nc/nm}(\text{observed}) = \text{nc/nm}(\text{partial melting}) \times \text{nc/nm}(\text{cumulate process})$$

For the sake of developing a model it has been assumed that the Ni and Cu ratios of the Råna magma were originally close to that of a high-MgO basalt (see Table 4). The author does not wish to imply that the Råna magma ratios were exactly these, but they will be used to illustrate the point. The assumed initial magma Cu/Pd is 7.2×10^3 and the Cu/Pd ratio is changed by a

factor of approximately 0.9 (assuming $F < 0.9$) to 6.5×10^3 by the formation of cumulates similar to those observed at Eiterdalen and Rånbogen. The Cu/Pd ratios of rocks from Eiterdalen and Rånbogen are 84×10^3 and 91×10^3 , an order of magnitude higher than either partial melting or crystallization alone would produce. At Tverrfjell the observed Cu/Pd ratio is 11×10^3 , while the calculated product of partial melting and sulphide fractionation is $7.2 \times 10^3 \times 0.359 = 2.58 \times 10^3$ (assuming 50% crystallization based on whole-rock geochemistry, Barnes 1986). Similar calculations on the other Ni and Cu to noble-metal ratios reveal the same result; namely that cumulate processes decrease the Ni and Cu to noble-metal ratios of the cumulate, which is the exact opposite effect on the Ni and Cu to noble-metal ratios to that needed for explaining the ratios in the Råna rocks. This result is fairly easy to understand, because noble metals have higher partition coefficients into sulphides than Ni and Cu, and therefore sulphides *must* have lower Ni and Cu to noble-metal ratios than the magmas from which they segregate. Consequently any rock containing these sulphides will have lower Ni and Cu to noble-metal ratios than the magma from which they form. Thus partial melting followed by crystallization cannot alone account for the Ni and Cu to noble-metal ratios observed at Råna.

Table 4. Model composition of the Råna rocks.

Description	Ni ppm	Cu	Co	Ir ppb	Pt	Pd	Au
Initial melt, based on a 20% partial melt of mantle	628	135	99	1.17	26	18.7	3.7
Melt after removal of 0.3% sulphides	401	86	85	0.058	1.3	0.93	0.18
Model of Eiterdalen consisting of 17.5% sulphides, 82.5% liquid, $F = 0.90$	3765	807	540	0.58	13	9.3	2
Model of Rånbogen consisting of 23% sulphides, 77% olivine, $F = 0.90$	3952	837	616	0.58	13	9.3	1.8
Melt after removal of 15% olivine and 0.15% sulphide	249	125	91	0.136	6.8	4.9	0.96
Model of Tverrfjell consisting of 0.39% sulphides, 30% liquid, 20% olivine and 50% plagioclase and pyroxene	429	141	102	0.27	13	9.3	1.8

Sulphide segregation

As outlined above sulphide accumulation *decreases* the Ni and Cu to noble-metal ratios in cumulates and the Ni and Cu to noble-metal ratios of rocks from Råna require a process that *increases* the Ni and Cu to noble-metal ratios. This leads to the suggestion, despite the presence of sulphides in the Råna cumulates, that they formed from a silicate liquid from which the sulphide liquid had been removed prior to its emplacement at Råna.

During Rayleigh fractionation the concentration of an element in the melt is governed by the equation:

$$C_1 = C_0 F^{(D-1)} \tag{4}$$

Fig. 8 shows the *change* in Ni and Cu to noble-metal ratio in the *magma* as sulphides are removed. For this calculation a partition coefficient of 1000 was assumed for noble metals between silicate liquid and sulphides. If a higher partition coefficient were used, smaller amounts of sulphides would be needed to achieve the same change in Ni and Cu to noble-metal ratios, but the trends would remain the same. ‘% sulphides removed’ on the abscissa refers to the amount of sulphides removed from the magma expressed as the wt % of the magma. If the Råna rocks are the product of the three processes partial melting, sulphide removal and cumulate processes, then

$$\begin{aligned} \text{nc/nm (obs)} &= \text{nc/nm(pm)} \\ &\times \text{nc/nm(sulphide removal)} \times \text{nc/nm(cp)} \end{aligned}$$

which can be rearranged to

$$\text{nc/nm (sulphide removal)} = \frac{\text{nc/nm (obs)}}{(\text{nc/nm(pm)} \times \text{nc/nm(cp)})} \tag{5}$$

From this equation and Fig. 8 the percentage of sulphides removed from the magma prior to emplacement at Råna may be estimated, e.g. at Eiterdalen

$$\begin{aligned} \text{Cu/Pd (sulphide removal)} &= \frac{\text{Cu/Pd (obs)}}{(\text{Cu/Pd (pm)} \times \text{Cu/Pd (cp)})} \\ &= \frac{84,000}{(7200 \times 0.9)} = 12.9 \end{aligned}$$

On the basis of the assumptions in this work, to obtain a change in Cu/Pd ratio of 12.9 by removal of sulphide from the magma, 0.3 wt % sulphides must be removed (Et in Fig. 8). Thus, by combining eq. 1 for partial melting and eq. 4 for

% SULPHIDES vs MELT RATIOS

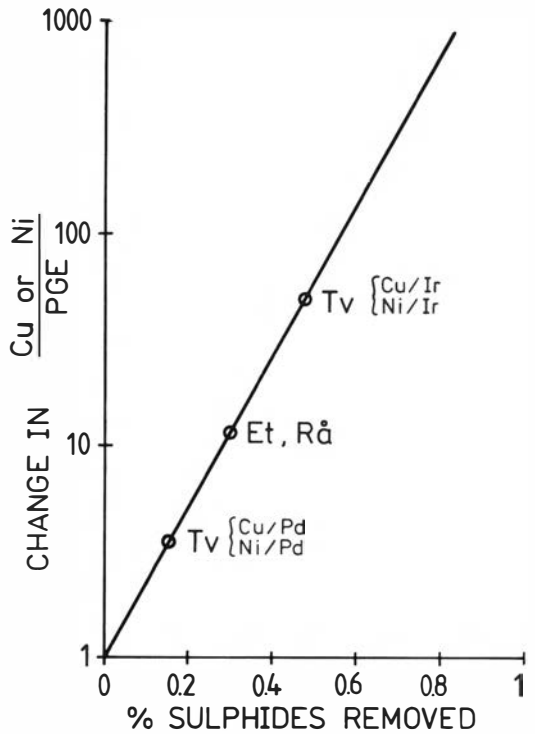


Fig. 8. Plot of change in (Cu or Ni)/noble-element ratios in the silicate melt with the percentage of sulphides removed from the melt.

sulphide segregation, the concentration of Ni and Cu and noble metals in the magma (C_1) at Eiterdalen can be modelled as having been derived from a 20% partial melt of the mantle and this melt experienced 0.3% sulphide segregation prior to emplacement of the magma at Eiterdalen (Table 4).

Equation 3 can then be used to model the cumulate containing minerals in the proportions presently observed in the rocks. In order to solve equation 3, F (the weight fraction liquid remaining) must be estimated. This can be done by means of Fig. 9, which is a plot of F versus the ratio of the concentration of an element in the cumulate (C_c) to the concentration of the element in the magma (C_1). For elements with high bulk partition coefficients into the cumulate, e.g. the Ni and Cu and noble metals, the concentration of the element in the cumulate falls rapidly as the degree of crystallization increases. At Eiterdalen the ratio of the cumulate to Pd in the cumulate

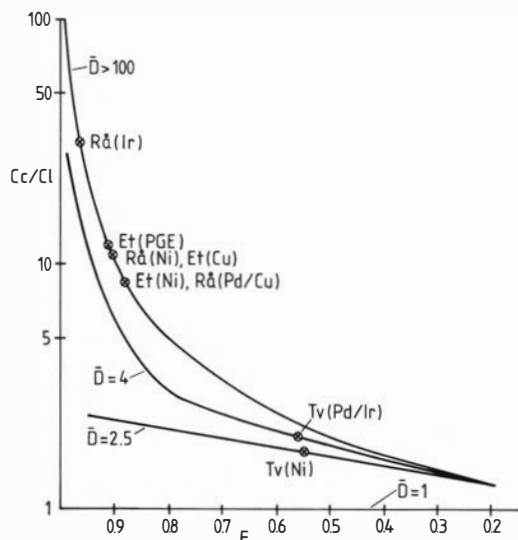


Fig. 9. Plot of concentration of the elements in the cumulate divided concentration of the element in the liquid vs the weight fraction liquid remaining (F).

to Pd in the magma = $11.4/0.93$ (Tables 2 and 4). This implies an F of 0.92 (Et PGE in Fig. 9). Used in a similar manner, Ni and Cu give a slightly lower estimate of F of 0.9 (Et Ni and Cu in Fig. 9). The results of the modelling are listed in Table 4.

Similar calculations at Rånboen indicate that approximately 0.3% sulphides were removed prior to emplacement of the magma at this locality. The rocks are principally olivine cumulates and in modelling the cumulate allowance was made for the presence of the olivine which increases the Ni content of the rocks. A satisfactory match was obtained between the observed and model rocks (Table 4).

At Tverrfjell the situation is more complicated. The degree of crystallization has a marked effect on the Ni and Cu to noble-element ratios (Fig. 7). On the basis of whole-rock geochemistry discussed elsewhere (Barnes 1986), approximately 50% crystallization has occurred. The change in Ni and Cu to noble-metal ratios due to cumulate processes is therefore approximately 0.35 (Fig. 7). On the basis of this assumption the Cu/Pd and Ni/Pd ratios indicate that approximately 0.15% sulphides were removed from the magma prior to emplacement at Tverrfjell (Fig. 8). In contrast the Cu/Ir and Ni/Ir ratios indicate approximately 0.5% sulphides have been removed. Obviously,

not both conclusions can be correct, so some other process must have disturbed the Ir relative to the other elements at Tverrfjell.

The most obvious difference between the Tverrfjell locality and the other two is that at Tverrfjell the rocks appear to have formed from a more fractionated magma than at the other two localities, e.g. the highest forsterite content observed in the olivines at Tverrfjell is 87% while at Rånboen it is 90%. Ir tends to behave in a compatible fashion during crystallization. If 15% olivine were removed from the initial magma (containing approximately 18% MgO) prior to its emplacement at Tverrfjell, the MgO content of the magma would fall to 12% and consequently the forsterite content of the olivine would fall to approximately 87%. The Ir might possibly be removed at the same time by chromite fractionation. A satisfactory match between the observed and modelled rocks at Tverrfjell can be obtained by assuming 0.15% sulphide and 15% olivine removal prior to emplacement at Tverrfjell followed by formation of a cumulate with the mineral proportions presently observed in the rocks (Table 4).

Summary

The segregation of small amounts (0.15–0.4%) of sulphides prior to emplacement of the magma at Rånboen may account for the Rånboen Layered Intrusion having such unusually high Ni and Cu to noble-metal ratios. This conclusion is supported by the olivine compositions observed at Rånboen; most of the olivines are depleted in Ni relative to normal layered intrusions (Fig. 4). If some sulphides had segregated from the magma prior to its emplacement at Rånboen, the magma would have been depleted in Ni and any olivines that formed in equilibrium with this magma would also be Ni depleted.

The unusual Ni and Cu to noble-metal ratios and the variations into Ni and Cu and noble-metal concentration between the different localities at Rånboen may be modelled as shown schematically in Fig. 10 and Table 4. Approximately 20% partial melting of the mantle took place to produce a MgO-rich tholeiite which intruded into the lower crust. Some of this magma intruded in the Eiterdalen and Rånboen areas; en route to these localities approximately 0.3% sulphides segregated. An olivine-sulphide cumulate consisting

FLOW DIAGRAM SHOWING THE DEVELOPMENT OF THE RÅNA INTRUSION SULPHIDES

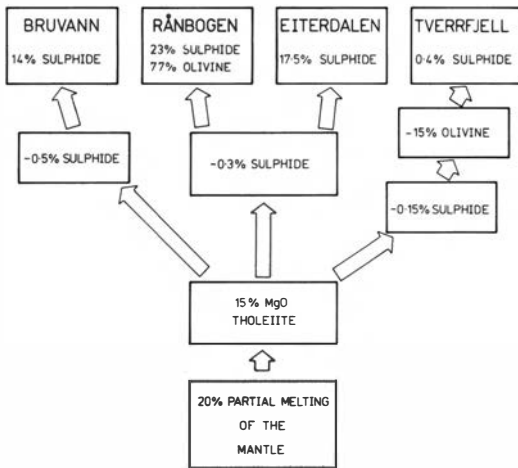


Fig. 10. Model for the development of the Rånå, Eiterdalen and Tverrfjell samples.

of 23% sulphide and 77% olivine developed at Rånå and a cumulate containing 17% sulphides developed at Eiterdalen. When modelling the Tverrfjell rocks, in addition to the removal of sulphides, olivine and possible chromite have to be removed from the magma prior to emplacement at Rånå. For the sake of completeness a model for the Bruvann Ni sulphide is also shown in Fig. 10; the data for this were taken from Boyd et al. (in press); the removal of 0.5% sulphides prior to emplacement of the magma at Bruvann could account for the unusual composition of the sulphides at this locality.

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Appendix: sources for Figs. 2 and 3

Mantle Location	Rock type	Source
Lesotho	garnet lherzolite	Mitchell & Keays (1981)
World	spinel lherzolite	Mitchell & Keays (1981)

Appendix: sources for Figs. 2 and 3 (contd)

Mantle Location	Rock type	Source
South USA	spinel lherzolite	Jagoutz (1979)
Ronda	spinel lherzolite	Stockman (1982)
Ronda	harzburgite	Stockman (1982)
West USA	harzburgite dts1	Govindaraju (1984)
West USA	harzburgite pcc1	Govindaraju (1984)
Thetford	harzburgite	Oshin & Crocket (1982)
<i>Komatiites</i>		
Kambalda	olivine spinifex	Keays et al. (1982)
Kambalda	dunite	Keays et al. (1982)
Kambalda	sulphide-rich peridotite	Keays et al. (1982)
Mt Edward	sulphide-rich peridotite	Naldrett (1981)
Lunnon	sulphide-rich peridotite	Naldrett (1981)
Munro	olivine spinifex	Crocket & MacRae (1986)
Munro	B-zone	Crocket & MacRae (1986)
Langmuir	sulphide-rich peridotite	Green & Naldrett (1981)
Texmont	B-zone sulphide rich	Barnes & Naldrett (1987)
Dundonald	B-zone sulphide rich	Barnes & Naldrett (1987)
Hart	B-zone sulphide rich	Barnes & Naldrett (1987)
Pipe	sulphide-rich peridotite	Naldrett (1981)
Hitura	sulphide-rich peridotite	Papunen (1986)
<i>High-MgO Lavas</i>		
Kating	komatiitic basalt	Barnes et al. (1982)
Donaldson	komatiitic basalt	Barnes et al. (1982)
Fred's flow	komatiitic basalt	Crocket & MacRae (1986)
Theo's Flow	high-MgO tholeiite	Crocket & MacRae (1986)
Australia	high-MgO basalt	Redman & Keays (1985)
Kanichee	high-MgO tholeiite	Naldrett (1981)
<i>Calc-alkaline Rocks</i>		
West USA	andesite, AGV-1	Govindaraju (1984)
Australia	basalt	Redman & Keays (1985)
<i>Ocean floor basalts</i>		
Jane de Fuca	basalt D10	Crocket & Teruta (1977)?
Troodos	olivine basalt	Becker & Agiorgitis (1978)
DSDP-37	olivine basalt	Crocket & Teruta (1977)

Appendix: sources for Figs. 2 and 3 (contd)

Mantle Location	Rock type	Source
Thetford	basalt	Oshin & Crocket (1986)
<i>Intrusive portions of ophiolites</i>		
Thetford	ultramafic to mafic rocks	Oshin & Crocket (1982)
Ronda	gabbro	Stockman (1982)
Oman	chromitite	Page et al. (1982)
Unst	chromitite	Gunn et al. (1985)
<i>Flood basalt related</i>		
West USA	basalt BCR-1	Govindaraju (1984)
West USA	diabase W-1	Stockman (1982)
Duluth	sulphide-rich gabbro	Naldrett (1981)
Great Lakes	sulphide-rich gabbro	Naldrett (1981)
Insizwa	sulphide-rich gabbro	Lightfoot et al. (1984)
Talnakh	sulphide-rich gabbro	Naldrett (1981)
<i>Layered Intrusions</i>		
Bushveld	chills	Sharpe (1982)
Jimberlana	peridotites to gabbros	Keays & Campbell (1981)
Montcalm	gabbro sulphide-rich	Naldrett (1981)
Kenbridge	gabbro sulphide-rich	Naldrett (1981)
Sudbury	gabbro sulphide-rich	Naldrett (1981)
Delta	peridotites to gabbros	Clark et al (1985)
Siika-Kam	gabbro sulphide-rich	Papunen (1986)
Kotalahi	gabbro sulphide-rich	Papunen (1986)
Laukunkan	gabbro sulphide-rich	Papunen (1986)
Vammala	gabbro sulphide-rich	Papunen (1986)
Koillisma	gabbro sulphide-rich	Lahtinen (1985)
Espedalen	gabbro sulphide-rich	Naldrett (1981)
Vakkerlei	gabbro sulphide-rich	Thompson et al. (1980)
<i>Platinum reefs</i>		
Stillwater	JM-reef	Barnes & Naldrett (1984)
Busveld	UG-2 reef	McLaren & de Villiers (1982) Gain (1985)
Bushveld	MR reef	Steele et al. (1975)
Lac des Iles	Roby Zone	Naldrett (1981)
<i>Cu-rich sulphides</i>		
Rathburn Lake	sulphide veins	Rowell & Edgar (1986)

Appendix: sources for Figs. 2 and 3 (contd)

Mantle Location	Rock type	Source
Sudbury	sulphide veins	Hoffman et al. (1979)
Donaldson	sulphide veins	Dillon-Leitch et al. (1986)
Kambalda	sulphide veins	Leshner & Keays (1984)

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