# CHAPTER 7

# DISCUSSION AND CONCLUSION

## 7.1 Formation of Skarn

Paragenetic studies of skarn minerals at the Khao Phra Ngam area and vicinity indicate that skarn evolution occurs in three stages. The first is represented by metamorphic stage due to the emplacement of diorite into the carbonate country rocks to form marble, diopsidic marble and a white zone of wollastonite surrounding chert nodules or rimming chert beds. This stage can be observed locally at the Khao Phra Ngam Sub-area and the Khao Phu Kha Sub-area.

The second, metasomatic, stage is dominated by skarn mineral assemblage such as wollastonite, clinopyroxene, and garnet associated with pyrite and magnetite. This stage is considered to represent prograde anhydrous skarn development. The third stage is dominated by hydrous minerals (epidote and chlorite) and ore minerals (chalcopyrite, bornite, covellite, and spharlerite) with Fe-oxide, considered to represent retrograde hydrous skarn development. The retrograde alteration stage was probably formed during the declining temperature of the diorite intrusion associated with an infiltration of meteoric water and silica-rich fluid from granodiorite intrusion.

In analogy with Einaudi, *et al* (1981)'s elaborate description of skarn deposits, the skarn formations together with the Fe-Cu mineralization at Khao Phra Ngam area and vicinity could be envisaged as follow:

As the dioritic magma intruded into the carbonate sedimentary sequence, contact metamorphism formed a zoned thermal aureole consisting of calcium-aluminum silicates in calcareous shale, calcium-magnesium silicates in dolomitic limestone, and wollastonite in cherty limestone (Figure 7-1A,B). The iron-poor calc-silicate marble and hornfels constituted the early metamorphic stage. Where impure carbonate rocks and calcareous shales are abundant, metamorphic calc-silicate may constitute a large portion of the skarn deposit. Composition of metamorphic calc-silicates reflected the composition of the original sediment protolith. The dominant impurities are magnesium and aluminum and the resulting calc-silicate minerals consist of grossularitic garnet and diopsidic pyroxene (Figure 7-2). Metasomatism began as crystallization of the magma released magmatic hydrothermal fluid and cause hydrofracturing of the pluton (Burnham, 1979) and in some cases, of previously formed hornfels (Figure 7-1B). This fluid which may mix with metamorphic water or at a later stage, with meteoric waters (Taylor, 1980), rose along the outer contact of the pluton and infiltrated the wall rocks along the intrusive contact as well as along fractures, preskarn dikes and sills, sedimentary contacts, and other permeable zones. The solution would be nearly neutral and enriched in iron relative to magnesium (Whitney *et al*., 1979). The metal and sulphur content depended on the temperature and pressure of equilibrium with the intrusive mass, the oxidation state of the system, and the halogen content of the magma (Holland, 1972; Burnham, 1979). Solution activity gradients resulted in an orderly zonal arrangement of early, generally anhydrous skarn assemblage: *endoskarn* formed in the intrusive and interbedded hornfels by introduction of calcium from carbonate rocks; *exsoskarn* formed in carbonate rocks by introduction of iron, silica, aluminum, and other components. Interaction of the skarn forming fluid with dolomite yielded magnesium skarn characterized by clinopyroxene and calcite, whereas limestone yielded calcite

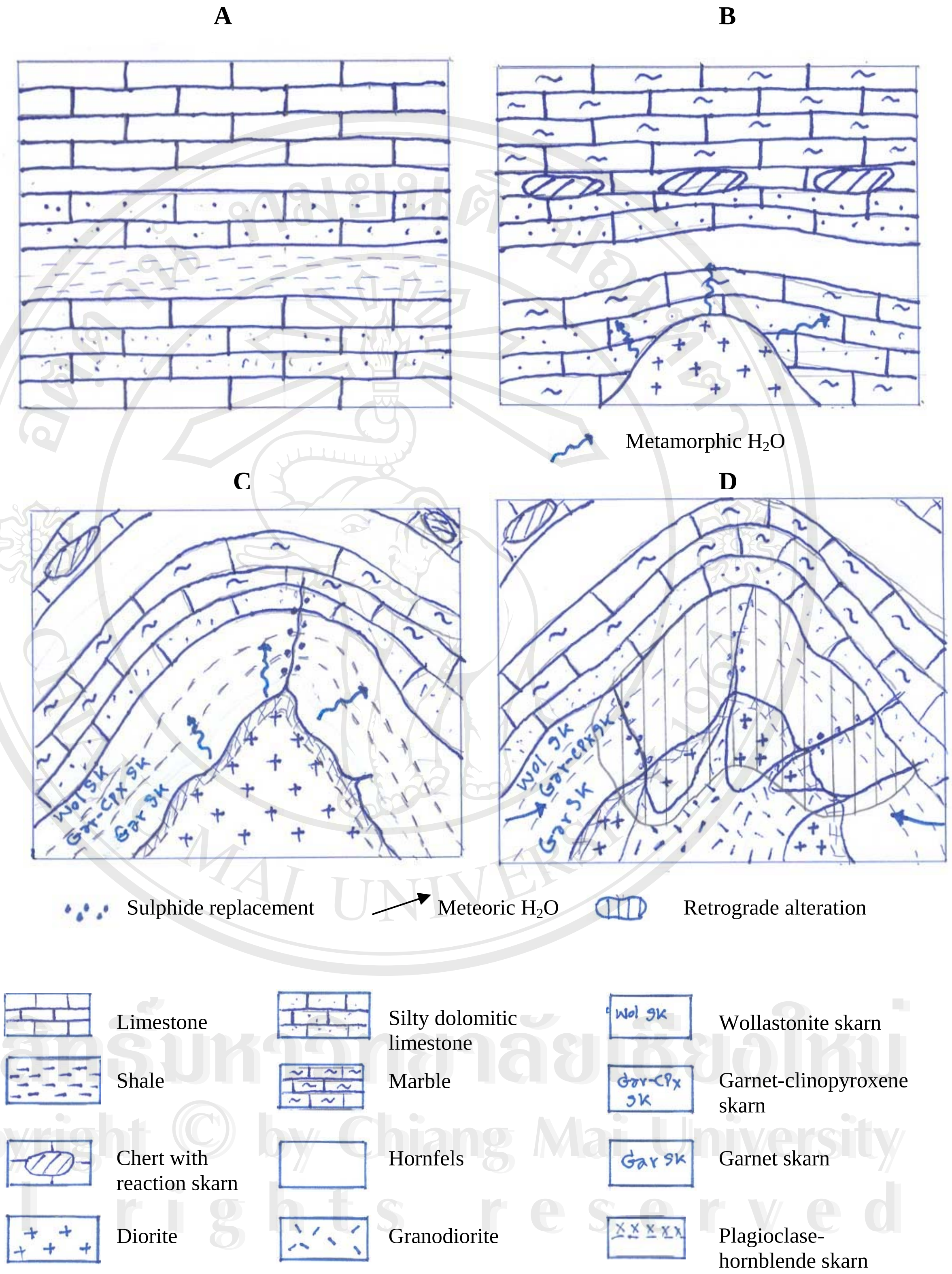
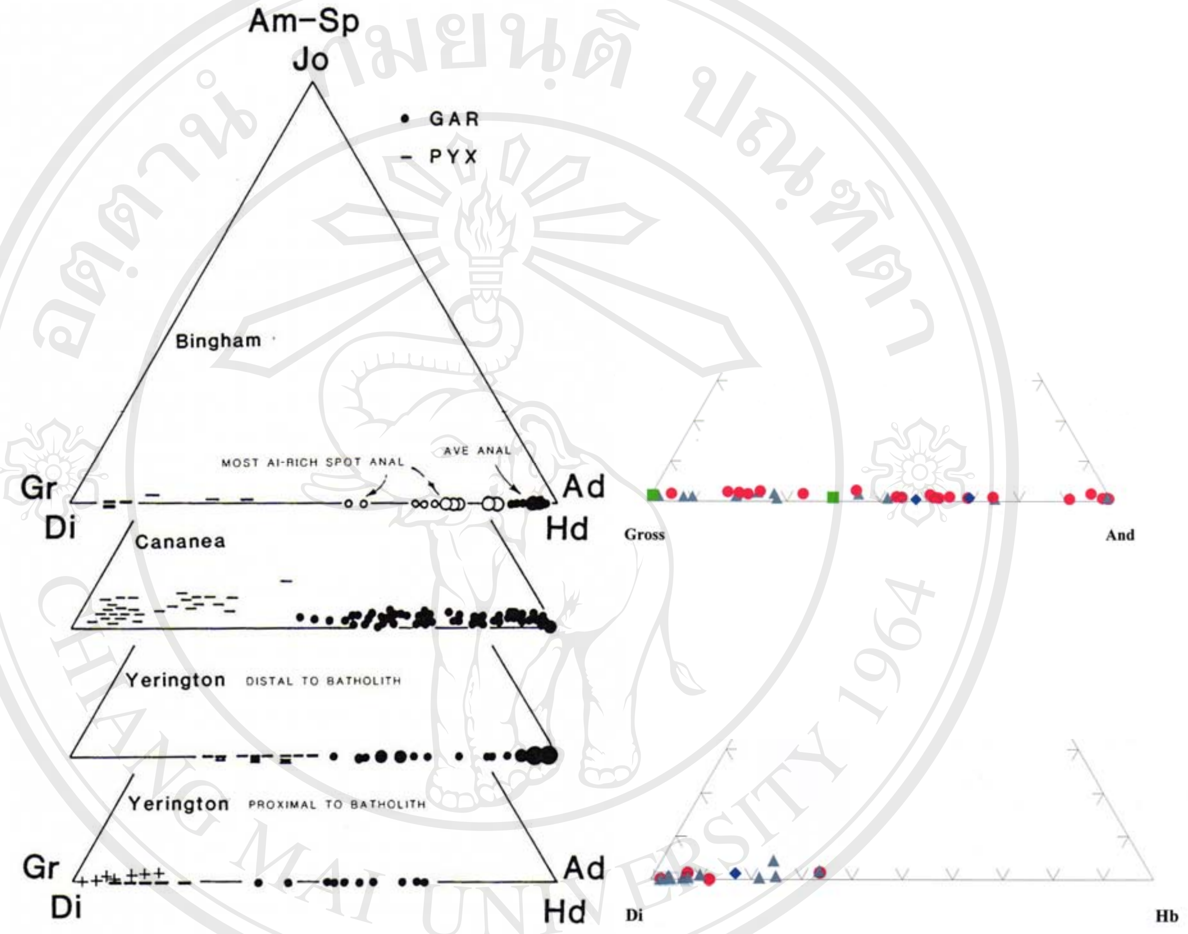


**Figure 7-1** Schematic diagram summarizing the stage of evolution of skarn in the Khao Phra Ngam area.



A B

**Figure 7-2** Composition of garnet (o and •) and pyroxene (+ = metamorphic; **-** = metasomatic) in copper skarn deposits (A) (Einaudi *et at*., 1981) compared with the Khao Phra Ngam area (B).

skarn characterized by garnet and pyroxene with outer zones of wollastonite, vesuvianite and/or pyroxenoid (Figure 7-1C). The early stage of anhydrous, zoned skarn growth was not accompanied by deposition of sulphide mineralization (Sminov, 1976; Zharikov, 1970). The late stages of prograde skarn growth showed a trend toward iron-enrichment and magnesium-depletion in the silicate. This evolution trend would be recognized by the development of late ferric rich (andradite) or ferrous- and manganese-enriched (hedenbergitic) pyroxene. Deposition of magnetite and sulphides generally commenced with this late stage of skarn growth (Sminov, 1976; Zharikov, 1970) but peaked during later skarn destructive stages. Probably the most characteristic opaque mineral of this stage is magnetite. Sulphides are less characteristic but may include low sulphur sulphides such as pyrrhotite, bornite, and chalcopyrite in garnet skarn zones, and sphalerite in outer pyroxene and pyroxenoid zone of wollastonite skarn. Extensive hydrous alteration of skarn silicates at this stage was rare. Alteration of the associated pluton (Figure 7-1D) may involve alkali metasomatism, further development of endoskarn or little megascopic alteration at all.

The calcic skarn zonal pattern from pyrite-chalcopyrite-magnetite associated with grossular-andradite garnet near pluton contacts to chalcopyrite-bornite association with wollastonite near marble contact reflects an outward decrease in total iron. The change from grossular-andradite garnet-chalcopyrite to wollastonite-bornite was explained by Burt (1972a,b) as the result of iron-rich oxidizing solution altering wollastonite to andradite. Precipitation of andradite caused change in the Fe/Cu ratio in the fluid and could cause the deposition of bornite rather than chalcopyrite.

Temperature and pressure of skarn formation in the Khao Phra Ngam area compared with other areas are listed in Table 7-1. These studies suggest temperature

**Table 7-1** Estimates of temperature, pressure, and fluid composition during skarn formation.

| **Locality, metals** | **Dominant ore minerals** | **Stage** | **Assemblage** | **Temperature (°C)** | **Pressure (kb)** | **$X_{CO_2}$** | **Reference** |
|---|---|---|---|---|---|---|---|
| *Mesozonal environments* | | | | | | | |
| **Osgood Mountains, Nevada W** | | Metamorphic | Forsterite-diopside; pyroxene-wollastonite-garnet | ~ 550 | 1.5-2 | <0.15 | Taylor and O'Neil (1977) |
| | Scheelite | Early skarn | Garnet-pyroxene | ~ 550 | <0.12 | | |
| | | | Andradite garnet | ~ 550 | <0.01 | | |
| | Magnetite, scheelite | Hydrosilicate | Amphibole-epidote-quartz | 480-350 | | | |
| | Pyrite-chalcopyrite | Sulphide-carbonate | Amphibole-epidote-quartz | 480-350 | | | |
| | | | Calcite + sulphides | | | | |
| **Castabonne, Pyrenees, France W** | | Early magnesian skarn | Calcite-forsterite; diopside-andradite | 550-450 | 1.4-2.8 | 0.2-0.1 | Guy (1979) |
| | Scheelite | Early calcic skarn | Grandite garnet | 550-450 | | 0.05 | |
| | Pyrite-sphalerite | Hydrosilicate | Quartz-tremolite-talc- serpentine-brucite | 450-350 | | | |
| | | Carbonate-sulphide | Calcite-sulphide-quartz | 350-300 | | | |
| **Sierra Nevada, California W** | Scheelite | Early skarn | Garnet-pryoxene | 650-600 | 1.5-2 | <0.1 | Kerrick (1977) |
| **King Island, Tasmania** | Scheelite | Early skarn | Grandite garnet-hedenbergite pyroxene | 800-425 | >0.65 (boiling) | 25-55 | |
| **Pine Creek, California W, Cu** | Scheelite | Metamorphic | Dolomite-forterite | 600-500 | 1-2 | 0.2-0.3 | Brown (1980), Brown and Bowman (1980) |
| | Sulfide | Skarn | Garnet-pyroxene | 550-450 | | <0.1-0.2 | |
| | | Hydrosilicate | Epidote-amphibole-sulphide-magnetite | | | | |
| **Elkhorn, Mountain** | | Metamorphic | Dolomite- Periclase | 575-615 | 0.7-1.3 | 0.05-0.1 | Bowman (1978) |
| | Magnetite-pyrrhotite | Early skarn | Garnet-pyroxene | 550-450 | | 0.04-0.25 | |
| | Pyrite-chalcopyrite | Hydrosilicate | Epidote-amphibole-sulphide-magnetite | | | | |

**Table 7-1** (Continued)

| **Locality, metals** | **Dominant ore minerals** | **Stage** | **Assemblage** | **Temperature (°C)** | **Pressure (kb)** | **$X_{CO2}$** | **Reference** |
|---|---|---|---|---|---|---|---|
| *Epizonal environments* | | | | | | | |
| **Ely, Nevada**<br>**Cu** | Magnetite<br>Chalcopyrite-pyrite<br>Pyrite<br>Sphalerite-galena | Early skarn<br>Hydrosilicate<br>Silica-pyrite<br>Late-vein | Garnet-pyroxene<br>Quartz-actinolite-magnetite<br>Quartz-pyrite-carbonate<br>Sphalerite-pyrite | 570-420<br>445-315<br>385-240<br>100 | 0.6-1.0<br>0.2-0.35<br>(boiling) | <0.06 | Huang (1976) |
| **Vancouver Island, B.C., Canada**<br>**Fe** | Magnetite-pyrite-arsenopyrite<br>Chalcopyrite-pyrite-pyrrhotite | Early skarn<br>Hydrosilicate<br>Quartz-calcite-sulfide | Garnet-pyroxene<br>Amphibole-calcite-chlorite<br>Quartz-chlorite-ilvaite | 465-402<br>340-290 | 0.5-1.0 | | Haug (1976) |
| **Washington Camp, Arizona**<br>**Cu, Pb, Zn, Ag** | Magnetite<br>Sulphide | Early skarn<br>Early skarn<br>Hydrosilicate | Andradite<br>Mn-salite, garnet<br>Quartz-calcite-talc | 490-390<br>440-400<br>380-210 | <0.5<br>(boiling) | <0.1 | Surles (1978) |
| **Santa Rita, New Maxico**<br>**Cu** | Magnetite, chalcopyrite<br>Pyrite, chalcopyrite | Early skarn<br>Hydrosilicate | Andradite-quartz-diopside<br>Chlorite-siderite-actinolite-quartz | 425-325<br>450-250 | 0.33-0.12<br>(boiling) | <0.1 | Ahmad and Rose (1980) |
| **Copper Canyon, Nevada**<br>**Cu, Au, Ag** | Magnetite<br>Pyrrhotite-chalcopyrite<br>Pyrite-chalcopyrite | Early skarn<br>Hydrosilicate<br>Late | Andradite-diopside<br>Actinolite-epidote<br>Calcite-quartz-hematite | 500-540<br>425-300<br>220-160 | 0.38<br>0.12<br>(boiling) | low | Theodore and Blake (1978) |
| **Khao Phra Ngam, Thailand**<br>**Fe, Cu** | Magnetite-pyrite<br>Chalcopyrite-pyrite-hematite | Metamorphic<br>Early skarn<br>Hydrosilicate | Diopside-wollastonite<br>Wollastonite-diopside-idocrase<br>Diopside-garnet-wollastonite<br>Garnet-diopside<br>Quartz-epidote-calcite | 650-700<br>475-660<br>350-520<br>350-520<br>300-350 | 0.5-1.0 | 0.1-0.3 | |

of prograde skarn formation of 650° to 400°C and indicate substantially higher temperatures of prograde skarn formation associated with higher pressure environments.

Chemical analysis of minerals from the Khao Phra Ngam area and vicinity shows that large proportions of the mineral are calcium-rich (diopside, grossular-andradite, epidote, calcite, sphene, and apatite). This observation suggests high calcium activity during skarn formation, most likely emanating from the solution of calcic carbonate protoliths. The mineral chemistry of prograde skarn minerals in the Khao Phra Ngam sub-area shows that: the wollastonite skarn contains wollastonite (Wo $_{99.86-99.63}$), clinopyroxene (Di $_{92-98}$, Hd $_{2-7}$) and garnet (Gr $_{60-98}$, Ad $_{0.4-39}$). The garnet-clinopyroxene skarn consists of wollastonite (Wo $_{99.25-99..50}$), clinopyroxene (Di $_{92-98}$, Hd $_{2-7}$), aniotropic garnet (Gr $_{24-91}$, Ad $_{7-75}$), and isotropic garnet (Gr $_{80}$, Ad $_{19}$). The garnet skarn is composed of aniotropic garnet (Gr $_{6-81}$, Ad $_{16-92}$), and isotropic garnet (Gr $_{81}$, Ad $_{16}$), clinopyroxene (Di $_{66-98}$, Hd $_{2-33}$) and epidote with 12.27wt% Fe. The plagioclase-hornblende skarn contains plagioclase ($An_1$), amphibole (actinolite, $Mg^{2+}$ / ($Mg^{2+}$+ $Fe^{2+}$) ratio ranges from 0.61 to 0.89) and some garnet (Gr $_{42}$, Ad $_{58}$). The mineral chemistry of the igneous mineral assemblage in this area is as follow; the diorite consists of amphibole (actinolite and actinolite-hornblende, $Mg^{2+}$ / ($Mg^{2+}$+ $Fe^{2+}$) ratio ranges from 0.61 to 1.0), plagioclase-feldspar (An $_{1.20-42.00}$ with some anorthite) and pyroxene (augite, MgO $_{13.23-14.23\ \mathrm{wt\%}}$ and FeO $_{12.31-13.53\ \mathrm{wt\%}}$). The granodiorite consists of pyroxene (augite, MgO $_{15.07\ \mathrm{wt\%}}$ and FeO $_{10.25\ \mathrm{wt\%}}$) and plagioclase-feldspar (An $_{24}$) and microcline.

In the Khao Thap Kwai Sub-area, the mineral chemistry of prograde skarn minerals shows as follow: the garnet-clinopyroxene skarn contains garnet (Gr $_{75}$, Ad

$_{23}$), clinopyroxene (Di $_{65\text{-}96}$, Hd $_{4\text{-}32}$) and some wollastonite (Wo $_{99.37}$). The garnet skarn is composed mainly of garnet (Gr $_{26\text{-}94}$, Ad $_{4\text{-}73}$) and zoned-garnet showing Al-rich core (Gr $_{70}$, Ad $_{28}$) and Fe-rich rim (Gr $_{20}$, Ad $_{79}$). The plagioclase-hornblende skarn contains mainly plagioclase (An $_{4\text{-}92}$). The mineral chemistry of the igneous mineral assemblage in this area is as follow; the diorite consists of amphibole (actinolite, actinolite-hornblende and magnesio-hornblende, $Mg^{2+}$ / ($Mg^{2+}$+ $Fe^{2+}$) ratio ranges from 0.67 to 0.91) and plagioclase-feldspar (An $_{0.2\text{-}79}$) with some anorthite (An $_{96\text{-}100}$). The granodiorite contains amphibole (actinolite-hornblende, $Mg^{2+}$ / ($Mg^{2+}$+ $Fe^{2+}$) ratio = 0.88) and plagioclase-feldspar (An $_{3\text{-}32}$).

The mineral chemistry of prograde skarn minerals in the Khao Phu Kha Sub-area shows that: the garnet-clinopyroxene skarn consists of garnet (Gr $_{81}$, Ad $_{18}$) and clinopyroxene (Di $_{73}$, Hd $_{22}$). The garnet skarn is composed mainly of garnet (Gr $_{0.2\text{-}49}$, Ad $_{50\text{-}99}$) and zoned-garnet showing Fe-rich core (Gr $_{0.00}$, Ad $_{99.62}$) and Al-rich rim (Gr $_{50}$, Ad $_{41}$) and epidote with 19.19-19.91 wt% Fe. The plagioclase-hornblende skarn contains clinopyroxene (Di $_{82}$, Hd $_{16}$) and garnet (Gr $_{30}$, Ad $_{89}$). The mineral chemistry of the igneous mineral assemblage in this area is as follow; the diorite consists of plagioclase-feldspar (An $_{22\text{-}35}$) with some K-feldspar and pyroxene (augite, MgO $_{14.43\ \mathrm{wt\%}}$ and FeO $_{13.63\ \mathrm{wt\%}}$).

Mineral chemical data also provides information which can be used to classify the skarn type. In their attempts to classify skarns on the basis of pyroxene composition, Nakano, *et al.* (1994) reported that Mn/Fe ratios in each deposits is relatively constant and that they tend to vary regionally in accordance with metal type. They found that tungsten skarn have pyroxene composition with an intermediate Mn/Fe ratio (average around 0.15), Cu-Fe deposits have low Mn/Fe ration (<0.1), whereas Zn-Pb deposits have high Mn/Fe ratios (>0.2). The average clinopyroxene Mn/Fe ratio of 0.04 at the Khao Phra Ngam Sub-area, 0.06 at the Khao Thap Kwai Sub-area and 0.14 at the Khao Phu Kha Sub-area are consistent with the Cu-Fe skarn of Nakano *et al.* (1994).

## 7-2 P, T, X $_{CO_2}$ , and $f_{O_2}$ Condition During Skarn Formation

In order to estimate the conditions where mineral assemblage in prograde skarn are stable, phase equilibria in the system $CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ were calculated systematically using the internally consistent thermochemical data for minerals compiled by Helgeson *et al*. (1978) based on experimental curves. The calculations were carried out for the following minerals: grossular, clinozoisite, anorthite, diopside, tremolite, quartz, calcite, and wollastonite. Thermochemical data for fugacity coefficients for $H_2O$ and $CO_2$ are taken from Burnham *et al*. (1969) and Majumdar and Roy (1956), respectively.

The T-X $_{CO_2}$ diagram calculated at 1 kbar is shown in Figure 7-3 a. The calculation was carried out with the following assumptions: (1) fluid pressure ($H_2O$ and $CO_2$) equal to total pressure, (2) constant volume exchange of reaction for the minerals, and (3) ideal mixing of $H_2O$ and $CO_2$.

The region where the mineral assemblages in prograde skarn indicated above are stable is hatched in Figure 7-3a. This region is bounded by the following univariant curves:

dolomite + 2 quartz = diopside + 2 $CO_2$ (1)

anorthite + calcite + quartz = grossular + $CO_2$ (2)

calcite + quartz = wollastonite + $CO_2$ (3)

As the pressure was estimated to be about 1 Kbar in the preceding section and the fluid inclusion study for quartz with a later stage product shows 290° to 350°C for the filling temperature (Muramatsu and Nambu, 1978), the prograde skarns are estimated to be formed in the temperature range from 350° to 700° and an $X_{CO2}$ range from 0.1 to 0.3. Figure 7-3 b shows the zonal arrangements of skarn corresponding to each region in Figure 7-3 a. This figure is constructed on the assumption that $Al_2O_3$ and MgO are inert composition, that CaO is a mobile component, that $H_2O$ and $CO_2$ are perfectly mobile components. The zonal arrangement of prograde skarn in the Khao Phra Ngam area is correspond to area 1, 2, 3 and 4 in Figure 7-3 a.

### 7.3 Comparison to Other Cu-Fe Skarn and Genetic Model.

Copper skarns are perhaps the world most abundant skarn type (Table 7-2). They are particularly common in orogenic zones related to subduction, both in oceanic and continental settings. Most copper skarns are associated with I-type, magnetite series, calc-alkaline, porphyritic plutons, many of which have co-genetic volcanic rocks, stockwork veining, brittle fracturing and brecciation, and intense hydrothermal alteration. These are all features indicative of a relatively shallow environment of formation. Most copper skarns form in close proximity to stock contacts with a relatively oxidized skarn mineralogy dominated by andraditic garnet. Other phases include diopsidic pyroxene, vesuvianite, wollastonite, actinolite, and epidote. Hematite and magnetite are common in most deposits and the presence of dolomitic wall rocks is coincident with massive magnetite lodes which may be mined on a local scale for iron. As noted by Einaudi *et al*. (1981), copper skarns are commonly zoned with massive garnet near the pluton and increasing pyroxene and finally vesuvianite and/or wollastonite near the marble contact. In addition, garnet may be colour zoned from proximal dark reddish-brown to distal green and yellow varieties. Sulphide mineralogy and metal ratios may also be systematically zoned relative to the causative pluton. In general, pyrite and chalcopyrite are most abundant near the pluton with increasing chalcopyrite and finally bornite in wollastonite zones near the marble contact.

The Khao Phra Ngam skarn shows many similarities and a few differences with other Cu-Fe skarn deposits (eg. Ely, Nevada, Bingham, Utah and Yerington, Nevada USA, Tables 7-1, 7-2 and Figure 7-2). The deposit occurs in carbonate host rocks that are associated with intermediate intrusion. These skarns are generally characterized by early anhydrous mineral assemblages that are overprinted by later hydrous retrograde mineral assemblages. The Khao Phra Ngam skarn is rich in hematite-magnetite and minor chalcopyrite, pyrite, bornite, spharlerite, and covellite.

The genesis of the Khao Phra Ngam skarn is demonstrated schematically in Figure 7-1 A., showing the development of the skarn following the Permo-Triassic diorite intrusion into the Permian carbonate rocks. Skarn developed in the carbonate horizons, which direct contact with the intrusion acts as a permeable connection. The Permian carbonate beds were overprinted by high-temperature early skarn within the unit due to the emanating fluid derived from the emplaced Permo-Triassic diorite after an initial isochemical metasomatism of the carbonate rocks. These early skarn assemblages were preferentially formed in carbonate rocks, which are chemically very reactive and have enhanced permeability.

During the prograde skarns forming, fluids were largely anhydrous and doritic derived, and no connection channels to focus fluids from meteoric sources from the

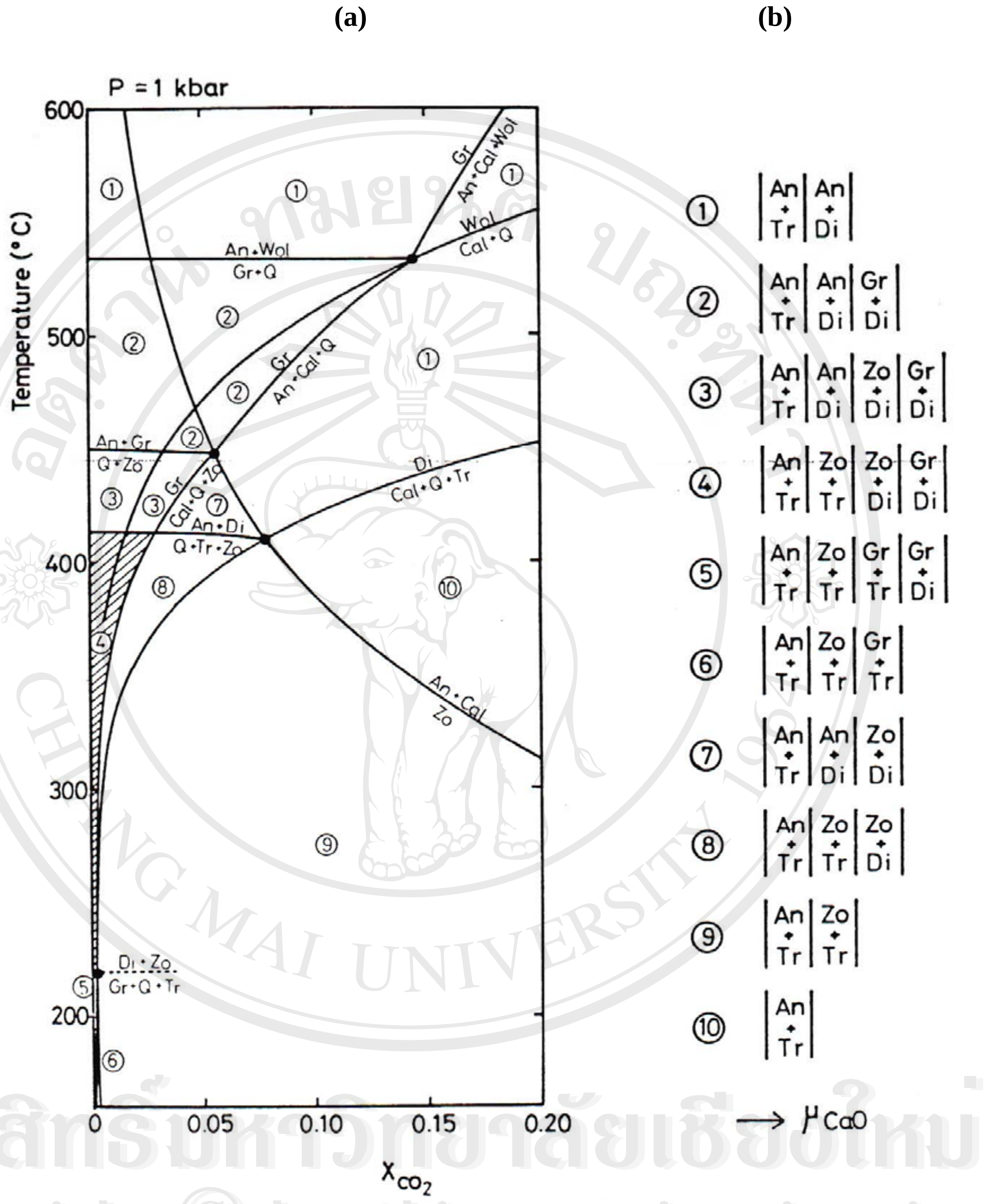


Figure 7-3 (a) T-Xco$_2$ diagram in the system CaO-MgO-$Al_2O_3$-$SiO_2$-$H_2O$-$CO_2$. $P_{total}$ = 1 kb. (b) Zonal arrangement of skarn predicted from (a). The circled numbers correspond to those of (a). This figure was constructed on the assumptions that $Al_2O_3$ and MgO are inert components, that CaO is a mobile component, that $SiO_2$ ia an excess component, and that $H_20$ and $CO_2$ are perfectly mobile components. Based on data from Helgeson *et al.* (1978) (modified after Uchida and Iiyama., 1982).

**Table 7.2** Major characteristic of the five classes of calcite skarn deposit (modified after Einaudi *et al.*, 1982).

| | **Iron** | **Tungsten** | **Copper** | **Zinc-lead** | **Tin-tungsten** |
|---|---|---|---|---|---|
| **Typical size** | 5-200 m.t. | 0.1-2 m.t. | 1-100 m.t. | 0.2-3m.t. | 0.1-3 m.t. |
| **Typical grade** | 40% Fe | 0.7% $WO_3$ | 1-2% Cu | 9% Zn, 6% Pb, 5oz/ton Ag | 0.1-0.7% Sn |
| **Metal associated** | Fe, (Cu, Co, Au) | W, Mo, Cu, (Zn, Bi) | Cu, (Mo, Zn, W) | Zn, Pb, Ag, (Cu, W) | Sn, F, W, (Be, Zn) |
| **Tectonic setting** | Oceanic island arc; rifted contnnental margin | Continental margin, syn- to late orogenic | Continental margin, syn- to late orogenic | Continental margin, syn- to late orogenic | Continental margin,late to postorogenic or anorogenic |
| **Associated igneous rocks** | Gabbro to syenite; mostly diorite, some diabase | Quartz diorite to quartz monzonite, rarely alaskite | Granodiorite to quartz monzonite | Plutons commonly absent: granodiorite to granite, diorite to syenite | Granite |
| **Cogenetic volcanics in ore zone** | Common; basalt; andesite | Absent | Rare; andesite, quartz latite | Absent | Absent |
| **Pluton morphology** | Large to small stocks, dikes | Lagre plutons, batholiths | Small stocks, dikes, breccia pipes | If present, stocks and dikes | Stocks, batholiths |
| **Alteration in igneous rocks** | | | | | |
| **Endoskarn** | Extensive in plutons, volcanics; epidote-pyroxene | Very local; pyroxene-plagioclase | Local; epidote-pyroxene-garnet | Local, but intense; epidote-pyroxene-garnet | Very rare |
| **Other** | Extensive Na silicates | Local quartz-biotite-muscovite-sulfide | Can be very extensive (e.g. porphyry Cu); biotite-orthoclase, quartz-sericite-pyrite | Local argillic, propylitic | Extensive greisen |
| **Exoskarn composition** | High in Fe; low in S, Mn | High in Al, Fe; low in S | High in Fe, S; low in Al, Mn | High in Fe, Mn, S; low in Al | High in Al, Fe; low in Fe, S |
| **Early minerals** | Ferrosalite (Hd$_{20-80}$), grandite (Ad$_{20-95}$), epidote, magnetite | Ferrosalite-hedenbergite (Hd$_{60-90}$, Jo$_{5-20}$ ), grandite (Ad$_{10-50}$), idocrase, wollastonite | Andradite (Ad$_{60-100}$), diopside (Hd$_{5-50}$), wollastonite | Manganoan hedenbergite (Hd$_{30-90}$, Jo$_{10-40}$ ), andradite garnet (Ad$_{20-100}$, Spessartine$_{2-10}$ ), bastamite, rhodonite | Idocrase, spessartine-rich grandite, Sn andradite, malayaite, danburite, datolite |
| **Late minerals** | Amphibole, chlorite, ilvaite | Spessartine ($_{5-35}$)-almandine ($_{5-40}$)-grandite, biotite, hornblende, plagioclase | Actinolite, (chlorite, montmorillonoids) | Mn actinolite, ilvaite, chlorite, dannemorite, rhodochrosite | Amphibole, mica, chlorite tourmaline, fluorite |
| **Ore minerals** | Magnetite, (chalcopyrite, cobaltite, pyrrhotite) | Scheelite, molybdenite, chalcopyrite, (sphalerite, pyrrhotite, magnetite, pyrite, biotite | Chalcopyrite, pyrite, hematite, magnetite, (bornite, pyrrhotite, molybdenite, tennantite) | Sphalerite, galena, pyrrhotite, pyrite, magnetite, (chalcopyrite, arsenopyrite) | Cassiterite, (scheelite, sphalerite, pyrrhotite, magnetite, pyrite, arsenopyrite) |

**Table 7-3** Characteristics of copper skarns (modified after Einaudi *et al.*, 1982).

| **Locally** | **Tonnage and grade, skarn ore** | **Age and morphology of intrusive rocks** | **Alteration and mineralization in intrusive** | **Calcic skarn Zoning of major minerals Stock → marble** | **Retrograde alteration** | **Magnesian skarn** | **References** |
|---|---|---|---|---|---|---|---|
| Christmas, Arizona | 100 m.t. 0.7% Cu | 62 m.y. granodiorite porphyey plug/dike complex, 0.5x0.5 km | Major potassic with chalcopyrite > bornite; very minor sericite; few meters endoskarn: pyroxene, garnet, idoclase, chalcopyrite > pyrite 0.05-0.1% Cu | Garnet-epidote-magnetite, pyrite> chalcopyrite → garnet, bornite > chalcopyrite, sphalerite $\text{Ad}_{72-91}$ | Minor calcite | Major occurrence: Forsterite, magnetite, brucite; chalcopyrite, pyrite (sphalerite) | Perry (1968, 1969) |
| Bingham, Utha | >100 m.t. 2% Cu + 150 m.t. 1,2%Cu 0.03% Mo, 0.4 oz Ag | 38 m.y. very irregular monzonite and quartz monzonite porphyry stock, 2x1.5 km; late quartz latite dikes; breccias | Major potassic with chalcopyrite-bornite and chalcopyrite>> pyrite; moderate sericitic with pyrite>chalcopyrite; 0.8% Cu, 0.04% Mo; minor epidote-amphibole endoskarn | Granet-pyroxene-magnetite, pyrite > chalcopyrite → wollastonite-garnet, bornite, chalcopyrite, (sphalerite, pyrite) $\text{Ad}_{60-100}$, Aug. $\text{Ad}_{98}$,$\text{Hd}_{5-35}$ | Major near stock in upper level; pyrite, chalorite,montmorillonite, talc, opal | Absent (no dolomite) | Atkinson and Einaudi (1978), Sweeney (1980) |

**Table 7-3** (Continued)

| | | | Calcic skarn | | | | |
|---|---|---|---|---|---|---|---|
| **Locally** | **Tonnage and grade, skarn ore** | **Age and morphology of intrusive rocks** | **Alteration and mineralization in intrusive** | **Zoning of major minerals Stock → marble** | **Retrograde alteration** | **Magnesian skarn** | **References** |
| Santa Rita, New maxico | > 100 m.t. 0.9% Cu | 56 m.y. elongate granodiorite and quartz monzonite porphyry stock, 1.2 x 2.8 km | Major potassic with pyrite > chalcopyrite; moderate sericitic with pyrite >> chalcopyrite; 0.1-0.3% Cu | Garnet-epidote-magnetite- chalcopyrite → garnet-pyroxene-pyrite-chalcopyrite→ garnet-sphalerite; avg. pyrite:chalcopyrite = 1:1 to 10:1 | Minor near sericitic alteration: pyrite, quartz, actinolite, chlorite, montmorillonite, epidote, siderite; 20-75% magnetite, 10-15% sulfide, pyrite:chalcopyrite = 10:1 to 25:1 | Absent (no dolomite) | Nielson (1970) |
| Ely, Nevada | > 100 m.t. | 110 m.y. abundant small stocks (0.5x0.5 km), sills of quartz monzonite porphyry | Minor potassic with pyrite-chalcopyrite; minor sericitic with pyrite > chalcopyrite; local advanced argillic 1% Cu | Garnet ($Ad_{90-100}$) – pyroxene ($Hd_{0-6}$) → wollastonite, pyroxene, idoclase, local green garnet ($Ad_{950-85}$) → pyrrhotite-magnetite-pyrite or galena-sphalerite | Minor quartz-calcite-magnetite-pyrite chalcopyrite veins with montronite envelopes in garnet, with actinolite ($Ft_{17-31}$) envelopes in pyroxene; major quartz-calcite-pyrite replacement of skarn and limestone | Absent (no dolomite) | James (1976) |

country rocks were formed. In the retrograde alteration stage, on the other hand, granodioritic fluids were concentrated with volatiles, mixed with meteoric fluids, and were focused into permeable early-formed skarn, which were dominantly hydrous. This late stage was also accompanied by the formation of retrograde skarn and hematite-chalcopyrite- pyrite mineralization.

### 7.4 Conclusion

**1.** The Khao Phra Ngam area is located at a contact zone between the Permo-Triassic diorite intrusion and Permian carbonate rocks of Khao Khad Formation. The intrusion had thermally metamorphosed the country rock into marble, diopsidic marble, and reaction skarn rimming chert nodules or chert bed, and subsequent formation of metasomatic skarns. Granodiorite was the late stage intrusion and intruded earlier skarn formation to form retrograde alteration and Cu-Fe mineralization. The zonation of prograde skarn is observed from the host rock side to the intrusive side as follows: marble with minor diopsidic marble, wollastonite skarn, garnet-clinopyroxene skarn, garnet skarn and plagioclase-hornblende skarn.

**2**. The principal skarn mineral assemblages at the Khao Phra Ngam area are garnet, clinopyroxene, wollastonite, calcite, and quartz, together with vesivianite, epidote, magnetite, hematite, chlorite, sphene and apatite as subordinated or accessory minerals. At least four stages of skarn formation and ore mineralization were recognized. Stage I, wollastonite + clinopyroxene ± quartz ± caclcite ± garnet; stage II, clinopyroxene + garnet ± wollastonite ± quartz ± calcite; stage III, garnet ± clinopyroxene ± feldspar ± magnetite ± pyrite; and stage IV, plagioclase + hornblende+ quartz ± pyroxene ± garnet. Retrograde alteration is characterized by a major development of hydrous mineral, such as epidote, chlorite, as well as quartz and calcite replacing the high temperature mineral assemblage. Metal-bearing skarn such as hematite + bornite + chalcopyrite ± pyrite also formed during this stage.

**3**. The chemical analysis of skarn mineral assemblages indicate that garnet belongs to grossular ($Ca_3Al_2Si_3O_{12}$) – andradite ($Ca_3Fe_2Si_3O_{12}$) series which isotropic garnet contains intermediate grossular-andradite composition and anisotropic garnet has little composition variation and contains mainly grossular component. Clinopyroxene belongs to diopside ($CaMgSi_2O_6$) and hedenbergite ($CaFeSi_2O_6$) series but closer to the diopsidic end-member. Wollastonite is almost pure wollastonite component.

**4**. The evolution of skarn formation can be divided into 3 stages: 1) metamorphic (isochemical) stage is characterized by the formation of thermal metamorphism that response to the emplacement of diorite into the carbonate and silicious rocks of the Khao Khad Formation; 2) metasomatic stage is characterized by the formation of prograde skarn and the development of these zonal skarn was likely a response to the mobility of elements as a small scale exchange of $CO_2$, Ca and Mg-rich fluid from the marble and Al, Si and Fe-rich fluid from the diorite. 3) retrograde alteration stage is characterized by a major development of hydrous mineral, such as epidote, chlorite, as well as quartz and calcite replacing the high temperature mineral assemblage. This stage was probably formed during the declining temperature of the diorite intrusion and an infilltration of silica-rich fluid form granodiorite intrusion along crack and fracture.

**5.** Estimates of P, T, $X_{CO_2}$ from the mineral assemblage and the stable phase equilibria in the system $CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ show that the prograde skarns were formed in the temperature ranging from 350° to 700° , pressure ranging from 0.5-1.0 kbar and an $X_{CO2}$ ranging from 0.1 to 0.3 mol%.

**6.** Chalcopyrite and bornite are the dominant sulphide with minor covellite together with spharlerite. Hematite is the main iron ores with minor magnetite and pyrite.

**7.** The skarn at Khao Phra Ngam can be classified as calcic iron-copper skarn deposit.