ELEMENT PARTITIONING AND THERMOBAROMETRY IN POLYMETAMORPHIC LATE ARCHEAN AND EARLY-MID PROTEROZOIC ROCKS FROM EASTERN LIAONING AND SOUTHERN JILIN PROVINCES, PEOPLE’S REPUBLIC OF CHINA*

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ABSTRACT. Quartzofeldspathic orthogneisses and a largely supracrustal section dominated by older mafic + ultramafic metavolcanics, with lesser amounts of younger pelitic schists, banded iron formations and marbles, have been subjected to at least three (probably four) stages of Precambrian orogeny and metamorphism in the northeastern portion of the Sino-Korean platform. The earliest recognizable event produced Late Archean, low-grade granulite/high-grade amphibolite facies assemblages, whereas Early Proterozoic recrystallizations generated low-rank amphibolites + greenschists, and Mid Proterozoic orogeny resulted in anchim metamorphic to greenschist facies associations. Most rocks exhibit effects of polymetamorphism, but individual specimens preserve the dominant phase configuration of each of the recrystallizations.

Samples lacking mineral zonations and replacement textures were selected for microprobe study. Systematic major element fractionations between coexisting clinopyroxene, amphibole, and layer silicates suggest a close approach to chemical equilibrium for the investigated rocks. Sparse low-variance assemblages and a variety of calibrated thermobarometers (garn + cpx; opx + cpx; garn + amph; garn + ru + ilm + sill + qtz; bio + garn; hornblende A1 content; white mica Si content; talc + cc + qtz + trem) allow assignment of the peak conditions of metamorphism: Late Archean = 700° ± 50°C, 5 to 7 kb, relatively low aH2O; Early Proterozoic = 500° ± 100°C, 4 to 6 kb; Mid Proterozoic = 400° ± 50°C, 1 to 3 kb, intermediate to high aH2O.

Moderately thick sialic crust (a minimum of 20 to 25 km) characterized by a thermal gradient comparable to a modern volcanic island-arc or continental-margin setting was present in the northeastern Sino-Korean shield as early as 2.7 to 2.8 by ago. Orogenies of progressively lesser intensities affected the region episodically over the next billion years, but the craton has behaved as a coherent block since Mid Proterozoic time.

INTRODUCTION

Eastern China consists of two polymetamorphic Precambrian nuclei, the Sino-Korean and Yangtse platforms, surrounded by later Phanerozoic fold belts (Huang, 1978, 1980). Figure 1 presents general geologic relations for this Circumpacific region. Miyashiro (1981) postu-

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Fig. 1. Regional tectonic setting of east Asia, showing continental margins and present-day convergent plate junctions, largely after Hamilton (1979), Li and others (1982) and Lee (1984). Precambrian cratons are indicated by dashed and ruled patterns; Phanerozoic granitoids are indicated in black. The area east of Bohai Bay and directly north of the Korean peninsula is the study area (rectangle defines area of fig. 2).

lated a progressive decrease in age of stabilization for the major Asiatic shields and a decrease in age of orogenic zones toward the Pacific Ocean: Zhang, Liou, and Coleman (1984) disputed this relationship, and Klimetz (1983) presented evidence that assembly of eastern China and amalgamation with the rest of the continental crust-capped Eurasian lithospheric plate was only accomplished in Mesozoic time (see also Li and others 1982). Broad regions in eastern China and nearby western Pacific archipelagos were subjected to felsic volcanic/plutonic igneous activity during Jurassic through Paleogene time (Wu and Qi, 1985;
Zheng, 1985): this widespread thermal event provided a pervasive overprint and partial obliteration of pre-existing Precambrian mineral parageneses. Thus, the cratonic nuclei that constitute the basement of eastern China have had complicated histories.

The northeastern Sino-Korean shield apparently contains the most ancient, well-documented Precambrian rocks in China (see Ma and Wu, 1981). An area of great interest lies directly west of Bohai Bay (Hebei Province) where the oldest radiometric dates have been obtained: here, geochronologic research groups have presented evidence that certain mafic inclusions in tonalitic gneiss formed about 3.3 to 3.5 by ago (CAGS, 1975; ASIG, 1978; Zhong and others, 1984; Jahn and Zhang, 1984; Huang, Bi, and DePaolo, 1986; Jahn and others, 1987—see also Zhu and Chen, 1984, for similar model lead ages). Northeast of Bohai Bay (eastern Liaoning and southern Jilin Provinces), amphibolitic rocks of komatiitic chemical affinities (Xu and Chen, 1984) are associated with tonalitic orthogneisses and charnockites. This region was selected for petrochemical investigation by Ernst, Cao, and Jiang (1988) in order to place such occurrences in a quantitative metamorphic framework: work emphasized the bulk-rock chemistry and sequence of mineral assemblages, because details of the parageneses and petrogenesis of the terrane had not previously been reported. In addition to documenting bulk-rock major element geochemistries and drawing on petrographic studies as well as published and unpublished radiometric data (Y. W. Chen, personal commun., 1984, 1985), the following provisional summary of crustal evolution of southern Jilin and eastern Liaoning Provinces was presented by Ernst, Cao, and Jiang (1988).

Separation of sialic crust from a relatively uniform mantle reservoir apparently began about 3.1 to 3.3 by ago in the northeastern Sino-Korean craton, with evolution of new and recycled materials continuing at least until the end of the Early Proterozoic: a widespread high-rank amphibolite/low-rank granulite facies metamorphic culmination occurred at about 2.8 to 2.9 by. Early Proterozoic dynamothermal events, producing greenschists and low-grade amphibolites, took place at 2.4 to 2.5 and 1.9 to 2.0 by. More feeble, local recrystallization occurred at 1.6 to 1.8 by. Contact metamorphism accompanied widespread Mesozoic calc-alkaline igneous intrusion about 130 to 250 my ago but was not studied by Ernst, Cao, and Jiang (1988).

Microprobe analyses of coexisting silicates and bulk-rock REE analyses from two Early Archean mafic inclusions in tonalitic gneisses from eastern Hebei Province are chemically similar to supracrustal lithologies analyzed in southern Jilin and eastern Liaoning Provinces (Ernst, in review). Although petrologic/crystallochemical similarity does not constitute proof, it supports the possibility that analogous 3.3 to 3.5 by old mafic protoliths exist in the study area as well: thus far, however, radiometric dating has not produced evidence of such ancient crust in Jilin and Liaoning Provinces.
REGIONAL GEOLOGY OF EASTERN LIAONING AND SOUTHERN JILIN PROVINCES P.R.C.

Fig 2. General geology of southern Jilin and eastern Liaoning Provinces, showing major lithologies, after Ernst, Cao, and Jiang (1988). Samples are located by dots and corresponding numbers (PRC-prefix omitted).
REGIONAL GEOLOGY

The most ancient, structurally deepest, Archean unit exposed in the northeastern part of the Sino-Korean shield consists of differing proportions of tonalitic gneisses, migmatites, metacharnockites, and lenses of tholeiitic + komatiitic amphibolite and metaperidotite. Many quartzofeldspathic units retain relict pyroxenes, providing evidence of low-rank granulite facies metamorphism, variably back-reacted to lower grade assemblages. The isofacial interlayered mafic + ultramafic units are high-rank amphibolites and hornblendites: paucity of cpx + opx appears to reflect a bulk compositional effect (quartz-normative, amphib-poor quartzofeldspathic rocks versus amphib-rich, silica-undersaturated nature of some mafic and all ultramafic lithologies). Intrusive into this complex and overlying it, metamorphosed to high grade at approx 2.8 to 2.9 by, is a series of younger Archean orthogneisses, supracrustal amphibolites, greenstones, felsic gneisses, and banded iron formations (BIFs). This entire series, plus the underlying gneiss complex, was recrystallized to low-rank amphibolite facies assemblages during the 2.4 to 2.5 by orogeny.

Lower Proterozoic rocks include layered schists, paragneisses, Mg-rich marbles, and BIFs which, in general, are better stratified and more continuous than Archean analogues. Metamorphic intensity during the 1.9 to 2.0 by orogeny was confined to epidote amphibolite and lower grades. Resting with angular unconformity on the Lower Proterozoic complex is a great prism of feebly metamorphosed and weakly deformed, well-ordered strata, consisting of carbonates, shales/slates, BIFs, and rare volcanics. These rocks in aggregate span the time interval 800 to 1950 my (Chen and others, 1981). The oldest portion of this chemically mature section was affected by the 1.6 to 1.8 by event: highest grade metamorphic assemblages produced were of the green-schist facies, but most rocks are less intensely recrystallized.

Regional geologic relationships are shown in figure 2. Southern Jilin and eastern Liaoning localities were investigated and sample numbers are indicated: PRC-prefixes are omitted in text, illustrations, and app. tables for brevity. Descriptions of the lithologic sections, general geology, and chemical petrology of the studied areas were presented by Ernst, Cao, and Jiang (1988).

METAMORPHIC MINERAL PARAGENESSES

One hundred-six specimens from 61 localities were examined microscopically. Major rock types are: (A) quartzofeldspathic orthogneisses (tonalitic gneisses, granulites/charnockites, metagranites); (B) mafic + ultramafic amphibolites (metamorphosed tholeiitic, komatiitic, and serpentinitic units); (C) magnetite quartzites/BIFs; and (D) paragaschists/paragneisses. Amphibolites can be subdivided into hornblende ± plagioclase- and talc ± serpentine-rich varieties, and paragaschists/paragneisses into marbles and pelitic schists. Quartzofeldspathic and mafic +
### Lithology

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### Fig. 3. Schematic composite mineral parageneses in southern Jilin and eastern Liaoning Provinces for metamorphic episodes at approx 2.8 to 2.9, 2.4 to 2.5/1.9 to 2.0, and 1.6 to 1.8 by ago, after Ernst, Cao, and Jiang (1988). Major phases are indicated by solid lines, accessory or less commonly present phases by dashed lines. Mineral assemblages for four principal lithologies are represented: (A) quartzofeldspathic; (B) mafic + ultramafic; (C) magnetite quartzite (BIF); and (D) pelitic + calcareous.
ultramafic lithologies dominate the Precambrian section of southern Jilin and eastern Liaoning Provinces.

Textural relations allow the relative sequence of mineral assemblage production to be established for the investigated rocks. The earliest, low-rank granulite facies/high-rank amphibolite facies phase compatibility preserved includes pyroxene-bearing quartzfeldspathic rocks, but few of the associated mafic and none of the metasedimentary supracrustal assemblages contain either opx or cpx; however, several metapelitic rocks contain sillimanite and/or garnet. The apparent difference in grade is probably a result of contrasting bulk-rock chemistries, the occurrence of cpx and opx versus amph being a function of silica saturation (Spear, 1981). Rocks metamorphosed under high-grade conditions during Late Archean time have been overprinted to a greater or lesser extent, first by amphibolite facies mineral assemblages, then variably retrograded during several episodes of Proterozoic metamorphism to epidote amphibolite, greenschist, and, probably, prehnite-pumpellyite to anchimetamorphic facies. Individual rocks, however, have retained mineral assemblages characterizing each of the orogenies. Insofar as can be determined, sections affected by the various metamorphic events are spatially coincident in southern Jilin and eastern Liaoning Provinces. A composite paragenetic diagram is illustrated in figure 3.

Significant contrasts in metamorphic mineral assemblages are recognized for the several rock types. Pyroxenes, monoclinic(?) K-feldspar, sillimanite, and almandine + pyrope-rich garnet seem to have been produced only during the 2.8 to 2.9 by recrystallization event. In lithologies affected by later orogenies, the K-feldspar is triclinic, and the nearly ubiquitous plagioclase tends to be more albite, as amphibole concomitantly changes from paragasitic-hastingsitic toward actinolitic chemistry. Early red or red-brown, titaniferous biotite trends toward lower Ti, olive-brown and green analogues. White mica becomes more celadonitic, and epidote grades to more pistacitic compositions in phase assemblages produced during the 2.0 to 2.5 by metamorphic episodes. Hematite, green biotite, and prehnite are confined to mineral associations formed in the 1.6 to 1.8 by recrystallization.

**MINERAL CHEMISTRY**

Coexisting phases from specific rocks were analyzed employing conventional electron microprobe techniques. After petrographic examination, samples were selected that were free from detectable alteration and weathering; an attempt was made to investigate only assemblages that show no evidence of chemical disequilibrium (replacement textures, zoning, and cetera). Whether microprobed samples represent stable metamorphic phase configurations or not remains an open question, but the general lack of zoning, mineral homogeneity, similar compositions of a phase from a particular rock type over its geographic distribution range, and systematic partionings of major
Fig. 4. Atomic proportions of cations in analyzed clinoamphiboles from the studied rocks (app. table A). Symbols for figures 4 to 15 are as follows: open circles = charnockites, tonalitic gneisses, metagranites; asterisk = mafic inclusion in orthogneiss; open triangles = amphibolites (metagabbro indicated as g); filled triangles = metakomatiites/ultramafics; and dots = metasedimentary rocks and paragneisses. (A) Cations occupying M(4).+ A structured sites; Mg + Fe are the major M(4) constituents in the grunerite. (B) Al^IV and Al^VI proportions.
elements between coexisting phases (next section) lend credence to the idea of a close approach to equilibrium during each metamorphic event. However, local mineral zonation, chloritic alteration, and the presence of two compositionally distinct populations of white mica in an orthogneiss (42b) and of chlorite in a pelitic schist (56) testify to the effects of incomplete overprinting in a few samples.

Microprobe techniques do not allow the distinction of ferrous and ferric iron, so in the mineral description and element partitioning studies, all iron is considered as ferrous for amphibole, pyroxenes, biotite, white mica, chlorite, talc, serpentine and garnet and as Fe₂O₃ for plagioclase and epidote. Although reasonable for most analyzed minerals, as indicated by a close approach of cation proportions to stoichiometric values, this approximation is probably too simplistic for some amphiboles and white micas, which may contain subequal amounts of Fe²⁺ and Fe³⁺.

For investigated phases, 4 to 6 spot analyses were obtained and averaged where nearly identical: in all cases, core and rim values were obtained, and where dissimilar, both are indicated. Analytical data are presented as app. tables A to H.

**Clinoamphiboles**

Twenty-eight clinohornblende analyses are listed in app. table A. As demonstrated by analyses from different parts of the thin section for sample 9, phase chemistry does not vary significantly from grain to grain; moreover, several detectably zoned core-rim pairs, 17d, 24, 27a, and 48c, display quite insignificant chemical contrasts. For the metagabbro, 17d, and two metakomatites, earlier aluminous hornblende is armored and replaced by more nearly endmember tremolite-actinolite. For BIF sample 24, the zoning is slight but in the reverse sense to that described above. Another specimen of meta-iron formation, 50b, contains an apparent equilibrium pair, hastingsitic hornblende + grunerite.

Although a spectrum of compositions exists, amphiboles cluster in three groups irrespective of rock type. The atomic proportions of K, Na, and Ca, and both Al⁴⁺ and Al⁶⁺

![Diagram](image)

Fig. 5. Atomic proportions of Ca, Mg, and Fe (Wo, En, and Fs) for analyzed pyroxenes from the studied rocks (app. table B). Symbols conform to usage of figure 4. Tie line links compositions of coexisting cpx and opx.
are illustrated in figure 4. Relatively potassium-rich pargasitic-hastingsitic hornblende characterizes the charnockitic and gray tonalitic gneisses; in such rocks, the mole fraction of iron in amphibole, X_{Fe}, ranges from 0.27 to 0.58. Interestingly, compositions of aluminous, iron-rich calcic amphibole from a quartzofeldspathic orthogneiss (28a) and that of the associated mafic inclusion (28) are virtually indistinguishable. Hornblende in a chemically evolved amphibolite, 34e, is similarly hastingsitic. In contrast to these lithologies, mafic amphibolites carry an actinolitic hornblende or actinolite, the Fe/(Fe + Mg) ratio of which is very low for rocks believed to represent metamorphosed komatiitic basalts (ranging from 0.19–0.28) and komatiite (X_{Fe} = 0.08–0.21). Hornblends from quartzofeldspathic gneisses and granulitic rocks also contain more TiO_{2} (av about 1.31 wt percent) than those from metamafic rocks (av about 0.29 wt percent).

**Pyroxenes and Olivine**

Analyses of six clinopyroxenes, two orthopyroxenes, and an olivine are listed in app. table B. Clinopyroxenes are only slightly subcalcic, low-Ti members of the diopside-hedenbergite series. The pyroxene quadrilateral is shown in figure 5. Four of the cpx from charnockitic rocks have closely similar X_{Fe} values of 0.31 to 0.32; the other is more iron rich at X_{Fe} = 0.44. The clinopyroxene from an amphibolite is characterized by an X_{Fe} of 0.19, reflecting the substantially more magnesian nature of the metakomatiitic basalt protolith.

Hypersthene in equilibrium with clinopyroxene from a granulite gneiss has an Fe/(Fe + Mg) ratio of 0.44. The orthopyroxene from a metabasalt of komatiitic affinities is very low in Al_{2}O_{3} (0.60 wt percent) and has an X_{Fe} of 0.35. The analyzed olivine from a komatiitic metaserpentinite is Fa_{17}, judging by its irregular, anhedral boundaries, it is evidently a relic of the original igneous assemblage rather than a neoblastic metamorphic phase. Its relatively high X_{Fe}, and important traces of Mn support the interpretation of high-temperature origin for the olivine.

![Graph](image)

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Fig. 6. Atomic proportions of Ti and X_{Fe} for analyzed biotites from the studied rocks (app. table C). Symbols conform to usage of figure 4.
Micas and Talc

Analyses of 21 biotites, 10 muscovites, and 4 talcs are provided in app. table C. Biotites from three charnockites, a felsic orthogneiss + its mafic inclusion, several other tonalitic gneisses, and an Archean metagranite are red or red-brown in color and contain about 3 to 6 wt percent TiO₂; iron contents are relatively high, with XFe ranging from 0.38 to 0.74. Variably retrograded granulitic gneisses and three mafic amphibolites contain olive-green biotite (TiO₂ = 1 to 2 wt percent; XFe = 0.27 to 0.45). Proportions of Ti and XFe are illustrated in figure 6 for the quartzofeldspathic, metasedimentary, and mafic + ultramafic rocks. An indistinct, positive correlation may exist between Ti content and the Fe/Fe + Mg ratio in the analyzed biotites, as noted by Guidotti, Cheney, and Guggenheim (1977).

The single analysis of a green, low-titanium biotite from a banded iron formation (24) possesses a puzzling deficiency in K₂O. This specimen was also analyzed for Bₐ, but none was detected. Repeated analyses yield a consistent composition, so if this analysis represents a mixture of biotite + chlorite, interlayering is regular on the scale of the effective microprobe beam diameter, 2μ. However, separate flakes of chlorite were not detected by microscopic examination of this rock. Substitution of part of the alkali by hydronium ion, H₃+, in the large interlayer cation site is another possibility but would not as clearly explain the computed biotite cation proportions.

Figure 7 demonstrates that TiO₂ is distributed systematically between coexisting biotite and calcic amphibole, with the former concentrating Ti relative to the latter. The

![Graph showing the distribution of TiO₂ in biotite and amphibole](image)

Fig. 7. Titania contents in coexisting analyzed clinoamphiboles and biotites from the studied rocks (app. tables A and C, respectively). Symbols conform to usage of figure 4. Tie line links compositions of coexisting hornblende and grunerite.
Fig. 8. Atomic proportions of Si and Fe + Mg for analyzed white micas from the studied rocks (app. table C). Symbols conform to usage of figure 4. Dashed line links compositions of white micas inferred to have been produced at two different P-T stages in 42b.

Fig. 9. Atomic proportions of silicon and iron per formula unit for analyzed chlorites from the studied rocks (app. table D). Symbols conform to usage of figure 4. Dashed line links compositions of two different P-T stages (inferred) of chlorite production in 56.
grunerite structure evidently disfavors Ti strongly in comparison with either biotite or tremolite-hornblende solid solution.

White micas analyzed from an Archean metagranite, a charnockite, three gneisses, and four paragneisses/pelitic schists are reasonably close to stoichiometric muscovite, with a mole fraction of celadonitic components, \((\text{Mg} + \text{Fe} + \text{Si} - 3.00)/2\), totalling about 0.15 to 0.38, and of paragonite, \(\text{Na}/(\text{K} + \text{Na})\), about 0.02 to 0.07. Phase composition does not appear to be closely correlated with bulk-rock chemistry. Silicon and \(\text{Fe} + \text{Mg}\) proportions are illustrated in figure 8. The divalent cation occupancy of octahedral sites in white micas appears to be about twice the excess of Si over 3.00, indicating that the substitution is not strictly the Tschermaks exchange, and involves trioctahedral solid solution and/or interlayer cation deficiency.

Perhaps of more interest is the observation that relict white mica (42b-Ms) from a tonalitic orthogneiss is comparable in chemistry to the four analyzed pelitic schist muscovites, whereas texturally indistinguishable phengitic mica (42b-Ms') in the same orthogneiss is similar to the more celdonitic micas of the other gneisses, the metagranite, and the charnockite. Apparently phengitic white mica represents a retrograde phase in most of the more deeply buried Early Proterozoic high-rank metamorphic rocks (mole fraction of paragonite in white mica \(\approx 0.02\)) but more nearly reflects the P-T peak of attendant physical conditions for the paragachs (mole fraction of paragonite \(\approx 0.05\)) metamorposed at shallower depths in Mid Proterozoic time. Because of similar low variance phase assemblages, these crystallochemical contrasts seem to be a function of different P-T conditions of recrystallization rather than reflecting disparate bulk-rock compositions. Paragonite was not detected in any of the studied specimens.

**Fig. 10.** Atomic proportions of 8-fold coordinated cations for analyzed garnets from the studied rocks (app. table E). Symbols conform to usage of figure 4.
Four samples of talc were analyzed—two from metakomatiites, one from a marble, and one from a banded iron formation. As shown in app. table C, the first three are virtually stoichiometric Mg$_3$Si$_4$O$_{10}$(OH)$_2$, whereas the BIF specimen represents a homogeneous 50:50 solid solution with minnesotaite.

**Chlorite and Serpentine**

Of the 13 analyzed chlorites presented in app. table D, samples from a komatiitic metabasalt, 14c, and a metakomatiite, 48c, possess rather low X$_{Fe}$ values of 0.28 and 0.12 respectively, compared to chlorites from charnockites, high-grade metagranitic rocks, a metagabbro, and a mafic inclusion in orthogneiss (X$_{Fe} = 0.33$ to 0.92). Analyzed chlorites, all apparently Proterozoic in age, exhibit a broad range of chemical variations as shown in figure 9. Chlorites from mafic amphibolites are highly magnesian, whereas those from quartzofeldspathic rocks tend to be pychonochlorites and rigidolites. Chloritites from metasedimentary rocks are chemically quite diverse, and for biotite-zone pelitic schist 56, different analyses suggest the possibility of either disequilibrium or localized domain equilibrium.

An analyzed serpentine mineral is from a rock that was probably a komatiite, now thoroughly hydrated. The exceedingly low iron content (X$_{Fe} = 0.04$) is characteristic of serpentines worldwide.

**Garnet and Tourmaline**

Analyses of garnets from an Archean metagranite, four gneisses, and a BIF are listed in app. table E. They are unzoned and chiefly almandine ± spessartine ± grossular rich; garnet 49c, however, contains important amounts of the Mg$_3$Al$_2$Si$_3$O$_{12}$ endmember. Approximate compositions are in the range Al$_{19.72}$Gros$_{05.75}$Spe$_{50.36}$Py$_{03.29}$, as illustrated in figure 10. Very low TiO$_2$ contents, 0.02 to 0.12 wt percent are noteworthy and quite unlike primary garnets from igneous rocks.

A single analysis of tourmaline is presented in app. table E. Assuming that it contains about 10 wt percent B$_2$O$_3$ and 4 wt percent combined H$_2$O + F, not detected by microprobe techniques, the analysis compares favorably with others in the literature. It is a complex uvite-dravite solid solution and occurs sporadically in several investigated metasedimentary rocks.

**Plagioclase**

Twenty-five plagioclase analyses are listed in app. table F. The Ab-rich corner of the ternary feldspar diagram is presented as figure 11. Duplicate analyses of different portions of 9 and 28a yielded identical results, An$_{83}$ and An$_{85}$ respectively. Zoning from a core value of An$_{17}$ to An$_{95}$ at the rim was measured in 10, a retrograded granulitic gneiss, and from An$_{28}$ to An$_{16}$ in 42c, an amphibolitic orthogneiss. Three charnockites, an Archean metagranite, an orthogneiss + its interlayered mafic inclusion, and six other quartzofeldspathic gneisses all possess calcic oligoclase of closely comparable compositions, An$_{18}$-33, the Or component is low, ranging from 0.5 to 1.7 mole percent. A single biotite + muscovite gneiss, 30c, carries nearly endmember albite, An$_{95}$. The plagioclase in paragneiss 49e is An$_{24}$ but is fairly rich in Or (1.3 mole percent). A metagabbro (An$_{98}$) and five amphiboles of komatitic chemical affinities (An$_{15}$-51) each contain homogeneous plagioclase, but compositions range slightly more widely from sample to sample. The KAlSi$_3$O$_8$ component is even lower than in the felsic rocks with values of 0.2 to 0.9 mole percent, doubtless reflecting the fact that plagioclases in the mafic rocks are not K-saturated.

The analyzed phases lie in the compositional range of the peristerite gap (Maruyama, Liou, and Suzuki, 1982); pairs of coexisting plagioclase were sought, but none were detected. Thus, Mid Proterozoic and younger thermal events appear not to have caused low-grade recrystallization of plagioclases in the investigated rocks.
Fig. 11. Atomic proportions of Ca, Na, and K for analyzed plagioclases from the studied rocks (app. table F). Symbols conform to usage of figure 4. Arrows point to rim compositions.

**K-feldspar Rims**

Potassium feldspars show somewhat irregular, optically indistinct zonations, with relatively Na-rich cores in the range Or$_{80-90}$. Only rims, therefore, could have been in equilibrium with the surrounding phases as they now exist. Accordingly, in app. table G, analytical data are given for margins of K-feldspar grains from three charnockites, an Archean metagranite, a retrogressed granulitic gneiss, four tonalitic gneisses, a paraschist, and a paragneiss. No consistent differences in composition are evident for the several occurrences: rim Or contents range from 91 to 99 percent.

**Epidote, Prehnite, Sphene, and Sillimanite**

Analyses for various other ferric iron-bearing silicates are presented in app. table H. Epidotes are essentially zoisite-pistacite binary solid solutions. Prograde specimens from an Archean metagranite, a charnockite, a retrogressed granulitic gneiss, and five tonalitic gneisses possess Al/(Fe$^{3+}$ + Al) ratios ranging from 0.67 to 0.77; corresponding values of X$_{Al}$ for epidotes from a chemically evolved metabasalt, a metagabbro, and a mafic inclusion in orthogneiss are 0.79, 0.74, and 0.67 respectively. A paraschist contains epidote with an X$_{Al}$ of 0.71. All these represent pistacite compositions. In contrast, clinzoisite in an amphibolite derived from a komatiitic basalt has an X$_{Al}$ of 0.91. Reflecting contrasts in minor element bulk-rock concentrations for the quartzofeldspathic + mafic versus ultramafic protoliths, clinzoisite from the latter is relatively enriched in Cr$_2$O$_3$ (0.18 wt percent) and impoverished in MnO (0.06 wt percent), whereas pistacites from all the rest are lower in Cr$_2$O$_3$ (0.00 to 0.08 wt percent) and relatively rich in MnO (0.10 to 0.39 wt percent).
The late-stage prehnite in an orthogneiss is somewhat more aluminous ($X_{Al} = 0.86$) than epidotes from other leucocratic rocks of similar bulk-rock composition. It was probably produced during the relatively feeble Mid Proterozoic recrystallization.

Analyzed sphaenes from an orthogneiss and its associated mafic inclusion, a retrograded and a tonalitic gneiss, a metagabbro, a fractionated metabasalt, and a metakomatitic amphibolite, are practically identical in composition. All exhibit minor departures from stoichiometry through substitution of $A_1^{VI}$ for Ti and $Fe^{3+}$ for Ca; $X_{Al}$ values range from 0.62 to 0.83, with the ultramafic sphaene having the most aluminous composition. In general, sphaenes from the granitic rocks are richer in $A_1$, $Fe^{3+}$, and $Mn$, with those from mafic rocks characterized by larger amounts of Ti.

Sillimanite from a paragneiss is virtually stoichiometric $A_1_2SiO_3$, with only very minor concentrations of chromium and ferric iron.

ELEMENT PARTITIONING AND THERMOBAROMETRY AMONG COEXISTING PHASES

General Statement

Principles governing fractionation of elements between competing rock-forming minerals were described by Ramberg and DeVore (1951). Subsequently, cation partitioning in coexisting minerals has been investigated by numerous authors; a summary of the theory and some natural examples were provided by Saxena (1978). Partitioning is a function of temperature, pressure, and for non-ideal solutions, the compositions of the participating phases. For major element distributions involving an exchange of the type $Fe_{bio} + Mg_{amph} \leftrightarrow Fe_{amph} + Mg_{bio}$, a distribution constant may be defined for fixed P and T as the ratio of the concentrations of exchangeable components in the coexisting phases: $K_D = (Fe/Mg)_{amph}/(Fe/Mg)_{bio}$. Where exchangeable element ratios for mineral pairs are plotted on log-log graphs, positively correlated linear trends result in favorable cases: if the slope is unity, ideal ion-for-ion exchange reactions describe the distributions. Other slopes reflect coupled substitutions among structural sites and/or the attendance of regular or non-ideal solution behavior. For situations in which several energetically distinct cation sites participate in the exchange reaction, a slope of 1.0 is not required for the log-log plots.

In general, actual data points scatter about but define a linear trend. Dispersion is due to non-equilibrium crystallization, later annealing, superposition of equilibrium partitioning values from assemblages that formed in contrasting P-T environments, coupled substitution of elements not considered in the exchange reaction, and analytical inaccuracies.

Observed Fractionations

Employing microprobe analyses of coexisting minerals listed in the appendices, distribution constants have been computed for iron $\leftrightarrow$ magnesium exchange reactions and are presented in table 1; lithologies, localities, and specimen numbers are also listed. Element partitioning in coexisting garnet/cpx, opx/cpx, garnet/amph and garnet/bio will be briefly discussed in the section dealing with thermobarometry. Among the rest
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Reported $K_D$ values are for Fe $\rightarrow$ Mg exchange except for plag/op, Fe$^{3+}$ $\rightarrow$ Al

* amphibole/serpentine
+ amphibole/talc
Fig. 12(A) Partitioning of iron and magnesium in cation proportions between coexisting clinopyroxene and amphibole from the studied rocks. Partition constant illustrated is average of five mineral pairs from quartzofeldspathic gneisses, assuming ion-for-ion exchange (that is, dashed line has a slope of 1.0 and an intercept of $K_D$). Amphibolite cpx + amph pair exhibits virtually no fractionation. (B) Relationship between amphibole Al$_2$O$_3$ content in wt percent and $K_D$ cpx/amph. Symbols conform to usage of figure 4.
of the observed fractionations, sufficient $K_D$ values are available in order
to deduce exchange behavior for the mineral pairs: cpx/amph; amph/
bio; amph/chl,talc or serp; and bio/ms. Chemographic relations are
plotted in figures 12 to 15. $Fe^{3+} \rightleftharpoons Al$ exchange between plagioclase and
epidote is also listed in table 1 and will be briefly treated.

cpx/amph.—Iron/magnesium ratios for six pairs of diopsidic, high-
Ca augite + pargasitic-hastingsitic (and actinolitic) amphibole are illus-
trated in figure 12A. Studied mineral pairs are from Archean rocks,
extcept for the most iron-rich gneiss, 37, of Early Proterozoic age. Five
samples from quartzofeldspathic gneisses exhibit a consistent $K_D$
value of $0.537 \pm 0.052$, with Fe markedly concentrated in hornblende relative
to clinopyroxene. In contrast, the cpx + amph pair from a mafic
amphibolite displays imperceptible fractionation, with a $K_D$ of 0.995:
perhaps in this rock, later amphibole replaced preexisting cpx, accept-
ing the Fe/Mg ratio of the precursor phase, but failing to equilibrate
with it. On the other hand, a distinct negative correlation exists in the
analyzed samples between $K_D$ cpx/amph values and aluminum contents
of the amphiboles, both as wt percent $Al_2O_3$ as illustrated in figure 12B,
and as $Al^{VI}$ per formula unit (p.f.u.). Aluminum is strongly fractionated
into amphib relative to coexisting cpx: in the former, $Al^{VI}$ dominantly
occupies the relatively small M(2) site, replacing chiefly magnesium—
hence for aluminous amphiboles, the Fe/Mg ratio is higher than it
would be in the absence of Al. Accordingly, the average partition curve
($K_D = 0.54$) illustrated in figure 12A seems appropriate for exchange
equilibria involving high-T/moderate-P hornblendes containing $\sim 12$
wt percent $Al_2O_3$ ($Al^{VI} \approx 0.52$ p.f.u.), whereas the single amphibolite
sample may be typical of non-fractionation between clinopyroxenes and
actinolites carrying approx 2 wt percent alumina ($Al^{VI} \approx 0.18$ p.f.u.).
Observed iron-magnesium distributions evidently are non-ideal, with
bulk-rock compositions in high-variance assemblages as critical as physi-
cal conditions. Data presented for higher pressure/lower temperature
metabasaltic rocks by Graham and Powell (1984) indicate that $K_D$
cpx/amph trends toward values of $\sim 0.5$ in some Phanerozoic eclogitic
rocks: the amphibole in such rocks is barroisitic, accordingly is similarly
high in $Al_2O_3$ content.

amph/bio.—The partitionings of Fe and Mg between 14 horn-
blende-actinolite + biotite pairs are shown in figure 13A. Analyzed
from a diverse set of parental lithologies—three metabasaltic amphibol-
ites, eight quartzofeldspathic gneisses, a mafic xenolith in gneiss, and
two samples of banded iron formation—in aggregate they display
essentially no fractionation, with an average $K_D$ of $1.046 \pm 0.218$.
Aluminous hornblends from gneissic rocks tend to be slightly enriched
in iron relative to biotites, whereas the situation is reversed for more
actinolitic amphiboles characteristic of the supracrustals. As noted in
the previous section, preferential concentration of Al in amphibole M(2)
sites causes an increased Fe/Mg ratio among the remaining octahedral
Fig. 13(A) Partitioning of iron and magnesium in cation proportions between coexisting amphibole and biotite from the studied rocks. Partition constant illustrated is average for 14 mineral pairs from various rock types, assuming ion-for-ion exchange.

cations for aluminous amphiboles, compared to the case where phases equilibrated in a low-$\text{Al}_2\text{O}_3$ environment (fig. 13B). Hence $K_D$\text{amph/bio}$ tends toward higher values in quartzofeldspathic units relative to interlayered isofacial mafic lithologies and the BIF specimens. Thus, fractionation of Fe and Mg between coexisting hornblende and biotite is a function of Al-content of the amphibole as well as T and P (see, also, Stephenson, 1977; Anderson, 1980). All these protoliths have Archean formational ages, so the observed distribution constants could have been produced by the Late Archean high-grade metamorphism.

$\text{amph/ch, talc or serp.}$—Iron/magnesium fractionation between hornblende or actinolite and the layer silicates chlorite, talc, and serpentine is illustrated in figure 14. For the twelve analyzed amphiboles coexisting with these Fe + Mg-rich layer silicates, one equilibrated with serpentine, three with talc, seven with chlorite, and one with both talc and chlorite. Parental lithologies exhibit wide-ranging compositions,
from komatiitic amphibolites to mafic amphibolite, metagabbro, quartzofeldspathic gneisses + a mafic xenolith, BIF, and marble. The partitionings are apparently systematic. Iron is slightly concentrated in chlorite relative to coexisting amphibole; for eight pairs, $K_D$ averages 0.862 ± 0.204. In contrast, for equilibrium with talc or serpentine, iron is markedly enriched in amphibole relative to the associated layer silicate; the average $K_D$ for four pairs (ignoring trace concentrations of Fe in phases from the marble, 58, where abundances are too low to yield meaningful numbers) is 2.34 ± 0.49. Other than the marble, all mineral pairs studied are from Archean rock types, so the observed fractionations could reflect the 2.7 to 2.8 by recrystallization event. However, because talc and serpentine (probably also chlorite) could have formed only at temperatures lower than the thermal maximum (700°C) attending Late Archean low-rank granulite/high-rank amphibolite facies metamorphism, the exchange equilibria documented here would have to represent latest Archean retrogression. Alternatively, some or all the
Fig. 14. Partitioning of iron and magnesium in cation proportions between coexisting amphibole and chlorite, talc and serpentine from the studied rocks. Tie line shows Fe/Mg of talc and chlorite coexisting with calcic amphibole. Partition constant of 0.86 is average of 8 chl + amph pairs; partition constant of 2.3 is average of four serp/talc + amph pairs. Ion-for-ion exchange assumed. Symbols conform to usage of figure 4.

Fe + Mg-rich layer silicates may be products of a Proterozoic stage of metamorphism, as is suggested by textural relationships summarized in figure 3. If so, element distributions presented in figure 14 may be metastable.

bio/ms.—Fe/Mg ratios for seven pairs of coexisting biotite and white mica are plotted in figure 15. Protoliths include six Archean quartzofeldspathic gneisses and a parashist of Early Proterozoic age. Two indistinctly different partition values may be recognized. Four of the gneisses display bio/ms $K_D$ values averaging $0.770 \pm 0.206$; phen-
Fig. 15. Partitioning of iron and magnesium in cation proportions between coexisting biotite and white mica from the studied rocks. Line connects compositions of two different micas from gneiss 42b, presumably of different generation ages. Partition constant of 0.77 is average of four bio + ms pairs which evidently equilibrated during the Early Proterozoic deep-seated metamorphism; partition constant of 0.38 reflects fractionation between bio and ms, probably generated during the Mid Proterozoic shallower recrystallization. Ion-for-ion exchange assumed. Symbols conform to usage of figure 4.

gitic white micas from these particular rocks have silicon contents that yield nominal temperatures of crystallization averaging 440°C (assuming a pressure of 5-6 kb) as will be discussed in the section dealing with thermobarometry. Two gneisses and the pararachshist contain white micas for which K_D averages 0.383 ± 0.089; these micas yield nominal temperatures of growth averaging 305°C (assuming a pressure of 2 ± 1 kb). Micas characterized by distribution constants that more closely
approach unity presumably formed during the Early Proterozoic, higher grade metamorphism, whereas micas displaying low $K_D$ values probably grew during the Mid Proterozoic, lower grade recrystallization. One rock, 42b, contains two optically similar but chemically distinct white micas; the less fractionated Fe/Mg partitioning evidently typifies the earlier-formed phase (this white mica is indicated in the tables and illustrations with a prime superscript).

\textit{plag/ep.}—The fractionation of Fe$^{3+}$/Al between coexisting plagioclase and epidote has been investigated, but the data exhibit considerable scatter and are not illustrated. $K_D$ values for eleven plag + ep pairs range from 0.0025 to 0.0251 and average 0.0082 ± 0.0073. The large associated standard error reflects near-background level concentrations of ferric iron in sodic plagioclase, which results in large percentage errors. Nevertheless, values listed in table 1 suggest a consistent distribution of elements for this mineral pair. Chemical behavior is sufficiently regular to postulate a close approach to equilibrium for the plagioclase-epidote reaction.

\textit{Summary of element fractionation study.}—Although the investigated rocks are part of a polymetamorphic sequence, systematic fractionations portrayed in figures 12 to 15 and listed in table 1 support the hypothesis that, for selected individual specimens, a close approach to chemical equilibrium was attained during recrystallization. Most, but not all, studied lithologies possess Archean ages of formation, and because of their preservation, the early, high-grade phase assemblages have been most thoroughly addressed. Nevertheless, effects of metamorphic overprinting are evident in these rocks, and later parageneses have been calibrated by reference to less intensely metamorphosed supracrustals of Proterozoic age (see fig. 3). Ambiguities admittedly exist, however, as to the ages of some phases, especially layer silicates.

\textit{Thermobarometry}

More quantitative assessment of physical conditions attending the described metamorphic events rest on experimental phase equilibrium studies and on thermochemical calibration of mineralogic thermometers and barometers. Derived values of $P$ and $T$ now to be discussed are listed in table 2.

First let us consider constraints provided by Fe/Mg partitioning between coexisting phases. The host rocks are chiefly granulitic orthogneisses but also include a high-rank paragneiss and a metamorphosed BIF. Only one rock (37, of Early Proterozoic age) is post-Archean. Quantitative data are provided by five garn-bio pairs, one garn/cpx pair, one opx/cpx pair, and three garn/amph pairs. Thermometric methods of Ferry and Spear (1978), Ellis and Green (1979), Lindsley (1983), and Graham and Powell (1984) were employed; most of these require—but are not highly sensitive to—an independent pressure estimate. For the Late Archean paragneiss, evaluation of the attendant lithostatic pressure during recrystallization may be approximated using
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Late Archean P-T values, underlined; Early Proterozoic P-T values, normal typeset; Mid Proterozoic P-T values, in parentheses.
the experimental results of Bohlen, Wall, and Boettcher (1983) for the reaction garnet + 3 rutile = 3 ilmenite + sillimanite + 2 quartz. As a first approximation, garnet was regarded as an ideal solid solution, a reasonable assumption for the low-Mn, low-Ca composition of 49e (0.024 and 0.088 atoms p.f.u. respectively; for more quantitative treatment, see Newton and Perkins, 1982), yielding pressure values at 600°C of 4.9 kb and 6.7 kb at 800°C. The pressure chosen is 6 kb at 700°C and represents a maximum inasmuch as sphene rather than rutile occurs in the assemblage. Bearing this proviso in mind, at 6 ± 1 kb, the various iron/magnesium fractionation studies previously referred to yield an average temperature of 696° ± 54°C for the Late Archean metamorphic event.

The Early Proterozoic recrystallization culminated at nearly as high grade, judging from nominal temperatures reported in table 2 for 37. The absence of barroisitic amphibole in this and in lower temperature Early Proterozoic assemblages indicates slightly lower maximum pressures of recrystallization compared to the Late Archean metamorphism, approx 4 to 6 kb (Ernst, 1979).

Presuming incipient formation of melt in quartzofeldspathic rocks for both 2.8 to 2.9 and 2.4 to 2.5 by old thermal events, presence of the plag + qtz + amph + bio + K-spar + mag ± sphene assemblage allows use of the total Al content of hornblende in order to determine the pressure of solidus recrystallization (Hammerstrom and Zen, 1986; Hollister and others, 1987). For five Late Archean low-rank granulite/high-rank amphibolite facies granitic gneisses (1,2,4,10,43a), this assumption allows calculation of a nominal average pressure of 7.1 ± 0.8 kb; for the Early Proterozoic gneiss (37), the corresponding value is 6.9 kb. Employing the AlIV contents of hornblendes in mafic amphibolites of Archean age (6,9,34e), assuming attending pressures as above, computed temperatures of Archean metamorphism according to the formulation of Nabelek and Lindsley (1985) average 648° ± 91°C, comparable to other values presented in table 2. Later (Mid Proterozoic?) actinolites formed at lower pressures at computed temperatures of about 400°C. In spite of large uncertainties inherent in these P-T calculations, they nonetheless support the conclusion that the Late Archean and slightly lower grade Early Proterozoic metamorphic events took place under roughly similar sets of physical conditions in crust at least 20 to 25 km thick.

Turning now to compositions of white micas in qtz + K-spar + bio-bearing assemblages, the silicon content of ms may be correlated with physical conditions of recrystallization (Velde, 1967; Massone and Schreyer, 1987). Using Si isopleths presented by the latter authors, white mica-derived physical conditions characteristic of the Early and Mid Proterozoic metamorphic episodes are obtained; phengite compositional variation is a sensitive function of pressure but is also related to temperature. All investigated white micas, which apparently recrystallized during the Early Proterozoic event, have Archean protoliths:
assuming a confining pressure of 5 to 6 kb, five samples yield an average nominal temperature of $408^\circ \pm 103^\circ$ C. Except for the two-ms Archean quartzofeldspathic gneiss (42b), the Mid Proterozoic white micas all developed in Lower Proterozoic host lithologies: for the five specimens analyzed, the average apparent temperature is $377^\circ \pm 54^\circ$ C, assuming a total pressure of 1 to 2 kb. The assignment of white micas to a particular Proterozoic metamorphism is highly problematic because these phases undoubtedly reequilibrated to some extent during thermal relaxation which terminated each of the two (or three) post-Archean orogenic events. Moreover, uncertainties reflect the fact that nominal temperatures obtained are critically dependent on the assumed pressure. The latter variable is not well constrained, especially for the lowest grade metamorphic event.

Fig. 16. Variation of wt percent titania in white micas from the studied rocks as a function of nominal temperature (derived from Si isopleths per formula unit presented by Massone and Schreyer, 1987). Filled circles denote white micas that are inferred to have formed at 5 to 6 kb, X symbols indicate white micas that apparently recrystallized at approx 1 to 2 kb. A pressure effect is not obvious. In gneiss sample 42b, line connects compositions of two different micas, presumably of different generation ages.
The titanium content of white micas (coexisting with sphene), which increases with rising temperature, appears to be relatively insensitive to pressure variation. As illustrated in figure 16, phengites thought to have crystallized at 5 to 6 kb roughly define the same T-X curve as those that apparently formed at about 1 to 2 kb pressure. Perhaps, in appropriate low-variance assemblages, experimentally calibrated Ti, combined with Si contents of white micas, could provide a method of quantitatively assessing both T and P during low-grade metamorphic recrystallization.

For the investigated Lower Proterozoic marble, 58, tremolite, calcite, quartz, and talc coexist, allowing analysis of the reaction 5 talc + 6calcite + 4 quartz - 3 tremolite + 6 CO₂ + 2 H₂O. Assuming a pressure of 2 kb for the Mid Proterozoic metamorphism, phase equilibria for this system, described by Skippen (1974), suggest a temperature of 400° to 440°C and an attendant aqueous fluid phase characterized by a mole fraction of CO₂ between 0.15 to 0.40.

Thermobarometric analyses all depend on a close approach to chemical equilibrium during the studied metamorphic event, without subsequent backreaction. However, as pointed out by England and Richardson (1977) and Spear and others (1984), metamorphic field gradients and the highest temperature stages of recrystallization are generally preserved in the rocks, rather than the actual metamorphic geothermal gradient. Culminations of the several events are reflected in the investigated mineral assemblages, but actual P-T-time recrystallization paths are not known for this area. What is evident from the present study, as illustrated in figure 17, is that distinctly different, declining sets of physical conditions accompanied Late Archean, Early Proterozoic, and Mid Proterozoic orogenies in the northeastern Sino-Korean shield.

PETROTECTONIC SUMMARY

Combined with previously published radiometric data and geologic studies (Ma and Wu, 1981; Zhong and others, 1984; Zhu and Chen, 1984; Xu and Chen, 1984; Zhai and others, 1985), the present mineralogic, thermobarometric, and element partitioning study allows distinction of at least three contrasting metamorphic episodes in southern Jilian and eastern Liaoning Provinces. The parageneses reflect successive dynamothermal events of decreasing intensity spanning the interval 2.8 to 2.9 to 1.6 to 1.8 by ago. Bulk-rock XRF and INAA data presented by Ernst, Cao, and Jiang (1988) and Ernst (in review) reinforce conclusions regarding the generation of continental crust in this portion of the Sino-Korean platform. Surviving Archean crust consists of primitive tonalitic, granulitic gneisses, associated chiefly older mafic + ultramafic amphibolites, and less voluminous, mostly younger, metasedimentary units, including banded iron formations. Chemically evolved granitoids episodically invaded the Proterozoic stratified supracrustal sequence.
Fig. 17. Petrogenetic grid after Ernst (1976) showing modern-day thermal gradients for contrasting plate tectonic settings, which may coincide with ancient metamorphic field gradients. Determined maximum physical conditions accompanying Precambrian metamorphism in southern Jilin and eastern Liaoning Provinces, as indicated by analyzed phase assemblages, are also illustrated. (1), (2), and (3) represent culminating P-T values attending Late Archean, Early Proterozoic and Mid Proterozoic metamorphic episodes, respectively.

and the underlying basement complex prior to final cratonization by Mid Proterozoic time.

Low-grade granulite/high-grade amphibolite conditions which accompanied the metamorphism at 2.8 to 2.9 by evidently approached 700° ± 50°C, 5 to 7 kb. For this Late Archean event, Sills and others,
(1987) have obtained analogous physical conditions for rocks exposed in eastern Hebei Province. In contrast, the low-rank amphibolite/green-schist assemblages characteristic of the 2.4 to 2.5 and 1.9 to 2.0 by old events (not separately distinguished in fig. 3) argue for attending temperatures near 400° to 600°C at about 4 to 6 kb total pressure in eastern Liaoning and southern Jilin Provinces. The greenschist and even lower grade recrystallization, which occurred about 1.6 to 1.8 by ago, probably culminated at no more than 400° ± 50°C and 1 to 3 kb.

Charnockitic rocks and associated mafic supracrustals appear to have annealed at rather low H2O activities, but younger, progressively lower grade assemblages may have been produced at higher values of aH2O. At least one Upper Archean BIF (50b) contains Cl-bearing biotite and hornblende, suggesting the possibility of important amounts of chlorine in the fluid phase and a lowered activity for H2O locally attending Late Archean metamorphism. Assuming a total pressure of 2 kb, the presence of the condensed assemblage cc + qtz + talc + trem in a Lower Proterozoic marble indicates that XCO2 during the 1.9 to 2.0 by recrystallization of this unit must have been approx 0.3 ± 0.2, with temperatures in the range of 420° ± 20°C.

The presence of relict phase assemblages in the rocks studied demonstrates that, although new crustal materials seem to have been added to the northeastern segment of the Sino-Korean shield, older portions were actively participating in the successive crustal remobilizations over the course of approximately a billion years. The declining P-T intensity of successive metamorphic events may simply reflect rate-related requirements for partial preservation of precursor assemblages, but mineral assemblages testify to the monotonic thermal relaxation and decompression of this part of the craton during Late Archean, Early, and Mid Proterozoic time. The recognized Precambrian recrystallization events seem to have involved culminating P-T conditions appropriate to regions characterized by moderately thick continental crust (a minimum of approx 20 to 25 km in Late Archean time), and volcanic island-arc or continental-margin type geothermal gradients, as illustrated in figure 17. During the Phanerozoic terrane assembly of east Asia, the Sino-Korean platform was invaded by Mesozoic granitoids principally adjacent to its margins (fig. 1), reflecting the fact that the craton has behaved as an integral unit ever since stabilization 1.6 to 1.8 by ago.

ACKNOWLEDGMENTS

Research reported here is the product of a cooperative scientific project initiated through the U.S. National Academy of Sciences and the P.R.C. Institute of Geochemistry, Academia Sinica. Partial support was also obtained through NSF grant EAR86-16624. I thank Professor Tu Guangzhi and Drs. Cao Ronglong and Jiang Jiyun for cooperative planning and scientific support which made this investigation possible.
Illuminating discussions with Academia Sinica members of the Institutes of Geology/Beijing and Geochemistry/Guiyang are also appreciated. Geologic teams in southern Jilin and eastern Liaoning Provinces guided me on field trips during September, 1984 and June–July, 1985 and freely shared scientific information. The manuscript has benefited from reviews by Frank S. Spear and Colin M. Graham.
## APPENDIX

### Table A

**Electron microprobe analyses of clinoamphiboles**

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Fe/(Mg+Fe) 0.455
## APPENDIX

### Table A

(continued)

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|                  |         |         |         |        |         |         |
| AlIV             | 1.334   | 1.384   | 1.626   | 1.684  | 1.349   | 1.697   | 0.113   |
| AlVI             | 0.403   | 0.376   | 0.748   | 0.398  | 0.482   | 0.439   | 0.007   |
| Ti               | 0.126   | 0.159   | 0.112   | 0.080  | 0.065   | 0.226   | 0.004   |
| Cr               | 0.006   | 0.009   | 0.002   | 0.001  | 0.014   | 0.002   | 0.012   |
| Fe²⁺             | 2.526   | 2.497   | 2.408   | 2.563  | 2.226   | 2.088   | 1.034   |
| Mn               | 0.058   | 0.064   | 0.065   | 0.289  | 0.059   | 0.005   | 0.039   |
| Mg               | 1.994   | 1.885   | 1.838   | 1.770  | 2.325   | 1.218   | 3.988   |
| Ca               | 1.913   | 1.899   | 1.818   | 1.897  | 1.862   | 1.870   | 1.904   |
| Na               | 0.383   | 0.414   | 0.517   | 0.518  | 0.433   | 0.538   | 0.047   |
| K                | 0.240   | 0.247   | 0.194   | 0.411  | 0.225   | 0.332   | 0.001   |
| **Total**        | 15.648  | 15.671  | 15.682  | 16.027 | 15.691  | 15.838  | 15.057  |
| Fe/(Mg+Fe)       | 0.559   | 0.581   | 0.567   | 0.601  | 0.489   | 0.725   | 0.206   |

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Fe/(Mg+Fe) 0.104 0.089 0.492 0.740 0.634 0.001

*chlorine-bearing
## APPENDIX

### Table B

**Electron microprobe analyses**

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W. G. Ernst—Polymetamorphic Late Archean
**APPENDIX**

**Table C**

*Electron microprobe analyses*

1. Biotites

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| Si     | 2.799 | 2.803 | 2.805 | 2.805 | 2.774  | 2.908  | 2.838 | 2.849  | 2.659     | 2.816   | 2.766   |
| AlᵥⅣ   | 1.201 | 1.197 | 1.195 | 1.195 | 1.226  | 1.092  | 1.162 | 1.151  | 1.341     | 1.184   | 1.234   |
| AlᵥⅠ   | 0.052 | 0.156 | 0.072 | 0.185 | 0.288  | 0.211  | 0.191 | 0.183  | 0.173     | 0.140   | 0.098   |
| Ti     | 0.282 | 0.271 | 0.238 | 0.098 | 0.165  | 0.071  | 0.093 | 0.105  | 0.020     | 0.183   | 0.178   |
| Cr     | --    | --    | --    | 0.011 | 0.002  | 0.013  | 0.016 | 0.002  | 0.001     | 0.001   | 0.002   |
| Fe²⁺   | 0.985 | 0.888 | 0.950 | 0.763 | 1.361  | 0.686  | 0.727 | 1.159  | 1.708     | 1.353   | 1.590   |
| Mn     | 0.007 | 0.006 | 0.009 | 0.005 | 0.021  | 0.012  | 0.004 | 0.017  | 0.029     | 0.018   | 0.022   |
| Mg     | 1.490 | 1.442 | 1.566 | 1.922 | 0.984  | 1.880  | 1.892 | 1.430  | 1.351     | 1.167   | 1.010   |
| Ca     | 0.002 | 0.001 | 0.001 | 0.004 | 0.001  | 0.002  | 0.002 | 0.003  | 0.001     | 0.001   | 0.001   |
| Na     | 0.002 | 0.008 | 0.006 | 0.038 | 0.003  | 0.001  | 0.037 | 0.003  | 0.000     | 0.006   | 0.011   |
| K      | 0.946 | 0.966 | 0.966 | 0.791 | 0.958  | 0.976  | 0.885 | 0.957  | 0.564     | 0.945   | 0.965   |

| Fe/(Mg+Fe)| 0.398 | 0.381 | 0.378 | 0.284 | 0.580  | 0.267  | 0.278 | 0.448  | 0.558     | 0.537   | 0.612   |
### APPENDIX

#### TABLE C (continued)

**1. Biotites (continued)**

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|     | 2.818  | 2.794  | 2.804  | 2.842  | 2.732  | 2.739  | 2.712  | 2.740  | 2.720  | 2.789  |
|     | 1.182  | 1.206  | 1.196  | 1.158  | 1.268  | 1.261  | 1.288  | 1.260  | 1.280  | 1.211  |
|     | 0.291  | 0.257  | 0.267  | 0.203  | 0.014  | 0.005  | 0.247  | 0.020  | 0.133  | 0.336  |
|     | 0.093  | 0.137  | 0.139  | 0.090  | 0.352  | 0.347  | 0.237  | 0.343  | 0.196  | 0.075  |
|     | 0.001  | 0.003  | 0.001  | 0.005  | 0.001  | 0.007  | 0.003  | 0.006  | 0.000  | 0.001  |
|     | 1.109  | 1.313  | 1.285  | 1.106  | 1.734  | 1.117  | 0.900  | 1.225  | 1.894  | 0.901  |
|     | 0.016  | 0.022  | 0.023  | 0.023  | 0.003  | 0.003  | 0.000  | 0.002  | 0.001  | 0.020  |
|     | 1.364  | 1.121  | 1.136  | 1.485  | 0.694  | 1.307  | 1.432  | 1.211  | 0.672  | 1.561  |
|     | 0.004  | 0.000  | 0.002  | 0.003  | 0.006  | 0.012  | 0.001  | 0.004  | 0.004  | 0.000  |
|     | 0.002  | 0.002  | 0.000  | 0.008  | 0.003  | 0.018  | 0.008  | 0.000  | 0.017  | 0.005  |
|     | 0.946  | 0.968  | 0.949  | 0.931  | 0.935  | 0.940  | 0.915  | 0.924  | 0.938  | 0.932  |
| Fe/(Mg+Fe)      | 0.448  | 0.539  | 0.531  | 0.427  | 0.714  | 0.461  | 0.386  | 0.503  | 0.738  | 0.366  |

* chlorine-bearing
### APPENDIX

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| Fe/(Mg+Fe)     | 0.600    | 0.697    | 0.449    | 0.652    | 0.802    | 0.619    | 0.573    | 0.354    | 0.532 | 0.635 | 0.096 | 0.056 | 0.506 | 0.020 |
### APPENDIX

#### Table D

**Electron microprobe analyses**

#### 1. Chlorite

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<td>0.009</td>
<td>0.000</td>
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| Fe/(Mg+Fe) | 0.543 | 0.473 | 0.427 | 0.514 | 0.284 | 0.423 | 0.521 | 0.557 | 0.121 | 0.344 | 0.330 | 0.590 | 0.924 | 0.035 |
### Table E

**Electron microprobe analyses**

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$\text{Fe/(Mg+Fe)} = 0.860 \quad 0.920 \quad 0.916 \quad 0.701 \quad 0.791 \quad 0.911 \quad 0.220$

*Contains about 10 wt% B$_2$O$_3$
## APPENDIX

### TABLE F

**Electron microprobe analyses of plagioclases**

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<th>7b-Plag</th>
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<th>10-Plag core</th>
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### Table G

Electron microprobe analyses of K-feldspar rims

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### APPENDIX

#### Table H

**Electron microprobe analyses**

1. Epidotes

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| Ti    | 0.008 | 0.029 | 0.009 | 0.007 | 0.004 | 0.013 | 0.013 | 0.022 | 0.000 | 0.022 | 0.010 | 0.007 | 0.011 |
| Cr    | 0.001 | 0.006 | 0.010 | 0.021 | 0.005 | 0.004 | 0.007 | 0.003 | 0.002 | 0.002 | 0.000 | 0.010 | 0.001 |
| Fe³⁺  | 1.640 | 1.933 | 1.604 | 0.529 | 1.513 | 1.985 | 1.349 | 1.129 | 1.880 | 1.509 | 1.555 | 1.606 | 1.701 |
| Mn    | 0.025 | 0.032 | 0.021 | 0.007 | 0.013 | 0.020 | 0.019 | 0.017 | 0.053 | 0.027 | 0.039 | 0.028 | 0.025 |
| Mg    | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 0.001 | 0.009 | 0.000 | 0.000 | 0.001 | 0.000 | 0.100 |
| Na    | 0.000 | 0.000 | 0.000 | 0.003 | 0.027 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| K     | 0.001 | 0.000 | 0.002 | 0.000 | 0.001 | 0.005 | 0.000 | 0.002 | 0.002 | 0.000 | 0.002 | 0.000 | 0.007 |
| Total | 15.960| 15.969| 15.990| 15.985| 15.954| 15.954| 15.964| 15.944| 15.977| 15.971| 15.959| 15.949| 15.996 |

Fe³⁺/(Al+Fe³⁺) 0.275 0.325 0.269 0.090 0.255 0.328 0.228 0.206 0.314 0.250 0.260 0.266 0.287
## APPENDIX

### Table H (continued)

**Electron microprobe analyses**

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REFERENCES


———, 1979, Coexisting sodic and calcic amphiboles from high-pressure metamorphic belts and the stability of barroisitic amphibole: Mineralog. Mag., v. 43, p. 269–278.

———, in review, Petrochemical comparison of 3.5 Ga old mafic amphibolite inclusions from eastern Hebei Province, with Archean mafic-ultramafic supracrustals of uncertain antiquity, southern Jilin/eastern Liaoning Provinces, China: Geochemistry, v.


