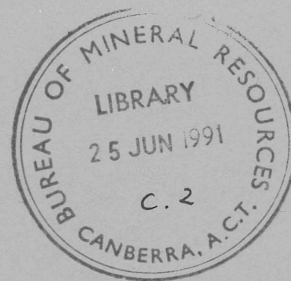
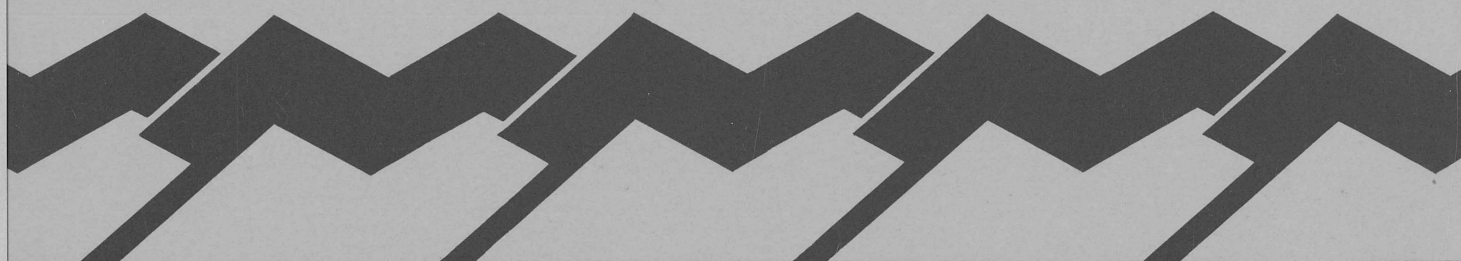


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TRACE METALS DISTRIBUTION PATTERNS IN BASALTS, PILBARA CRATON,
WESTERN AUSTRALIA, WITH STRATIGRAPHIC-GEOCHEMICAL IMPLICATIONS

A.Y. Glikson , R. Davy and A.H. Hickman

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**TRACE METALS DISTRIBUTION PATTERNS IN BASALTS, PILBARA CRATON,
WESTERN AUSTRALIA, WITH STRATIGRAPHIC-GEOCHEMICAL IMPLICATIONS**

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SUMMARY

The distribution patterns of transition trace metals [Ti, V, Cr, Mn, Co, Sc, Ni] and chalcophile metals [Cu, Zn, Pb] in metamorphosed tholeiitic basalts [TB] of the Archaean Pilbara Craton, Western Australia, are reported with reference to their potential application as stratigraphic/geochemical fingerprints. Two petrological series can be discerned with respect to Ni distribution: [1] high-Ni low-Mg/Ni basalts associated with komatiites [Apex Basalt, basalts of the Gorge Creek Group and partly the Whim Creek Group, Nymerina Basalt and Kylenea Basalt (west Pilbara Craton) Dolerite]; [2] low-Ni high-Mg/Ni basalts of commonly low Mg' values accompanied by only a minor komatiite component [Talga Talga Subgroup, Kylenea Basalt]. Trace metal fractionation indices [V/Cr, Co/Ni, Ti/Ni] suggest [1] a relatively highly fractionated nature of TB of the Talga Talga Subgroup [North Star Basalt and Mount Ada Basalt]; [2] low fractionation of TB of the Apex Basalt; [3] generally low-to-intermediate degree of fractionation of Gorge Creek Group basalts [Charteris Basalt and Honeyeater Basalt] [with the exception of high Co/Ni in the latter] and Whim Creek Group basalts [Warrambie Basalt, Loudon Volcanics and Mount Negri Volcanics]; [5] low fractionation of Mt Roe Basalt samples, with the exception of high V/Cr ratios; [6] high to very high fractionation of the Kylenea Basalt tholeiites, and [7] variable fractionation of TB of the Nymerina Basalt and Maddina Basalt. The Ti/Ni ratio, which can be diagnostic of magmatic fractionation, is high in the Talga Talga Subgroup tholeiites and the Kylenea Basalt and low in tholeiites associated with high-Mg basalts. Variations in trace metal abundances in TB of different stratigraphic units commonly correlate with variations between associated high-Mg basalts and even peridotitic komatiites, suggesting a primary magmatic inheritance of these differences. Some of the more pronounced variations are [1] the low Mg' values [40-55], low Ni [high Mg/Ni], high Ti/Ni, low Cr [high Mg/Cr], high V and high V/Cr, high Zn and low Cu of basalts of the Talga Talga Subgroup; [2] higher Mg' values [55], high Ni [low Mg/Ni, low Co/Ni], low Ti and Ti/Ni, high Cu and low V/Cr of Apex Basalt [Salgash Subgroup] tholeiites which are commonly associated with komatiites; [3] a magnesian character of Gorge Creek Group and some of the Whim Creek Group tholeiites [Mg' values about 55-65] and their low Ti and V levels; [4] the evolved composition of Fortescue Group basalts [$Mg' = 30-50$], their generally low Mn and V and high variability in Ni and Cr, characterizing particular volcanic units. Stratigraphically significant differences between the ratios of the high field strength elements reflect high levels of Zr, Y, Nb and P relative to Ti in TB of the late Archaean Fortescue Group, Whim Creek Group, and to some degree the Honeyeater Basalt, as compared to early Archaean basalts of the Warrawoona Group and Charteris Basalt. The relative enrichment in incompatible elements may be accounted for in terms of changes in the source lithosphere and/or an increase in the importance of crustal assimilation from the level of the Gorge Creek Group and upwards.

I. INTRODUCTION

This report is concerned with the dispersion of the transition trace metals [Ti, V, Cr, Mn, Co, Sc, Ni] and chalcophile metals [Cu, Zn, Pb] in tholeiitic basalts [TB] from the Archaean Pilbara Craton, Western Australia, in an attempt to identify stratigraphic - geochemical markers, or "geochemical fossils", as an aid for the mapping of this Archaean province. This report discusses mainly geochemical variations in tholeiitic basalts (TB), in order to minimize variations arising from fractionation, and although some comparisons are made between high-Mg basalts and high-Al basalts. The volcanics include material from the early Archaean Warrawoona Group, the Gorge Creek Group, the Whim Creek Group and late Archaean Fortescue Group, dated within the time range of $3.5 - 2.7 \times 10^9$ years [Hickman, 1990]. The regional geology and stratigraphy of the Pilbara Group have been comprehensively documented by Hickman [1983, 1990]. The data on which this paper is based have been collected during a regional geochemical survey by the BMR and the Geological Survey of Western Australia [Glikson and Hickman, 1981a, 1981b; Glikson et al., 1986a, 1986b; Glikson et al., 1987]. Stratigraphic and location information for volcanic units referred to in this report is presented in Fig. 1 and Table 1. For information on analytical methods, accuracy and precision refer to Glikson and Hickman [1981a]. In this report the data are present in frequency columnar histograms [Figs 2-13] and as averages and standard deviations [Table 2]. For the full set of individual analyses refer to Glikson et al., 1986a.

Mg' values [molecular MgO/MgO+FeOt] of the TB [Fig. 2] vary with time from a main range of 40-55 for the Talga Talga Subgroup [lower Warrawoona Group] to a mode of 55 in the Apex Basalt [Salgash Subgroup], while TB correlated with the Salgash Subgroup in the western Pilbara have a main modal range of 40-55. TB of the Gorge Creek Group [Charteris Basalt, Honeyeater Basalt] and part of the Whim Creek Group [Warrambie Basalt, Loudon Volcanics] are dominated by magnesian types [modal range 55-65]. By contrast TB of the Fortescue Group are more iron rich, with main modal ranges for Mg' of 30-50. As will be shown below, whereas Mg' values reflect fractionation which controls trace metal levels, the Mg/trace metal ratio varies considerably between the basaltic suites, which in some instances allows their stratigraphic / geochemical characterization.

II. NICKEL

Nickel crystal/melt partitioning coefficient (K_d) values for olivine decrease with increasing temperature and with higher MgO of the magma, from about 15 at 8% MgO to about 5 at 24% MgO [Irving, 1978]. Similar trends apply to K_{dNi} values for other ferromagnesian phases. This renders variations in the Ni levels of rocks of similar Mg' value significant with regard to the physical conditions of petrogenetic processes. Ni-Mg relationships vary between continental basalts [CONB], ocean island basalts [OIB], midocean ridge basalts [MORB] and arc-trench basalts [ATB] which plot in distinct fields on Mg-Ni diagrams [Glikson, 1983]. Mg and Ni levels tend to be high in MORB, low in CONB and intermediate in OIB. ATB have very low Ni and very high Mg/Ni ratios above 800. Because of high K_{dNi} coefficients the Mg/Ni ratio increases significantly with magma fractionation and is about 320 in average MORB [Hoffman et al., 1988] compared to 132 in model primitive mantle [McDonogh, 1987; Sun and McDonough, 1989].

Pilbara volcanics show positive correlation coefficients [mostly r above 0.50] between Ni and other metals. In order of decreasing affinity correlations are indicated with Co, Cr, Mg, Fe, and occasionally with V, Sc, Pb, Cu and Ca. As a group, tholeiitic basalts of the Pilbara Craton show a Ni frequency peak at about 50 ppm, significantly lower than the median of 160 ppm of tholeiitic basalts of the Eastern Goldfields, Yilgarn Block [Glikson, 1983].

Ni abundances in Pilbara tholeiitic basalts [Fig. 3] are mainly low in the Talga Talga Subgroup [NSB av. Ni = 69+/-40 ppm, av. Mg/Ni = 572; MAB av. Ni = 63+/-26 ppm, av. Mg/Ni = 567], are higher in tholeiitic basalts associated with high-Mg basalts and peridotitic komatiites of the Salgash Subgroup [Apex av. Ni = 102+/-40 ppm, av. Mg/Ni = 429; Euro av. Ni = 115+/-69 ppm, av. Mg/Ni = 360], and fluctuate in younger volcanic units. Thus, the Honeyeater Basalt and Charteris Basalt are distinct from each other with respect to Ni and Mg/Ni values.

The Mt Roe Basalt contains high-Ni [av. Ni = 136 \pm 86 ppm] tholeiitic basalts with distinctly high Ni/Cr ratios [0.3]. Low-Mg basalts of the Kylena Basalt are notable for their low Ni values [av. Ni = 45 \pm 11 ppm, av. Mg/Ni = 594], while the Nymerina Basalt contains distinctly high-Cr basalts [av. Mg/Cr = 101]. The fields of dolerite and gabbro overlap with those of tholeiitic basalts, and a continuous transition is seen with high-Mg basalts [Mg' = 60-80; Ni = 100-400 ppm]. The average values of HMB of the Talga Talga Subgroup [Ni = 167 \pm 81 ppm; av. Mg/Ni = 401] and the Salgash Subgroup [Apex Basalt: Ni = 190 \pm 105; av. Mg/Ni = 362; Euro Basalt: Ni = 212 \pm 98 ppm; av. Mg/Ni = 325] are consistent with the relations between the stratigraphically corresponding tholeiitic basalts, namely the younger high-Mg basalts are richer in Ni and have lower Mg/Ni ratios. Similar Mg/Ni relations are seen between peridotitic komatiites of the Talga Talga Subgroup [1529 \pm 436 ppm; av. Mg/Ni = 106] and those of the Apex Basalt [1435 \pm 195; av. Mg/Ni = 80]. Mg/Ni values of basalts of the Kylena Basalt in the western Pilbara [Wallace and Hoatson, 1990] are low [av. TB: Ni = 108 ppm; av. Mg/Ni = 411; av. HMB: 573 ppm; av. Mg/Ni = 175].

Andesitic volcanics and high-Al basalts of the Pilbara Supergroup may have Ni values close to those of arc-trench tholeiites [below 40 ppm] or are similar to the basalts, suggesting that some of these rocks are altered equivalents of the latter. The high Mg/Ni ratios of high-Al basalts [av. 766 for Talga Talga Subgroup HALB] is consistent with ATB. Clear compositional gaps occur between high-Mg basalts and peridotitic komatiites; there is a 400-1000 ppm gap in rocks of the Talga Talga Subgroup, a 700-1000 ppm gap in rocks of the Salgash Subgroup and no gap in the Kylena Basalt. Clearly, two petrological series can be discerned with respect to Ni distribution: [1] high-Ni low-Mg/Ni basalts associated with komatiites, such as those of the Salgash Subgroup, Kylena Basalt [in the western Pilbara Craton], and [2] low-Ni high-Mg/Ni basalts of commonly low Mg' values and accompanied by only minor komatiite component. In some instances a continuous spectrum occurs between ferroan tholeiites and high-Mg basalts, as for example in the Honeyeater Basalt [Mg' = 40-70; Ni = 20-200 ppm; Mg/Ni = 400-800].

Lateral geochemical variations in the composition of stratigraphically equivalent units are seen. For example, the Ni levels of tholeiitic basalts of the Apex Basalt vary between sections sampled at Spinaway Creek, Sandy Creek and Tambourah Creek - suggesting either variations in source and degree of fractionation/contamination or problems in stratigraphic correlations of these sequences. If geochemical compositions may be applied for stratigraphic correlations - an approach open to question in view of such lateral variations - the following observations can be made: tholeiitic basalts from sequences correlated with the Salgash Subgroup in the western Pilbara, namely at Cleaverville and Karratha, have moderate Ni values [111+/-30 ppm; av. Mg/Ni = 398] which, apart for the paucity of high-Mg basalts in these sections, indicate a general similarity with Ni values in east Pilbara basalts. Sequences correlated with the Talga Talga Subgroup and Salgash Subgroup in the Strelley area, central Pilbara, both have relatively low Ni abundances. Tholeiitic basalts from the Tambourah section, central Pilbara, correlated with the Apex Basalt, also have low Ni levels [30-70 ppm].

III. COBALT

The behaviour of Co relative to MgO is the reverse of that of Ni and Cr. Compared to primitive mantle [104 ppm; Mg/Co = 2652; Hoffman, 1988] Co is enriched relative to Mg in MORB [average 47 ppm; Mg/Co = 1175]. Relationships between Co and Fe [total iron as FeO] show a decrease in relative abundance of Co from primitive mantle [Fe/Co = 563] to MORB [Fe/Co = 1720] [Hoffman, 1988]. Cobalt levels in peridotitic komatiites of the Talga Talga Subgroup [98+/-21 ppm; Mg/Co = 2011] are close to primitive mantle values. Since $Kd_{Co}^{Ol/melt}$ values are normally in the 2-7 range [Irving, 1978], the Mg/Co mantle-like values, which imply a low $Kd_{Co}^{Ol/melt}$ value of about 1.0, suggest high temperatures partial melting conditions in agreement with conclusions derived from Mg/Ni values above. Little variation of Co with Mg' values is seen between high-Mg basalts and tholeiitic basalts, with the common abundance range being 40-50 ppm [Fig. 3], but the Mg/Co ratios vary from about 1600 in HMB to 1300-1000 in TB, reflecting enrichment of Co relative to Mg in the magmas with fractionation as contrasted with the depletion of Ni and Cr.

Positive correlation coefficients [r above 0.50] demonstrate the close association between Co and Fe and HMB of the Talga Talga Subgroup. Other correlations are shown in some instances with Mn and Zn. Unlike Ni and Cr, Co shows little systematic variation between the Talga Talga Subgroup and Salgash Subgroup basalts, nor between older and stratigraphically higher basalts [Fig. 4], although the average Mg/Co ratios can be low in some of the Fortescue Group basalts [Mt Roe Basalt = 558; Kylena Basalt = 798], reflecting relative enrichment of cobalt. Though Ni and Cr are strongly depleted in the Kylena Basalt, Co levels are not depleted, averaging 41 ± 1.3 ppm, underscoring the different behaviour of this element.

Co/Ni ratios and Fe/Co ratios vary systematically between TB associated with little HMB, and TB associated with HMB and PK. Co/Ni ratios in Talga Talga Subgroup TB [0.6-0.7] are significantly higher than in Apex Basalt TB [av. 0.39]. High ratios in the Honeyeater Basalt [av. 0.65] and Kylena Basalt [av. 0.90] compare with low to intermediate values in other units. The Co/Ni variations support correlations between east, central and western Pilbara TB made by Hickman [1983]. Thus, the average ratios at Strelley, central Pilbara, are 0.94 for Talga Talga Subgroup TB and 0.50 for Salgash Group TB. In the western Pilbara the average ratio for TB from volcanic sequences correlated with the Salgash Subgroup is 0.43. Fe/Co ratios, which generally increase with fractionation [PK = 800-1000; HMB = 1300-1900; TB = 1800-2600], are higher in the TB of the Talga Talga Subgroup [1800-2600] than in TB associated with komatiites [Apex Basalt: 1800-2100].

IV. CHROMIUM

With its low Kd_{Cr} Ol/melt [0.5-1.0] and high Kd_{Cr} opx/melt [2-10] and Kd_{Cr} cpx/melt [1.5-2.0] coefficients, chromium is more strongly concentrated in normative pyroxene-rich basic magmas than Ni, as shown by variations between the Mg/Cr ratios of model primitive mantle [Cr = 2915 ppm, Mg/Cr = 87, McDonough, 1986] and MORB [Cr = 289, Mg/Cr = 185; Melson and Thompson, 1971], reflecting a lesser degree of Cr loss relative to Mg than is the case with Ni relative to Mg. Cr levels in MORB and OIB are similarly

high whereas CONB have lower levels and ATB have very low Cr and very high Mg/Cr ratios. Like Ni, Cr abundances vary with stratigraphy throughout the Pilbara volcanic sequence: Tholeiitic basalts of the Talga Talga Subgroup have low Cr [averaging 160-180 ppm, with many values below 100 ppm; Mg/Cr = 210-230] whereas the Apex Basalt has higher averages [295+/-198 ppm; Mg/Cr = 149]. TB of the Euro Basalt are more like those of the Talga Talga Subgroup. Stratigraphically higher tholeiitic basalts show a wide scatter of Cr values, but the majority of samples of the Mt Roe Basalt and in particular the Kylena Basalt have low to very low Cr abundances [Fig. 5]. The latter unit has extremely high Mg/Cr ratios, averaging 1145. The Mg/Cr ratios of high-Mg basalts [Talga Talga Subgroup average 94, Apex Basalt averages 112] are close to primitive mantle [87], suggesting little selective partitioning of Cr between melt and residue upon high degree of partial melting. Kylena Basalt [west Pilbara Craton] rocks have particularly high Cr [average HMB: Cr = 2190 ppm; Mg/Cr = 45; average TB: Cr = 324 ppm; Mg/Cr = 142]. Positive correlation coefficients [r above 0.50] indicate associations, in decreasing order, with Ni, Mg, Sc, V, Mn and Zn.

When considering the distribution of Cr with respect to stratigraphic correlations, the following observations appear valid: [1] Volcanics correlated with the Apex Basalt in the Tambourah Creek area, central Pilbara, have Cr levels about or lower than 100 ppm, namely less than the Apex Basalt; [2] Lateral variations of stratigraphically well correlated sequences occur, i.e. variations in Cr levels are seen between laterally equivalent tholeiitic basalts of the Apex Basalt in the Kelly belt, i.e. between the Sandy Creek section [high-Cr] and the Spinaway Creek section [low-Cr]; [3] high-Mg basalts of the Apex Basalt associated with peridotitic komatiites at Camel Creek are more magnesian than those at Sandy Creek, reflecting higher degrees of melting; [4] the basaltic sequences correlated with the Apex Basalt in the western Pilbara have moderate Cr abundances [av. Cr = 201+/-71 ppm; Mg/Cr = 219], similar to the east Pilbara equivalents; [5] The Honeyeater Basalt at Soanesville includes distinct high-Cr and low-Cr tholeiitic basalt groups.

V. VANADIUM

Vanadium shows a more than 3-fold enrichment from model primitive mantle [82 ppm; Fe/V = 740] [McDonough, 1986] to average MORB [289 ppm; Fe/V = 280] [Melson and Thompson, 1971], due to very low K_d Ol/melt [0.04] values. Vanadium resides mainly in pyroxenes [K_d Opx/melt = 2.8; K_d Cpx/melt mostly 1-10 under low f_{O_2} conditions] and is enriched in late-stage ferroan basalts where most concentrates in magnetite [K_d mt/melt below 60 at low f_{O_2}] and iron-titanium oxides [K_d ilmenite/melt = 12]. It shows a wide scatter with a distribution peak at 300-350 ppm in the Warrawoona Group and about 170-230 ppm in stratigraphically higher volcanics [Fig. 6]. Anomalously high vanadium values about 400-500 ppm are shown by some Mount Ada Basalt [Talga Talga Subgroup] basalts. The Fe/V ratio shows a corresponding increase from the Warrawoona Group [240-340] to the Whim Creek Group and Fortescue Group [330-500]. These differences are stratigraphically useful, as they suggest that basic volcanic rocks with above 300 ppm vanadium are far more likely to belong to the Warrawoona Group than to stratigraphically higher units - the Honeyeater Basalt being an exception with values up to about 350 ppm. The systematic increase in V/Cr ratios with lower Mg' numbers is expressed in the Talga Talga Subgroup by the rise from the average of PK [0.03] to HMB [0.31], TB [1.8] and TA [4.5]. Stratigraphic variations in these parameters indicate that TB of the Apex Basalt [Salgash Subgroup] are less fractionated [V/Cr = 0.89] than the Talga Talga Subgroup [V/Cr = 2.0], in agreement with variations discussed earlier. Significant correlation coefficients [r above 0.50] indicate the closest association between V and Ti and Fe, occasional associations with Mn, Sc, Cu, Zn, Pb, Cr and Ni, and common correlation with large ion lithophile elements including P, Y, La, Zr and Nb. These relationships can be interpreted in terms of the general increase in V along with incompatible elements with fractionation and its residence in P-rich vanadiferous magnetite.

VI. SCANDIUM

The Scandium level of model primitive mantle [15 ppm] and MORB [41 ppm] [Hoffman, 1988] indicate the relatively low compatibility of this element with mantle residues [$K_{d_{Sc}Ol/melt} = 0.26$, 0.37 ; $K_{d_{Sc}Opx/melt} = 1.4$, 0.53 , Irving, 1978] and its concentration in clinopyroxene [$K_{d_{Sc}Cpx/melt} = 7-1$ with higher temperature] and magnetite [$K_{d_{Sc}magnetite/melt} = 3.3-0.8$]. Sc^{+3} shows a close coherence with Fe^{+2} and is captured due to the strong ionic Sc-O bond, although less so than the smaller-radius vanadium. Scandium is concentrated in early pyroxenes and has very high Kd coefficients in garnet [$K_{d_{Sc}garnet/melt} = 27.6$]. Average Sc abundances in TB of the Talga Talga Subgroup [50+/-35 ppm] and Salgash Subgroup [33+/-5 ppm] at Strelley, central Pilbara, and in the western Pilbara [34+/-6 ppm; 41+/-3 ppm, respectively] [Fig. 7] are similar to those of modern basalts. Modal values in stratigraphically higher units are mostly in the 20-30 ppm range. High-Mg basalts have similar values, for example 38+/-5 ppm at Strelley. Significant correlation coefficients [r above 0.50] mainly occur with vanadium. With the increased fractionation of the rocks, the Sc/V ratio decreases from HMB [0.18] to TB [0.09] due to the near-constant Sc level and increase in V, the reverse trend of the predicted.

VII. MANGANESE

The similarities between Mn^{+2} and Fe^{+2} ions in terms of their ionic radius [Mn: $R = 0.80$; Fe: $R = 0.75$], electronegativity and ionic potential result in a common compatibility between Mn and residual silicates and particularly with oxides [$K_{d_{Mn}Ol/melt} = 1.0+/-0.5$; $K_{d_{Mn}Opx} = 0.7-0.8$; $K_{d_{Mn}Cpx/melt} = 0.4-1.0$; $K_{d_{Mn}Mt/melt} = 1.7-1.8$]. The enrichment of Mn along with Fe is reflected in its rising concentration from model primitive mantle [1053 ppm] to MORB [1239 ppm]. However, in the Warrawoona Group MnO shows little variation between PK [0.21+/-0.04%], HMB [0.21+/-0.03%] and TB]. TB of the Warrawoona Group display a principal range of 0.16-0.24% MnO [av. 0.22+/-0.05%] and a FeOt/MnO range of 50-70 [Fig. 8]. Concentrations of MnO in the Fortescue Group tend to

be low compared to Warrawoona Group and Gorge Creek Group TB. Low MnO values are shown by TB of the Mt Roe Basalt [av. 0.13+/-0.04%; FeOt/MnO = 30-50], Kylena Basalt [av. 0.15+/-0.03%; FeOt/MnO = 70-75], Nymerina Basalt [av. 0.15+/-0.03%; FeOt/MnO = 65-75] and the Maddina Basalt [av. 0.15+/-0.02; FeOt/MnO = 60]. There is a tendency for high MnO along with high Fe in TB of the western Pilbara Craton, namely TB of the Talga Talga Subgroup [av. 0.24+/-0.04%; FeOt/MnO = 52] and the Salgash Subgroup [av. 0.25+/-0.07; FeOt/MnO = 47]. Positive correlation coefficients [r above 0.50] indicate associations between Mn and Fe, Ti and Zn [Talga Talga Subgroup], Fe, Cu, Zn, U, La, Ce [Charteris Basalt], and Fe, Mg, Ca, Sc, V, Cr and Ni in some localities - suggesting residence of Mn in pyroxene and in some instances in magnetite, amphibole and/or mica.

VIII. TITANIUM

Titanium can be a significant minor constituent of pyroxenes due to ionic radius [$R_{Ti}^{IV} = 0.68$] and electronegativity [$Kd_{Ti}^{opx/melt} = 0.11$; $Kd_{Ti}^{cpx/melt} = 0.1-1.0$] similar to those of Fe^{+3} , however its commonly incompatible behaviour results in parallel enrichment with large ion lithophile [LIL] elements (Zr, Y, Nb, REE), except where fractionation of Fe-Ti oxide has taken place. Ratios between Ti and LIL elements in primary ultrabasic magmas are similar to those of the mantle sources [Nesbitt and Sun, 1976; Sun and Nesbitt, 1978]; the change in ratios in more evolved rocks reflects the extent of magmatic fractionation, mainly of Fe-Ti oxides. Thus, variations between model primitive mantle and average MORB reflect the marked increase of Ti relative to the major compatible components [Fe, Al and Ca] and its closer coherence with the incompatible LIL elements [P, Zr, Y, Nb]. The increase in Ti/trace metals ratios in MORB, as compared to primitive mantle ratios, is represented, by Ti/Co [from 11 to 206], Ti/Mn [from 1.2 to 6.7], Ti/Sc [from 73 to 234], and Ti/V [from 15 to 29], reflecting an increased fractionation order through Co, Mn, Sc, V and Ti. Distinct Ti-Zr-Nb-Y relationships were indicated for basalts of distinct modern tectonic provinces [Pearce and Cann, 1973; Pearce and Norry, 1979]. In particular TiO₂ is strongly depleted in arc-trench basalts [below 1.0%] and is commonly high in continental plateau

basalts [above 1.5%]. The coherence between incompatible elements in Pilbara basalts is represented by correlation coefficients. These are very high in some units [r above 0.80] between Ti and P, Zr and Y, and high [r above 0.50] between Ti and Nb, Ce, La, V, Zn and Ga. Ti-Fe correlations are high only in some instances.

Titanium displays significant stratigraphic variations through Pilbara volcanic succession [Glikson and Hickman, 1981; Glikson et al., 1986], showing a marked tendency for intermediate to high levels in TB of the Talga Talga Subgroup, low levels in the komatiite-rich Apex Basalt of the Salgash Subgroup, intermediate levels in the Euro Basalt, low levels in the Gorge Creek Group, and intermediate levels in Fortescue Group TB [Table 2; Fig. 9]. Peridotitic komatiites and high-Mg basalts of the lower and upper Warrawoona Group show a consistent decrease in TiO₂ [NSB and MAB PK: 0.47 \pm 0.21%, HMB: 0.83 \pm 0.28%; Apex Basalt PK: 0.18 \pm 0.04%, HMB: 0.58 \pm 0.18%]. These stratigraphic/geochemical variations are broadly consistent in the eastern Pilbara, although lateral variations are observed, for example between basalts of the Apex Basalt at Spinaway Creek [about 1.0%] and at Sandy Creek [about 0.6%]. No systematic variations such as those of the eastern Pilbara are observed in the Warrawoona Group at Strelley [central Pilbara], or in the western Pilbara. The high TiO₂ levels of basalts of the Tambourah succession, central Pilbara, earlier correlated with the Apex Basalt may agree with the older age of these rocks indicated by U-Pb zircon studies [McNaughton et al., 1988]. TiO₂ levels of the Salgash Subgroup in the western Pilbara are likewise higher [1.0-1.6%] than in the eastern Pilbara. TiO₂ levels in the Mt Roe Basalt vary between the Glen Herring section [0.7-0.9%] and the Yandicoogina section [0.8-1.3%]. Likewise the Nymerina Basalts shows variations between the Meentheena section [0.8-1.3%] and the Hay Creek section [1.2-1.7%]. Clearly, lateral geochemical variations are important in the Pilbara Craton as vertical stratigraphic trends.

Stratigraphic variations between the ratios of the high field strength elements in Pilbara volcanics [Glikson et al., 1986] include high levels of Zr, Y, Nb and P relative to Ti in tholeiitic basalts of the Fortescue Group, Whim Creek Group, and to some degree the Honeyeater Basalt. Thus, basalts of the Warrawoona Group and Charteris Basalt typically have Ti/Zr ratios of 70-120, Ti/Y ratios of 260-350, Ti/Nb ratios of 1200-2000 and TiO₂/P₂O₅ ratios of 8-15. The corresponding ratios in strati-

graphically higher units, including the Honeyeater Basalt in part, are Ti/Zr 10-60, Ti/Y 140-280, Ti/Nb 200-1600 and TiO₂/P₂O₅ 4-8. The relative enrichment of these LIL elements can be readily accounted for in terms of progressively increased role of the assimilation of sialic crustal rocks by basic magmas from the level of the Gorge Creek Group and upwards.

IX. COPPER

Due to their similar ionic radii Cu⁺² [$r = 0.72$] substitutes for Fe⁺² [$R = 0.75$] in ferromagnesian silicates. However, the strongly covalent Cu-O bond relative to the Fe-O bond results in the increase in the Cu/Fe ratio of the magma on fractionation until combination with S produces sulphides. These relationships are reflected in the partitioning coefficients of Cu, which are low in olivine [$Kd_{CuOl/melt} = 0.2-0.5$ and higher in clinopyroxene [$Kd_{CuCpx/melt} = 1.5-2.4$]. Consequently Cu increases markedly from model primitive mantle values [28 ppm] to MORB [74 ppm]. Cu levels in PK [av. 37+/-18 ppm] and HMB [av. 83+/-54 ppm] follow this trend but there is a wide scatter of values within TB, with moderate to high values in the lower and upper parts of the Warrawoona Group, respectively [NSB and MAB 40-100 ppm, Apex Basalt 140-160 ppm], low ranges in the Honeyeater Basalt [Shay Gap section: 50-60 ppm] and Loudon Volcanics [40-60 ppm] and contrasted levels in different units of the Fortescue Group [Mt Roe Basalt: 50-110 ppm; Kylena Basalt: 30-60 ppm] [Fig. 10]. Fe_{total}/Cu ratios are commonly low for high-Cu basalts [i.e. Apex Basalt: 600-900; Mt Roe Basalt: 700-1100] and high for low-Cu basalts [i.e. Honeyeater Basalt: 1000-1500; Kylena Basalt: 1200-1800], suggesting little correlation between the two elements. The differences in Cu levels between TB of the Talga Talga Subgroup and Salgash Subgroup are also observed in volcanic successions correlated with these units in the central and western parts of the Pilbara Craton [Hickman, 1983, 1990] and are thus stratigraphically useful. Anomalously low Cu levels [10-20 ppm] occur in some Talga Talga Subgroup basalts at Strelley, central Pilbara. Positive correlation coefficients [r above 0.50] for TB of some units indicate associations between Cu and V, Co and Zn [Apex Basalt], Mn [Charteris Basalt], Fe, Zn [$r = 0.73$] and Pb [$r = 0.91$] [Honeyeater Basalt], Fe, Pb, Ga and Ni [Mt Roe Basalt]

and Fe, Zr, Nb, La and Ce [Nymerina Basalt]. The association with large ion lithophile [LIL] elements suggests an occurrence of Cu in micas in some instances. The Cu levels of basalts, particularly those classified as altered on the basis of LMPR plots [Beswick and Soucie, 1978], display a wide dispersion due to secondary mobility of copper.

X. ZINC

The Zn-O bond is more strongly covalent than the Fe-O bond and the Zn/Fe ratio tends to increase with magmatic fractionation. Zn often shows good correlation with Fe and may reside in pyroxene [$Kd_{Zn_{pyx}/melt} = 1-2.5$], and/or it may be incorporated in sulphides. The average Zn level of MORB [122 ppm] is about twice the model abundance of Zn in primitive mantle [56 ppm] but comparisons of Zn levels between basalts of different tectonic environments suggest a wide variability, possibly related to the incompatibility and secondary remobilization of this metal. The average Zn content in the Talga Talga Subgroup increases from PK [61+/-10 ppm] to HMB [78+/-18 ppm] to TB [96+/-28 ppm]. The mode for Zn in tholeiitic basalts of the lower Warrawoona Group is 80-100 ppm whereas stratigraphically higher TB commonly show lower modes in the 70-80 ppm range. Average Zn values in the Apex Basalt are lower than in the Talga Talga Subgroup [PK: 34+/-5 ppm; HMB: 67+/-12 ppm; TB: 72+/-13 ppm]. The Charteris Basalt has low Zn values [63+/-22 ppm] [Fig. 11]. The decrease in Zn levels from the lower to the Salgash Subgroup is consistent with stratigraphically correlated variations in the central Pilbara [Strelley section: Talga Talga Subgroup - 112+/-35 ppm; Salgash Subgroup - 90+/-18 ppm] and the western Pilbara [Talga Talga Subgroup - 173+/-118 ppm; Salgash Subgroup - 90+/-13 ppm]. In Pilbara volcanics positive correlation coefficients [r above 0.5] pertain in some units between Zn and Fe, Mn, Ti, P, and Zr [Talga Talga Subgroup], Fe, Ti, P, Zr, V, Y, La and S [Apex Basalt], Fe, Ti, Pb, Th, Zr, Nb, Y, Ce, and La [Salgash Subgroup, west Pilbara], Fe and Pb [$r = 0.94$], Cu and Nb [Honeyeater Basalt], Fe, Pb, V, Cr, Co, Sc and Cu [Mt Roe Basalt]. The different relationships suggest contrasted host phase compositions, which on the basis of the common association with large ion lithophile [LIL] elements include amphibole and/or mica. The Zn-

S correlations in TB of the Apex Basalt [$r = 0.51$], the Charteris Basalt [$r = 0.71$], Loudon Volcanics [$r = 0.56$] and the Mt Roe Basalt [$r = 0.8$] suggest a concentration of zinc in sulphides in at least some basaltic suites.

XI. LEAD

Lead is concentrated in residual melts and resides in apatite, mica and feldspar. In many instances Pb occurs in sulphide in feldspar and mica. The more covalent Pb-O bond as compared to the Sr-O bond results in an increase in the Sr/Pb ratio with fractionation. The secondary dispersion of Pb associated with late-magmatic and metamorphic alteration, such as in the Pilbara rocks, results in uncertainties concerning the significance of Pb data with respect to igneous processes. The generally low Pb levels in high-Mg basalts [mostly below 5 ppm] indicate primary low levels, while isolated values above 5 ppm may be products of alteration effects. At these low ranges analytical inaccuracies are large and must be taken into account. These relationships are represented by correlation coefficients, which are often high [above 0.50] between Pb and K, Rb, U and Th, and in some instances between Pb and H₂O+ and CO₂ - reflecting both the residence of lead in feldspar and/or mica and its secondary mobility. Other significant but sporadic correlations occur between Pb and Fe, Ti, V, Cu, Ga, Zr, Nb, Y, Ce and La; however the inconsistency of these correlations underlines the secondary redistribution of lead in connection with hydrous alteration. A secondary enrichment of lead derived from felsic materials is suggested by the common positive anomalies on primitive mantle-normalized spidergram plots. All Pilbara TB show 5-10 times Pb enrichment relative to oceanic tholeiites (Figs 14, 15). Most Pb values of basalts of the Talga Talga Subgroup lie in the 4-8 ppm range and the Apex Basalt in the 2-4 ppm range, in accord with the generally less fractionated compositions of the latter [Fig. 12]. The generally low [below 5 ppm] Pb levels in basalts correlated with the Salgash Subgroup in the Karratha-Cleaverville area, western Pilbara, supports this correlation. There is a wide scatter of values, including very low values for the Honeyeater Basalt [mostly below 2 ppm], in the Gorge Creek and Whim Creek Groups. Fortescue Group basalts show a relatively high modal range of 4-

12 ppm. Differences between Pb levels in different sections may be explicable in terms of volatile contents; for example, the generally higher Pb levels of basalts of the Mount Roe Basalt in the Glen Herring area compared with those of the Yandicoogina area may be related to higher CO₂ and lower H₂O levels. Basalts classified as 'altered' on the basis of LMPR diagrams [Beswick and Soucie, 1978] tend to have high Pb levels.

XII. SULPHUR

Variations between chalcophile metals and sulphur may be indicative of the role of sulphides and thus the potential for mineralization where S levels are high. Sulphur levels in the analyzed volcanic rocks are generally low and vary between stratigraphic units: Talga Talga Subgroup TB are mostly very low in S [below 100 ppm], although the more heavily altered and volatile-rich Mount Ada Basalt TB show a wider scatter of values [Fig. 13]. TB of the Apex Basalt in the eastern and western Pilbara and of the Charteris Basalt and Whim Creek Group tend to have somewhat higher modal peaks [100-200 ppm] than Talga Talga Subgroup TB. Most Fortescue Group tholeiites contain 100-200 ppm Pb, with the Kylena Basalt having higher values [mode 500 ppm]. The generally low S in the volcanics and poor correlations between sulphur and trace metals suggest a minor role of sulphides in controlling the distribution of these elements.

XIII. STRATIGRAPHIC TRACE METAL DISTRIBUTION

In this report comparisons between basaltic suites are facilitated by dendogram plots where abundances are normalized to mid-ocean ridge basalt [N-MORB] composition. The order of elements in these plots is based on the increasing ratio [M/P] between the concentrations in N-MORB [Hoffman, 1988] and model primitive mantle [MPM] [McDonough, 1986], in the sequence of Ni [M/P=0.07], Cr [M/P=0.1], Mg [M/P=0.2], Co [M/P=0.45], Mn [M/P=1.18], Fe [M/P=1.38], Zn [M/P=2.17], Sc [M/P=2.8], Pb [M/P=2.8], Cu [M/P=2.65], V [M/P=3.5], Al [M/P=3.75], Ca [M/P=3.5] and Ti

[M/P=8.9]. Comparisons between the reference N-MORB and tholeiitic basalts from Pilbara volcanic units show that distinct spidergram patterns apply to some of the units. The patterns provide geochemical/stratigraphic fingerprints which allow comparisons between and testing of potential correlations between volcanic units across the Pilbara Craton. The distinct spidergram patterns allow identification of stratigraphically unclassified basaltic outcrops provided a sufficient number of rocks is analysed [10-20] and compared with type sections within the same general area [@ 50 km]. On the other hand, comparisons between spatially distant basaltic successions in the western and central Pilbara Craton face difficulties due to lateral heterogeneities arising from source mantle variations and/or petrogenetic processes. In the following some of the main comparisons are indicated [Table 2, 6; Fig. 14]:

Mg/Ni - typically high, as compared to N-MORB, in the Talga Talga Subgroup, Honeyeater Basalt and Kylenea Basalt.

Mg/Co - high in the Apex Basalt, Honeyeater Basalt, Loudon Volcanics and Nymerina Basalt.

Mg/Cr - generally high as compared to MORB. Very high ratios in the Kylenea Basalt and very low ratios in the Nymerina Basalt are diagnostic to these units.

Fe/Ti - generally high ratios as compared to MORB reflect the low TiO₂ of the basalts, especially in the Apex Basalt, Gorge Creek Group and Loudon Volcanics.

Fe/Mn - the ratios are similar or slightly higher than N-MORB.

Fe/Co - high ratios pertain in the Talga Talga Subgroup and low in the Whim Creek Group and the Mt Roe Basalt.

Fe/V - high ratios pertain from the Whim Creek Group to the Fortescue Group.

Fe/Zn - generally high ratios apply, reflecting the ferroan composition of the basalts.

Ni/Cr - low ratios pertain in the Warrawoona and Gorge Creek groups and commonly high ratios in higher parts of the sequence.

Co/Ni - ratios are generally higher than those of N-MORB.

V/Cr - with the exception of the Apex Basalt, Charteris Basalt and Nymerina Basalt, ratios are higher than N-MORB.

Ti/Ni - The Ti/Ni ratio offers a useful differentiation index in that it may reflect the ratio of pyroxenes and Ti-bearing oxides to olivine. High ratios are diagnostic of the North Star Basalt, Mount Ada Basalt and Kylenea Basalt, whereas low ratios pertain to the Apex Basalt, Charteris Basalt, Loudon Volcanics and Mt Roe Basalt.

In so far as high-Mg basalts [HMB] can be regarded as primary or near-primary magmas, rather than cumulates [Nesbitt and Sun, 1976; Sun and Nesbitt, 1978], their composition, uncomplicated by the fractional crystallization history which affected the tholeiitic basalts, may facilitate stratigraphic correlations. Comparisons between profiles and averages of high-Mg basalts from various units [Fig. 15; Tables 4 & 5] indicate that most HMB of the Apex Basalt, Charteris Basalt, Honeyeater Basalt and Loudon Volcanics have higher Mg' values and lower Fe, Mn, Zn, V and Ti compared to HMB of the Mount Ada Basalt and the Euro Basalt, in accord with comparisons between TB of these units. Similarly, most peridotitic komatiites of the Apex Basalt have lower Fe, Cr, Mn, Zn, V and Ti than PK of the North Star Basalt - suggesting differences between their primary magmas.

High-Mg basalts of the Mount Ada Basalt have high Ti/Ni ratios and those of the Apex Basalt low Ti/Ni ratios compared to the North Star Basalt equivalents. The highly magnesian [average $MgO = 16.5 \pm 3.2\%$; $Mg' = 75 \pm 3$] HMB of the Kylenea Basalt [west Pilbara Craton] have high Ni and Cr and low siderophile element levels [very low Ti/Ni and V/Cr] as compared HMB of other units. HMB of the Nymerina Basalt have high Ni and Ti as compared to HMB of the Talga Talga Subgroup. HMB of both the Kylenea Basalt [west Pilbara Craton] and Nymerina Basalt units are characterized by lower Mg/Ni ratios than any older units, which may signify lower temperature melting of Fortescue primary magmas compared to older Archaean volcanism. As in tholeiitic basalts, Pb levels are highly variable and mostly very high, reflecting secondary assimilation/alteration processes.

The possible distinct grouping of tholeiitic basalts in accord with their stratigraphic classification has been tested using a Q-mode cluster analysis by Bonham-Carter [1976]. Only the ferromagnesian elements [total Fe as FeO, MgO, MnO, TiO₂, Ni, Cr, Co, V, Cu and Zn] are considered in this analysis. Samples from the Warrawoona Group fall into several clusters in which TB from particular units dominate [Fig. 16]. However, there is no clear discrimination as most clusters contain mixed sample populations. The clustering, while supporting overall empirical distinctions between stratigraphic/geochemical groups, does not allow the classification of unknown samples. A more useful method for stratigraphic/geochemical discrimination of TB samples is the R-mode cluster analysis, which graphically reflects the correlation coefficients of the elements. The differences displayed between correlation patterns of the different stratigraphic units [Fig. 17] may have potential use in the classification of statistically adequate samples from stratigraphically unclassified outcrops.

High-Al basalts of the Talga Talga Subgroup show few differences from the tholeiitic basalts. Dendrogram profiles of andesitic basalts of the various units, defined on the basis of SiO₂ above 55% level, show a coherent grouping in some instances, suggesting they represent original igneous compositions. In other instances, compositional scatter and marked depletion in Ca suggest secondary mobility of some of the ferromagnesian elements in altered/silicified equivalents of the tholeiitic basalts [Glikson and Hickman, 1981a]. A comparison between basalts and andesites of the Talga Talga Subgroup indicates that the latter form a coherent group which overlaps the compositional range of TB but is somewhat depleted in Mg, Fe, Ca and most trace metals compared with TB. Andesites of the Loudon Volcanics and Mount Negri Volcanics form coherent profiles which are only distinguished from the corresponding basalts by lower Mg, Ni, Cr and Ca [Loudon Volcanics] or lower Cu, V and Al [Mount Negri Volcanics]. Comparisons between TB and andesites of the Mt Roe Basalt indicate commonly high Cr, Zn and V, and low Cu and Ca in the latter, which may represent altered basalts. Few or no differences are observed between TB and andesites of the Kylena Basalt. Andesites of the Nymerina Basalt tend to be somewhat depleted in Ca relative to TB, while andesites of the Maddina Basalt are somewhat enriched in Pb - both suggestive of alteration.

XIV. CONTROLS OF TRACE METAL DISTRIBUTION

The compatibility of trace metals with silicate and oxide phases is related to their ionic radii, electric charge, ionic potential and bond type, as reflected by melting point data [Taylor, 1965]. On the basis of ionic size and melting point data the decreasing order of compatibility of divalent ions is Mg^{+2} , Ni^{+2} , Co^{+2} , Fe^{+2} . Ni^{+2} [$R=0.69$] (R -ionic radius) and Co^{+2} [$R=0.72$] have high partition coefficients [K_d] in olivine whereas Cr^{+3} [$R=0.63$] and V^{+3} [$R=0.74$] are charge unbalanced in, and thus excluded from, olivine but are accepted in pyroxene crystal lattices. Because of its larger ionic radius Co^{+2} is less able to enter Mg^{+2} positions than is Ni^{+2} but is captured in early Fe^{+2} positions. Consequently the Co/Ni and Fe/Co ratios tend to increase with magmatic fractionation. Due to its strong ionic bond with oxygen Cr^{+3} is preferentially captured in Fe^{+3} positions and is thus rapidly depleted in the magma upon early crystallization of pyroxene. Since Ni and Cr typically occupy divalent and trivalent positions in minerals, respectively, the Ni/Cr ratio depends on the mineral mode and is not a useful fractionation index, although the ratio may help to indicate the role of olivine versus pyroxene fractionation. The substitution of V^{+3} for Fe^{+3} results in higher concentrations of vanadium in pyroxenes and magnetite. The high ionic potential of V^{+3} results in its complexing in volatile-rich magmas and thus concentration in fractionated melts. This, together with the large ionic radius of V^{+2} as compared to Cr^{+3} , renders the V/Cr ratio a useful differentiation index. Likewise the large ionic radius of Sc^{+3} [$R = 0.81$] relative to V^{+3} renders the Sc/V ratios positively related to differentiation. Another useful differentiation index is furnished by the Ti/Ni ratio, given the relative incompatibility of titanium [residing in pyroxene and oxides] as compared to the strong partitioning of Ni into olivine.

The application of trace metal ratios as fractionation indices for basic rocks does not suffer from problems inherent in the application of rare earth elements [REE] and large ion lithophile elements [LILE], which may be selectively enriched in basic magmas through assimilation and metasomatism. For example, the source lithosphere of basic magmas may already have been characterized by light REE enrichment [O'Nions and McKenzie, 1988] and

the enrichment of primitive high-Mg basalts in light REE, as documented for example in the Mount Negri Volcanics [Sun and Nesbitt, 1978], may well reflect source characteristics and/or wall rock contamination as in the model of Huppert and Sparks [1985], rather than magmatic differentiation. Clearly, tholeiitic basalts of volcanic units which commonly include high-Mg basalts and komatiites, namely the Apex Basalt, Honeyeater Basalt, Louden Volcanics and Nymerina Basalt, show relatively little fractionation. The generally low to intermediate degrees of fractionation of Apex Basalt, Gorge Creek Group and Whim Creek Group basalts, as indicated by trace metal relationships, are consistent with REE data, namely flat mantle-normalized REE patterns or depletion in light REE of tholeiitic basalts of the Apex Basalt, Euro Basalt, Charteris Basalt, Honeyeater Basalt and Warrambie Basalt [Glikson et al., 1986]. The REE, LILE and high field strength elements [HFSE] data allow a three-fold division of the volcanic sequence, as follows [ages after Hickman, 1990]:

[1] Talga Talga Subgroup [3.50–3.46 Gyr] marked by tholeiitic basalts with positive (Ce/Yb)_N ratios [1.0–3.0] and HFSE enrichment orders of Ce above Zr above Nb above Ti above P above Y relative to chondrites.

[2] Salgash Subgroup [3.45 Gyr], Gorge Creek Group [~3.3 Gyr], Warrambie Basalt marked by tholeiitic basalts with lower (Ce/Yb)_N ratios [1.0–2.3] and variable HFSE enrichment orders.

[3] Louden Volcanics, Mount Negri Volcanics [2.99 Gyr], Fortescue Group [2.77 Gyr] marked by very high total REE, high (Ce/Yb)_N [3.4–6.3] and high HFSE abundances.

It has been suggested that the Archaean basaltic sequences may have a bimodal origin, arising by [1] repeated partial melting in an Archaean low velocity zone, giving rise to tholeiitic basalts and minor proportions of high-Mg basalts, and [2] mantle diapiric events triggering large degrees of melting giving rise to high-Mg and peridotitic komatiites [Glikson, 1983]. The present study indicates that tholeiitic basalts associated with abundant komatiites are less fractionated than those not associated with a significant komatiitic component, and were more likely produced by crystal fractionation of the komatiitic magmas rather than concomitant melting in a low velocity zone.

The variations in Mg/Ni, Mg/Co and Mg/Cr between basalts of the Talga Talga Subgroup and the komatiite-rich Apex Basalt may reflect variations in the physical conditions of magma genesis. Thus, higher melting temperatures would result in lower olivine/melt partitioning coefficients for Ni, Co and Cr [Irving, 1968], with consequent higher abundance of these trace metals in the partial melts. This supports the two-source model, whereby melting temperatures in uprising mantle diapirs would exceed those in a low velocity zone. The latter zone would have produced magmas ranging in composition from high-Mg basalt to tholeiitic basalt, as indicated by their compositional continuity and the common occurrence of minor proportions of HMB in tholeiitic sequences. Evidence for the existence of mantle diapirs hinges on the occurrence of peridotitic komatiites, which show a well pronounced compositional gap with high-Mg basalts with respect to Mg' values, Al and trace elements [Glikson, 1983]. If so, HMB derived from a low velocity zone may be expected to have different chemical characteristics from those derived from mantle diapirs. The data presented here are inconclusive in this regard and, although HMB and PK of the Apex Basalt have marginally higher Mg/Ni ratios than equivalents in the Talga Talga Subgroup basalts, more data are required to test this possibility.

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Table 1 - Stratigraphy of volcanic successions of the northern Pilbara Craton, Western Australia

Fortescue Group [@ 2.77 Gyr]

Maddina Basalt [TB, TBA, TA]
 Kuruna Siltstone
Nymerina Basalt [TB, TBA, TA, HMB]
 Tumbiana Formation [carbonates, tuff]
Kylena Basalt [TB, TBA, TA, TAA]
 Hardey Formation
Mount Roe Basalt [TB, TBA, HALB, TA, HMB]

Mt Negri Volcanics [TB, TA, HMB]
Louden Volcanics [TB, TBA, TA, HMB, PK]

Whim Creek Group [@ 3.0 Gyr]

Rushall Slate
 Mons Cupri Volcanics [felsic tuff, rhyolite]
Warambie Basalt [TB, TBA, TAA]

De Grey Group

Mallina Formation [siltstone & slate]
 Lalla Rookh Sandstone [conglomerate, feldspathic arenite]

Gorge Creek Group

Honeyeater Basalt
 Cleaverville Formation [banded iron formation]
Charteris Basalt [TB, TA, HALB, HMB]
 Corboy Formation [quartzite, feldspathic arenite]

 Wyman Formation [porphyritic rhyolite] [3.325 Gyr]

Warrawoona Group [3.5-3.45 Gyr]

Salgash Subgroup

Euro Basalt [TB, HMB, HALB]
 Panorama Formation [rhyolite]
Apex Basalt [TB/HMB/PK, TA]
 Towers Formation [chert]

Duffer Formation [andesite, dacite, rhyolite, dolerites]

Talga Talga Subgroup

Mount Ada Basalt [TB, TA, HALB, HMB, PK]
 McPhee Formation [felsic to andesitic volcanics & sediments]
North Star Basalt [TB, HALB, TA, HMB, PK]

Intrusive granite contacts

* TB - tholeiitic basalt [including doleritic varieties]; TBA - amygdaloidal TB; TA - tholeiitic andesite; TAA - amygdaloidal TA; HALB - high-alumina basalt; HMB - high-Mg basalt; PK - peridotitic komatiite.

Table 2 - Mean and standard deviation values for tholeiitic basalts [TB] from volcanic units, Pilbara Craton.

Unit*	N number of samples	Mg'	MgO %wt	FeOt %wt	TiO2 %wt
N-MORB		56	7.6	10.4	1.6
MB	7	48+/-9.0	4.9+/-1.4	9.1+/-0.2	0.88+/-0.15
NB	21	47+/-1.4	5.8+/-2.0	10.9+/-1.4	1.28+/-0.21
KB	42	44+/-4.5	4.5+/-0.6	10.0+/-0.9	1.15+/-0.18
MRB	40	39+/-8.7	3.9+/-1.4	10.7+/-3.9	0.94+/-0.26
NEGV	6	43+/-8.8	4.7+/-1.3	10.6+/-3.2	1.21+/-0.26
LV	18	61+/-14.0	8.6+/-3.7	8.9+/-1.3	0.54+/-0.30
WB	12	40+/-8.4	4.6+/-1.8	12.2+/-1.6	1.24+/-0.38
HB	46	56+/-7.4	6.9+/-1.1	9.7+/-1.8	0.62+/-0.22
CB	14	57+/-8.9	7.4+/-1.3	10.0+/-1.9	0.70+/-0.34
EB	11	47+/-12.6	6.6+/-2.2	12.9+/-2.6	1.29+/-0.51
AB	23	55+/-6.3	7.0+/-1.0	10.3+/-1.8	0.80+/-0.33
MAB	56	43+/-7.8	5.7+/-1.7	13.4+/-1.8	1.54+/-0.43
NSB	54	48+/-7.8	6.3+/-1.3	11.8+/-1.8	1.26+/-0.49

* N-MORB [average mid- ocean ridge basalt, from Hoffman, 1988 and Melson and Thompson, 1971]; MB - Maddina Basalt; NB - Nymerina Basalt; KB - Kylena Basalt; CP - Kylena Basalt [west Pilbara Craton] volcanics; MRB - Mount Roe Basalt; NEGV - Negri Volcanics; LV - Loudon Volcanics; WB - Warrambie Basalt; HB - Honeyeater Basalt; CB - Charteris Basalt; EB - Euro Basalt; AB - Apex Basalt; MAB - Mount Ada Basalt; NSB - North Star Basalt

MnO %wt	V ppm	Cr ppm	Sc ppm	Co ppm	Ni ppm
0.19	289	289	41	47	149
0.15+/-0.02	203+/-47	95+/-38	28+/-8	41+/-6	76+/-23
0.15+/-0.03	195+/-47	358+/-362	22+/-7	38+/-7	132+/-91
0.15+/-0.03	214+/-17	25+/-12	27+/-1.5	41+/-1	45+/-11
0.13+/-0.04	207+/-45	101+/-156	25+/-3.8	51+/-13	137+/-87
0.15+/-0.01	234+/-36	155+/-3	24+/-1.0	50+/-4	97+/-32
0.15+/-0.02	180+/-36	155+/-140	33+/-17	47+/-6	138+/-71
0.21+/-0.06	228+/-73	103+/-63	25+/-10	48+/-5	111+/-38
0.19+/-0.04	251+/-56	172+/-118	21+/-14	46+/-4	71+/-21
0.17+/-0.03	227+/-58	306+/-234			127+/-76
0.19+/-0.04	305+/-70	152+/-171			116+/-69
0.20+/-0.03	264+/-45	295+/-199		40+/-6	102+/-40
0.21+/-0.03	341+/-67	168+/-293		45+/-5	63+/-26
0.22+/-0.05	316+/-71	176+/-185		45+/-6	69+/-40

Cu ppm	Zn ppm	Pb ppm	S ppm
74	122	0.49	1000
90+/-34	90+/-8	7+/-2	160+/-46
126+/-44	102+/-32	5.5+/-4.4	267+/-295
46+/-10	83+/-13	8.1+/-3.7	345+/-204
81+/-31	107+/-67	6.9+/-4.9	354+/-815
114+/-7	83+/-4	7.5+/-4.6	654+/-454
59+/-22	68+/-21	9.4+/-13.5	336+/-341
140+/-76	103+/-14	7.8+/-6.3	266+/-91
64+/-26	75+/-20	3.9+/-2.3	197+/-175
81+/-40	63+/-22		412+/-532
139+/-44	96+/-22	15.5+/-19.1	698+/-583
99+/-47	72+/-14		324+/-365
74+/-32	103+/-27	5.6+/-3.2	614+/-556
56+/-35	96+/-28	4.1+/-2.7	298+/-438

Table 3 - Mean ratios of ferromagnesian elements for tholeiitic basalts [TB] from volcanic units, Pilbara Craton.

Unit*	N	Mg/Ni	Mg/Co	Mg/Cr	FeO/TiO₂	FeO/MnO
N-MORB		306	971	154	6.4	55
MB	7	389	722	310	10.3	61
NB	21	263	902	97	8.5	73
KB	42	594	659	1096	8.7	67
MRB	40	171	461	231	11.4	82
MEGB	6	295	569	184	8.8	71
LV	18	376	1091	334	16.5	59
WB	12	252	583	272	9.8	58
HB	46	587	905	242	15.6	51
CB	14	352		146	14.3	59
EB	11	344		263	10.0	68
AB	23	412	1055	143	12.8	51
MAB	56	543	772	205	8.7	64
NSB	54	547	850	216	9.4	54

* refer to Table 2 for legend of unit abbreviations

Fe/Co	Fe/V	Fe/Zn	Ni/Cr	Co/Ni	V/Cr	Ti/Ni
1725	280	664	0.5	0.31	0.97	64
1731	348	786	0.8	0.54	2.1	69
2230	434	831	0.37	0.29	0.5	58
1905	363	936	1.8	0.91	8.6	153
1631	402	777	1.4	0.37	2.0	41
1555	352	992	0.62	0.51	1.5	75
1472	384	1017	0.89	0.34	1.2	23
1976	416	921	1.1	0.43	2.2	67
1639	300	1005	0.41	0.64	1.5	52
	342	1234	0.41		0.74	33
	329	1044	0.76		2.0	67
2001	303	1112	0.34	0.39	0.89	47
2315	305	1011	0.37	0.71	2.03	146
2038	290	955	0.39	0.65	1.79	109

Table 4 – Average element abundance and ratios in high-Mg basalts from volcanic units of the Pilbara Craton.

Unit*	N	Mg'	MgO %wt	FeOt %wt	TiO2 %wt
NB	6	56+/-2	8.5+/-0.7	12+/-0.9	1.26+/-0.14
KB	6	75+/-3	16.5+/-3.2	9.5+/-0.5	0.48+/-0.08
HB	13	67+/-5	10.8+/-2.1	9.4+/-1.2	0.53+/-0.18
CB	7	65+/-4	9.7+/-0.86	9.2+/-1.2	0.52+/-0.07
EB	8	59	9.5+/-1.5	11.6+/-1.1	1.2 +/-0.25
AB	32	67+/-5.5	11.7+/-3.0	10.1+/-1.3	0.57+/-0.18
NSB&MAB	19	63+/-5.7	10.6+/-2.1	10.9+/-1.4	0.83+/-0.23

	MnO %wt	V ppm	Cr ppm	Sc ppm	Co ppm	Ni ppm	Cu ppm
NB	0.17+/-0.01	231+/-38	837+/-54	29+/-3	47	261+/-46	101+/-
KB	0.14	149+/-14	2254+/-621	26+/-2		602+/-135	44+
HB	0.19+/-0.04	236+/-49	628+/-432	31+/-3	46	144+/-51	58+
CB	0.18+/-0.02	194+/-35	662+/-142			187+/-62	82+
EB	0.2+/-0.03	269+/-39	682+/-412	31+/-1.5	50	212+/-99	151+
AB	0.19+/-0.03	214+/-24	862+/-638	36+/-6	53	225+/-143	81+
NSB&MAB	0.21+/-0.03	257+/-44	828+/-513		49	168+/-81	83+

Zn ppm	Pb ppm	S ppm
92+/-5	2.4+/-1	200+/-126
58+/-5	4.3+/-3.3	65+/-7
57+/-11		100+/-88
58+/-8		285+/-178
80+/-7		367+/-513
69+/-14		169+/-139
78+/-18	3.7+/-2	187+/-60

* refer to Table 2 for legend of unit abbreviations

Table 5 – Average trace metal ratios of high-Mg basalts of volcanic units, Pilbara Craton.

unit*	av.	Mg/Ni	Mg/Co	Mg/Cr	Ni/Cr	Co/Ni	V/Cr	Ti/Ni
NB		202	1013	62	0.33	0.27	0.29	29.4
CP[=KB]		167		45	0.27		0.07	5.2
HB		490	1151	240	0.43	0.35	0.95	24
CB		347		93	0.30		0.30	19.5
EB		305	1133	97	0.29	0.20	0.46	37.6
AB		457	1394	174	0.49	0.31	0.69	21.1
NSB&MAB		427	1350	105	0.25	0.35	0.46	37

* refer to Table 2 for legend of unit abbreviations

Table 6 - relative trace metal abundance levels in Pilbara volcanic units (1) compared to MORB (2) compared to Talga Talga Subgroup tholeiitic basalts

(1) comparisons with MORB

Unit	high levels	low levels
North Star Basalt	Mn,V,Pb	Mg,Ni,Cr,Zn,Cu,Al, Ca,Ti
Mount Ada Basalt	Mn,Pb,V,Al	Mg,Ni,Cr,Zn,Ca,Ti
Apex Basalt	Mn,Cu,Al	Mg,Ni,Fe,Zn,V,Ca,Ti
Euro Basalt	Cu,V,Al	Mg,Ni,Cr,Mn,Fe,Zn,Ca
Charteris Basalt	Cu,Al	Fe,Mn,Zn,V,Ca,Ti
Honeyeater Basalt	Pb,Al	Mg,Ni,Cr,Fe,Zn,Ca,Ti
Warrambie Basalt	Pb,Al	Ni,Cr,Zn,Sc,V,Ca,Ti
Louden Volcanics	Pb,Al	Fe,Zn,Sc,Cu,V,Ca,Ti
Negri Volcanics	Pb,Cu,Al	Mg,Ni,Cr,Fe,Mn,Zn,Sc V,Ca,Ti
Mt Roe Basalt	Pb,Al	Mg,Cr,Fe,Mn,Zn,Sc,V, Ca,Ti
Kylena Basalt, Nymerina Basalt, Maddina Basalt	Pb,Al	Mg,Ni,Cr,Fe,Mn,Co,Zn, Sc,V,Ca,Ti
	Cu (Nymerina)	Cu (Kylena)

(2) comparisons with Talga Talga Subgroup tholeiitic basalts

Apex Basalt	Ni,Cr,Cu	Pb
Euro Basalt	mostly similar to Talga Talga Subgroup	
Charteris Basalt	Ni,Cr	Fe,Mn,Zn,V,Ti,Pb
Honeyeater Basalt	Cu	Fe,V,Zn,Ti
Warrambie Basalt	Cu	
Louden Volcanics	Ni,Cr	Mn,V,Ti
Negri Volcanics	Ni,Cu	Mn,V
Louden Volcanics	low Ti, V and Cu compared to Negri Volcanics	
Mt Roe Basalt	Ni,Cu	Mg,Cr,Mn,V,Ca
Kylena Basalt	Pb	low abundance ranges of all the ferromagnesian elements as well as Ca and Al, and are only high in Pb. Low Ni, Cr, Co and Cu but high Mg as compared to the Mt Roe Basalt.
Nymerina Basalt	Pb	Mn,V,Sc
Maddina Basalt	Pb,Cu	

LEGEND

Fig. 1 - Geological sketch map of the northern Pilbara Craton including locations of principal volcanic type sections considered in this report as follows: TC - Talga-Coongan; T - Talga River; MR - McPhee Reward; SH - Shark Centre; ST - Strelley Gorge; W - Withnell Creek; WH - Whundoo; B - Bowls Gorge; BA - Bamboo Creek; SC - Sandy Creek; MS - Mount Sholl; CC - Camel Creek; T - Tambourah Creek; SP - Spinaway Creek; K - Karratha; CL - Cleaverville; MC - Miralga Creek; BC - Budjan Creek; EC - Emu Creek; C - Charteris Creek; S - Soanesville; SR - Strelley Creek; SG - Shay Gap; WR - Warrambie Station; PR - Pyramid Road; MN - Mount Negri; MO - Mons Cupri; OW - Opaline Well; BR - Mt Brown; Y - Yandicoogina; GH - Glen Herring; WC - Whim Creek; CP - Cooya-Pooya; P - Pelican Pool; ME - Meentheena; HC - Hays Creek.

Figs 2-13 - Frequency distribution histograms of Mg' value ($100\text{Mg}/(\text{Mg}+\text{Fe})$), Ni, Co, Cr, V, Sc, MnO, TiO_2 , Cu, Zn, Pb and S in tholeiitic basalts of volcanic units of the Warrawoona Group, Gorge Creek Group, Whim Creek Group and Fortescue Group. Vertical lines signify the mean and standard deviations.

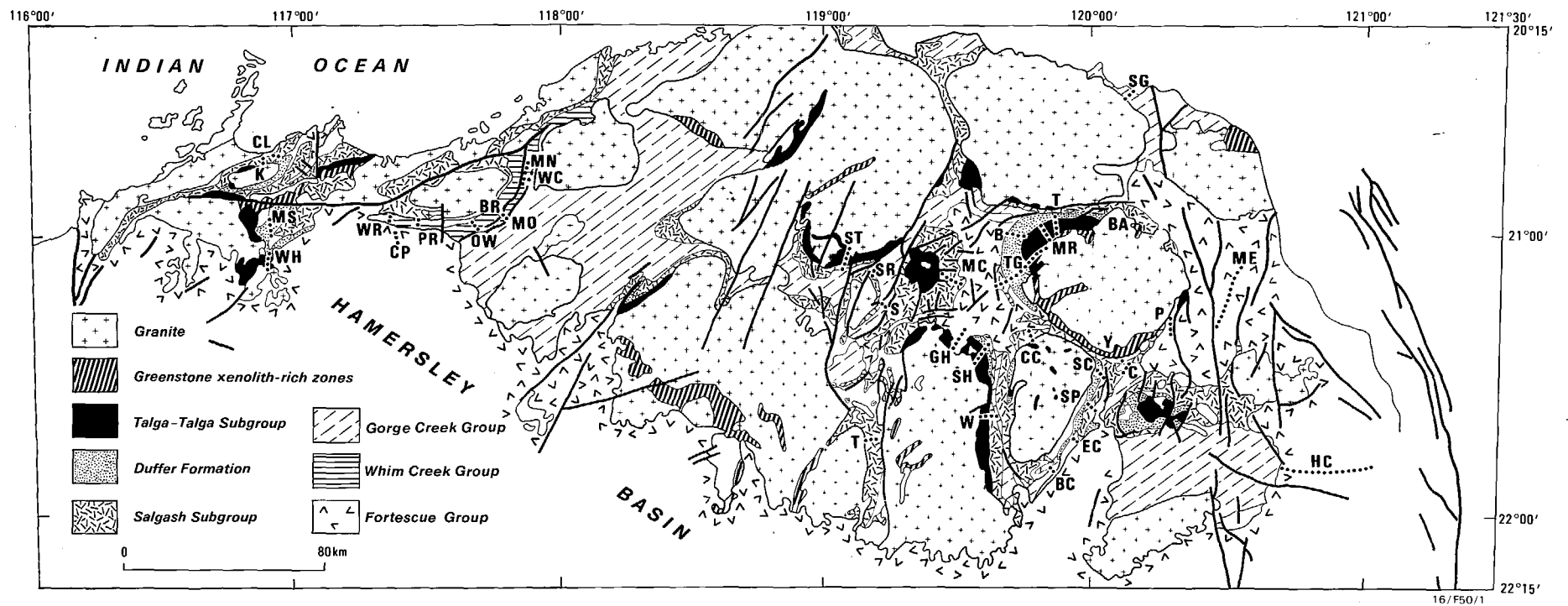
Fig. 14 - Spidergram plots (element concentration normalized to element concentration in mid-ocean ridge basalts [MORB] displaying the distribution of Ti, Ca, Al, V, Cu, Pb, Sc, Zn, Fe, Mn, Co, Mg, Cr, Ni (arranged in a decreasing order of enrichment in MORB relative to chondrites) in tholeiitic basalts of volcanic units of the Warrawoona Group, Gorge Creek Group, Whim Creek Group, Loudon Volcanics, Mount Negri Volcanics and Fortescue Group.

Fig. 15 - Spidergram plots for high-Mg basalts as in Fig. 14.

Fig. 16 - A Q-mode cluster analysis plot (Bonham-Carter, 1967) of tholeiitic basalts, showing groupings of samples according to their stratigraphic unit affiliation.

Fig. 17 - R-Mode cluster analysis plots for tholeiitic basalts, showing distinctions in inter-element correlations between the different volcanic units.

Fig. 1



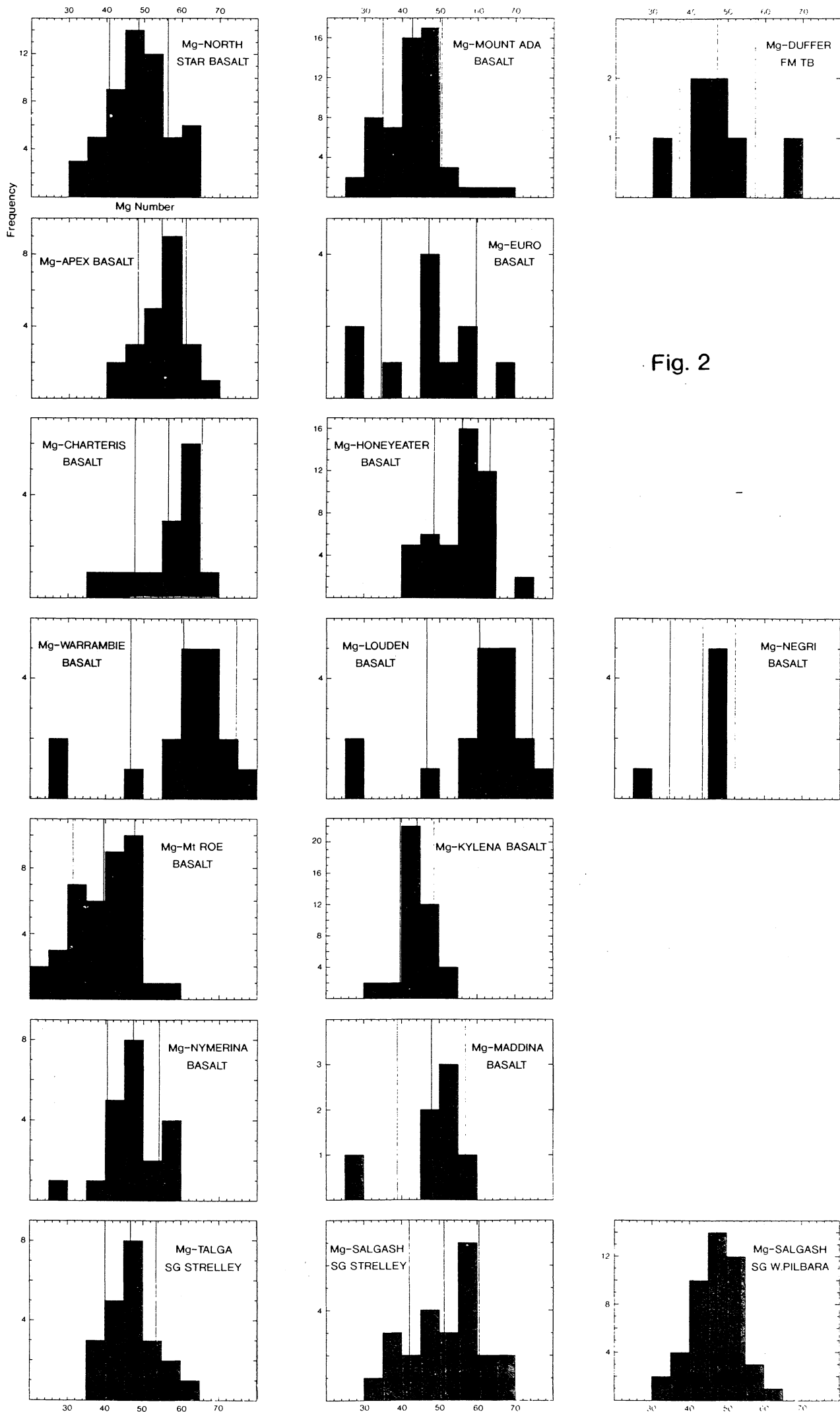


Fig. 2

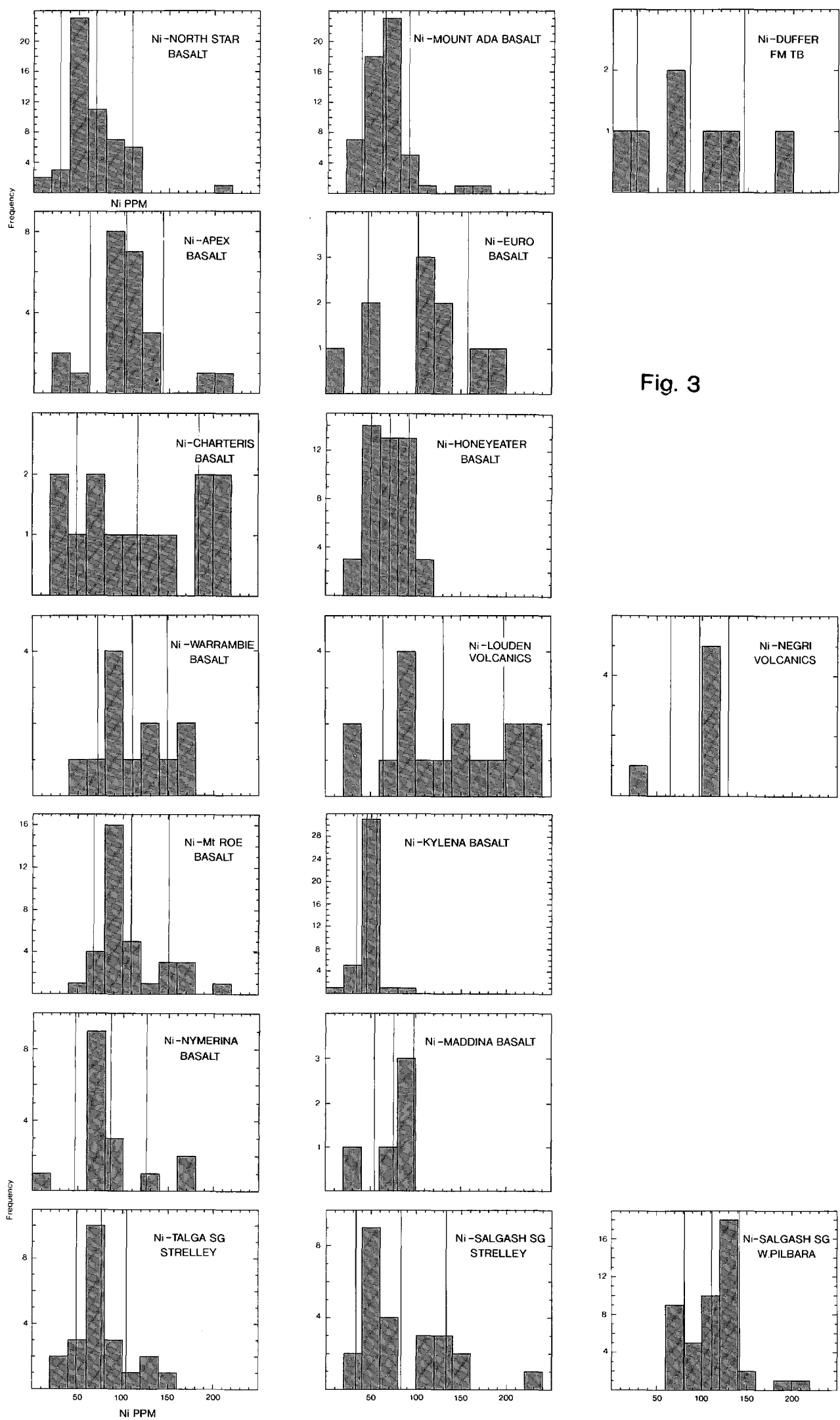


Fig. 3

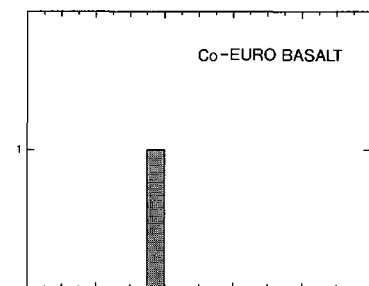
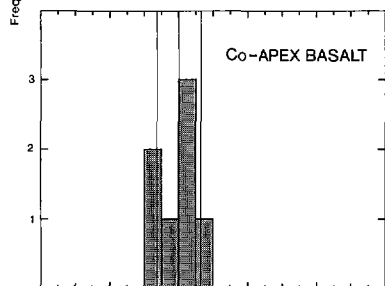
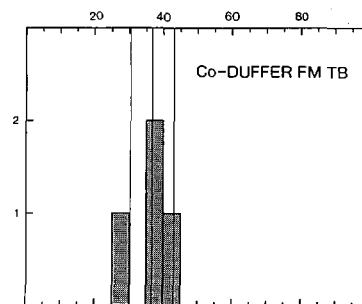
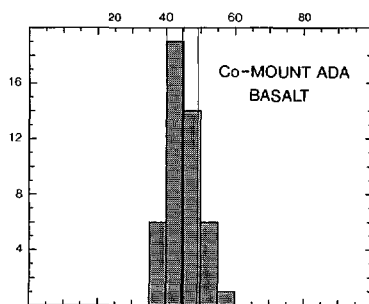
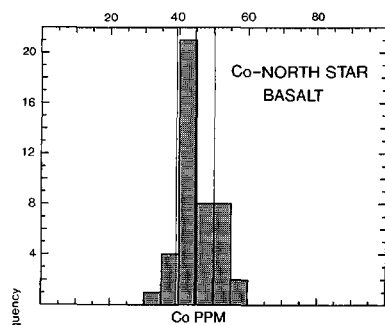
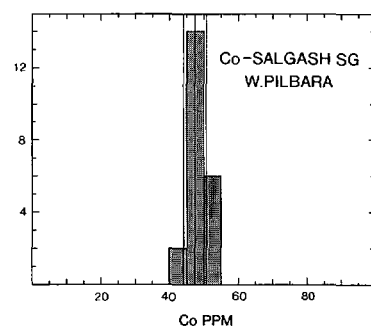
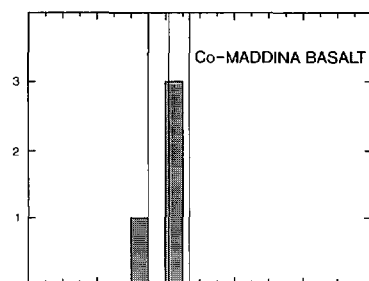
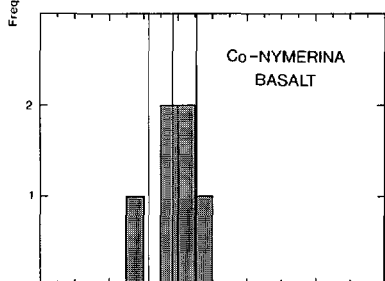
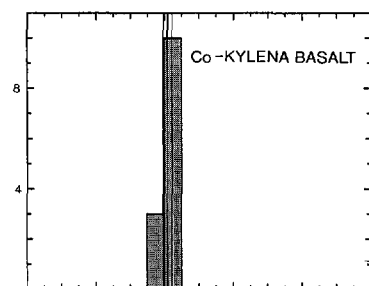
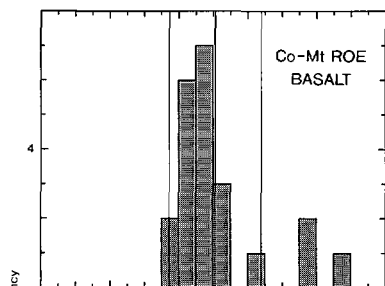
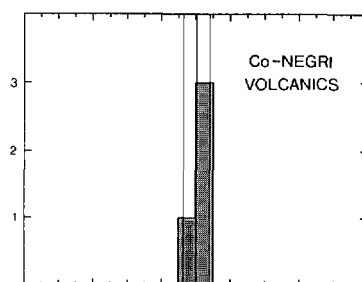
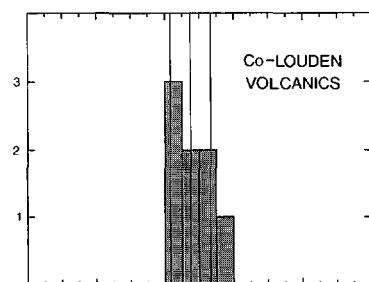
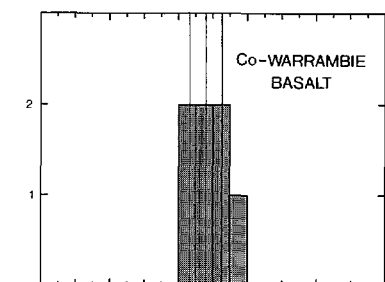


Fig. 4



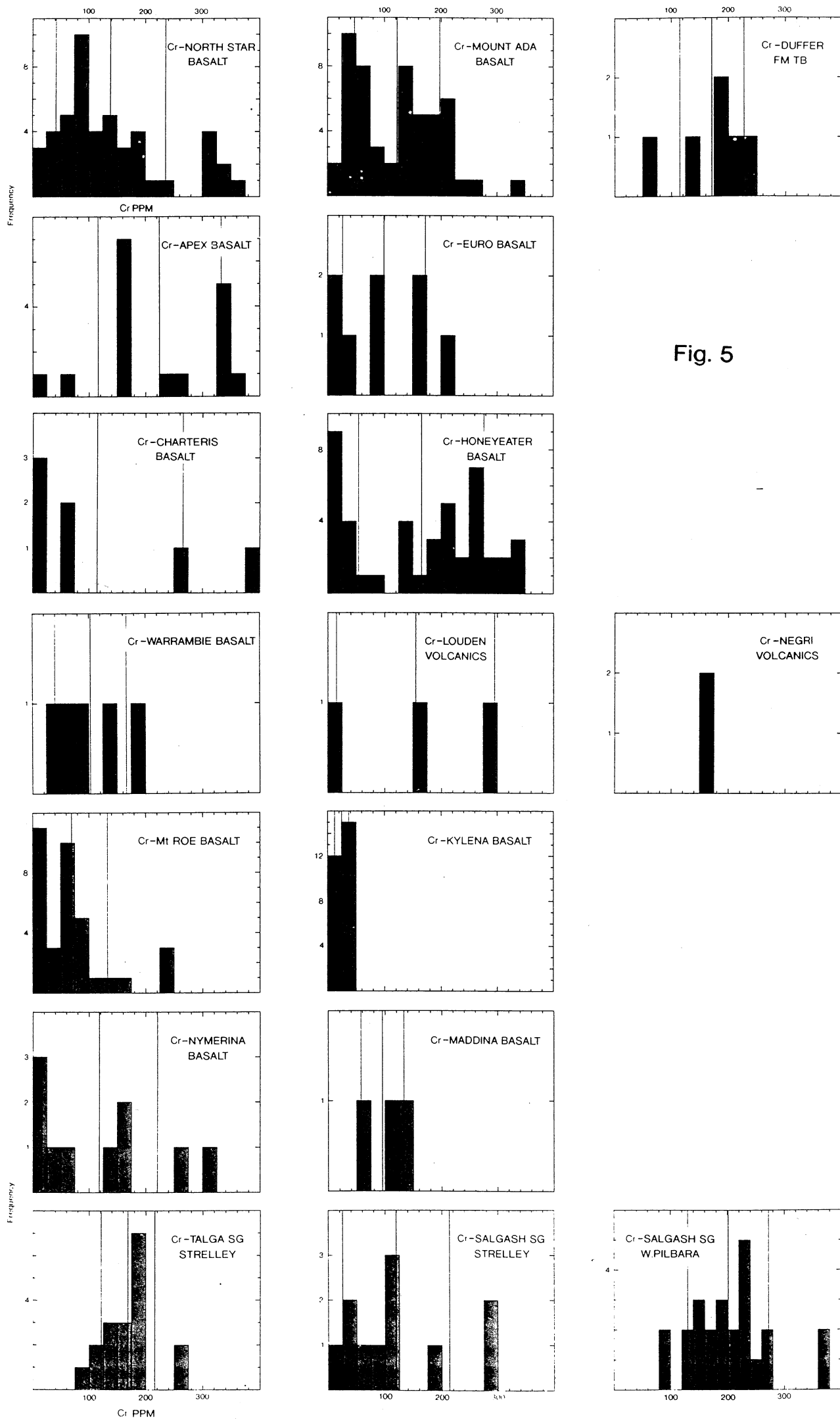


Fig. 5

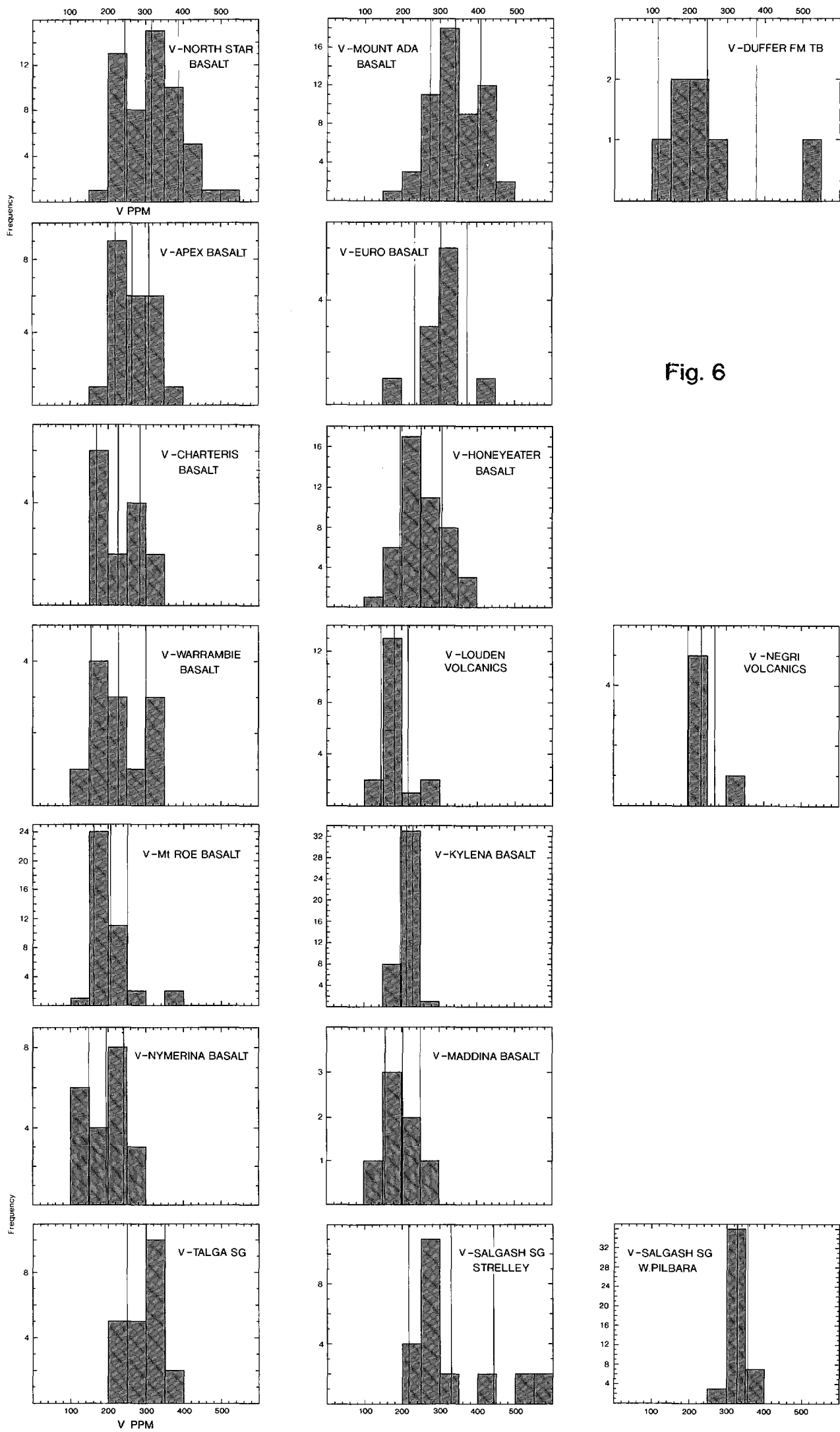


Fig. 6

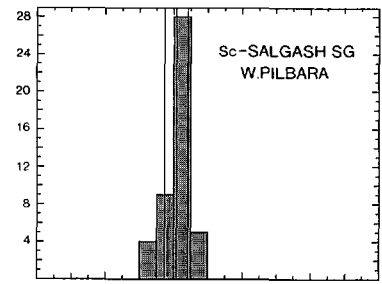
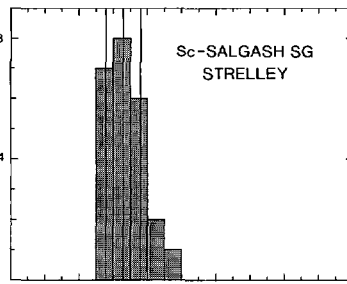
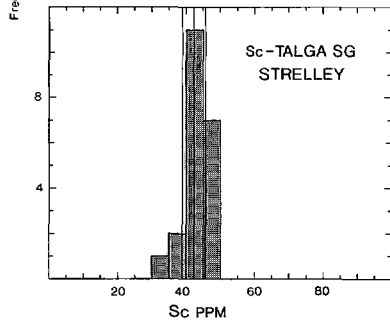
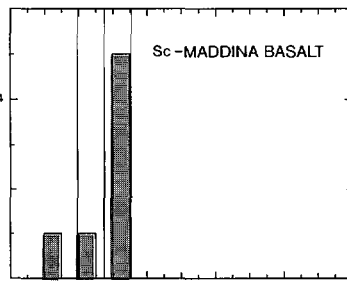
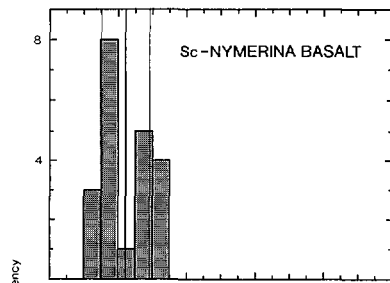
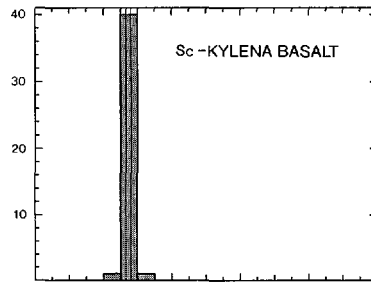
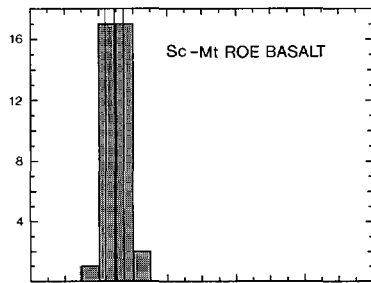
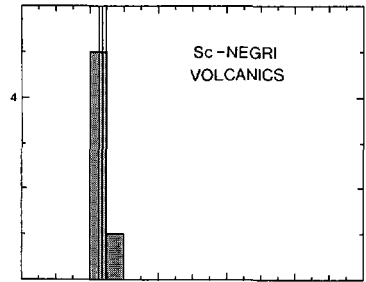
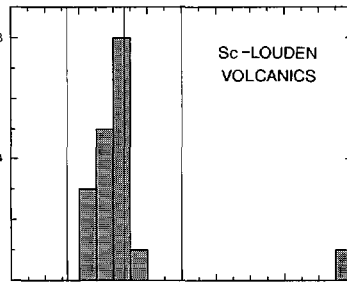
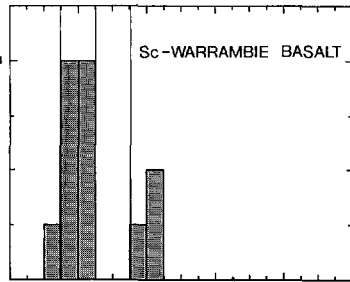
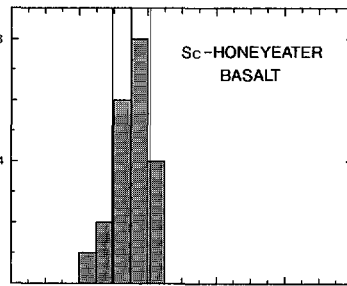
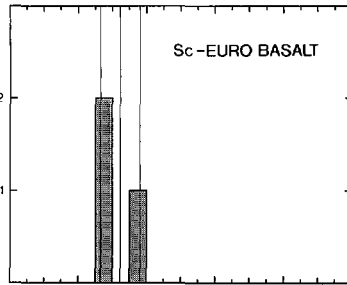
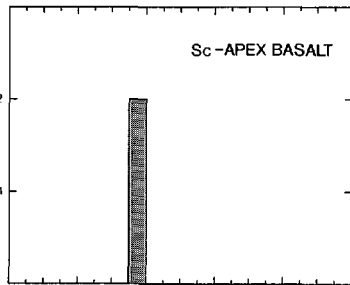
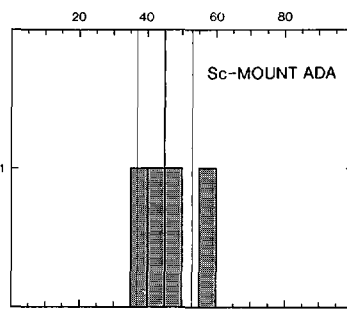
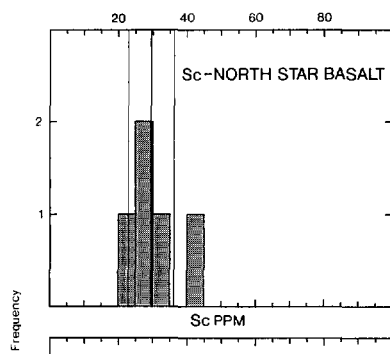


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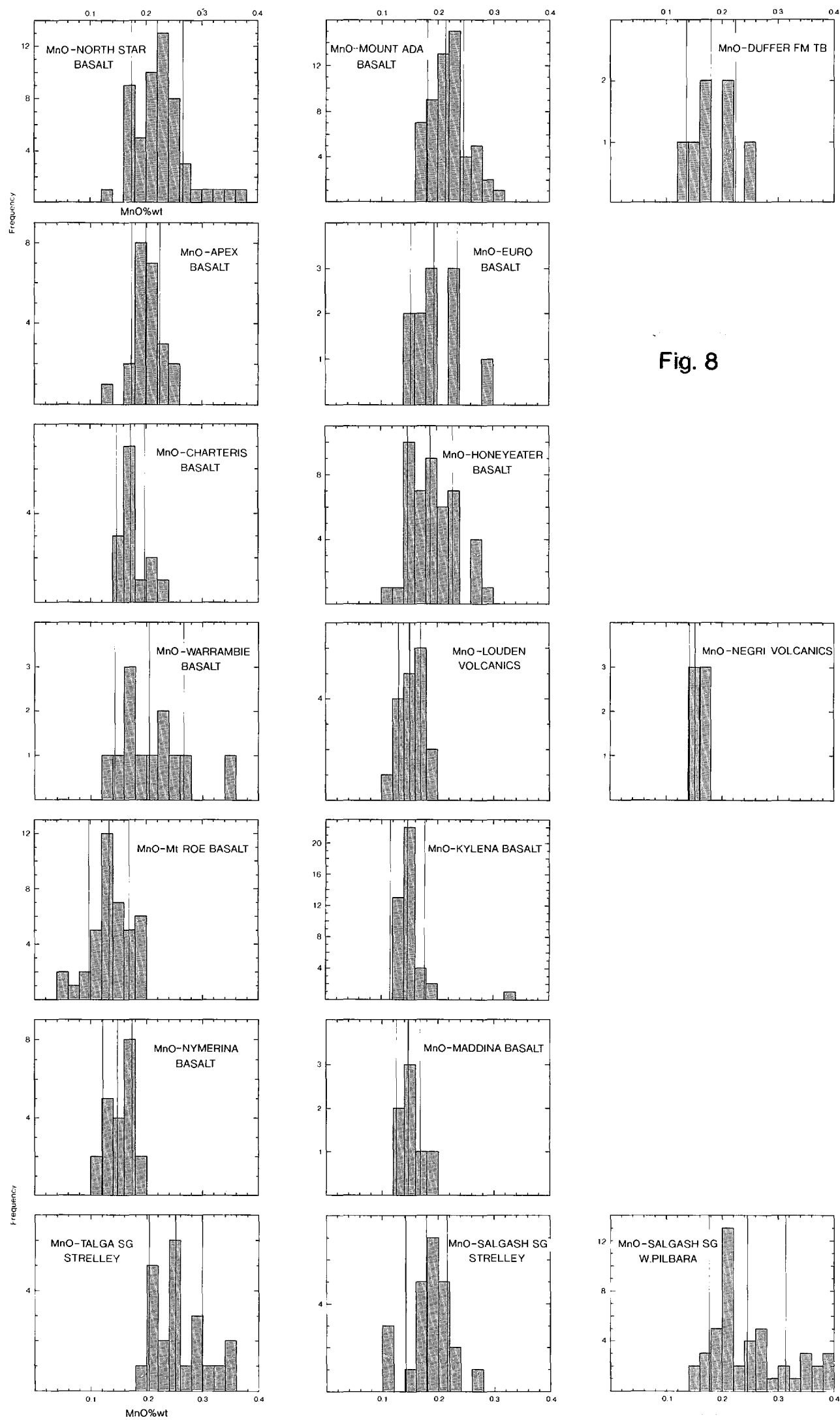


Fig. 8

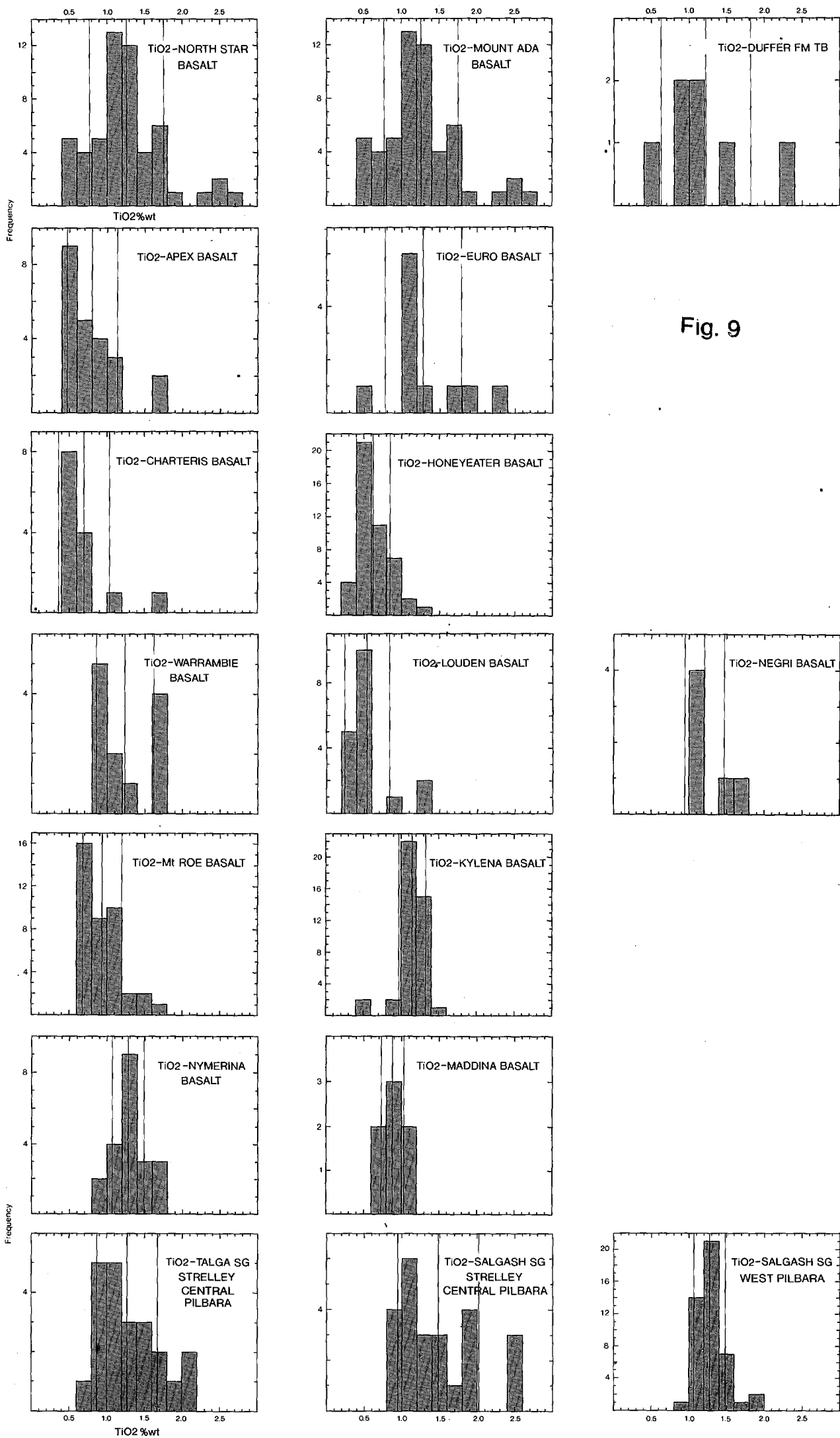


Fig. 9

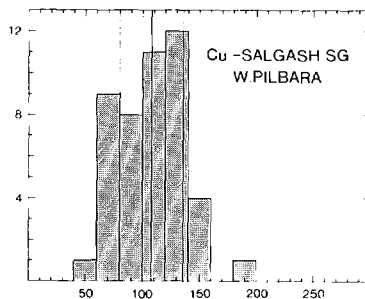
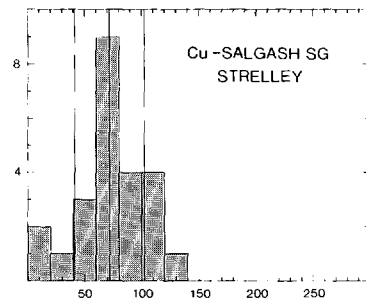
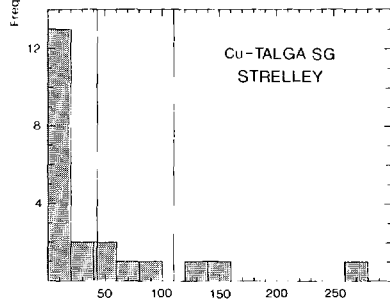
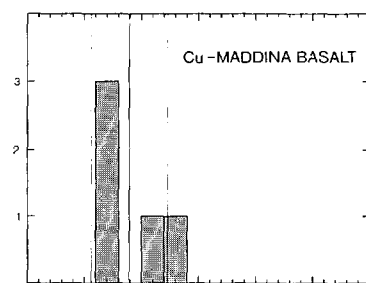
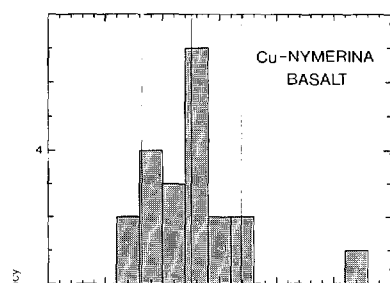
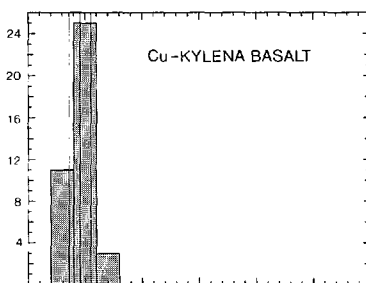
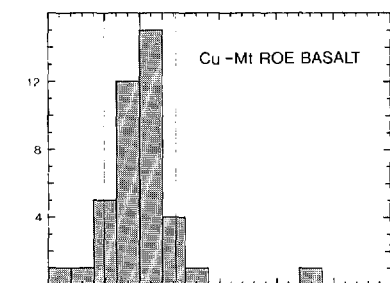
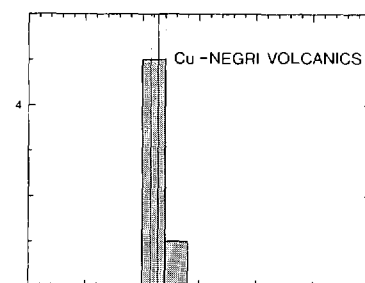
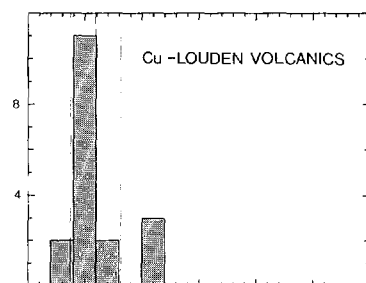
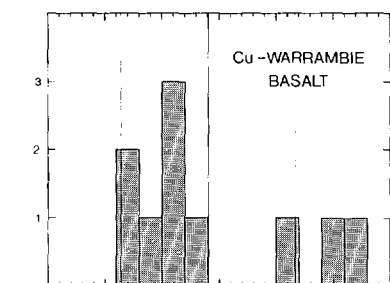
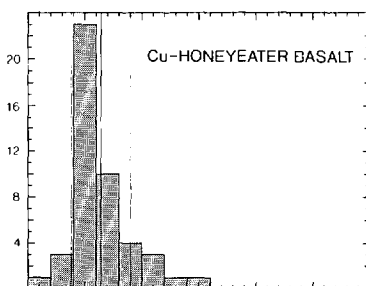
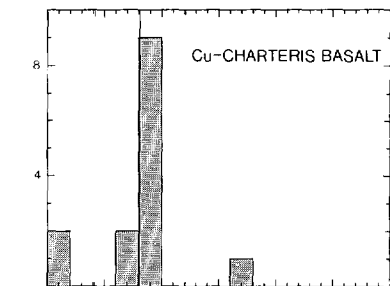
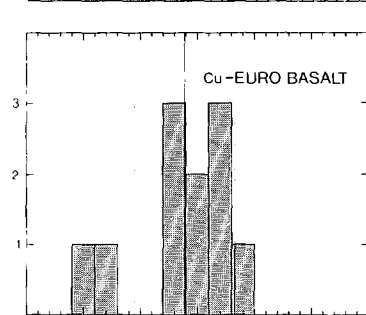
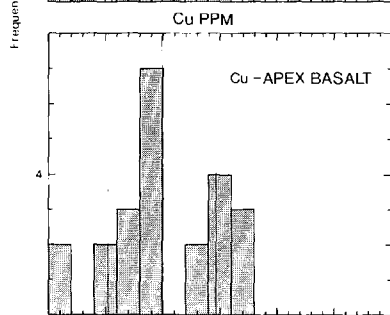
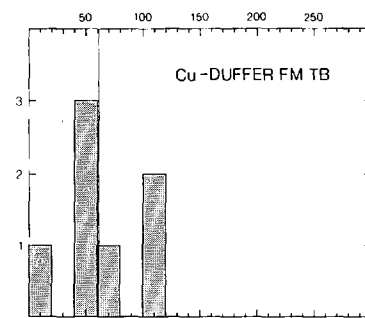
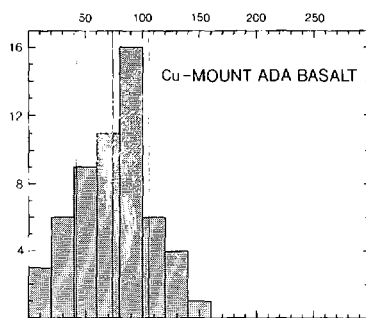
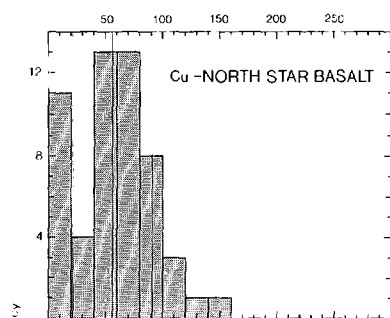


Fig 10

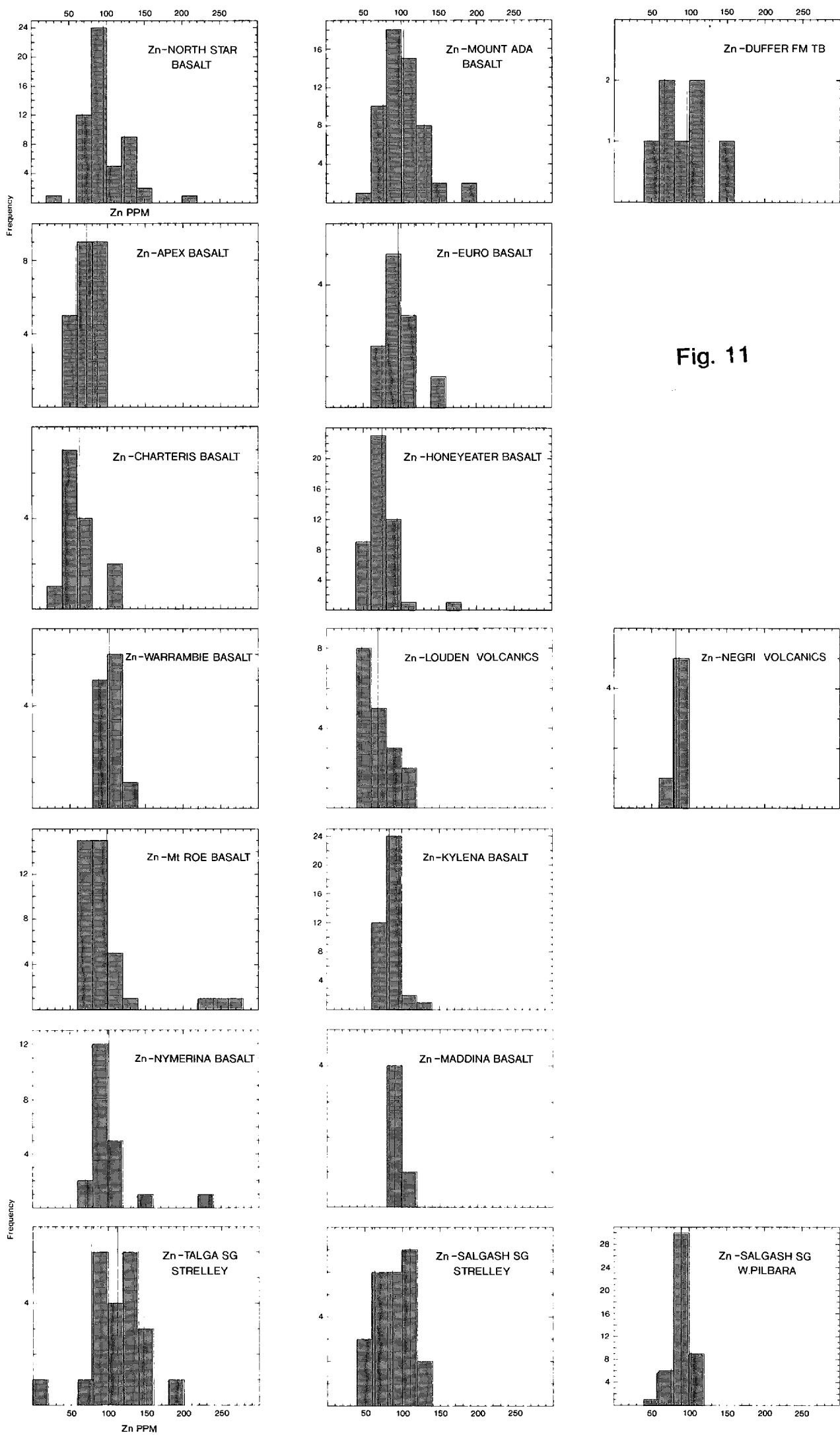


Fig. 11

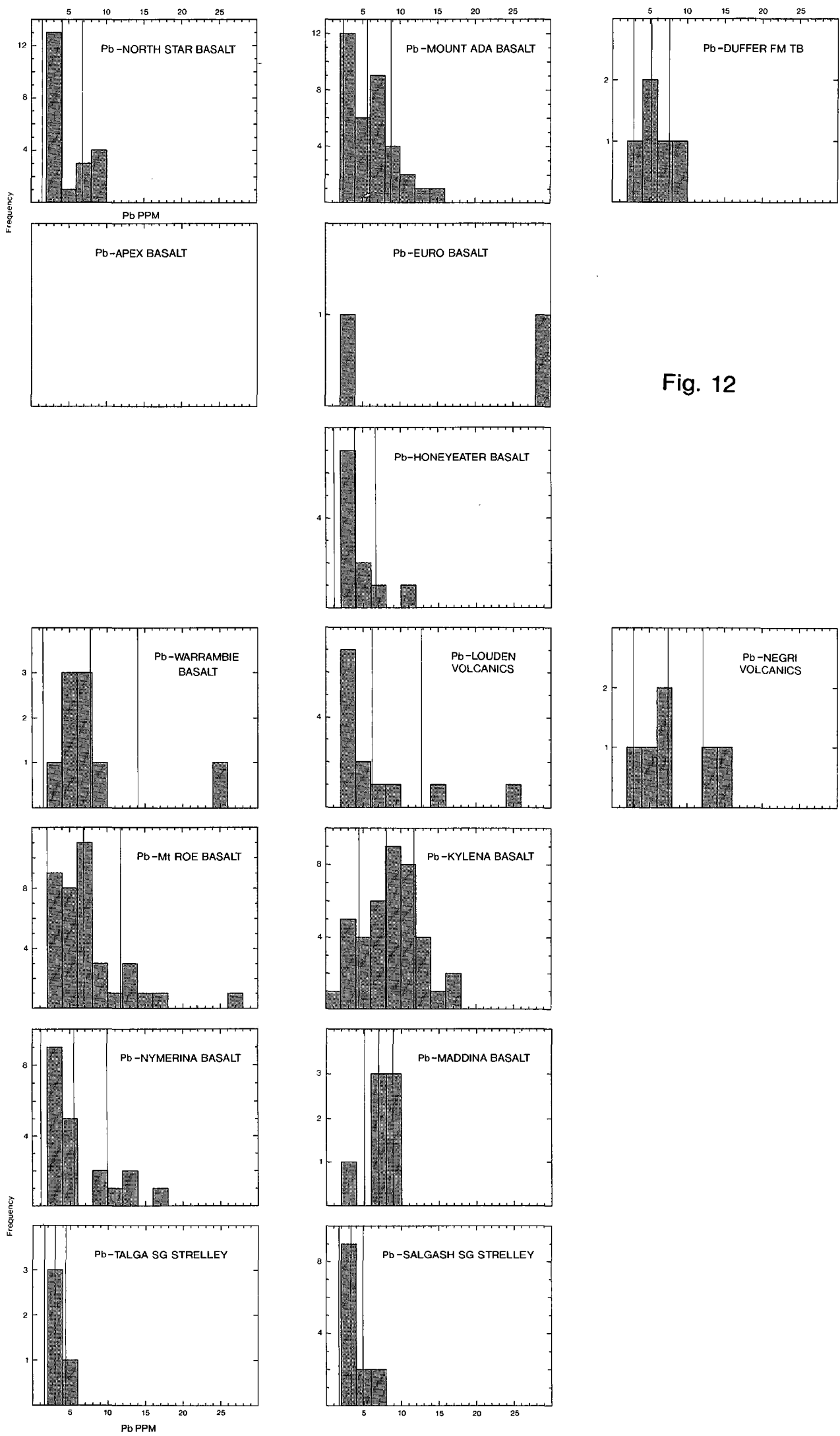


Fig. 12

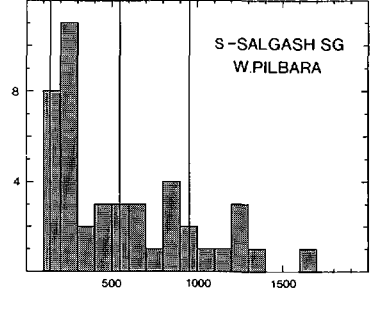
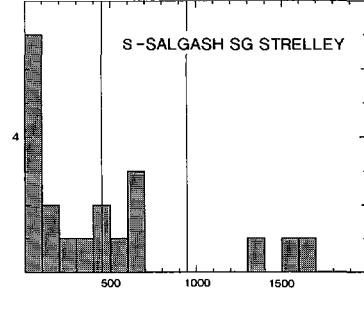
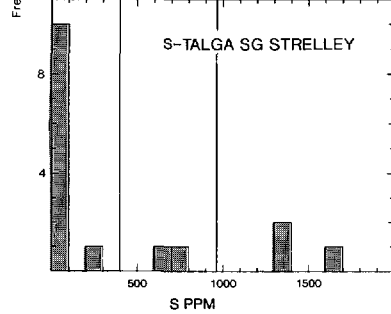
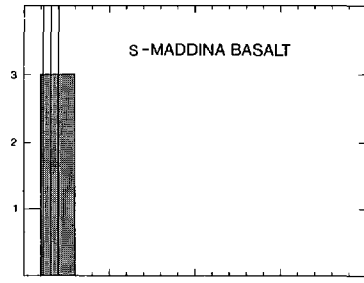
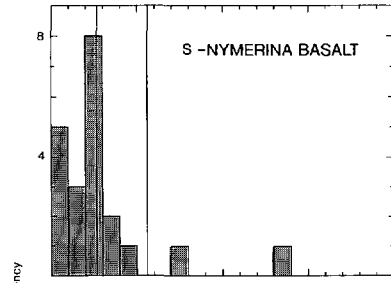
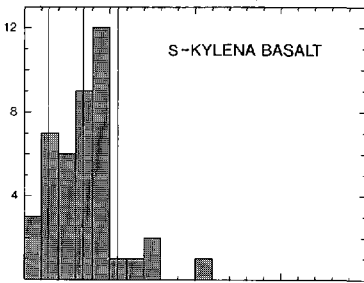
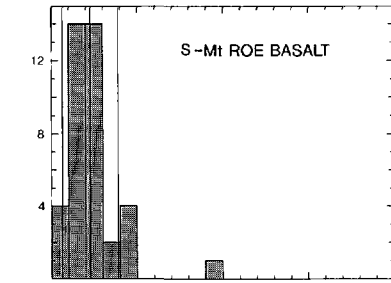
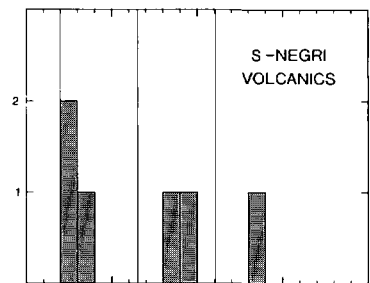
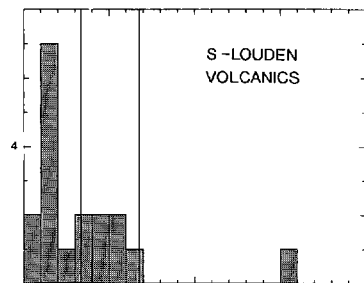
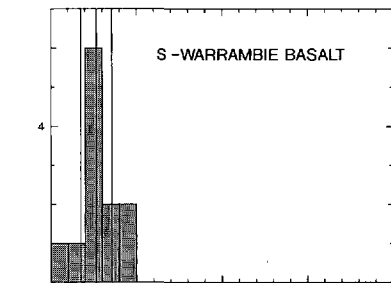
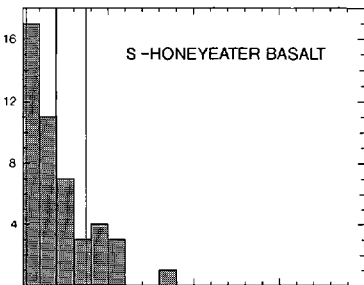
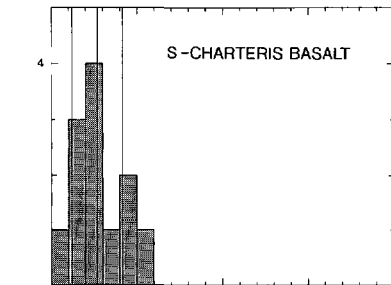
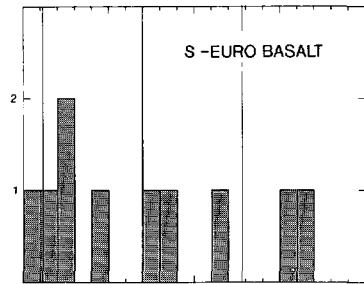
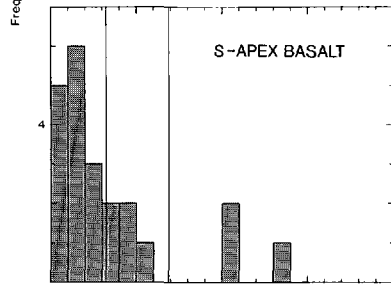
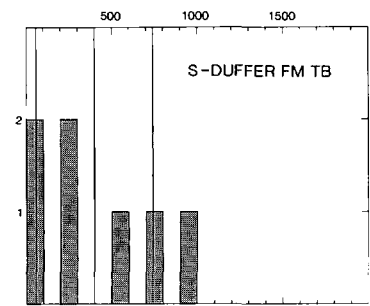
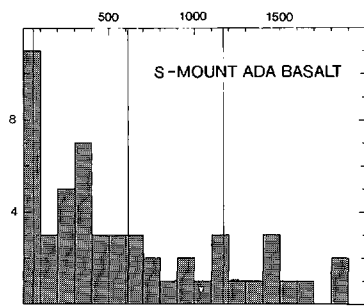
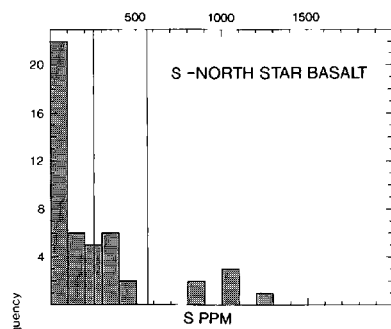


Fig. 13

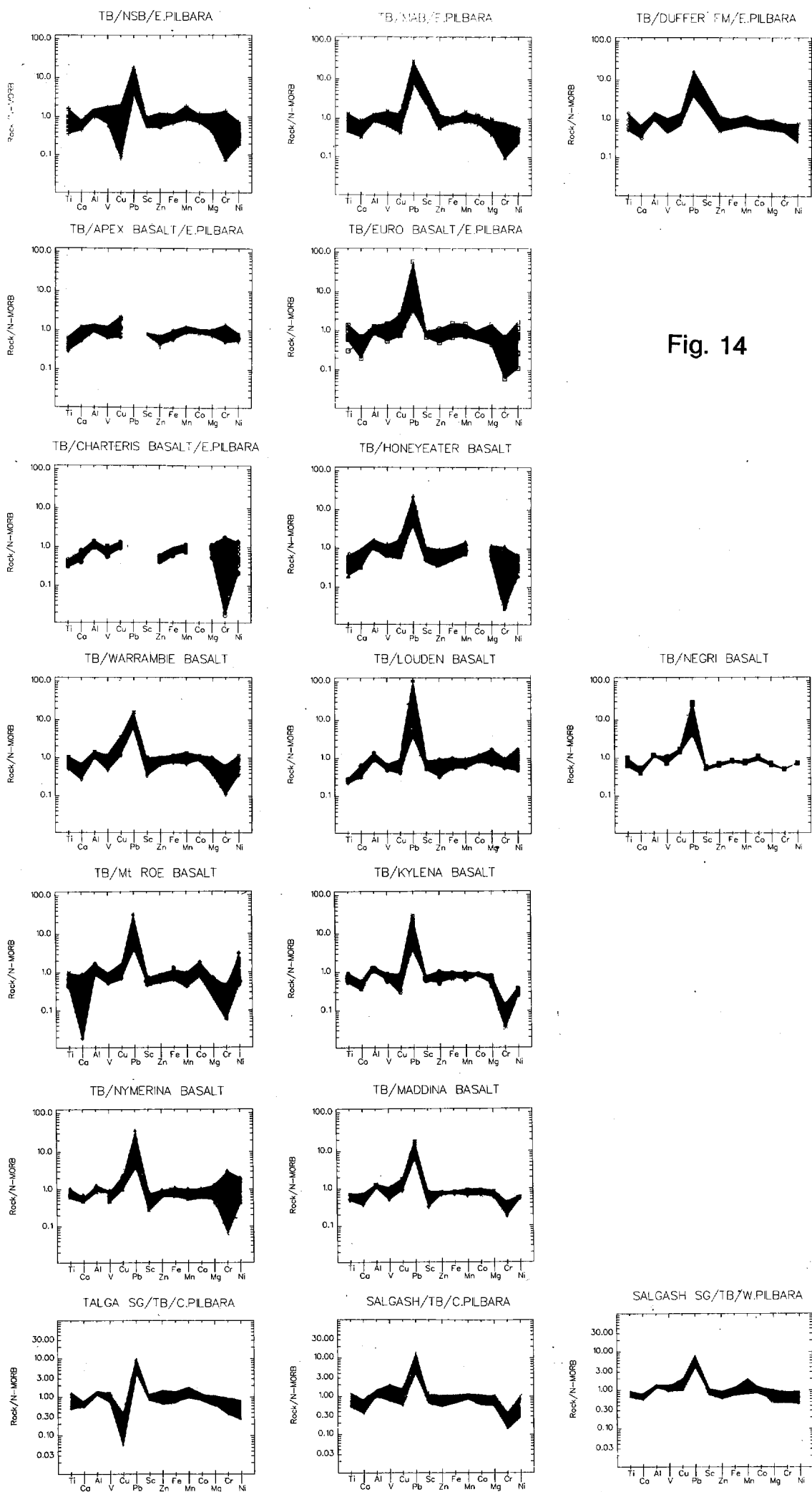


Fig. 14

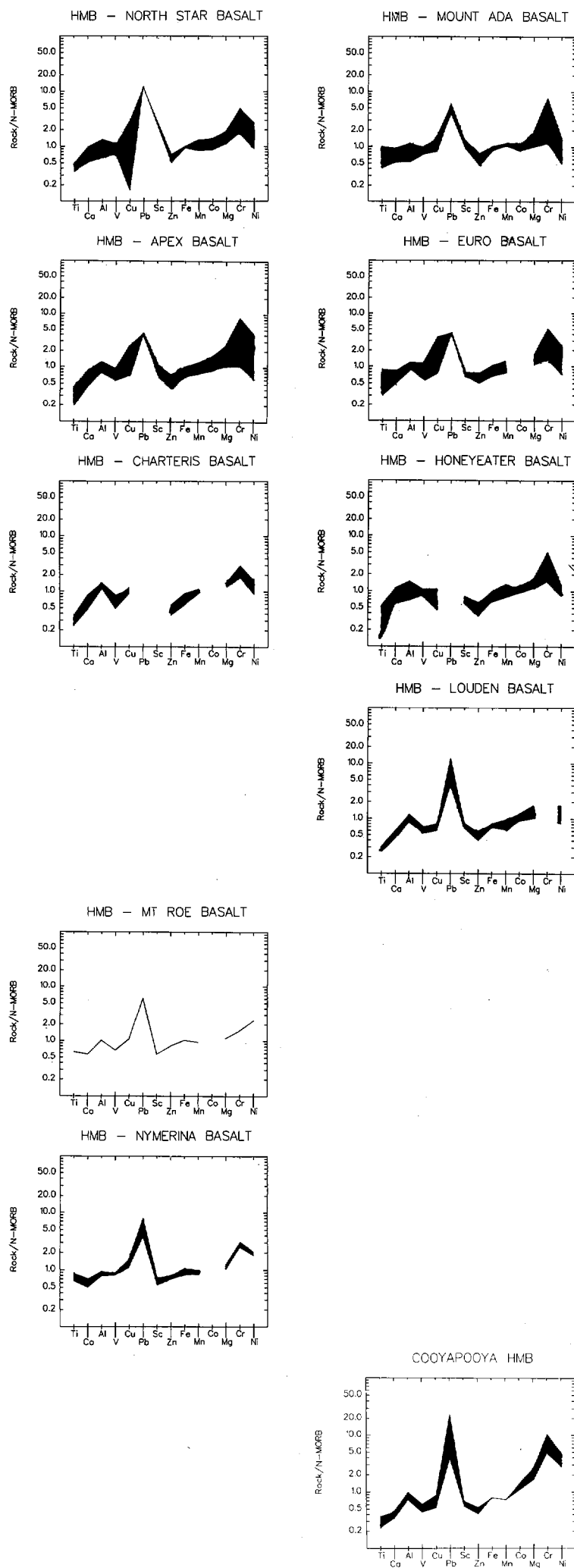


Fig. 15

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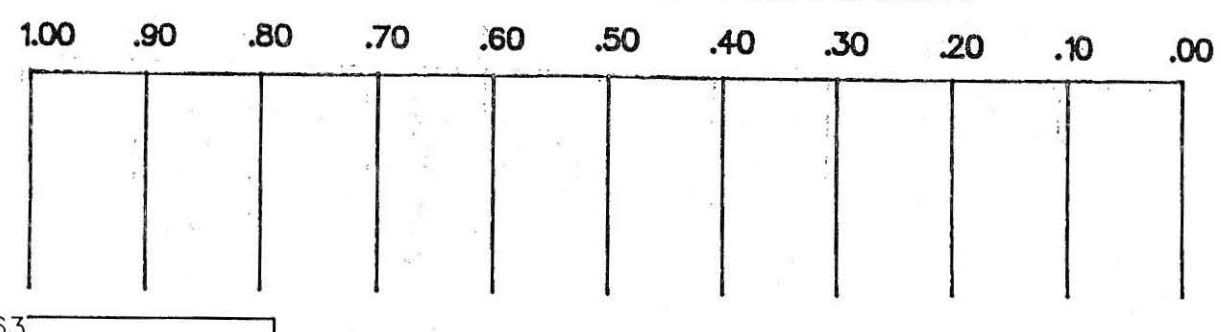


Fig. 16

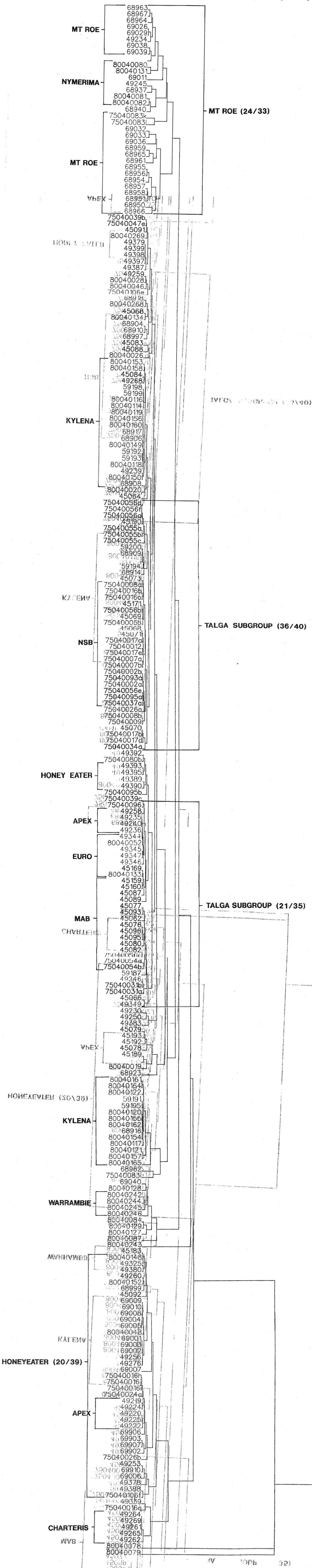


Fig. 17a

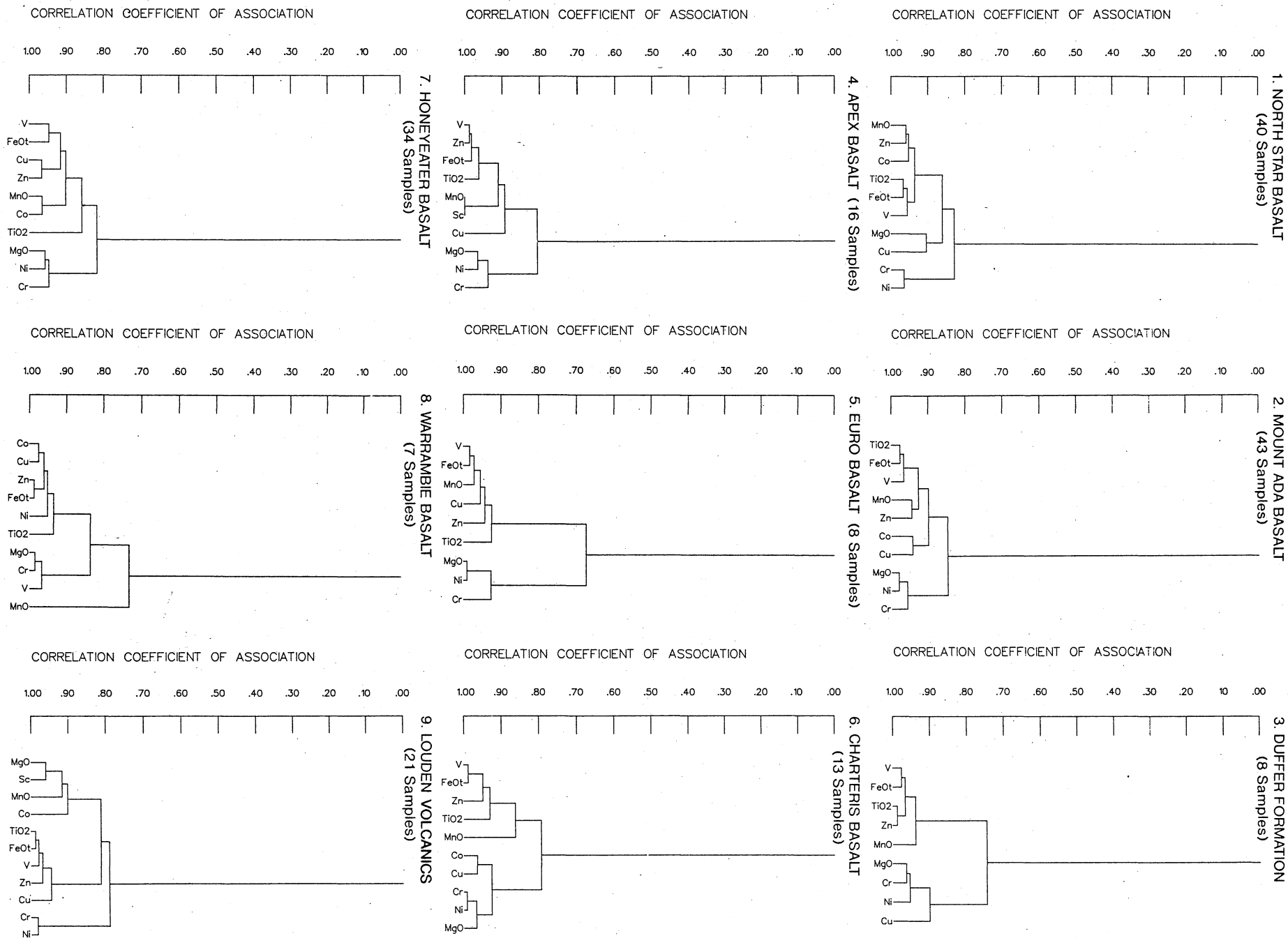


Fig. 17b

