muth-ikunolite-bismuthinite-joseite A (Fig. 2). The rarity of ikunolite and the commonly reported association of bismuth with bismuthinite suggest that very special conditions are necessary for its formation. Ikunolite may, perhaps, be stable over a limited P-T range or form only in the presence of significant amounts of selenium and tellurium. A solution to this problem, however, must await a detailed study of the system Bi-Bi_2S_3-Bi_2Te_3.

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THE DISTRIBUTION OF Ni, Co, Cr, Cu, Ba AND Sr BETWEEN BIOTITE-GARNET PAIRS IN A METAMORPHIC SEQUENCE

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INTRODUCTION

One of us (Phinney, 1962) has made a systematic study of the mineralogy and major element chemistry of a sequence of rocks from a regional metamorphic terrane in Nova Scotia. The rocks, collected from St. Paul Island and Cape North, Nova Scotia, are represented by one from the garnet zone, 19 from the staurolite zone, two from the kyanite isograd, and one from the kyanite zone. The results of that study indicate that though the rock as a unit might represent an equilibrium facies characteristic of the temperature and pressure under which it was formed, there are distinct inhomogeneities in mineral composition on the hand specimen and thin section level.

The suite of coexisting biotites and garnets used in that study were analyzed for Ni, Co, Cr, Cu, Ba and Sr to determine what the effect of metamorphic grade is on the distribution of these elements between the two phases.

The emission spectrographic methods for Co, Cr and Sr have been described by Turekian and Carr (1961). The other elements were determined by the same methods, using iron lines for internal standards for Ni and Cu, and a calcium line for Ba. The precision is about 10% coefficient of variation, and each sample was run in duplicate.

RESULTS

Table 1 presents the analyses of the garnets and biotites with increasing metamorphic grade reading down. In all cases strontium was below the level of detection, 4 ppm Sr.

TABLE 1. Ni, Co, Cr, Cu, Ba, AND Sr IN COEXISTING GARNETS AND BIOTITES[1]

	Garnets							Biotites					
	Numbers (Phinney, 1962)	Ni	Co	Cr	Cu	Ba	$\frac{\text{moles Fe+Mg}}{\text{100 grams}}$	Ni	Co	Cr	Cu	Ba	$\frac{\text{moles Fe+Mg}}{\text{100 grams}}$
Garnet zone	CN 13	10	25	168	46	38	.400	189	118	237		590	.534
Staurolite zone	CN 27	18	18	198	20	38	.531	105	47	215	32	800	.531
	SP 87	8	29	156	11	34	.497	117	52	296	76	960	.557
	SP 99	26	62	174	28	30	.538	157	76	170	25	990	.530
	SP 92	18	26	167	15	30	.536	130	52	276	20	940	.538
	SP 84	9	29	145	9	34	.468	174	73	218	34	1050	.535
	SP 66	11	27	145	190	34	.511	124	81	145	56	910	.534
	SP 51	7	31	124	3	13	.513	116	65	197	10	760	.538
	SP 42	7	28	123	11	13	.493	150	91	125	11	700	.541
	SP 38	7	30	97	9	11	.530	122	90	106	15	580	.547
	SP 35	6	24	111	8	13	.460	152	91	166	9	930	.558
	SP 34	7	31	177	10	16	.510	149	93	156	25	1230	.553
	SP 33	9	31	157	33	14	.528	87	76	192	24	1410	.549
	SP 28	10	24	103	16	14	.535	94	64	105	16	785	.540
	SP 14	7	21	165	10	12	.491	109	61	185	12	910	.533
	SP 13	18	23	130	9	12	.497	84	61	199	18	680	.533
	SP 12	9	21	134	48	12	.510	80	69	201	10	690	.537
	SP 9	8	42	132	19	22	.510	101	44	179	24	780	.530
	SP 109B	12	16	154	10	30	.516	38	17	271	20	820	.537
Kyanite isograd	SP 106	9	18	129	12	33	.514	63	40		14	42	.529
	SP 109A	7	26	288	4	26	.556	162	85	178		1040	.517
Kyanite zone	SP 110	7	38	168	7	25	.514	198	99	253	8	550	.513

[1] Results are listed with increasing metamorphic grade. All results are in parts per million. In all determinations strontium was below the level of detection, 4 ppm.

Discussion

The array of data in Table 1 may be asked several questions: (1) for a particular metamorphic facies are there equilibrium distributions between the two phases for the trace elements, (2) what are the variations in trace-element distribution as a function of metamorphic grade, and (3) what is the gross structure of trace-element distribution between the coexisting minerals under study?

The 19 coexisting biotite-garnet pairs from the staurolite zone provide an opportunity to check if the several trace elements studied are in equilibrium distribution. Kretz (1959) has made a similar study for some gneisses from the Grenville province and finds that manganese obeys the Nernst distribution law whereas chromium does not. For the discussion of Ni and Co, we have used the fraction of the trace element to the molar sum of iron plus magnesium as an index, as the sites occupied by these elements are the likely ones for the incorporation of cobalt and nickel. From Figs. 1 and 2 it is evident that no clearly defined curve (either a straight line if the sites were chosen correctly and ideal solution laws were obeyed, or a curved line, otherwise, going through the origin) can be drawn, and the scatter is fairly large, especially for nickel. The large spread is outside the limits of analytical errors, and we must conclude that for the trace elements we have studied equilibrium does not seem to be observed from hand specimen to hand specimen.

There are also no obvious trends for any of the trace elements as one proceeds from the low-grade assemblages to the higher grade assemblages. The ratio, $(\mathrm{Co/Mg})_{\mathrm{biotite}}/(\mathrm{Co/Mg})_{\mathrm{gatnet}}$, however, of the one sample of the garnet zone is .094 while for the other zones it is in the range of 0.5. This is in the same direction as that reported by Carr and Turekian (1961) comparing pairs from the amphibolite and the epidote-amphibolite facies, but the ratios are about 2 and 0.6 respectively.

Despite the fact that precise equilibrium distributions of the trace elements are not evident, there are nevertheless marked distribution effects controlled by the mineral structures. In the garnets there are 8, 6 and 4 coordination sites whereas in the biotite there are 12, 6 and 4 coordination sites. The trace elements are presumed as a first approximation to fit into sites which most closely resemble their ionic radius requirements. In the garnets studied all the Mg and Fe is in the 8 coordination site, and it is to be expected that Mn, Ni, Co, Cu, Ca, Cr, Sr and Ba should be found in this site. The Cr may be in the 6 coordination site as well. In the biotites the 6 coordination site is the locus of the Mg and Fe and presumably also of the Mn, Cr, Ni, Co and Cu. The Ti may either be in this site or in the tetrahedral site.

In this general context the observed distributions are as follows: *Nickel*

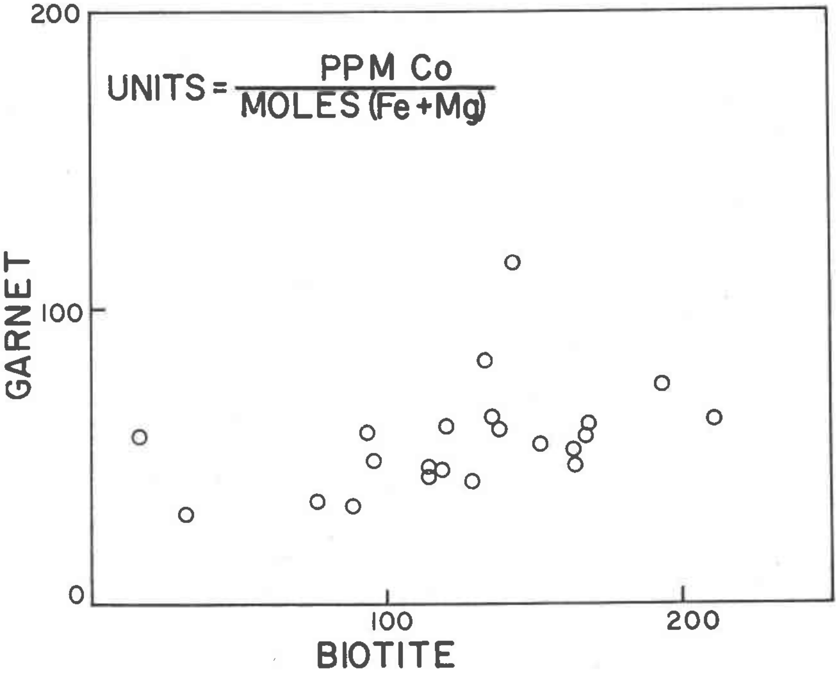

Fig. 1. Distribution of cobalt between coexisting garnets and biotites.

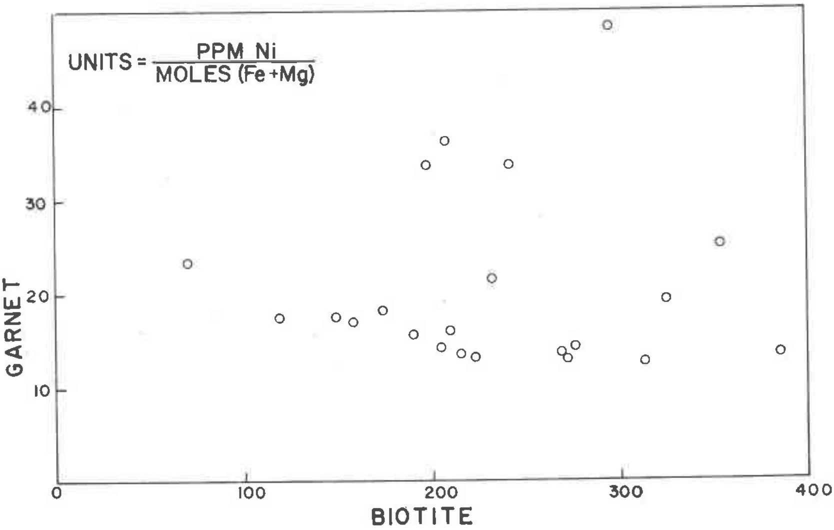

Fig. 2. Distribution of nickel between coexisting garnets and biotites.

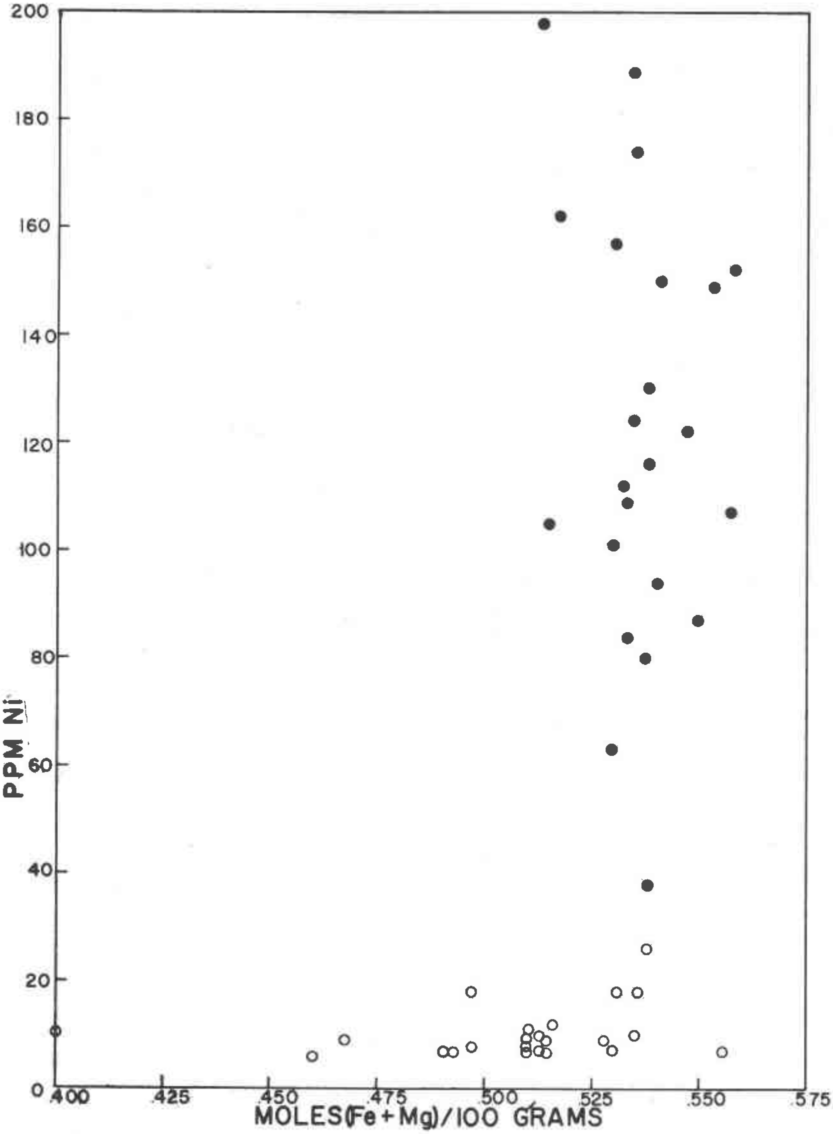
200
180
160
140
120
100
80
60
40
20
0
PPM Ni
.400
.425
.450
.475
.500
.525
.550
.575
MOLES(Fe+Mg)/100 GRAMS

FIG. 3a

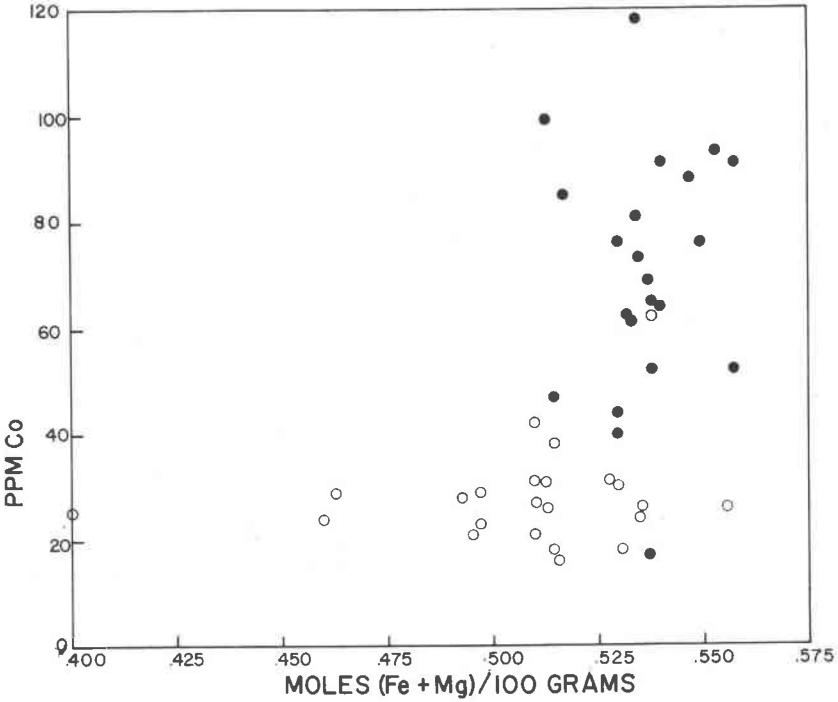

FIG. 3b

is heavily discriminated against by the garnet site (Fig. 3a). The data in DeVore (1955) show a similar discrimination. *Cobalt* is also favored by the biotite octahedral site, but the disparity is less than nickel for the two lattices (Fig. 3b). *Chromium* is only slightly favored by the biotite (Fig. 3c) and *copper* appears to be randomly distributed between the two phases.

Strontium is almost completely excluded from both lattices (<4 ppm Sr), while *barium* is found in great abundance in the 12 coordination site in the biotite and is present to about 20 ppm in the garnet structure. This implies that there is a very much more important sink in the system for strontium than either of the mafic minerals, while the barium is more generally distributed. This sink for strontium is undoubtedly the plagioclase.

CONCLUSIONS

Our study reinforces the conclusions implicit in the work of DeVore (1955) and Kretz (1959) on other suites of metamorphic rocks, *viz.* (1) rarely in samples of hand specimen size are equilibrium distributions of

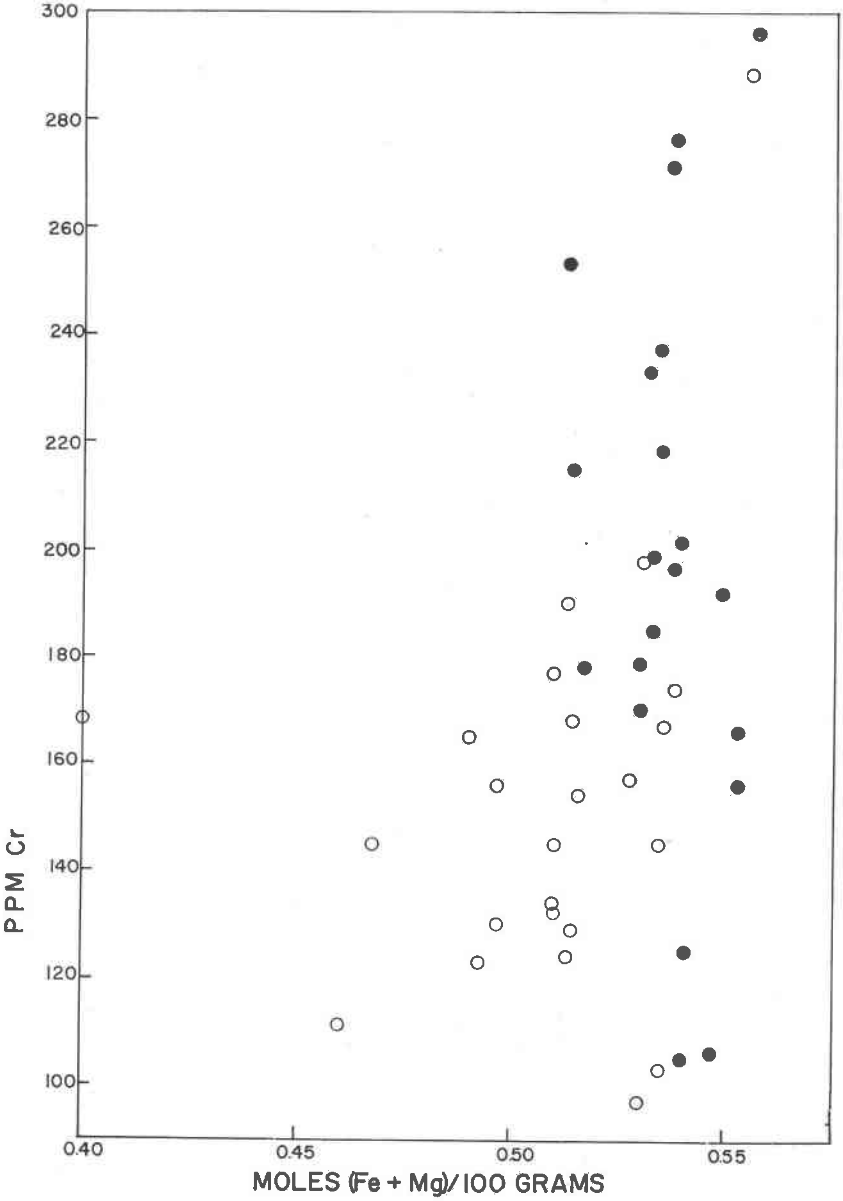

FIG. 3c

FIG. 3. Nickel, cobalt and chromium concentrations as a function of iron and magnesium concentrations for garnets (open circles) and biotites (black circles).

trace elements between coexisting phases observed in metamorphic sequences, and (2) the laws governing the inclusion of a trace element in different coexisting crystal lattices are more than those based on any single parameter such as ionic radius.

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INTERCRYSTALLIZED APATITE AND ANKERITE FROM THE NEW ALBANY SHALE OF INDIANA[1]

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A core that penetrated the New Albany Shale (upper Devonian and lower Mississippian) was obtained from Clark County in southeastern Indiana. An unusual specimen of intercrystallized apatite and ankerite was found within the black shale. This sample, which is 0.1 foot thick, was obtained approximately 1 foot stratigraphically below the top of the New Albany Shale. Similar material has been seen in approximately the same stratigraphic position at five other localities in Indiana; the sample from Clark County best illustrates the relationships described in this note.

More than 90 per cent of a thin section cut from this sample is composed of intercrystallized apatite and ankerite. Pyrite, quartz and gypsum(?) as well as separately crystallized ankerite and apatite, also are present. The intercrystallized apatite and ankerite has wavy extinction, a birefringence between apatite and ankerite, and refractive indices ranging from 1.648 to 1.576 (Na light). Discrete areas of intercrystallized

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