4.METALLOGENESIS OF FLUORITE

4.1 Temperature-Pressure Conditions of Fluorite Deposition in Northern Thailand

The homogenization temperature of fluorite deposition at Fang, Mae Tha and Ban Hong deposits is mostly between 410-250°c for the first stage, and 280-57°c for the second stage of deposition (Appendix D , Table D-5). Mae La Noi and Ban Muang Ngai (Chiang Dao) fluorite deposits show similar homogenization temperature to those of Fang, Mae Tha and Ban Hong. Amphoe Pai fluorite reveals narrow range of temperature, inclusions mostly homogenized between 155-160°c, with only one inclusion homogenized at 309°c. At Tha Song Yang and Ban Sop Lan (Omkoi), homogenization temperatures are similar to those of Amphoe Pai.

In Fang, Mae Tha, and Ban Hong deposits, there are two types of fluorites formed at greatly different temperature and pressure conditions. The open-space filling fluorite with rock fragments at Fang, the granular fluorite associated with stibnite at Mae Tha, and the pale yellowish brown fluorite with rock fragments at Ban Hong contain gaseous inclusions (Type 4). They are formed at high temperatures of 250-410°c (251.3-357.2°c at Fang, 271.7-410°c at Mae Tha, 281.8-379.8°c at Ban Hong). This type of fluorite distributed throughout the veins at Fang, Mae Tha and Ban Hong, but mostly concentrated in the lower portions of the ore bodies. The shape of most gaseous inclusions is irregular, since they are trapped between grains of fluorite. Botryoidal and concentrically layered fluorite around rock nuclei, and aggregates of fine radiated crystals are formed at lower temperatures (57-280°c).

Most of the inclusions are of Type 2 and 3 , and are negative of the crystals or related to crystal growth zones. They were formed throughout the temperature range below the first stage, but most of them were suddenly deposited at certain temperature intervals, as shown by the histograms (Figs. 3.15,3.18,3.19). These inclusions tend to occur in the upper parts of ore bodies.

The pressure of formation of the high temperature fluorite can not be determined by using a decrepitation temperature-pressure curve, a method in use for quartz, because such a curve for fluorite is not available at present. Fluorite with Types 2 and 3 inclusions was deposited later than the high temperature-pressure fluorite of the first stage. The pressure was low, possibly very close to atmospheric pressure, as indicated by mineralization in Pleistocene gravel beds in some places and related to recent topography. This fluorite is related to the hot springs, as will be discussed later.

The other studied deposits in northern Thailand also show two generations of fluorite deposition, as in Fang, Mae Tha, and Ban Hong. But the stage of high temperature-pressure fluorite indicated by gaseous inclusions is not as clear. Most of the fluorite is colour-layered fluorite or well-crystallized fluorite, formed at temperatures less than 200°c. In Amphoe Pai, it occurs in the upper portions of veins in the region. This type of fluorite is quartz-free. There are also four inclusions from fluorite intergrown with cryptocrystalline quartz homogenized between 259.1 and 309.4°c. This type of fluorite is usually found at lower elevation in this region.

In Tha Song Yang and Ban Sop Lan (Omkoi), homogenization temperatures are uniform. They range from 200 to 125°c. There are no gaseous inclusions. The deposition consist of well crystallized cubic fluorite formed by only one generation of deposition.

4.2 Association with Hot spring : Model for Fluorite Deposition

The study of the fluorite deposits in the previous chapters indicates that they were formed under similar conditions of deposition. Most of them occur around Cenozoic structural basins, along major structural alignments, and associated with present-day hot springs in most places (Shouls, 1972).

The subsurface reservoir temperatures from hot springs in Chiang Mai were calculated by Premgamol and others (1976) and later by Barr and others (1977), using the water chemistry of the hot springs as " silica geothermometer " and " Na-K-Ca geothermometer "(Appendix F , Table F-1). The subsurface temperatures of the hot springs in the mine areas and others are in the same range as the temperatures of second stage fluorite deposition determined from fluid inclusion studies. First stage fluorites formed at much higher temperatures. At SP Mine, Mae La Noi, the subsurface temperature of the hot spring near the fluorite deposits is estimated at 152°c by silica geothermometer, while the surface temperature is 80°c (Appendix F , Table F-1). The hot spring 1.2 km north of the Fang fluorite deposit has 183°c subsurface temperature, and 100°c surface temperature. The warm water in the fluorite vein is about 40°c at the surface. Hot pools in the fluorite vein at Thepnithi claim, Mae Tha are at 42°c, and the surface temperature of water in the Universal vein is 27°c, the same as the surrounding temperature in winter. Both waters contain 25 ppm fluorine (Ratanasathien 1979). Hot pool in the fluorite vein in the Thai Fluorspar claim at Ban Hong show a temperature about 40-50°c at the surface. The temperature of hot pools in the Pai River close to Mahalanna vein was not determined.

Subsurface reservoir temperatures of hot springs in all areas of northern Thailand range from 65 to 200°c by the silioa geothermometer. This range is the same as for most inclusion homogenization temperatures determined, and for the probable true formation temperatures. The subsurface temperatures of several hot pools in fluorite deposits are still under investigation.

Chemical analyses of the hot spring (Appendix F, Table F-2) indicate that the fluorine content of the thermal waters ranges from 11-167 ppm. The range of fluoride values found in the ground water in the world is only 0.5 to 1.5 ppm (Graham and others, 1975).

Shouls (1972) observed that in Ban Kong Khak fluorite deposit, 70km SW of Chiang Mai , is still being deposited from hot springs. He noted that hot springs have cemented a recent pebble bank, and adjacent to some of the hot spring vents botryoidal encrustations of fine grained , radiating fluorite are found around replacement mineralization.

Thus, a close association between hot springs and fluorite deposits is indicated by :-

(a) the homogenization temperatures of inclusions reveal the same range of temperature as subsurface reservoir temperatures of hot springs in fluorite deposits and at other localities possessing similar geologic settings.

(b) hot spring water is unusually rich in fluorine.

(c) fluorite is still being precipitated.

Ramingwong and others (1978) suggested the geologic setting of hot springs in northern Thailand as :-

1) The associated rocks and possibly reservoir rocks of the thermal water systems are predominantly granitic rocks of various ages or sedimentary rocks near the granites. Some springs are associated with volcanic rocks. At Fang, Mae La Noi, and Ban Hong, hot pools in or near veins are in limestones and the other rocks, while the pool at Mae Tha is in volcanic rocks close to limestone.

2) Most of the hot springs occur in the areas of natural discharge and therefore may not be immediately above the heat source. The general flow component of the thermal water system is vertical, although there are some indications of horizontal (lateral) flow component (e.g. at Thepanom hot springs, Amphoe Mae Cham). Where lateral flow is present, the thermal water undoubtedly follows a local ground water flow pattern. As a result of this, thermal water will mix with local ground water and subsurface temperatures as calculated from this type of thermal water will yield relatively low temperatures.

3) Faults and fractures which have been reactivated during the Late Cenozoic are definitely related to the thermal water system. They are though to act as convenient flow channels for

discharging thermal waters, and have raised heated rocks close to the surface (Fig. 4.1). Moreever, considerable heat is thought to have been added to the adjacent rocks as a result of the movement of the rocks

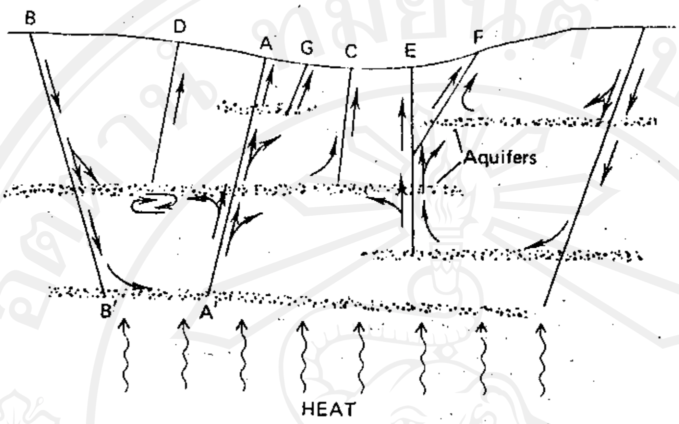


Fig 4.1 Schematic model of a hot-spring system having a heat source of unspecified nature and interconnected permeability.
(after Fournier and others, 1974)

along the fault zone. Fracturing is of great importance as regards storage capacities, recharge and discharge quantities.

4) Thermal water is of local meteoric origin as evidenced from isotopic analysis, D/H and $0^{18}/0^{16}$ ratio, and low salinity. It is derived from altitudes some what higher than the discharge area.

Ramingwong and others (1978) concluded that most of the hot springs are the result of deeply circulating, locally derived meteoric water that has accquired heat and chemical constituents by percolation through fractured granitic plutons and surrounding wall rocks to considerable depth. The heated water found access to the surface along fractures and faults in the plutons. If the geothermal gradient in northern Thailand is, on average 40-50 °c/ km, and a maximum

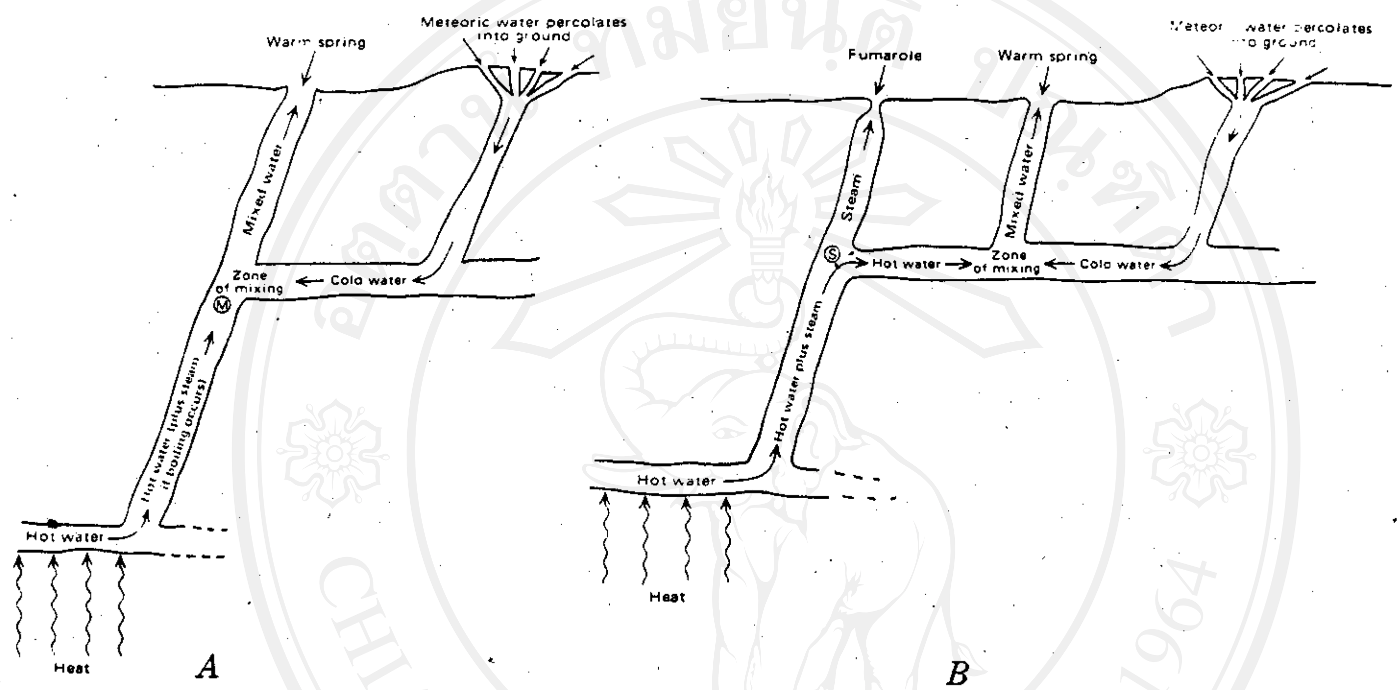


Fig. 4.2 Schematic model (A) for obtaining a mixed-water warm spring in which both the enthalpy and silica content of the hot-water content are the same as in the original deep water (model 1) and schematic model (B) in which the hot-water component has lost steam before mixing with cold water (model 2). (after Fournier and Truesdell, 1974).

subsurface temperature as calculated by the chemical geothermometer is 180° c, this would suggest that water reached a depth of 1.6-2 km. Relatively recent faults may have a vertical displacement in the order of 2 km (Ramingwong and others, 1978).

The hot springs in the fluorite deposits seem to be different from the normal hot springs. The faulting and fracturing of rocks, natural discharge, and the nature of the reservoir rock are similar, but

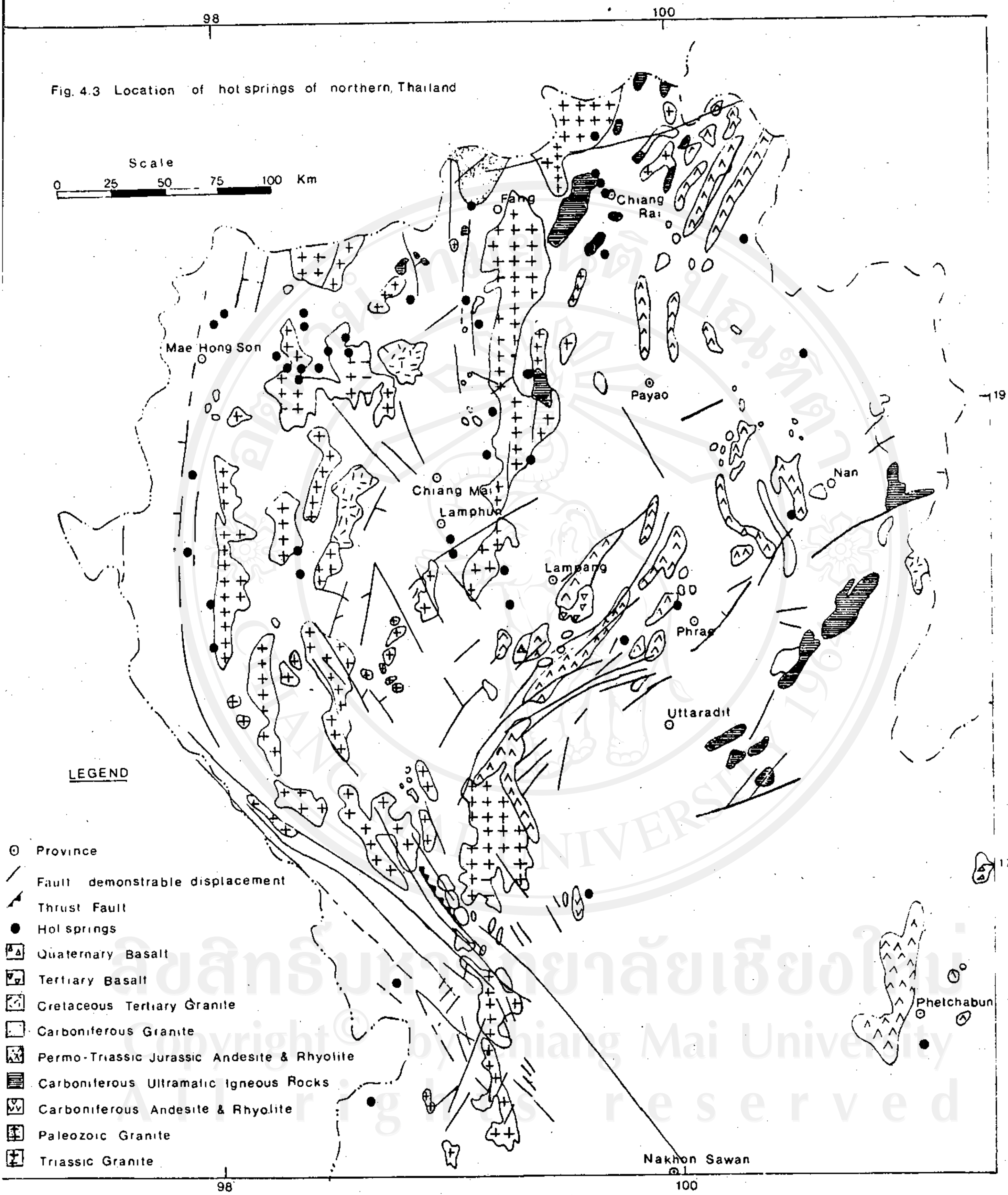


Fig. 4.3 Location of hot springs of northern Thailand
Scale
0 25 50 75 100 Km
98
100
Fang
Chiang Rai
Mae Hong Son
Payao
19
Nan
Chiang Mai
Lamphun
Lampang
Phrae
Uttaradit
17
Phetchabun
Nakhon Sawan
LEGEND
Province
Fault demonstrable displacement
Thrust Fault
Hot springs
Quaternary Basalt
Tertiary Basalt
Cretaceous Tertiary Granite
Carboniferous Granite
Permo-Triassic Jurassic Andesite & Rhyolite
Carboniferous Ultramafic Igneous Rocks
Carboniferous Andesite & Rhyolite
Paleozoic Granite
Triassic Granite

the sources and fractions of waters in the hot springs (that is, the amount of meteoric water,and the amount of magmatic water-the ordinary composition of most hot springs ranging from 5-10 % by volume), is different. In fluorite-forming hot springs, there must be a huge volume of high temperature fluorine-rich magmatic water (evidenced by gaseous inclusions in replacement fluorite and open space filling fluorite near rock nuclei in deposits associated with hot springs) mixed with some local ground water at depth. Fluorine-bearing water ascends from depth along a channel way such as a structural fault or joint, and mixes with shallow cold ground water near the surface, usually at the edge of a Cenozoic basin, before flowing laterally to the river. At the depth of mixing, the weight of the overlying column of cold water is greater than the weight of warm mixed water. Thus, the pressure relations are such that oold water enters the hot-water channel and the mixture flows to the surface and is discharged as a warm spring (Fig. 4.2 A.) Figure 4.2B. shows a case in which a fumarole occurs because steam escaped before the hot water mixed with ground water.

In fluorite-forming hot springs, the mean temperature of original hot magmatic waters was about 2.0-2.86 times greater than after mixing. This is evidenced by comparing homogenization of the first stage fluorite containing gaseous inclusions and second-stage fluorite containing gas-liquid inclusions (Appendix D , Table D-5). At the zone of mixing, super-saturation of fluorite occurred, and fluorite was deposited from the zone of mixing to the surface. Because the rate of temperature decrease was progressively greater upward to the surface, the fluorite ore body is usually wedge-shaped with the upper part (near surface) wider than the lower part of ore body, e.g. at Fang, Mae Tha, and Ban Hong. Below the mixing zone, the fluorite is scarcely deposited. Some fluorite may be deposited along the channel way from the magma chamber up to the zone of mixing, and to the surface by reaction of fluorine vapour with the wall rock, but not because of supersaturation.

To understand the nature of the hot spring model for fluorite deposition, it is necessary to study the limit of solubility for deposition of fluorite in the low-temperature water, and the mode of formation of fluorite at low temperatures, and the associated gangue minerals such as stibnite, quartz, etc.

4.3 Chemistry of Fluorite Deposition

In low temperature systems (under 250°c) fluorite is only sparingly soluble in water (Strubel, 1965). The solubility in pure water rises from about 9 ppm CaF_2 (4.5 ppm F) at 25°c, to 16 ppm CaF_2 (8 ppm F) at 100°c (Fig. 4.4). Solubility at temperatures up to 100°c is doubled in 0.1 N NaCl solution and tripled in 2 N NaCl solution, presumably because of the formation of complexes or ion pairs. Amorphous silica in solution increases the solubility of fluorite, but the change in solubility with temperature is little affected (Ellis and Mahon, 1964). Cooling from saturated solution will precipitate fluorite in only small amounts from about 100°c down to surrounding surface temperature. Fluorite can precipitate readily at 25°c from moderately supersaturated solutions (Roberson and Schoen, 1973). At 1 atm pressure

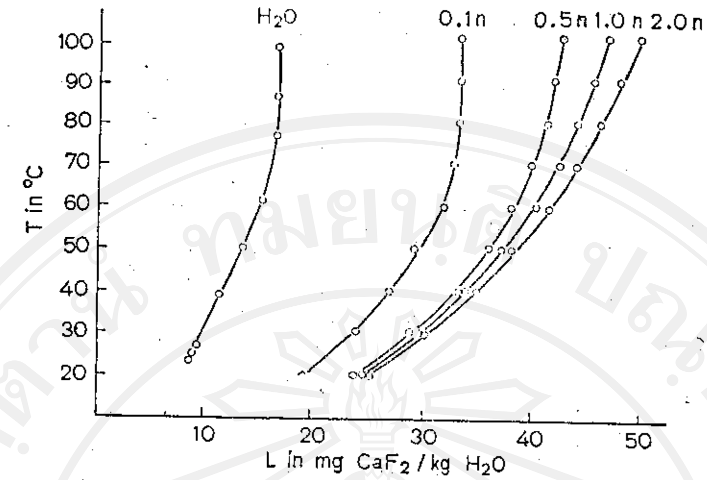


Fig. 4.4 Solubility of fluorite in the system CaF_2—NaCl—H_2O in solutions of constant NaCl concentrations. (After STRÜBEL, 1965)

and neglecting ionic strength effects, a solution which is saturated at 100°c would be supersaturated by a factor of 3 if the solution is cooled to 25°c (Roberson and Schoen, op. cit.). They also pointed that some thermal water sources of the Snake River Basin, Idaho, are near saturation with respect to fluorite. The amount of fluorite which can be deposited by cooling low-temperature fluorite-saturated solutions has been discussed by Holland (1967). He showed that under optimum conditions, 25 mg of fluorite could be precipitated from 1 kg of water (25 gm / Ton) if the saturated solution was cooled from 101.5°c to 20°c. Saturated solutions with calcium and fluorite not in equivalent proportion would precipitate less fluorite. The solubility of fluorite decreases with increasing Ca^{++} content in the water.

Thus mixing of water from different lithologic assemblages could occur as water moves towards a thermal spring orifice, and supersaturation with respect to fluorite could result in the mixture. If other conditions were favourable, precipitation could occur at the mixing point or beyond it in flow path, especially if the temperature of water decreased significantly.

The mode of formations of northern Thailand fluorite has been studied by Shouls (1972). He described four possibile causes of fluorite precipitation :-

1) From modern thermal water.

In modern thermal water, salinities up to about 500 ppm occur (Appendix F , Table F-2). This represents an electrolyte concentration of about .01 N., which is enough to affect the solubility of fluorite, even allowing for dilution of thermal water by unheated low salinity ground waters. Spring water to which calcium is added from other sources, e.g. from calcium rich rocks, or by mixing with calcium rich waters can precipitate fluorite.

In northern Thailand, limestone and other sources of calcium are abundant. The alternating wet and dry monsoonal climate provides a mechanism where this mixing could be achieved, especially where permeable hill areas provide fluctuating hydrostatic pressure at the base of slopes. The more constant hydrostatic pressure from the thermal water allows the interface between the ground water of meteoric origin, and the geothermal water to move seasonally, and thus spreads the zone of mixing and reaction through an appreciable thickness of rock.

2) Cooling of fluorite-saturated solutions.

Shouls (1972) suggested that some deposits show low temperature textures. However, he suggested that this method of deposition can not account for major fluorite occurrences such as the Ban Hong deposit. He calculated a heat balance for the Ban Hong deposit by assuming that optimum cooling conditions occurred in the fluorite saturated solution. He assumed that the deposit formed in a million years, and calculated the annual heat loss for each square centimeter of wall. This comes to 8800 cal/cm^2/year. This figure may be compared with the average surface heat flow of about 40 cal/cm^2/year for the Earth's land surface, and a maximum value of about 341 cal/cm^2/year in a geothermal area in Japan (Holmes, 1965). On this basis a period of about 25 million years would have been necessary to account for the formation of the deposit. Hence this cause of deposition is unlikely to have been of great importance.

3) Release of pressure.

In a high pressure-high temperature system, a release of pressure lowers the solubility of fluorite. The system however insensitive to pressure changes at low temperatures, and therefore pressure change are discounted as being of major importance in low temperature fluorite formation. However, in a chemical system rich in fluoride ions, release of pressure and boiling may form a fluoride-rich vapour phase which may :

(a) react with calcium-rich rock to form fluorite as in the equation :-

$$\underset{\text{in solution}}{2H^{+} + 2F^{-}} + \underset{\text{solid}}{2CaCO_3} \longrightarrow \underset{\text{solid}}{CaF_2} + \underset{\text{in solution}}{2(HCO_3)^{-} + Ca^{++}}$$

This gives a volume reduction of 60 %, and consequently viods are formed.

(b) dissolve in water to precipitate fluorite directly if the water is rich in calcium, or form a secondary fluoride-rich water either by condensation or solution.

4) Supersaturation

Supersaturated solutions can exist in the calcium fluoride - water system. Shouls suggested that significant supersaturation is unlikely to have existed during the formation of deposit at Ban Kong Khak because the fine grained banded texture of fluorite indicates the existence of many centers of crystallization during deposition. He suggested that long-term supersaturated solutions can not be the main source of the deposit, although slight temporary supersaturation may have affect local deposition of ore within the vein.

Shouls (1972) finally concluded that thermal water in northern Thailand, of the same origin in both modern and earlier times, are the parent fluids of the fluorite deposits by the process of indirect mixing and reaction with Ca-rich rocks as outlined in 1). Fluoride-rich vapours as outlined in 3) may have been additional sources of fluorite.

The results of the present study relate to the mode of formation. Temperature of homogenization and type of fluid inclusions from many deposits suggests that the earliest fluorite was deposited by release of pressure (3) and supersaturation(4), and later fluorite was deposited by addition of addition of calcium (1). The early fluorite homogenized at $410-250^{\circ}$c with vapour-dominated inclusions ; the source was the vapour phase of the late stage of magma which probably

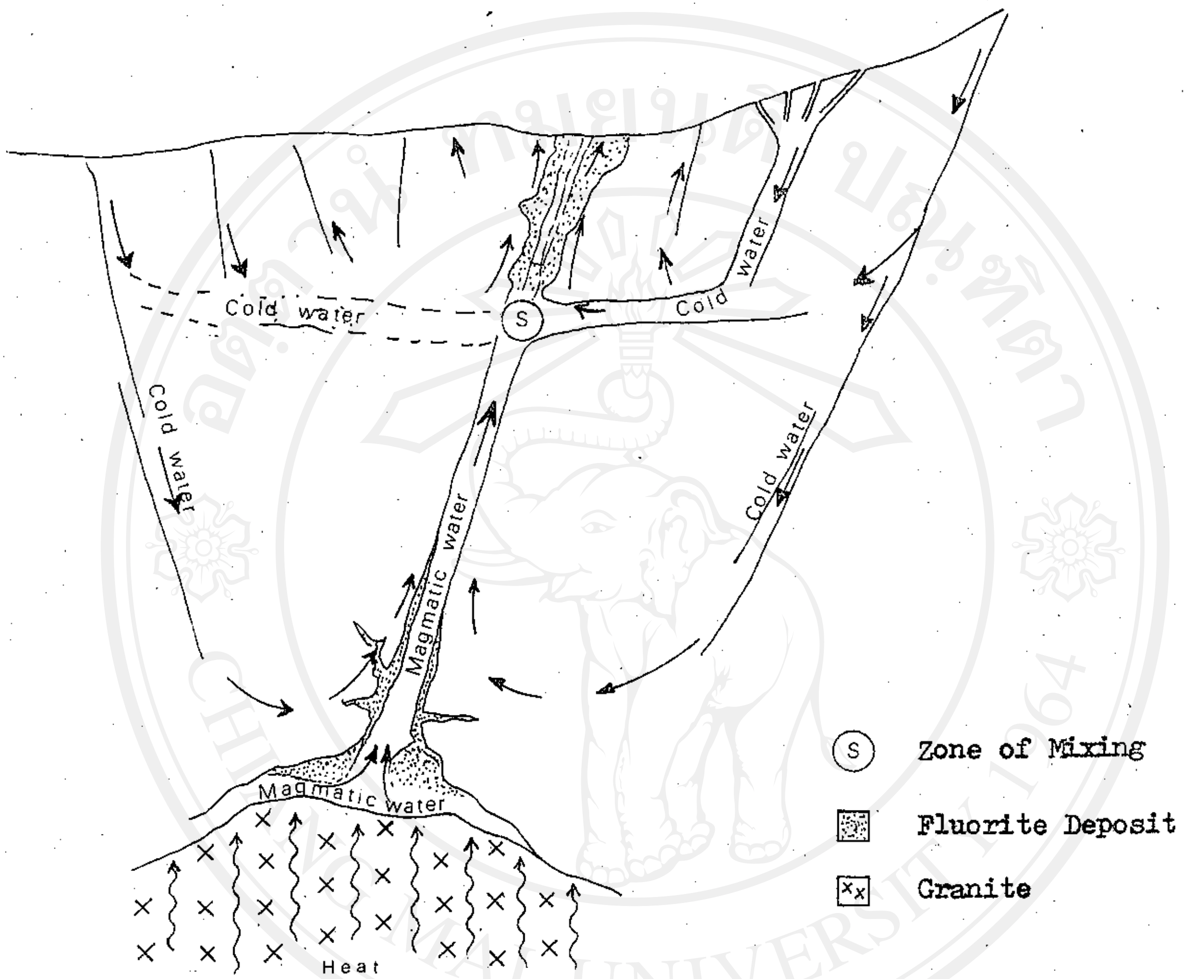


Fig. 4.5 Schematic model for early stage fluorite deposition. Mixing of magmatic water and cold shallow ground water during early deposition ; deposition effected mostly by the methods 3 and 4. (Note : the fluorite replaced country rocks near magma chamber).

concentrated in the upper part of a magma chamber and migrated upward along structural faults. Because of release in pressure, fluorite would deposit by methods 3a and 3b. These high temperature gaseous inclusions are abundant in deposits inwhich the country rock is limestone, such as Fang, Mae Tha, and Ban Hong. The processes 3b and 4 are suitable for deposits inwhich country rocks are not limestone, (hence 1? and 3a not operative), but Ca-water may be supplied from Ca-saturated ground water. Supersaturation (4) may also occur at the zone of mixing with ground water near the surface. This process may be operated for the open-space filling in granitic country rock, such as the Mahalanna Mine (Amphoe Pai) and Ban Sop Lan (Omkoi) deposits. The processes of adding calcium (1) and cooling (2) may also have occurred but would not have been so important during the initial period inwhich the fluorite-saturated magmatic water rose upward.

The later fluorite homogenized at 57-280 °c with gas-liquid or entirely liquid inclusions. Addition of Ca (1) and cooling (2) are likely to be the only processes active in the later period.

In the period of magmatic water, the fluorine vapour could react with country rocks along the channel beyond the magma chamber up to the near-surface ore body (Fig. 4.5). At present, activity has ceased , and there may be only hot spots underneath the deposits. The circulation of modern thermal waters in hot springs with salinity up to 500 ppm (Appendix F , Table F-2), may dissolve fluoride originally deposited from magmatic waters in the deeper parts of channel ways (1.6-2 km). Thermal water ascends along the channel to the near-surface ore

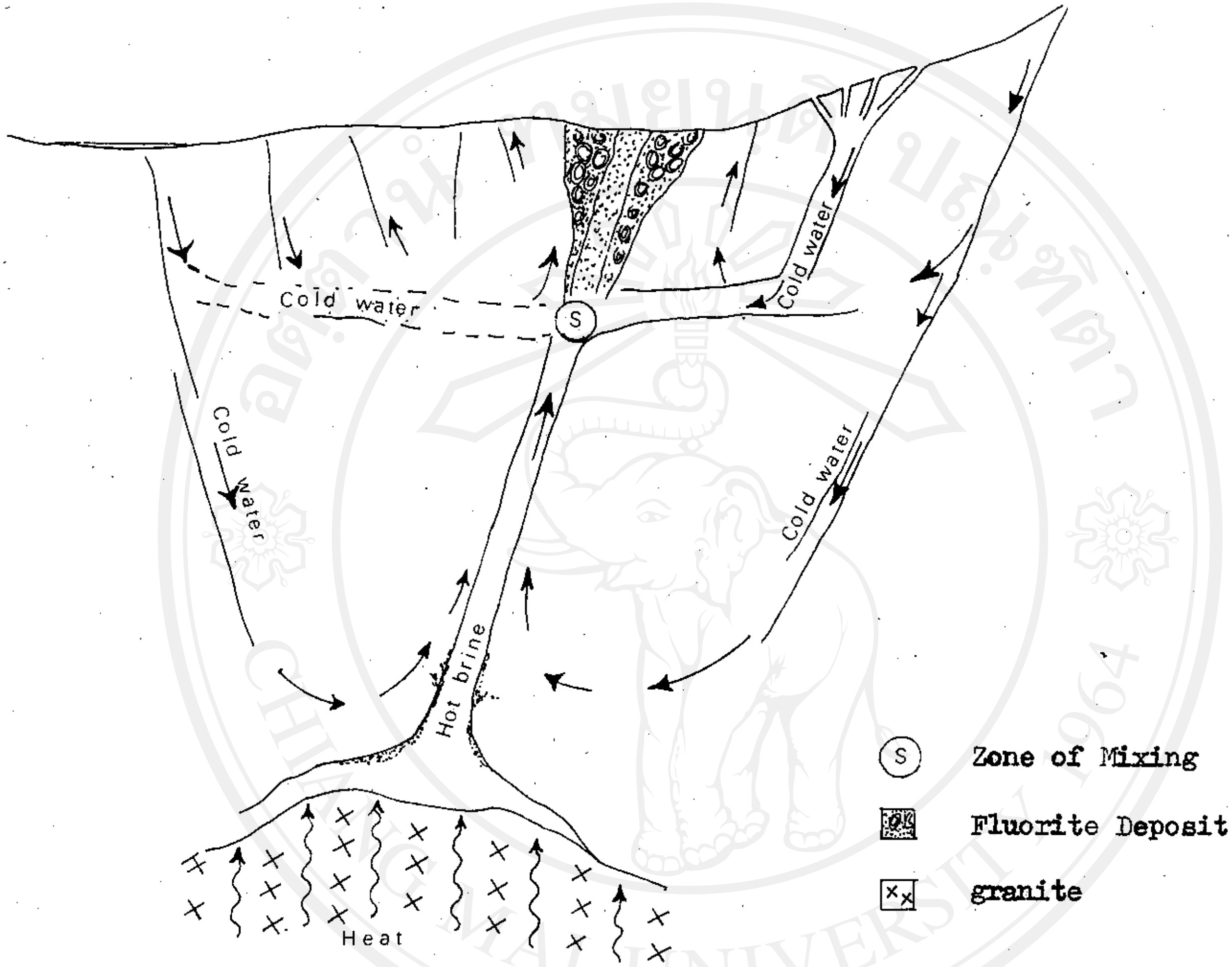


Fig. 4.6 Schematic model for late stage fluorite deposition. Mixing of recent thermal water with cold shallow ground water at the stage later than magmatic F-solution. The remaining heat provided the energy to circulate the thermal (brine) water and dissolved F from the underlying rocks, redeposited in the same zone of mixing, and increasing the size of fluorite veins. (Note : the smaller quantity of replaced fluorite near the magma chamber).

body. Fluorite would redeposit by cooling (2) or by mixing with Ca-saturated shallow ground water (1). This fluorite forms fine grained banded masses around the earlier-formed fluorite (Fig. 4.6).

In Mae La Noi, the fluorite replaced limestone, with relicts of original texture. Mixing with calcium rich water could have caused the later precipitation as layering around the replacement type, or as coating layers in the vugs. Later the fluoride content is reduced to a level of unsaturation and the calcium carbonate in the water becomes relatively saturated during the temperature drop at the hot spring orifice. Calcite then precipitated as interstitial fillings in the remaining space in the vug.

Some deposits contain cryptocrystalline quartz (mainly chalcedony) intergrown with fluorite e.g. some veins in Mahalanna Mine, and some parts in Fang, Mae Tha, and Ban Hong. Pothisat (1973) explained the relationship between fluorite and silica by using the following equation :-

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \qquad 1$$

$$3SiF_4 + 3H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6 \qquad 2$$

$$H_2SiF_6 + 3CaCO_3 \longrightarrow CaF_2 + H_2O + 3Co_2 + SiO_2 \qquad 3$$

$$SiF_4 + 2CaCo_3 \longrightarrow 2CaF_2 + SiO_2 + 2CO_2 \qquad 4$$

Silica has the very close relation to fluorite deposition, especially that was redeposited by cooling (2) and (1) because it can be dissolved in high concentrations, up to 400 ppm in thermal spring (Wedepohl and others, 1972). The silica contents of hot spring water in the world range from 46-529 ppm (White and others, 1963) while those in northern Thailand range from 85.6 to 278.0 ppm (Appendix F , Table F-3). It can simultaneously deposited with fluorite, in cryptocrystalline form as chalcedony and other varieties. In the 1st stage of fluorite deposition (much higher temperatures indicated by gaseous inclusion homogenization temperatures), silica is not prominent. The fluorine vapour escaped from the upper part of magma chamber was probably quartz-free or contained only small amount of quartz.

4.4 Evidence of Mixing of Fluorine-rich Water with Shallow Ground Water

Important features of the thermal water model are the mixing of fluorine rich magmatic water in the first stage, and of fluorine-rich brine in the second stage, with shallow cool ground water near the surface. The evidences from this study are :-

1) The temperature of formation of fluorite suddenly drops to about a half or a third of its original value.

2) The phase ratio of fluid inclusions changes from an abnormally high gas-liquid ratio (Type 4 ; gas 50 % by volume) to liquid inclusions (Type 1) or gas-liquid inclusions (Types 2,3).

3) The shape of inclusion changes from irregular, trapped between coarse granular fluorite, to regular-angular , trapped in the crystals, indicating different rate of cooling. The former indicated very fast cooling, while the latter indicates slower cooling.

4) Critical temperatures of gaseous inclusions, suggested by the rate of homogenization, are in nearly the same range of temperature, even in different deposits. But temperatures of gas-liquid inclusions vary greatly even between inclusion with the same phase ratio.

Their degree of fillings are usually greater than the critical density. This suggests that volatile fluorine came from a single source, and is mixed with other liquids.

5) The histograms of homogenization temperatures reveal sharp peaks in the inclusion populations, starting at a definite temperature in each deposit. This mean that although fluorite was formod continuously during temperature drop, it mostly deposited at a certain point of temperature. This almost certainly represents sudden cooling.

6) Some inclusions show two immisible liquids in the same inclusion.

7) The elevation of ore bodies are the same or nearly the same as recent shallow ground water of the basins.

8) Gradation of temperature within many deposits further supports mixing and lowering of temperature with time.

In Mahalanna Mine, fluorite veins show a temperature decrease from wall rock towards the centre. In Vein no. 5, the mean temperatures change from 156.5-158.4 $^{\circ}$c in pale violet, pale green, and colorless fluorite at the middle part of the 4 m. thick vein to 164.6 $^{\circ}$c in colorless fluorite near the wall rock. The temperature decreased across the vein is 4 $^{\circ}$c/m. Concentrically layered fluorite shows a systematic decrease in temperature outwards. (samples BH(U) 0.2 and 0/1, Ban Hong p.281, Appendix D, Table D-4.3). Botryoidal fluorite show a decrease in temperature outward (p. 270). Zones of inclusions from core at Fang show a temperature decrease upwards the ore body (Core TDH 9, p.279). At Mae Tha, gaseous inclusions show a similar range of temperature all across the deposit, but gas-liquid inclusions show increasing temperature eastwards probably towards the source of thermal waters (p.280, Appendix D , Table D43); this is supported by the higher temperatures in the present thermal springs in the eastern part of the deposit (p.291)

Observed and inferred differences between normal hot springs and those associated with fluorite deposits are listed in Table.

Table 4.1. Comparison of the characteristics of hot springs associated with fluorite deposits and normal hot springs

<table>
<tr><th>Hot springs associated with fluorite deposits</th><th>Normal hot springs</th></tr>
<tr><td colspan="2">1. Occur in strong tectonic zones ; especially along extensional faults near margins of Cenozoic basins.</td></tr>
<tr><td colspan="2">2. Near or in granite.</td></tr>
<tr><td>3. Country rocks are normally limestone.</td><td>3. Country rocks are mostly granite.</td></tr>
<tr><td colspan="2">4. Young age (Pleistocene-Recent)</td></tr>
<tr><td>5. May or may not be near natural discharge.</td><td>5. Usually occur near natural discharge.</td></tr>
<tr><td>6. Present temperature of the spring in the vein is relatively low (40-60°c), subsurface is not much studied (152°c at SP Mine)</td><td>6. Present temperature of the hot spring is 50-100°c at surface, 100-180 or 200°c subsurface.</td></tr>
<tr><td colspan="2">7. Heat energy from magmatic source.</td></tr>
</table>

8) Volatile fluorine ascending to the spring orifice from depth.	8) No direct source of volatile fluorine.
9) Magmatic water or brine is major component of hot-spring water during early stage of hot-spring processes.	9) No magmatic water involved, the hot spring water is less saline.
10) Mixing of magmatic water and hot brine with shallow cold ground water caused supersaturation and deposition of fluorite.	10) May or may not show mixing with shallow cold ground water.

The nature of the country rocks is closely related to fluorite deposition. Ca-rich country rocks and Ca-saturated shallow ground water are closely associated with fluorite deposition from hot springs. The volatile fluorine from magmatic water can react with Ca-rich rock and form replacement deposits. The fluorine in water can react with Ca-saturated shallow ground water and deposit fluorite during cooling to a half or a third of the original temperature, at the mixing zone. If the amount of volatile fluorine emerging at the spring orifices is the same, areas with limestone country rock will contain fluorite deposits more than granites or other country rocks which are less calcic. Furthermore, the later stage deposition by hot spring processes, subsequent to volatile fluorine emanation, will occur more readily in the Ca-Saturated shallow ground waters in limestone areas than in ground water in granite or other kind of rocks.

The uniformity of grain size relates to the range of temperature of homogenization. The more uniform and larger the crystal size, the narrower the range of temperature, especially in country rocks other than limestone or Ca-rich types. The histograms of homogenization temperature suggest that the temperatures dropped only a few tens of degrees during deposition of the whole ore body. This certain fluorite formed by supersaturation of the fluorite- saturated brine ? at the mixing zone with shallow ground water at the spring orifice ?. The rate of supply of fluorine saturated brines to mixing zone must be very constant for a long period of time in order to get equal amounts of ore as those in the regions of Ca-rich rocks. The rate of cooling must be very slow at the mixing stage. The temperature dropped to about half at the mixing zone, and remained at that certain temperature for a long period of time during the deposition of epithermal well-crystallized fluorite. The decrease in fluorite concentration in brine during mixing with ground waters must be very small.

Table 4.2 Comparison of deposits in limestone country rocks with those in granites and other rock types.

Deposits in limestone country rocks	Deposits in other rocks
1) Shape of ore bodies partly regular along fault zones and partly irregular as cavity filling and replacement.	1) Shape of ore bodies are normally regular in open spaces such as fault zones.

2) Replacement fluorite common to predominant.	2) Replacement fluorite very rare.
3) Mainly fine grained crystalline ; concentrically layered and botryoidal.	3) Mainly well-crystallized, as large cubic crystals or flat - layered fluorite.
4) Colour of fluorite mainly grey and colorless, pale colours and original colour of limestone.	4) Colour of fluorite variable (e.g. deep green, purple, colorless, etc.)
5) Fluid inclusions concentrated locally, especially in well crystallized parts; zones of inclusions common.	5) Fluid inclusions randomly distributed.
6) Shape of primary inclusions irregular to regular angular (box shaped or pyramid)	6) Shape of primary inclusions prismatic, box shaped, as negative of crystals.
7) Fluid inclusions of Types 1,2, 3 and 4. The phase ratio of inclusions ranges from 0-100 % gas	7) Fluid inclusions mainly of Type 3, with constant phase ratio.
8) Broad range of crystallization temperature.	8) Narrow range of crystallization temperature.

4.5 Genesis of Minor Sulphides Associated with Fluorite.

The thermal water is effectively free from heavy metal ions, but traces of sulphides are found quite frequently in the fluorite deposits. The most famous occurrence is the stibnite associated with fluorite in the Mae Tha deposits. There are at least 2 stages of stibnite mineralization in the paragenetic sequence (Fig. 2.25). Stibnite is associated with fluorite at Mae Phu, Amphoe Thoen where the stibnite increases in quantity with depth, and at Tha Song Yang deposit. At Amphoe Pai, small bladed stibnite crystals are found locally with fluorite. Pyrite is found only in small amounts in most fluorite deposits.

Shouls (1972) believed that the sulphides associated with fluorite were deposited during mixing of a hydrothermal liquid containing fluoride and sulphide ions with a ground water containing calcium and heavy metal ions. The commonest heavy metal ion in northern Thailand ground water is iron; the commonest sulphide in fluorite should be pyrite. The sulphide ion concentration in the waters is less than 1 ppm (possibly about 0.1 ppm). The amount of pyrite precipitate from ground water-thermal water mixing should be thus one or two orders of the magnitude less than the fluorite, and this is found at Ban Kong Khak for sample.

The stibnite can not be explained as in the case of pyrite. Antimony is not common in ground water. The close association of stibnite-fluorite in various kinds of country rock also indicates that antimony has not come from country rock. Antimony must be hydrothermal in origin. Stibnite probably precipitated from saturated solutions associated with fluorite.

Transportation and deposition of stibnite from hot spring waters can take place by a variety of processes. Dickson and

Tunell (1968) suggested the following processes 1 : deposition from simple H_2O with concentrations in parts per million ; (2) from boron-containing solutions with concentrations ranging from parts per million to thousands of parts per million at high boron contents ; (3) from sulfide solutions with high concentration. The process (3) is reasonable for stibnite-fluorite deposits in northern Thailand which contain as much as 5 % by volume of stibnite (Mae Tha), 90 % by volume (Tha Song Yang), 10 % by volume (Mae Phu). The sulfide solution may be the immisible liquids with fluorine vapour. The $(SbS_3)^{3-}$ ion may be important in the transportation of antimony in aqueous solution rather than $(SbS_2)^-$, $(HSbS_2)^-$ or $(Sb_4S_7)^{2-}$ (Brookins, 1972). Dickson and Tunell (1968) also pointed out that the solubility of stibnite in every instance is greatly enhanced with increasing alkalinity. The temperature coefficients are strongly positive. In solution with the presence of H_2S with Sb_2S_3 , solubility increases as a function of increasing temperature (Brookins, 1972). Deposition of stibnite could take place by temperature decrease, decreasing alkalinity, increasing acidity or by oxidation of sulfur-bearing species to $SO_4^=$. Which mechanism operated in specific areas of recent stibnite deposition depends on the physico-chemical history of the hot springs involved.

Hot spring waters contain Cl^-, $SO_4^=$, $CO_3^=$, and HCO_3^- and rare anions seem to have no particular association with waters from which stibnite originated.

The solubility of stibnite in pure H_2O is about 65 ppm at 250°c and 100 bars, which is sufficiently high for H_2O to act as an ore-carrying solution. Solubility in H_2O is 20 ppm at 100°c, and much dissolved Sb_2S_3 would precipitated from saturated solution originally at elevated temperature and cooled to 100°c or lower (Dickson and Tunell, 1968).

Stibnite would be less soluble in CO_2-H_2O than in pure H_2O. Ratanasathien (personal communication, 1979) explained the recent deposition of stibnite crystals from vapour from hot spring in the Thepnithi claim, Mae Tha, as due to the CO_2 concentration of the vapour near the surface where the country rock is limestone.

The stibnite deposited with fluorite in Mae Tha, Tha Song Yang and Mae Phung may reflect supersaturated or saturated sulfide solutions immiscibly associated with supersaturated fluoride vapour or saturated fluoride solutions. Deposition occurred during the drop of temperature at the mixing zone with ground water saturated with CO_2-H_2O in areas of limestone country rock. The increase of CO_2 in H_2O towards the limestone country rocks (probably by the reaction of fluoride with the limestone to form fluorite deposition) increased the rate of deposition of stibnite. This may explain the prismatic stibnite aggregates found throughout the fluorite deposit at Mae Tha and Mae Phu . The formation of stibnite by at least 2 stages of sulfide-saturated solution occurred in the Mae Tha region.

4.6 Tectonic Setting of the Fluorite Province

4.6.1 Relation to Granites

The fluorite province is closely related to granites in northern Thailand. Most deposits are in granites, at the contact zones, or in the nearby sedimentary or metamorphic rocks. The age of granites should therefore be related to the age of fluorite mineralization.

The granites and crystalline rocks crop out primarily in three approximately north-south striking structural units (Fig. 4.7):

1) the central crystalline complex west of Chiang Mai.

2) the chains of granite bodies east of Chiang Mai.

3) the chains of granite bodies west of Chiang Mai.

The central crystalline complex contains gneiss and schist and comprises Precambrian to Carboniferous rocks. Unstressed porphyritic granite, mostly Triassic in age is present in the central complex (G.G.M. Report, 1976).

Granites of the eastern chain yield Early Triassic dates (Fig. 4.7). Whole rock isochrons yield Early Triassic dates of 232 ± 31 m.y., 235 ± 5 m.y., and 236 ± 14 m.y., respectively, for the Fang Mae Suai, the Ban Hong, and the Li intrusions of the eastern granite chain (G.G.M. Report, 1976).

The Mae Sariang granite of the western chain intruded during Ladinian to Earliest Jurassic times. Dating of the westernmost Mae Lama granite by Rb/Sr whole rock analyses indicated 70-80 m.y. and K/Ar analyses of muscovite and biotite revealed about 69 m.y. and 60 m.y., respectively (G.G.M. report, 1976).

For the granite veins at the western margin of the central crystalline complex, the ages determind for muscovite and biotite suggest a quick termination of thermal influences in Late Cretaceous time (G.G.M. Report, 1976). Much younger dates were found for mica from four nearby granite bodies, by the K/Ar and Rb/Sr methods ;

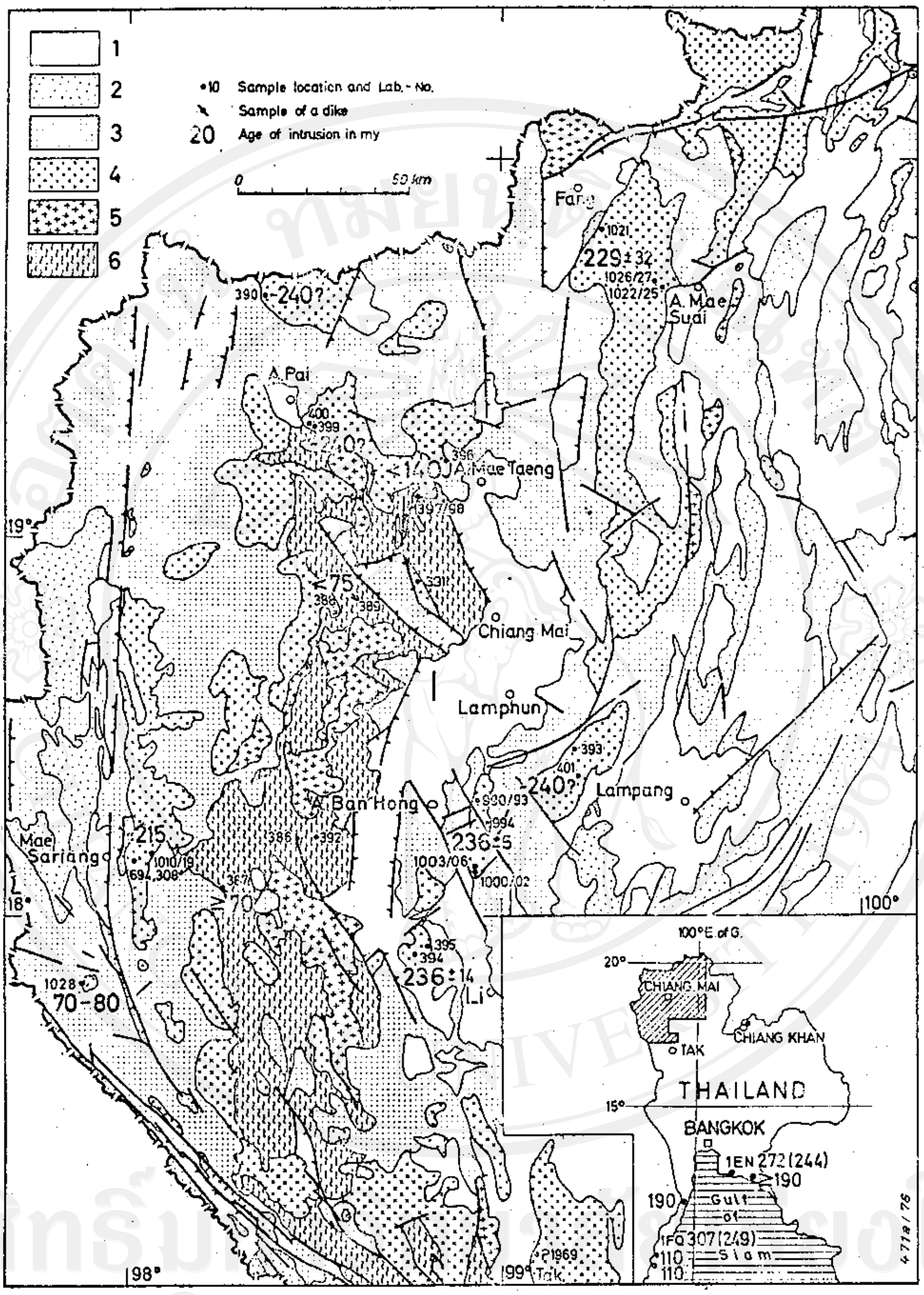


Fig. 4.7 Generalized geological map with sample localities and ages of intrusions. 1 = Cenozoic; 2 = Mesozoic; 3 = Paleozoic; 4 = mainly Mesozoic granite; 5 = foliated granite and orthogneiss, presumably Carboniferous and older; 6 = gneiss and migmatite, mostly Precambrian. (Map adapted from BfB Final Report, 1972; ages on the insert map from BURTON & BIGNELL 1969.)

this indicate " Mixed ages " caused by incomplete loss of radiogenic isotopes during at least one Tertiary thermals event. K/Ar biotite ages is 18.6, 19.6 m.y. showing that these Tertiary influences did not end earlier than the Early Miocene in the eastern parts of the central crystalline complex (G.G.M., 1976).

Teggin (1975) reported that Mae Sariang granite is 213 m.y. ; Samoeng 195 m.y. ; Khuntan 206 m.y. ; Tak (the white granite) 208 m.y. and Tak, (the pink granite) 212 m.y. He stated that most granites are generally potassic in character.

Granite plutonism in northern Thailand has been closely linked to orogenic events. In the Early Triassic , there were renewed movements especially in the regions of Chiang Rai and Mae Sariang. Elsewhere comparatively stable conditions prevailed until Post-Carnian/ Norian time when a major folding phase affected northern Thailand. The final shape of the present fold structures is mainly due to two phases, Late Triassic, and Jurassic/Cretaceous (G.G.M., 1972). Intense lateral compression in some areas produced overturned and isoclinal folds or upthrusts, in others only gentle folding and warping. Direction and degree of overturn of fold structures changes considerably in different parts of northern Thailand. During the Mesozoic (Post Carnian/Norian), numerous stocks of biotite granite were emplaced.

The Carboniferous granites did not yield any mentionable fluorite mineralization (G.G.M., 1972). Mesozoic granites are very important for tin-tungsten mineralization. Some minor fluorite is associated with this tin-tungsten mineralization. Tin-tungsten deposits are intimately related to Middle Triassic quartz veins and their equivalents occurring near the top, or in the marginal portions of Middle Triassic granite stocks or in the overlying metasediments. Fluorite is found as gangue mineral in tin-tungsten deposits at Mae Lama district. Fluorite commonly occurs in separate veins from the wolfram-bearing quartz veins at Mae Lama Mine (Panupaisal, 1978). Small crystals of light green fluorite were found within the cassiterite bearing vein at Pa Mark Mine. At Huai Luang Mine, fluorite occurs as colorless and pale green crystals in cassiterite-wolframite bearing greisen. These evidences indicate that fluorite is closely associated with tin-tungsten mineralization. The age of mineralization is believed to be nearly the same as that of the Mae Lama adamellite -not older than Late Cretaceous. Fluid inclusion study by Panupaisal (1978) indicated that the fluorite formed at temperatures ranging from 475 to 390° c.

Another recent discovery of W-F mineralization is at Doi Ngom, Amphoe Long, Phrae Province. Here, the mineralogy is complex including ferberite-stibnite-fluorite with quartz and chalcopyrite gangues. The ores occur as fracture-filling in brecciated silicified country rocks of the Lampang Group? The age of mineralization is still not known.

Most fluorite deposits of northern Thailand are probably related to the youngest granite phase,(Neogene), (G.G.M., 1972). These late intrusions generally occurred within the older granite areas, and their subsequent manifestations most probably caused a partial mobilization of the more volatile components of older intrusive bodies.

Fluorine was carried in solution into structurally and lithologically favourable zones where fluorite was precipitated (G.G.M., 1972). Favourable regions for fluorite deposits are major fault zones in the vicinity of Mesozoic and/or Tertiary granites.

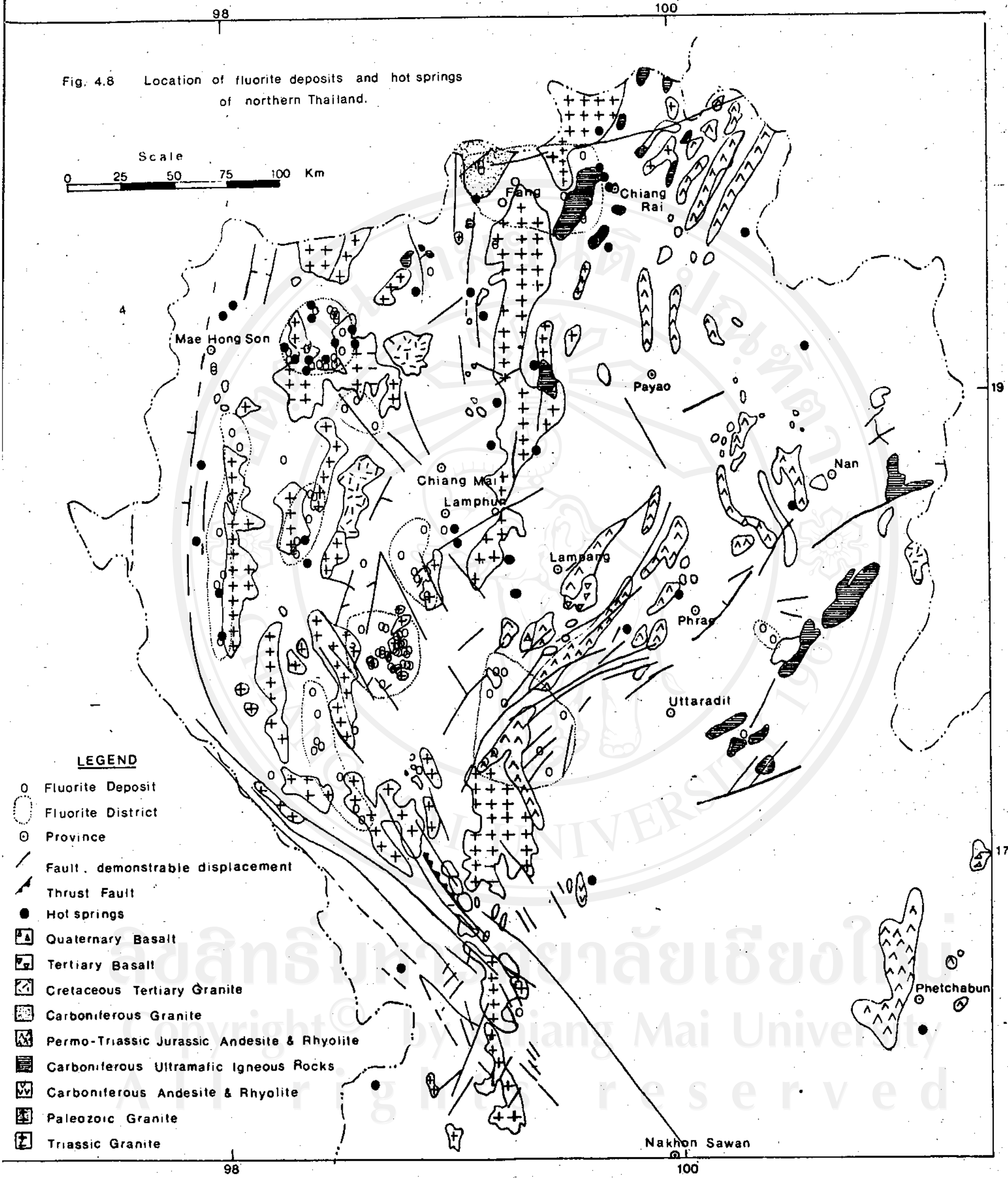
4.6.2 Relation to Cenozoic Fracturing

Late Cenozoic faulting influenced much of the present day topography of Thailand. Many young, frequently antithetic faults run parallel to previous thrust-folding, thus sometimes forming graben-like structures. This has resulted in a mozaic of tectonic blocks, the subside parts of which form local basins. Locally the vertical displacement is considerable(e.g., the block of the Fang Basin was displaced down along its western main fault about 2,000 m).

Fluorite deposits are found at the edges of the fault blocks, and in minor blocks within the basins. Hot springs present in some parts of the region, are similar in geologic setting to the fluorite deposits. The basins are generally bounded by faults which follow older tectonic patterns rejuvenated during Cenozoic time. They contain Tertiary and Quaternary sediments of lacustrine or fluviatile origin (e.g. 1,300 m thick in the Fang Basin) which in some basins may be as old as Paleocene (Buravas, 1975). Faulting has continued into Quaternary times, as indicated by faults affecting terraces of Late Tertiary or Pleistocene age.

Some fluorite deposits and hot springs are associated with faults at the margins of granite batholiths e.g. Amphoe Pai, and Ban Omkhut, and major fault zones. The Nam Mae Yuam fault zone runs

Fig. 4.8 Location of fluorite deposits and hot springs of northern Thailand.



from south of Mae Sariang, northwards to the Burmese border. Mineralization is known only on the east side of the structure, the side closest to the granite batholith ; fluorite occurs at Mae Sariang, Mae La Noi, Mae La Luang and others associated with hot springs. Nam Mae Cham fault is a minor north-south trending structure about 50 km east of Mae Sariang. Fluorite mineralization appears to be minor, and some correlation with hot springs is evident, particularly at Ban Kong Khak. Stibnite and lead occur further from the hot springs than the three fluorite localities. Amphoe Pai deposits are situated north of the preceding area at the center of an intersecting set of strong lineaments in granites and nearby sedimentary and metamorphic rocks. The structures could be interpreted as the fractured top of a dome. The area is well mineralized and numerous hot springs correlate closely with the structural line and mineralization.

4.6.3 Age of Mineralization

It is evident that mineralization mainly post-dates the major faulting. The age of mineralization may be therefore be estimated from th date of the block faulting. The fault-bounded Mae Moh Basin, Lampang Province contains the youngest sediments known in the Tertiary basins, dated as lower to middle Pliocene (Von Koeningswald, 1959 ; outside* age limits of 7 and 4 m.y., according to Funell, 1964). Faulting in this area must be Pliocene or Younger. The recognition of the latest possible date for the block faulting is also difficult, as a lower to middle Pleistocene age has been suggested for the sediment above the unconformity at Nakhon Sawan (Von Koeningswald,1959), and mid or late

Pleistocene movements are suggested by the high level terrace (near Amphoe Mae Taeng, 40 km north of Chiang Mai).

The more recent igneous activity in Thailand was the extrusion of basaltic magmas which occurred in Late Cenozoic time throughout Thailand and South East Asia. Age dating and paleomagnetic studies indicate that extrusions in northern Thailand occurred during the last 600,000 years (Barr and others, 1976). The occurrence of basalt is scattered in northern Thailand and its distribution does not show any obvious correlation with that of hot springs and fluorite deposits.

Fluorite is closely associated with Neogene gravel beds in some areas. At Ban Hong, fluorite mineralization cuts Tertiary conglomerate (G.G.M., 1972). The conglomerate is faulted against Permian limestone, and the fluorite was deposited in the fault zone and partly filled in the Tertiary conglomerate. At the Thepnithi Mine, Fang, the upper part of the veins consists of many rounded fluorite pebbles (" egg ore "). This fluorite is concentrically layered around rounded pebbles of the Neogene gravel beds. The mineralization is therefore Neogene or younger. At Saeng Thong Mine, south of Amphoe Hod, fluorite occurs as replacement in Tertiary conglomerates (G.G.M., 1972). At Ban Pong Nam Ron, King Amphoe Klong Lan, Amphoe Muang, Kamphaeng Phet Province, fluorite was deposited as layer surrounding rounded pebbles isolated in the clay matrix of gravel beds (Bunopas, 1976). The age of this semi-consolidated conglomerate is Pliocene to Pleistocene (Bunopas, 1976). Thus most districts contain fluorite in Neogene beds.

Fluorite is still being deposited from hot springs at Ban Kong Khak (Shouls, 1972). Ratanasathien (personal communication, 1979) stated that fluorite is still being deposited from hot springs in the Thepnithi Mine, Mae Tha. At Pa La Door deposits which belongs to Sahachart Mining Co., fluorite is also still being precipitated from the hot springs within the vein.

In summary, the fluorite deposits in northern Thailand show similar geologic setting and age. Age of mineralization is very young, probably ranging from late Tertiary-Recent? The mineralization in the early stage was related to magmatic water, and in the later stage to hot springs processes.

4.7 Comparison with Other Major Fluorite Provinces in the World

4.7.1 Regional Setting of the Deposits

Fluorite deposits in northern Thailand are similar in geologic setting, age of mineralization, temperature (& pressure) of formation and mineralogy with other major fluorite provinces in the world. Their location is shown in Figure 4.8. Van Alstine (1976) showed that major fluorspar districts are localized chiefly along and near continental rift zones and lineaments. In western U.S.A., more than 45 fluorite districts are cited along the Rio Grande graben of New Mexico and the Colorado Plateau, and along this rift projected northward through Colorado, Wyoming, Idaho, Montana, British Columbia, Yukon Territory and Alaska, and projected southward into Mexico. The graben is bounded by normal faults and cross faults.

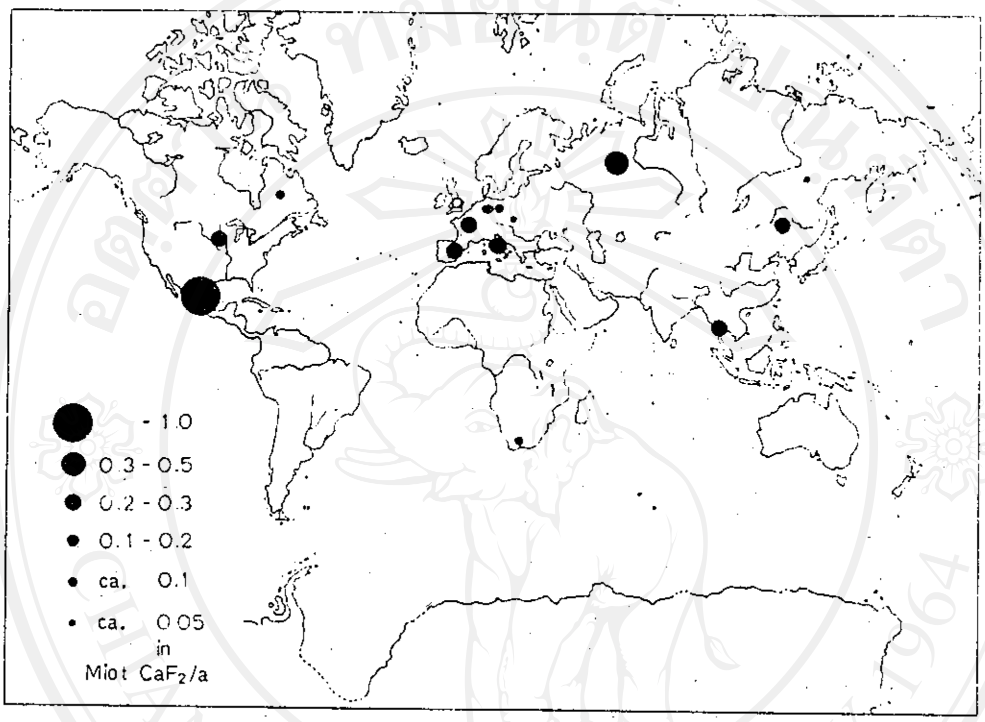


Fig. 4.9 The main fluorite producing countries of the world (after JACOBI, 1971)

Others U.S.A. fluorspar districts are similarly associated with tensional rifts and lineaments in Illinois, Kentucky, Oregon, Nevada, Ontario, Neva Scotia and Newfoundland.

The 6,400-km-long Afro-Arabian rift zone is also associated closely with major fluorspar districts and alkalic and silicic igneous rocks (Baker and others, 1972 ; Logatchev and others, 1972). Fluorspar deposits and districts are found along this rift in Kenya, Tanzania, Malawi, and Mozambique.

The Rhine graben (Bederke, 1966 ; Illies, 1972) is associated with alkalic igneous rocks and major fluorspar districts in Germany and northeastern France. Along its extension to the south, the Rhine depression in eastern France also has major fluorspar deposits near it. Further south along this Tertiary continental rift are the large fluorspar deposits of Sardinia, Italy (Van Alstine, 1976).

One of the world's largest fluorspar provinces is in eastern Transbaikalia, U.S.S.R., between Lake Baikal and Manchuria ; it contains more than 200 known deposits (Yakzhin, 1962). This fluorspar province adjoins the Baikal rift zone, a linear system of grabens that extends for about 3,000 km (Florensov, 1966). Fluorite deposits, grabens, and volcanic rocks are found along and within 65 km of a northeast - trending regional fault (Ivanova, 1974).

At Amba Dongar, Gujarat, India, very large fluorspar deposits associated with carbonatite, syenite, and other potassium-feldspar rocks in a ring complex have been found about 5 km north of a major Tertiary rift dissecting the Deccan Plateau (Deans and others).

Other fluorspar deposits are near this rift along the Narmada Valley, 80 km west and 200 km east of the Amba Donga deposits.

Fluorspar deposition thus seems to be genetically related to rifting, which evidently provided access for the volatile fluorine from depth.

The well-documented U.S.A. deposits show close similarity to those in northern Thailand. In western U.S.A., there are two broad belts of fluorite deposits, the western and the eastern belts (Shawe, 1976). The epithermal deposits in western United States are similar to those in northern Thailand. There is close spatial association of epigenetic fluorite with major fault zones as in Thailand, especially in areas of tension along the margin of uplifts. Many deposits occur as veins along tensional faults or as replacement deposits in fractured rock close to the faults. The distribution of the fluorite deposits closely follows the Basin-Range structures. The distribution in belts suggests an association with strike-slip fault zones that seem to constitute a fundamental structural framework of the continental crust. The deposits are associated with high fluorine igneous rocks which are predominantly Tertiary in age. The mineralization in western U.S.A. is Tertiary, younger than 32 m.y. (worl, 1972) ; no deposits are demonstrably younger than 6 m.y., except for a few hot - spring apron deposits such as Ojo Caliente, New Mexico, currently being deposited. This 6-32 m.y. age range does not concide with the age distribution of andesitic-basaltic volcanism in western U.S.A. , the deposits formed locally after volcanism.

In western United States, the deposits are chiefly veins along tensional normal faults, stockworks, and pipes. At a few localities, ore solutions migrated from the faults, replaced carbonate rocks at favourable horizons, and formed strata bound or manto deposits.

Fluorine-bearing thermal waters are found near the rifts. At Ojo Caliente, New Mexico, and Poncha swamp, Colorado, fluorite was reported in travertine deposited from the thermal waters.

The temperature of the fluorite deposition in western United States was low (below 200°c), and pressure was also (Van Alstine, 1976). Most deposits are epithermal, similar to those in northern Thailand. Grain size ranges from coarsely crystalline to very fine grained material that commonly is fibrous, banded or crustified. Fluid inclusions suggest that this type of fluorite formed from very dilute solutions probably a mixture of hydrothermal and shallow meteoric water (Van Alstine, 1976). This is similar to the hot spring models and magmatic waters described in the previous chapter.

4.7.2 Relation of Fluorite Deposits to Geophysical Properties

Fluorite deposits in both northern Thailand and western United States are in region of high heat flow. In western U.S.A., the heat flow values exceed 2 HFU (2×10^{-6} cal/cm^2/sec) in broad regions that coincide remarkably with the distribution of fluorine-rich igneous rock and fluorite deposits (Shawe, 1976). Present heat flow may be different from that in the Middle to Late Tertiary when fluorine mineral deposits were forming. However, some of the fluorine-rich rocks are as young as 3 m.y. and the occurrence of fluorite in modern hot-spring aprons indicates that the episode of fluorine mobility likely extends from Tertiary to Holocene. Probably the episode of fluorine-rich magmatism and fluorine mineral deposition that commenced about 30 m.y. (Middle Tertiary) in western U.S.A. is still manifested by high heat flow throughout the region.

In northern Thailand, the heat flow values are high. The geothermal gradient measured in an oil well in the Fang Basin indicate 70-90°c/km or more.(Barr and others, 1977). The heat flow value is probably 2-5 HFU (Barr and others, 1977). The heat flow values at Amphoe Mae Sod, Tak Province = 2.62 HFU ; in comparison the heat flow values at Khorat Plateau are less than 1 HFU and in the Andaman Sea 5.27 HFU (Barr and others, 1977).

In western U.S.A., the low gravity regions concide with fluorspar districts, ranging from less than -250 to -150 milligals. These low gravity regions broadly represent crustal zones intruded by significant volumes of silicic igneous rock. Moore (1962) suggested a correlation between high potassium content of Cenozoic igneous rock and low Bouguer gravity values in the western United States. Low gravity contours also roughly outline topographically high region :- the mountainous parts of the country - that have risen isostatically in response to their low density. In northern Thailand, there has been no regional study of Bouguer gravity and other geophysical properties of rocks. Teggin (1975) reported that the granites of northern Thailand mostly are potassic in character. They are probably similar to those in the western U.S.A.

A broad region of low (less than 8 km/ sec) upper mantle seismic velocity is present in western United States and this region quite closely encompasses the region of Middle to Late Tertiary volcanism and fluorine mineralization. This region of low velocity in upper mantle is likely characterized by above -normal temperatures, and this condition generally accords with high heat flow in the overlying crust. Woolard (1968) proposed that the region of low seismic velocity in the upper mantle may reflect a phase transition from normal mantle material of dunite composition, high seismic velocity, and density of 3.35 into mantle material of eclogite composition, lower seismic velocity, and higher density. The compositional change resulting from the phase transition suggested by Woolard may have involved fractionation of materials from the upper mantle into the overlying crust, and this event may have taken place in the recent geologic past, from Middle Tertiary time onward. Possibly these materials included high fluorine-basaltic and rhyolitic magmas and fluorine-rich fluids that penetrated upward toward the surface of the crust, to account for the fluorine-rich igneous rocks and fluorine mineral deposits of Middle Tertiary and younger age in the province.

Shawe (1976) suggest that magmatism and fluorine mineralization may have originated within the crust, but in response to high heat flow from mantle and to related processes. In any case, the spatial coincidence of the region of low upper-mantle seismic velocity with a region of high heat flow, Middle to Late Tertiary fluorine-rich magmatism, and Middle to Late Tertiary fluorine mineralization indicates a strong mantle control on the magmatism and fluorine mineralization.

Table 4.3 Comparison of northern Thailand fluorite province and western United States province

Northern Thailand	Western United States
1) Occur in major fault zones and rift zones.	1) Occur in major tensional fault zones.
2) Closely related to granites (some in contact zones or nearby sedimentary rocks).	2) Closely related to fluorine-rich igneous rocks.
3) Igneous rock normally is potassic granite.	3) Igneous rock is potassic granite?(alkaline)
4) Regions show high heat flow and high geothermal gradient.	4) Region shows high heat flow values.
5) Low gravity region ?	5) Low gravity region.
6) not known.	6) Area has low seismic velocity.
7)Occurs near back-arc continental margin, source of fluorine may be from magma from assimilated mantle wedge.	7) Strong mantle control on magmatism and fluorine mineralization.
8) Young age of mineralization (Pleistocene-Recent).	8) Young age of mineralization (32-6 m.y.), with some more recently formed.
9) Epithermal deposits.	9) Epithermal deposits.
10) Grain size coarse crystalline to very fine grained.	10) Grain size coarse crystalline to very fine grained.

4.8 Sources of Fluorine

Because of the similarity in the environments and geology of fluorite deposition in northern Thailand and western United States, it is useful to consider the possible source of fluorine in western United States, suggested by Shawe (1976).

The possible sources of fluorine which formed fluorite deposits near the continental rifts zones or lineaments include :

1) Volatile emanations from a crystallizing alkalic or silicic magma, closely associated.

2) Remelting of late-fluorine rich alkalic fractions of underlying intrusive masses.

3) Melting of fluorapatite, hornblende, or other fluorine-bearing minerals in ultramafic mantle rocks.

4) Melting of fluorine minerals in descending crustal rocks in a nearby paleosubduction zone : hornblende and other fluorine-bearing minerals in basalt or gabbro, or fluorapatite in marine phosphate rock and nodules.

In northern Thailand, the sources of fluorine are most probably from volatile emanations from younger potassic granites, (source 1) in the region of older granite (G.G.M., 1972).

4.9 Plate Tectonic Model of Fluorite Mineralization in Northern Thailand

The distribution and origin of mineral deposits including fluorite have recently been interpreted in terms of plate tectonics. The hypothesis is shown to be useful in explaining the origin of host rocks of fluorite and also the deposits themselves. Fluorite mineralization occurs in different periods of time, in different tectonic settings at plate boundaries (Mitcholl and Garson, 1976), as described below :-

1. Intra-continental volcanic belts.

This type is unrelated to subduction. Fluorite-tin-tungsten-niobium ores occur in sodic granite and associated pluton with ring complexes. The source of fluorine may be from the mantle. High trace metal contents are present locally in young oceanic igneous rocks adjacent to hot spots ; but the initial Sr^{87}/Sr^{86} ratios suggest a continental crustal source for at least part of the granite and hence possibly also for the associated metals. The age of mineralization was Jurassic.

2. Magmatic belts related to subduction.

Tin-tungsten-and fluorite mineralization is present in the eastern Andes of Bolivia and Peru. Mineralization is of Late Tertiary age, and its genesis has been related to a Benioff zone in or near the position of the present one. Deposits are associated with alkaline or other granites.

3. Continental collision magmatic belts related to tin-tungsten-fluorite associated.

Post-tectonic tin-tungsten-fluorite bearing granites of southwest England were generated in the underthrust continental plate following continental collision in a setting analogous to that of the Late Tertiary Malarkachung granite in the Himilayas. Most post collision granites intruded tightly folded and thrust metamorphosed sediments, commonly of flysch facies, a lithology that characteristically contains very low trace amounts of tin. These sediment host rocks were probably deposited oceanic crust, but were underthrust by continental crust prior to intrusion by granites, and hence were not present at deep crustal levels to form a source for the magma and metals. Limited evidence suggests that the granites and probably the tin are derived from the lower continental crust.

4. Back-arc continental margins.

Around the western Pacific margins and in SE Asia, continental margins are mostly bordered by marginal basins of Late Mesozoic to Tertiary age and by island arcs. In East and SE Asia, some of these margins include belts of Late Mesozoic to Early Tertiary granitic plutons with associated deposits of tin and tungsten and minor molybdenum and bismuth ; fluorite is commonly present. Examples are the Late Mesozoic mineralized granites of peninsula Burma and Thailand bordered by the Andaman-Nicobar arc, and the South China tungsten province of Late Mesozoic age.

In South East Asia, the widespread association of fluorite and tin deposits near back-arc continental margins has been related to the rise of fluorine with other volatiles from deep levels of an outwardly migrating Benioff zone during marginal basin development. The rising fluorine can extract tin from deep levels of already emplaced but still hot granitic bodies and deposit it around the upper levels of the intrusions.

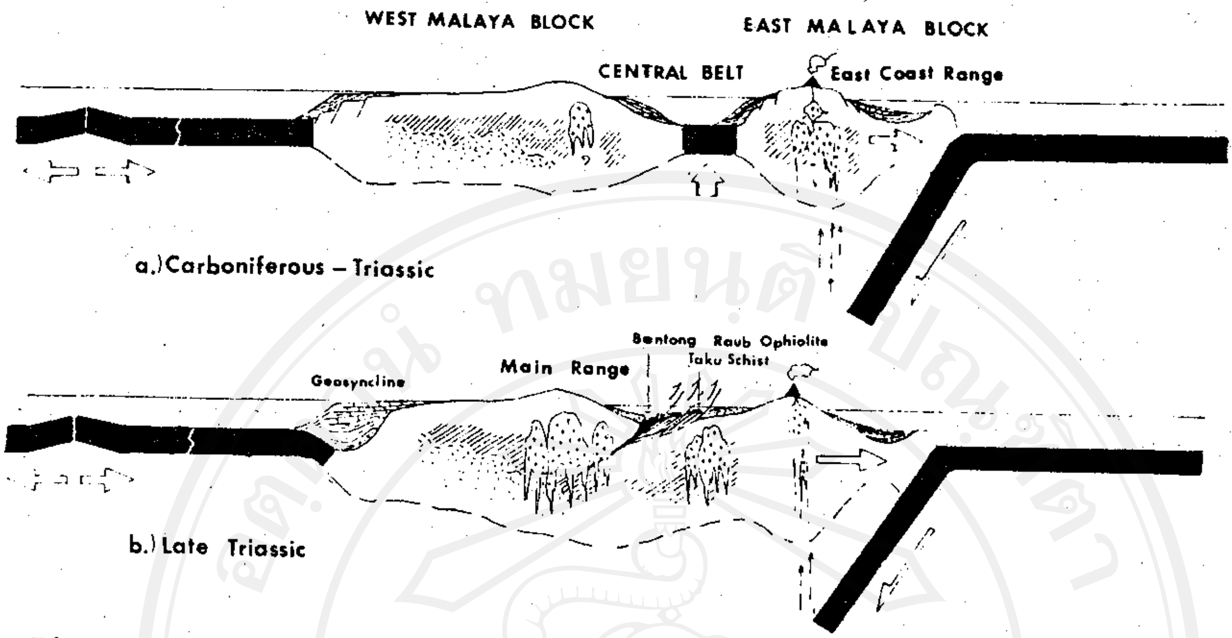


Fig. 4.10 Tectonic setting of Malay peninsula during the Carboniferous to Late Triassic. (after Asanachinda, 1978).

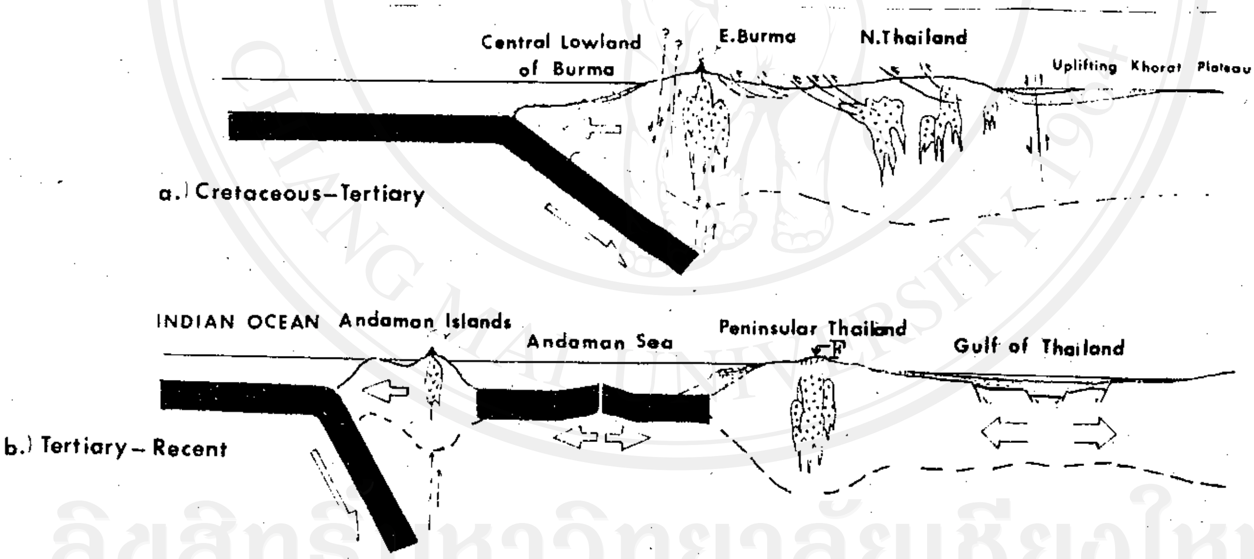
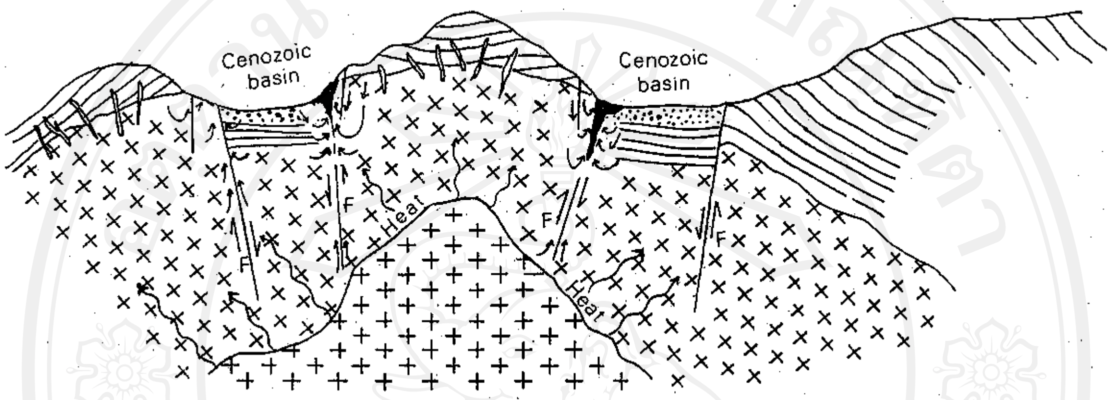


Fig. 4.11 Post–Jurassic evolution of Burmese Malayan orogen. (after Asanachinda, 1978). Epithermal fluorite deposits(F) occur in peninsular Thailand.



Younger granite (Cenozoic)

Older granite (Mesozoic)

Epithermal fluorite deposit (Pleistocene-Recent)

Mesothermal ? fluorite deposits (pegmatite, greisen, contact metasomatic - Mesozoic ?)

Sedimentary rocks and metamorphic rocks.

Fig. 4.12 Model for fluorite generation and deposition in northern Thailand.

Since most economic epithermal fluorite deposits in northern Thailand are Pleistocene to Recent age, they must be related to the plate tectonic evolution in Cretaceous-Tertiary, and Tertiary to Recent times. In Cretaceous-Tertiary time, back-arc extensional tectonic possibly occurred at the end of the Mesozoic era leading to back-arc updoming along with thermal events (Burton and Bignell, 1969), and formation of the intracratonic Gulf of Thailand basin (Pariwatvorn,1977). This may have been caused by weakening of the east-west stress field due to the progressively decreasing subduction rate northward along strike of the trench axis in particular. The suggestion proposed here is supported by Stauffer (1973) who mentioned the clockwise rotation of the whole peninsular region during the Cenozoic (Asanachinda, 1978).

Post-Jurassic back-arc extension occurred in two distinct periods of time, namely Late Cretaceous to Early Tertiary (Fig.4.11A.), and during the Miocene (Asanachinda, 1978). The latter has been found to be responsible for the formation of Andaman Basin (Rodolfo,1969), (Fig. 4.11 B.). In the Tertiary-Recent, the dip of the plate under the Andaman Islands was steeper than in Cretaceous-Tertiary (Asanachinda, 1978).

The subduction-related model was applied to the mineralization in the Western Tin Belt by Mitchell and Garson (1972). They suggested that the main period of mineralization was contemporary with the marginal basin development. The upward migrating volatiles generated during such development leached tin from the lower part of the still hot granitic rocks and deposited it at high levels with possibly addition of mantle-derived tin simultaneously with the rise of fluorine from an anomalous mantle wedge underlying the back-arc region. This mechanism of mineralization could be well explain the origin and genesis of apparently young vein types of fluorite, stibnite, and stibnite-ferberite-fluorite-quartz association particularly in northern Thailand (Asanachinda, 1978).

Volatile fluorine rose to the fault zones in northern Thailand, and formed fluorite deposits since the begining of mineralization (about Pleistocene). The most suitable areas for deposition are the upper parts (near surface) of Pleistocene tensional faults at the margins of Tertiary basins. Volatile fluorine in the deeper parts may react with the country rocks and deposits . But the hot brines of hot springs can dissolve, transport, and redeposit the fluorite at/or near the surface if the heat energy used for convection and circulation of water in hot springs is still enough. The fluorites have been recently deposited by hot spring processes since the upward rise of volatile fluorine ended.