THE ULTRATRACE ELEMENT GEOCHEMISTRY OF TIN ORES AND BRONZE USING ICP-MS AND THE MINING AND METALS TRADE IN PREHISTORIC THAILAND

Thesis submitted by

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The geochemical variation of tin ore deposits is examined at both the genetic level and on a regional scale. The influence of tectonic, magmatic and geologic history on the distribution of tin deposits is discussed. Multielement and isotopic analysis of ultratrace elements in ores and metals, by Inductively Coupled Plasma Source Mass Spectrometry (ICP-MS), is used to determine those elements which may be used to characterise the tin component of archaeological bronzes from Thailand. The efficiency of ICP-MS for this work on tin ore provenancing is evaluated and the data analysed to provide information on the technology and trade in the early southeast asian metals industry. Documented information on the pre-industrial mining industry of Southeast Asia is examined together with the economic theory of small-scale mining and metals trade to present a scenario for the influence of an early metals industry on the culture of Thailand in the 1st millennium BC. This scenario is examined in the context of the analytical data presented and the current views of southeast asian archaeology and anthropology.
Abstract. 2
Table of Contents. 3
List of Figures and Tables. 8
List of Plates. 15
Acknowledgements. 17
Abbreviations. 19

1. INTRODUCTION 22
  1.1 The Aims of the Project. 22
  1.2 The Theory. 23
    1.2.1 The Geology and Geochemistry. 23
    1.2.2 The Metals. 24
    1.2.3 The Analytical Method. 25
    1.2.4 Mining and Metallurgical History. 26
  1.3 The Research Method. 26

2. GEOLOGY 28
  2.1 Geology of Southeast Asia and Thailand. 28
    2.1.1 Granite Provinces. 28
      i) Tectonic Evolution of Southeast Asian Mineralised Granites. 33
      ii) Tin Ores and Their Relationship to the Granites. 37
    2.1.2 Metalliferous Regions and Zoning of Elements. 42
      i) General. 42
      ii) Deposits other than Tin. 57
        a) Copper and Lead/Zinc. 57
        b) Barite. 58
        c) Bismuth. 58
        d) Antimony and Mercury. 58
        e) Chromite. 59
        f) Gold. 60
        g) Zircons. 60
        h) Tungsten. 61
        i) Uranium. 62
  2.2 Tin Geology. 62
    2.2.1 Types of Tin Deposit. 62
      i) Tin Provinces. 62
      ii) Tectonic Environments. 65
iii) The Classification of Tin Deposits. 66
   a) Pegmatites. 68
   b) Veins and Stockworks. 70
   c) Greisens. 70
d) Skarns. 71
e) Altered Primary & Secondary Deposits. 72

2.2.2 Geochemistry of Tin. 77
i) Previous Research. 77
ii) Diagnostic Elements in Cassiterite Concentrates. 80
   a) Rare Earth Elements (Lanthanides). 80
   b) Niobium and Tantalum. 82
c) Tungsten and Titanium. 83
d) Indium. 83
e) Scandium. 83
f) Zirconium. 84
g) Lithium. 84
h) Gallium. 84
i) Other Elements. 84
iii) Diagnostic Elements in the Study of Tin Bronzes. 85
iv) Elements and their Mineralogical Associations. 86

2.2.3 Tin Regions relevant to Southeast Asia. 88
i) South China. 88
   a) South China Fold System. 88
   b) Daxinganling and Jilin-Heilungjiang Fold System. 89
c) Sanjiang Fold System. 89
   ii) India. 90
   iii) South Thailand. 92
   iv) North Thailand. 92
   v) Central Thailand. 94
   vi) West Malaysia. 95
   a) Kinta Valley. 97
   vii) East Malaysia. 99

3. ANALYSIS 104
  3.1 Instrumentation. 104
  3.1.1 ICP-MS. 104
3.2 Analytical Procedure.

3.2.1 Basic Problems.
1) Contamination of Reagents.
2) Preparation Methods.
3) Polyatomic and Isobaric Overlap.
4) Partitioning of Trace Elements.

3.2.2 Sample Preparation.
1) Cassiterite and Tin.

3.3 Analytical Results.

3.3.1 Description of Samples.
1) Tin Samples.
2) Copper Samples.
3) Bronze Samples.
   a) Non Chai.
   b) Tham Ong Bah.
   c) Kok Makamtao.
   d) Ban Na Di.
   e) Ban Don Ta Phet.
4) Lead Samples.

3.3.2 Statistical Procedures.

3.3.3 The Use of Lead Isotopes.

3.3.4 ICP-MS Spectra.

3.3.5 Analytical Results.
1) Introduction.
2) Copper Samples.
3) Lead Samples.

4) Tin Samples.
   a) High Thorium Tin Sources.
   b) High Yttrium Tin Sources.
   c) High Tungsten Tin Sources.
   d) High Gold Tin Sources.
   e) Categorisation of Tin Sources.
5) Bronze Samples.
   a) Notes on Some Elements.
Summary of the Bronzes. 

4. MINERALS AND METALS INDUSTRY

4.1 Trade and Economics: the Present and the Past.

4.1.1 The Socio-Cultural Context
- in brief.

1) The Red River Valley.
2) The Southeast Asian Tin Belt.
3) The Chao Phraya-Paklong Depression.
4) The Tongle Sap Plains and Mekong River.
5) The Khorat Plateau.
6) The Sichuan-Yunnan Region.

4.1.3 Trading Economy.
1) Bronze Production and Trade.
2) Tin Mining in the Historical Period.
3) The Identification of Sites.
4) The Working of Different Tin Deposits.
5) Pilok, Kanchanaburi.
6) Khlong Thom, Bang Saphan, Prachuap Khiri Khan.
7) The Peninsular Coast.
8) Ban Bo Kaeo, Samoeng, Chiang Mai.
9) Song Toh, Kanchanaburi.
10) Summary.

3) Historical Information on Social Contexts.
1) Mining.
2) Customs.
3) Smelting Tin.

5. DISCUSSION, CONCLUSIONS AND FUTURE WORK

Appendix 1. Reduction Methods.
a) Hydrogen Reduction.
b) Carbon Reduction.

Appendix 2. ICP-MS Operating Conditions.

Appendix 3. Lead Mining at Song Toh, Kanchanaburi.

Appendix 4. Geochemical Tables.

Appendix 5. Mineralogical Determination of Ore
Figure 111. Orientation Map of Thailand. encl.
Figure 112. Orientation Map of South China. encl.
Figure 211A. Southeast Asian Metalliferous Zones. 29
Figure 211B. Southeast Asian Granite Provinces. 31
Figure 211C. Plate Tectonic Reconstruction for the Southeast Asian Tin Belt. 33
Figure 211D. Major Tectonic Events Capable of Mobilising Tin from Precambrian Continental Basement. 35
Figure 211E. Metallogenic-Tectono-Magmatic Provinces of Southeast Asia. 36
Figure 211F. The Tin Fields of Southeast Asia in Relation to the Granites. 38
Figure 212A. Tin Occurrences Related to the Structural Zones of South China. 44
Figure 212C. Metalliferous Zones of Thailand. 46
Figure 212D. Major Southeast Asian Structural Zones. 49
Figure 212E. Sn-Nb-Ta Deposits in Relation to Malaysian Mineralised Belts. 50
Figure 212F. Mineral Zonation in Kinta Valley, Perak. 54
Figure 212G. Schematic of the Deposit Zonation in the Dachang Ore Field. 54
Figure 212H. Complex Mineral Zonation in the Herberton Tin Field, Australia. 55
Figure 212I. Vertical Zonation of Mineralisation in the Dachang Tinfield, South China. 56
Figure 221A. The Greisen Environment. 64
Figure 221B. Environments of Placer Deposition. 77
Figure 223A. Tin Deposits in India. 91
Figure 223C. Map of the Pilok Tin-Tungsten Mineralised Field. 93
Figure 223D Major Primary Deposits of the Kinta Valley. 98
Figure 223E. Distribution of Significant Stanniferous Hydrothermal Veins, Pegmatites and Aplites in Malaysia. 101
Figure 223F. Distribution of Significant Stanniferous Skarns in Malaysia. 102
Figure 311A. System Diagram of Plasma-Source Mass Spectrometer. 108
Figure 312A. Full Range Profile of Bronze BND-1101. 111
Figure 312B. Expanded Spectrum of BND-1101 Showing Tin Peaks.

Figure 312C. Expanded Spectrum of BND-1101 Showing Barium and Lanthanides.

Figure 312D. Expanded Spectrum of BND-1101 Showing Silver, Tin and Barium/REE Peaks.

Figure 312E. Spectrum of BND-1101, Reduced Vertical Scale to Show Tin Peaks.

Figure 312F. Spectrum of BND-1101 Showing Iron/Manganese Peaks.

Figure 312G. Expanded Spectrum of BND-1101 Showing Lead/Bismuth Peaks.

Figure 312H. Lead Isotopes in Bronze.

Figure 321A. ICP-MS Spectrum of an Aqueous Tin Solution in 500ng/ml, Illustrating the Occurrence of Tin-Related Polyatomic Interferences.

Figure 321B. ICP-MS Spectrum for 1ug/ml Ta, Indicating the Presence of TaO+ on Au at 197 amu.

Figure 321C. ICP-MS Spectrum for 1ug/ml Nb, Indicating the Presence of NbO+ Interference on Ag at 109 amu.

Figure 321D. Full Range Profile of 3% HCl Acid Blank.

Figure 332A. Chart Showing Copper Anomaly in Ratchaburi Cassiterite.

Figure 332B. Chart Showing Effect of Removal of Ratchaburi Tin Anomaly.

Figure 332C. Chart Showing Copper, Lead and Zinc Anomalies in Cassiterite Samples.

Figure 332D. Chart Showing Effect of Removal of Major Copper, Lead and Zinc Anomalies.

Figure 332E. Bar Chart of Lead and Zinc in Bronze.

Figure 332F. Log. Chart of Lead and Zinc in Bronze.

Figure 332G. 3-D Chart of Lead and Zinc in Bronze.

Figure 333A. Variations in Lead Isotope Plots.

Figure 334Aa. ICP-MS Part-Spectrum of Cassiterite from Makhon Sri Thammarat.

Figure 334Ab. ICP-MS Part-Spectrum from Phuket showing Lead Anomaly.

Figure 334Ba. ICP-MS Full-Spectrum of Cassiterite from Nakhon Sri Thammarat.

Figure 334Bb. ICP-MS Full-Spectrum of Cassiterite from
Figure 334Ca. Lanthanide Spectrum for a Cassiterite-Sulphide Ore.
Figure 334Cb. Lanthanide Spectrum for Phuket Alluvial Concentrate.
Figure 334Da. ICP-MS Part-Spectrum of Takua Pa Cassiterite Concentrate Fraction.
Figure 334Db. ICP-MS Part-Spectrum of Takua Pa Cassiterite Middlings Fraction.
Figure 334Ea. Spectrum of Cassiterite Ore Sample from Phuket, not Katthu.
Figure 334Eb. Spectrum of Cassiterite Ore Sample from Katthu, Phuket.
Figure 334Fa. ICP-MS Full-Range Spectrum of Cassiterite from Nakhon Sri Thammarat.
Figure 334Fb. ICP-MS Full-Range Spectrum of Cassiterite from Uthai Thani.
Figure 334Fc. ICP-MS Full-Range Spectrum of Cassiterite from Chiang Mai.
Figure 334Fd. ICP-MS Full-Range Spectrum of Cassiterite from Phuket.
Figure 334Ga. ICP-MS Full-Range Spectrum of Cassiterite from Kanchanaburi.
Figure 334Gb. ICP-MS Full-Range Spectrum of Cassiterite from Takua Pa Concentrate.
Figure 334Gc. ICP-MS Full-Range Spectrum of Cassiterite from Phuket.
Figure 334Gd. ICP-MS Full-Range Spectrum of Cassiterite from Takua Pa Middlings.
Figure 334Ha. ICP-MS Full-Range Spectrum of Cassiterite from Ranong.
Figure 334Hb. ICP-MS Full-Range Spectrum of Cassiterite from Chumporn.
Figure 334Hc. ICP-MS Full-Range Spectrum of Cassiterite from Kanchanaburi.
Figure 334Hd. ICP-MS Full-Range Spectrum of Cassiterite from Katthu, Phuket.
Figure 334Ia. ICP-MS Full-Range Spectrum of Cassiterite from Carnon Valley, Cornwall.
Figure 334Ib. ICP-MS Full-Range Spectrum of Cassiterite
from Goss Moor, Cornwall.
Figure 334c. ICP-MS Full-Range Spectrum of Cassiterite from Par, Cornwall.
Figure 334d. ICP-MS Full-Range Spectrum of Wood Tin, Cornwall.
Figure 334ja. ICP-MS Full-Range Spectrum of Lead Sulphide Ore, Song Toh, Kanchanaburi.
Figure 334jb. ICP-MS Full-Range Spectrum of Lead Sulphide Ore, Pha Daeng, Tak.
Figure 334jc. ICP-MS Full-Range Spectrum of Lead Sulphide Ore, Kong La, Pattalung.
Figure 334jd. ICP-MS Full-Range Spectrum of Lead Sulphide Ore, Phrae.
Figure 334ka. ICP-MS Full-Range Spectrum of Lead Ingot of Unknown Origin.
Figure 334kb. ICP-MS Full-Range Spectrum of Lead Oxide Ingot from Song Toh, Kanchanaburi.
Figure 334kc. ICP-MS Part-Range Spectrum of Lead Ingot of Unknown Origin.
Figure 334kd. ICP-MS Part-Range Spectrum of Lead Ingot from Sichang 3 Wreck, Chonburi.
Figure 334la. ICP-MS Full-Range Spectrum of Lead Ingot from Sichang 3 Wreck, Chonburi, Metal Portion.
Figure 334lb. ICP-MS Full-Range Spectrum of Lead Ingot from Sichang 3 Wreck, Chonburi, Whole Ingot.
Figure 334lc. ICP-MS Part-Range Spectrum of Lead Ingot from Sichang 3 Wreck, Chonburi, Corrosion Fraction.
Figure 334ld. ICP-MS Part-Range Spectrum of Lead Ingot from Sichang 3 Wreck, Chonburi, Whole Ingot.
Figure 334ma. ICP-MS Part Spectrum of High Lead Ban Don Ta Phet Bronze.
Figure 334mb. ICP-MS Part-Spectrum of Ban Don Tha Phet Low Lead Bronze.
Figure 335a. Geographical Distribution Relationship of Zirconium and Niobium in Cassiterite.
Figure 335b. Geographical Distribution Relationship of Titanium and Tantalum in Cassiterite.
Figure 335c. Geographical Distribution Relationship of Titanium and Zirconium in Cassiterite.
Figure 335e. Geographical Distribution Relationship of
Figure 412A. Geographical Regions of Southeast Asia. 223
Figure 413A. The Malay Clay Furnace. 258
Figure A3.1. Lead Smelter, Song Toh, Kanchanaburi. 282
Figure A6a. Orientation Map of Thailand. 297
Figure A6.1. Barite Deposits of Thailand. 298
Figure A6.2. Antimony Deposits of Thailand. 299
Figure A6.3. Tungsten Deposits of Thailand. 300
Figure A6.4. Tin Deposits of Thailand. 301
Figure A6.5. Copper/Lead/Zinc Deposits of Thailand. 302
Figure A6.6. Zinc Deposits of Burma. 303
Figure A6.7. Tin Deposits of Burma. 304
Figure A6.8. Barite Deposits of Burma. 305
Figure A6.9. Chromite Deposits of Burma. 306
Figure A6.10. Antimony Deposits of Burma. 307
Figure A6.11. Tungsten Deposits of Burma. 308
Figure A6.12. Lead Deposits of Burma. 309
Figure A6.13. Tin/Tungsten/Fluorite Deposits of Southeast Asia. 310
Figure A7.1. Diagrammatic Representation of the Primary Tin Deposits of Southwest England. 315
Figure A7.2. Diagrammatic Representation of the Types of Primary Tin Deposits in Southeast Asia. 315
Figure A7.3. Diagrammatic Representation of Environments of Primary Tin Deposition in Southeast Asia. 316
Figure A7.4. Types of Tin Deposit. 317
Figure A7.5. Depositional Environments. 318
Figure A8.1. Supported Sluice Box. 320
Figure A8.2. Dammed Stream with Palong. 320
Figure A8.3. Riffles. 320
Figure A9.1. Paired Shafts, Song Toh, Kanchanaburi. 327
Figure A9.2. Shafts, Bang Saphan, Prachuap Khiri Khan. 328
Figure A9.3. Shafts, Samoeng, Chiang Mai. 328
Figure A9.4. Adits, Pilok, Kanchanaburi. 327

Table 212A. Metallogenic Components of the Shan-Tenasserim Province. 51
Table 212B. Some Documented Mineral Associations of Southeast Asia. 52
Table 221. Mineral and Metal Associations of the Southeast Asian Tin Deposits. 68
Table 221A. Provenances of Some Placers Containing Tin and REE Species. 75
Table 221B. Classification of Tin-Bearing Placers. 76
Table 222A. Some Important Minerals & Their Compositions. 86
Table 321A. Isobaric and Polyatomic Ion Interferences for Tin in HCl Acid Medium. 121
Table 321B. Polyatomic Ion Interferences Arising from Minor Elements in Cassiterite. 122
Table 321C. Equivalent Concentration Data for 500ppm Tin Polyatomic Ion Interferences. 123
Plate 1. A Small Mining Community, Peninsular Thailand. 19
Plate 2. ICP-MS Plasma Impinging on the Sampling Cone. 103
Plate 3. General View of the Phu Lon Copper Mining District. 219
Plate 4. Overgrown Mining Site, Kanchanaburi Province. 235
Plate 5. Simple Palong into which Ore Slurry is Washed, Kanchanaburi. 236
Plate 6. Abandoned Tin Mining District Showing Lack of Revegetation. 236
Plate 7. Tree Ferns on Land Contaminated by Heavy Metals. 237
Plate 8. Small Mining Adits, Pilok, Kanchanaburi Province. 238
Plate 9. Simple Mining Shafts, Prachuap Khiri Khan Province. 240
Plate 10. Washing Ore, Prachuap Khiri Khan Province. 240
Plate 11. Hummocky Terrain in a Kanchanaburi Mining District. 242
Plate 12. Alluvial Mining Region on Coastal Plain, Ranong. 242
Plate 13. Small-Scale Alluvial Mining, Phangnga. 243
Plate 14. Reservoir and Sluice at Top of a Hush Gully. 245
Plate 15. Miners Breaking Ore to be Shovelled into a Raised Palong, Chiang Mai. 246
Plate 16. Old Mining Shaft, Samoeng, Chiang Mai Province (b/w). 247
Plate 17. Simple Palong, Samoeng, Chiang Mai Province (b/w). 247
Plate 18. Small Boy Working the Outflow of a Raised Palong (b/w). 248
Plate 19. Bamboo Water Pipe, Samoeng, Chiang Mai (b/w). 249
Plate 20. Stone-Lined Stream, with Palongs, Artificially Deepened by Prolonged Mining, Samoeng, Chiang Mai. 250
Plate 22. Lead Slags at Abandoned Mining/Smelting Site, Bo Ngam, Kanchanaburi Province. 262
Plate 23. Ancient Bamboo-Lined Mine Shaft, Buried in Yellow
Laterite, Song Toh, Kanchanaburi Province. 279
Plate 24. Sinkhole in Limestone Directly Above Song Toh
Open Pit Lead Workings. 280
Plate 25. View Across Abandoned Smelting Site, Song Toh
South West, Kanchanaburi Province. 283
Plate 26. Ancient Mining Adits, Song Toh Lead Mine,
Kanchanaburi. 284
Plate 27. Ancient Galleries, Song Toh, Kanchanaburi
Province. 284
Plate 28. Cave Entrance Leading to Cavern Containing
Hearth, Troughs etc., Kanchanaburi Province. 285
Plate 29. Primitive Palong, Riffles Placed Directly into
Stream Channel, Chiang Mai. 321
Plate 30. Primitive Palong, Boarded Trough Dug to Process
Ore Slurry Washed from the Face by a Monitor. 322
Plate 31. Lanchut, Phuket Island. 323
Plate 32. Raised Palong, Chiang Mai Province. 324
Plate 33. Panners Working Stream Channels, Phuket Is. 324
Plate 34. Mining Shafts Sunk Through Alluvium to Ore-
Bearing Strata, Kanchanaburi Province. 329
Plate 35. Bamboo-Lined Shaft, Kanchanaburi Province. 330
Plate 36. Simple Palong in Stone-Lined Gully, Samoeng. 331
Plate 37. Complex Galleries, Kanchanaburi Province. 332
Plate 38. Reservoir to Provide Water to Small Raised
Palong, Lohasiri Mine, Ratchaburi Province. 333
Plate 39. Dulang Washers Working a Stream Below a
Palong. 334
Plate 40. Construction of Bamboo-Lined Shaft. 335
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<tr>
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<td>Trace Element Profile</td>
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<tr>
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<td>BND</td>
<td>Ban Na Di</td>
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<td>Cornwall/Devon</td>
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<tr>
<td>RSD%</td>
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"Peace be with thee, O Tin-ore;  
In the beginning dew became water,  
    The water became foam,  
    The foam became rock,  
Come forth from thy stony lair.  
If thou wilt not obey my call,  
Thou wilt be a traitor before Allah.  
Hey! Tin-ore that drifts hither and thither,  
Drifts on the sea, roams on the land,  
Float to the surface of my pool,  
If thou wilt not float thou wilt be a rebel before Allah,  
A traitor to Mahomed and disloyal to Baginda Rasul Allah."

A Malay Pawang's Charm to call tin ore to a mine. Quoted in Scrivenor, 1928.
Plate 1. A Small Mining Community, Peninsular Thailand.
1.1 THE AIMS OF THE PROJECT

This is a multidisciplinary thesis investigating the use of a new, sophisticated, analytical technique to study variations in the geochemistry of southeast asian tin ores, their influence on the composition of early metal artefacts and the applicability of this to the economic interpretation of trade in prehistory.

This study approaches the problem from three directions:-

1. The initial study of the geology, geochemistry and mineralogy of the Southeast Asian Tin Belt provides, as far as possible, a database from which details of regional geochemical variations can be extracted.

2. The ultratrace element and isotopic analysis of ore and metal samples generates comparative data which can be statistically examined to highlight anomalies in elemental compositions and isotopic ratios which could indicate a source region for the ores. To do this a new analytical technique is used and is, in itself, evaluated as to its performance in this work.

3. The development of mining technology and modern small-scale mining are discussed briefly and the data are used, together with previous research, to theorise on southeast asian socio-economic development with respect to the metals trade.

For various reasons, which are explained below, the research concentrates on tin ores and the tin bronzes characteristic of thai metallurgy, but an appendix on lead and lead mining is included.

In an attempt to eliminate trace element interference from other sources, lead and copper ores were also analysed as
well as tin, lead and copper metal. For comparison some
Cornish tin and tin ores were also analysed.
In addition to this, several methods of preparation of the
tin prior to analysis were tried, in an attempt to simulate
the original smelting process. This is further discussed in
Chapter 3.

Any study of this kind relies heavily on background data in
a variety of subjects. In many instances the necessary data
are not available or only partially so and therefore the
conclusions which can be drawn are severely limited and in
some cases reduced to mere inference and hypothesis, until
further data are obtained from other disciplines.

1.2 THE THEORY

1.2.1 THE GEOLOGY AND GEOCHEMISTRY

The geology and geochemistry of cassiterite have been
studied by a number of researchers over many years and have
yielded a wealth of varied and important [and occasionally
unsubstantiated] data on the variability of the mineral
(Taylor, 1979).

It is this variability of cassiterite and cassiterite
deposits that suggests it may be a useful tool in
archaeological provenancing.

The variations in the trace element and mineralogical
associations of cassiterite are of practical importance:-

1. They can be used to determine the genetic environment
of the deposit as classified by Taylor (1979).

2. Because there are so many different genetic
environments and geochemical associations of
cassiterite, it may be possible to significantly reduce
the number of possible sources of the tin.
3. In Thailand, and Southeast Asia generally, the different types of ore deposit are well represented.

4. Variations occur on a local and regional scale. 10 different elemental assemblages were recognised and 3 different tectonic environments (Hutchison and Taylor 1978). Furthermore, 4 chemically varied granitic provinces were described by Cobbing et al. (1986)

The genetic environment of a deposit may be recognised in one of two ways:-

1. By the relative amounts of a certain trace elements or minor elements.

2. By the presence or absence of a particular trace element or combination. For the purpose of this study an anomalous presence of any element is a concentration above the background levels of that element and allowing for a degree of known environmental or analytical contamination. Figures are given in Appendix 4.

1.2.2 THE METALS

In the use of these factors in archaeological work however, it must be realised that the trace element chemistry of a tin bronze does not bear a simple direct relationship to the original tin ore and other factors have to be considered:–

1. More than one ore may have been used in the production of the bronze.

2. The behavior of trace elements during smelting is unpredictable and largely unresearched. Enrichment or depletion may occur. Therefore only identification by the presence or absence of elements is feasible. This reduces the number of genetic environments traceable.

3. Contamination during smelting may occur.
4. Modern concentrates have usually undergone greater separation, especially of magnetic components, than early ores.

5. Recycling of metal may occur.

6. Corrosion products may confuse the analyses of metals.

With regard to points 1 and 5, however, the abundance of cassiterite in Thailand makes it unlikely that ores were mixed and the mixing of metals would depend on a number of factors which are discussed later. Corrosion products may be avoided by careful sampling but corrosion does not appear to affect the analyses.

1.2.3 THE ANALYTICAL METHOD

While it is possible that trace element analysis of tin could be a useful archaeometallurgical tool, much depends on the analytical method used. The low concentrations of the elements in the ore and the need to determine the presence or absence of any element require an extremely sensitive analytical technique. Similarly, the number of analyses required to obtain an acceptable database of information needs a rapid throughput of samples and simultaneous elemental analysis. Inductively Coupled Plasma Source Mass Spectrometry was chosen and is discussed in Chapter 3.

Lead isotopes have been used, with some success, to identify ore sources in antiquity and are discussed by Farquhar and Fletcher (1984), Branigan (1982), Farquhar and Vitali (1985), Northover and Gale (1982), Farquhar et al. (pers. comm.), Stos-Fertner and Gale (1978) and Gale (1978) and the role of lead in early thai and chinese metallurgy needs to be considered.
1.2.4 MINING AND METALLURGICAL HISTORY

It has long been a sound geological principle that the present is the key to the past [James Hutton's Principle of Uniformitarianism] and, within reason, this applies no less to mining technology.

Basic mining techniques of rock breaking, mucking, tramming and hoisting remained much the same from the Neolithic search for stone and pigment to the Industrial Revolution. Similarly ore beneficiation methods and smelting technology, once developed, changed little. Early texts however, are few and tend to be devoid of details as the authors were rarely conversant with the techniques, processes and implements involved.

This study is concerned with early tin bronzes consisting of copper, tin and often lead. The development of copper metallurgy, as opposed to the use of native copper, probably post-dates the earliest lead metallurgy, as evidenced by the finds at Catal Huyuk, Turkey. (Mellaart 1967, Gale and Stos-Gale 1981). Ores of both lead and copper are widely distributed and so is evidence of their early use. Tin ores however, have restricted geographical occurrence and the development of tin metallurgy is confined to the tin belts of the world. The disparate methods of bronze production in Southeast Asia probably reflect this distribution: China developing sophisticated lead-bronze metallurgy while tin-bronze metallurgy developed in the tin belt further south.

In the context of this thesis, interpretation has been made from the point of view of mineral economics and mining culture in order to compare this with current archaeological and anthropological theories.

1.3 THE RESEARCH METHOD

A. Initially a literature search was undertaken to decide whether there was enough background information to support
B. Samples were collected from Thailand to include cassiterite ores, lead ores, copper ores, lead metal, and tin metal. Bronzes and copper were already available at the Institute of Archaeology. At the same time, as much supporting information as possible, on geology, geochemistry, mineralogy, mining, metallurgy and relevant archaeology was obtained.

C. A development stage was initiated, with the British Geological Survey, to determine the best sample preparation method and to optimise the instrument for analysis of high matrix concentration samples, especially the binary and ternary matrix of metal alloys.

D. Analysis of as many samples as possible was done according to the agreement with the BGS.

D.ii. Mineralogical examination of ore samples was done using a binocular microscope and studies of thin and polished sections are intended.

D.iii. Dissolution residues were analysed by X-ray diffraction to provide supporting information.

E. Alternative analytical data on some of the samples were obtained from other sources, as a comparative method was not practicable at the time.

F. All the available information was examined, correlated and compared to determine if the data could be used to support or illuminate the economic interpretations of aspects of the early metal age in Thailand.

High Tin Bronze is defined as Sn > 10%.
South China is defined as Yunnan, Guangxi and Guangdong.
Regional Divisions of Thailand are Defined in Appendix 10.
2.1 GEOLOGY OF SOUTHEAST ASIA AND THAILAND

2.1.1 GRANITE PROVINCES

The region can be divided into three distinct metallogenic provinces (Hutchison and Taylor, 1978):

1. A peripheral Cenozoic volcanic arc incorporating maritime Southeast Asia.
2. A Mesozoic Sundaland core i.e. mainland Southeast Asia.

To describe it in metallogenic terms: the first is a major modern producer of copper with silver and gold; the second, in which this study is primarily interested, is the Southeast Asian Tin Belt producing tin with secondary tungsten and antimony; the third is a major tungsten and antimony province with subordinate tin and mercury (Figure 211A). Theoretically, the variations between 2 and 3 may be useful in differentiating southeast asian metallurgy from chinese.

Taylor (1979) described the regional geology of the tin belt as:

Province Type 1d, Deposits associated with passive and/or batholithic magmatic environments.
- Southeast Asia - Erzgeberge Style: a major orogenic zone intruded by granitoids with a late Cambrian miogeosynclinal environment to the west and eugeosynclinal to the east separated by a geanticlinal ridge. Limestones are common to the west and andesite/rhyolite volcanics to the east. Post-Upper Triassic uplift and erosion led to terrestrial sedimentation. The general structural trend is NNW-SSE with the three major zones perhaps bounded by major wrench faults.
Figure 211A.

SE Asian Metalliferous Zones

103° 113° 93° 93°

PHUKET

KINATA

W Sn

Mo

Sn

Cu

Pb

Sb & Hg

Au

Sn

W (Sb)

0 200 600 800 km

BANKA

BILLITON

113°
In the southeast asian tin province the tin mineralisation is spatially related to the acid granitoids, of Permo-triassic age in Indonesia and the Malay Peninsula and of Cretaceous age in Phuket and Tenasserim. Within these environments the different mineralogical and metal associations of the deposits have limited regional distribution.

Four chemically varied granitic provinces have been recognised, as shown in Figure 211B, (Cobbing, Mallick, Pitfield and Teoh 1986). These are:

1. The Main Range Province.
   Endogenous greisen-bordered vein swarms of cassiterite and wolframite.
2. The Eastern Province.
   Magnetite-cassiterite skarns + base metal sulphides, with antimony in Thailand.
3. The Western [Peninsular Thailand-Burma] Province.
   Endogenous greisen-bordered vein swarms and pegmatites of cassiterite and wolframite.
4. The North Thailand Migmatite Province.
   Endogenous vein and skarn replacement scheelite and fluorite deposits with some tin and antimony.

The mineralogy and geochemistry of the Tin Belt is, at least partially, related to that of the tin-bearing granites; which in turn can affect the geochemistry of the cassiterite ores used in prehistoric metallurgy. However the relationship between tin ores and their host granite is not clear cut.

A considerable body of data has been accumulated on granites, both stanniferous and barren, throughout the world including Southeast Asia and it is necessary to give a brief description of the events leading to the formation of the several granitic mineralised belts of Southeast Asia.
Figure 211B. S.E. Asian Granite Provinces. (Cobbing et al., 1986)
Recent evidence suggests that economic concentration of tin requires continental crustal remelting (Hutchison and Chakraborty, 1979; Lehman, 1982; Hutchison, 1988) rather than the existence of a primary crustal tin anomaly (Pollard et al. 1983). Magmatic-tectonic events including metamorphism and anatexis progressively differentiate the crust with respect to tin. Polycyclic events of this kind result in increasing tin concentration with increasing crustal involvement.

The southeast asian stanniferous granites, like those of S.W. England, are classified as S-type (Chappell and White 1974) or the Ilmenite Series of Ishihara (1977). These granites are derived from a source region within the continental crust as opposed to the I-type granites [Magnetite Series] derived from a deeper, upper mantle source. It is apparent, on a global scale, that many I-type batholiths are spatially related to current subduction of oceanic lithosphere such as the Philippine intrusives which are related to the subduction of both the South China Sea from the west and the Philippines Sea from the east. It should be noted that the porphyry copper-molybdenum deposits are associated with the I-type subduction-related granitoids. A fact which is pertinent to the mineralised zones of Southeast Asia. On the other hand the tin-bearing S-type granites bear no such relationship to subduction zones. The alternative tectonic model which could account for a batholithic scale belt of S-type granites is continent-continent collision or continent-arc collision. However, such collisions occur when an ocean or marginal basin closes as a result of subduction and therefore a belt of I-type granites should occur on the continent side of younger S-type granites. Figure 211C shows this situation in Thailand, based on Rb-Sr whole rock isochron ages (Beckinsale, 1979).

Beckinsale (1979) discusses the geochemical and geochronological data for the thai granites in relation to
Figure 211C. Plate Tectonic Reconstruction for the S.E. Asian Tin Belt. (Beckinsale, 1979).
the tectonic model proposed by Mitchell (1977). The I-type, granites of Thailand and East Coast Belt of Malaysia, which Hutchison and Taylor (1978) describe as the remains of a volcano-plutonic arc, and the Permo-Triassic volcanic arc which incorporates the copper deposits of Loei and the copper district extending southward through Central Thailand, are the result of the eastward subduction of a Permian marginal basin occupying Central Thailand. In Triassic times the marginal basin closed with a continental collision, generating the main tin-bearing, S-type granites of the Central Belt of Thailand and the Main Range in Malaysia. During Lower Cretaceous times a marginal basin lying to the west of Thailand was subducted eastwards giving rise to the I-type granites of west Thailand at Mae Lama and Phuket. In the Middle Cretaceous this basin closed, resulting in the richly mineralised S-type granites of Khao Daen and Phuket. Therefore in Southeast Asia, the model implies that tin previously concentrated in continental crust, is remobilised when an anatetic-fractional crystallisation cycle is initiated by continental collisions and the generation of S-type granites.

Hutchinson (1988) expands this model by including pre-rift thermal reworking of continental crust resulting in sub-alkaline granites of crustal origin (Figure 211D). Such areas of updoming and trap volcanism forming 'spot' granites, rather than belts, are characteristic of the margins of the South China Sea (Figure 211E).

On the whole, Hamilton's (1972) summary serves to indicate the complexity of southeast asian tectonic history. He describes Southeast Asia and "Sundaland" as an aggregate of small continental fragments. Late Palaeozoic subduction westwards beneath Malaysia and Thailand [granite in east Malaysia and melanges in Laos and Cambodia] ended when Indochina collided with them. Early and Middle Triassic subduction was eastwards, beneath the west side of the aggregate. Late Triassic and Jurassic subduction was then from the north and ended with the collision of the
Figure 211D. Major Tectonic Events Which Can Mobilise Tin from the Pre-Cambrian Continental Basement.

Tin mobilisation is important in: Malayan-type Collision Belts and Pre-rifting Districts of Crustal Re-working with Sub-alkaline Granites.
aggregate with China. Early Cretaceous subduction was again from the west. Late Cretaceous subduction was beneath the east side of the aggregate and followed continental rifting there. Cenozoic subduction, from the west once more, ended, in the north, when the aggregate collided with India but still continues in the south.

**Tin Ores and Their Relationship to the Granites.**

Primary tin mineralisation is spatially related to particular granites as illustrated in Figure 211F. For example: the hydrothermal vein swarms in roof cusps of granite intrusions at Mawchi Mine and Hermingyi Mine, Burma; the disseminated deposits in extensively greisenised rock of Haad Som Pan, Thailand (Aranyakanon, 1961) and the varied pegmatites and aplites in the roofs of intrusions and in the surrounding country rock. Although the spatial relationship is undisputed, the geochemical relationship is not fully understood and there is some doubt as to whether the stanniferous pegmatites fractionated from the same magma that produced the host granite. Neither is the origin of the hydrothermal fluids, involved in the formation of vein swarms nor the pneumatolytic alteration responsible for the Haad Som Pan deposits, fully understood.

Pitakpaivan (1969) analysed various tin granites for their tin and tungsten contents and it is apparent the Sn or W contents of the granites do not necessarily reflect the occurrence of ores. In the Mae Bo Kaew deposits, Chiang Mai, the granite is recorded as having moderate tin content and low tungsten [60-75 ppm Sn, 5-8 ppm W] and yet high grade Sn/W ores occur. Similarly, the granites at I-Pu, Pilok only record 30 ppm Sn and 15 ppm W when there are some local rich deposits of tin and tungsten.

However, certain differences between tin-bearing granites and tin-barren granites are recognised (Rosler and Lange, 1972). Tin granites are generally late-stage, biotite or two-mica paligenetic granites and sometimes tourmaline granites. They are albite and lithium-rich with cassiterite, topaz, tourmaline and fluorite accessories and
Submarine granites with tin deposits locally?

Figure 211F. Tin Fields of Southeast Asia and their Relation to the Granites. (Hosking, 1969).
1. Belugyun Island
2. Heinz Bay.
3. Palou.
4. Mergui/Tenasserim Islands.
5. Ranong.
7. Thai Muang.
8. Phuket.
9A. Rayong.
10. P. Lankawi.
10A. Penang.
11. Lumut.
12. Malacca.
15. Singkep.
tin, gallium, fluorine and lithium in the dark micas. Tin-barren granites, on the other hand, are often migmatitic, single phase, synorogenetic intrusives of hornblende granites and granodiorites. They contain little albite but are richer in iron/magnesium biotites as well as titanite, allanite and apatite. They are richer in calcium, magnesium, manganese and titanium and the dark micas contain lead, nickel and copper. Unlike the tin-bearing granites, autometasomatism is rare.

Although in general the tin mineralisation in Thailand is related to the Cretaceous and Triassic granites, it has been suggested that the pyrometasomatic Skarn-type deposits of Pinyok Mine, Thailand and perhaps the bedded cassiterite-pyrrhotite-magnetites of east Malaysia and Billiton, may in fact be volcanogenic in origin and considerably older than the intruding granites (Hutchison and Taylor 1978). Hosking (1988) also notes that these deposits may not be easily defined.

This being so, the theory that the geochemical and isotopic study of the tin-bearing granites can be applied to the geochemical study of the related ores is in some doubt. However the ores mined from the Quaternary placers inevitably contain accessory minerals derived from the host granite as well as the tin pegmatites. For this reason care must be taken to differentiate between geochemical data on ores from primary sources and those from alluvial sources. Unfortunately most of the available literature is concerned with the geochemistry of granites or cassiterite and few deal specifically with ores/concentrates.

In the earliest phase of the metallurgical age primary mixed ores were probably used, rather than alluvials, but at the height of the bronze era nearly all cassiterite would derive from secondary sources if those were available, although evidence of underground or surface exploitation of primary sources needs to be obtained. In this area, only two major underground tin mines exist at present, those at Sungei Lembing near Kuantan, Malaysia and
Kelampa Kempit Mine in Billiton, Indonesia. There are however, numerous small scale, low technology operations. It is the existence of the small-scale operations which suggests that underground mining of primary deposits in the past was not beyond the capabilities of the early miners, especially the Thais or Mon-Khmer, if alternative sources were not available. A survey of all mining operations in Southeast Asia to determine whether there are any indications of early mining would be most illuminating.

However, the dividing line between easily exploitable, alluvial deposits and difficult to exploit, primary ores is not so clear cut. There are also the highly altered and weathered primary ores, which are soft enough to be easily exploited even in prehistory, to be considered. Such deposits, including those at Pilok, Samoeng and Phuket in Thailand, to mention but a few, are exploited both as the weathered primary and the associated alluvials.

There are therefore three types of ore geochemistry to consider:

1. Primary ores, which may or may not reflect the geochemistry of the granite host.

2. Secondary ores, in which the accessory minerals may reflect the granite host.

3. Combined primary and secondary ores which must be treated as secondary ores even though the accessory minerals derived from the granite host may be significantly reduced.

Primary tin deposits in the roofs of granites also intersect the country rock. Therefore the accessory minerals in a secondary deposit may include those derived from its metamorphic aureole as well as those from a stanniferous granite.

In order to determine the ore sources used in the
production of tin or tin-bronze there are five types of geological/geochemical data to be examined:-

1. The specific geochemistry of cassiterite and the corresponding chemistry of the metal product.

2. The geochemistry of the ore as a whole, including heavy mineral accessories included in the smelt and therefore reflected in the final products of metal or slag.

3. The mineralogy of ore remains found at a production site.

4. Rock samples found at the production site especially granite or metamorphics.

5. The chemistry of the slag found at a production site.

From such data a picture of what was being mined and where it was going can be obtained as well as the possible production sites of a metal artefact. If enough basic data is accumulated it may be possible to relate the bronze's chemical characteristics to a production site and/or an ore source or mining region.

2.1.2 METALLIFEROUS REGIONS AND ZONING OF ELEMENTS

General.

Metalliferous deposits are not uniformly distributed across Thailand. Two regions in particular are virtually barren of metals. These are the Khorat Plateau and the Great Plain of the Chao Phrya River depression.

However a regional elemental zoning throughout Southeast Asia must be considered. Unfortunately much of the data is based on production rather than occurrence and extreme caution is advised when considering 'mineral-free' regions.
On a regional scale, Hutchison and Taylor (1978) recognised the importance of the Sn-W-Sb-Hg association in that the Chinese Sn-W belt is abruptly separated from that of Southeast Asia by the Red River. Divisions between N.W. Thailand/Burma and W. Yunnan/Sechuan are less apparent, the west part of the Sanjiang Tin Province being considered an extension of the Thai Tin Belt (Figure 212A), (Chen and Wang, 1988). Xu Keqin and Zhu Jinchu (1988) note that there is a tendency for W deposits to concentrate in the eastern part of the Chinese Sn/W belt, whereas Sn deposits concentrate in the west. The Sn-W deposits lie in between. However, they account for the Sn/W occurrences in western Yunnan by placing them in the Southeast Asian Tin Belt. They also note a regional zonation of Sn/W and Sn-sulphide deposits from south Jiangxi westward to south Hunan as follows:

<table>
<thead>
<tr>
<th>West</th>
<th>East</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn W skarns+Sn</td>
<td>W/Sn</td>
</tr>
<tr>
<td>Cass. Scheelite + sulph.</td>
<td>Wolf./Qz veins</td>
</tr>
<tr>
<td></td>
<td>Wolf.Qz veins</td>
</tr>
</tbody>
</table>

In peninsular Southeast Asia, W and Sb occur together in the more continental parts of the region, whereas in China the two tend to occur separately. The tin occurs with tungsten in both areas. Hg is not a common associate of tin south of the Red River but increases in significance further north.

The South China tin deposits are of mainly cassiterite-sulphide type and their derivatives, but show four different mineral assemblages:

1. Pegmatite: Li-Be-Nb-Ta-REE
2. Cassiterite skarns: W-Sn
3. Cassiterite skarns: Fe-Sn
4. Cassiterite-sulphide: Sn-Cu-Pb-Zn-Sb

(Li Xiji, 1988).

Within the polymetallic belt of south China, Yang Jiachong
Figure 212A. Tin Occurrences Related to the Structural Zones of South China.
(Chen Xin and Wang Zhitai, 1988).
et al. (1988) recognised three geochemically anomalous zones with sub-divisions:

1. Tin polymetallic zone.
   a. Mangchang anomalous subzone: Sn-Pb-Zn-Sb-As
   b. Dachang anomalous subzone: Sn-Cu-Zn-W-Sb-As-Ag
   c. Furongchang anomalous subzone: Pb-Zn-Sb-Sn-As-Hg
2. Sn-Hg zone.
3. Hg zone.

Other researchers (Chen Yuchuan, 1988; Liu Yuanzhen, 1988) have also recorded assemblages within the Dachang deposits:

1. Cassiterite-sulphide association: Pb-Zn-Sn-Sb-As
2. Zn-Cu deposit association: Zn-Cu-Sn-W-As-Sb
3. W-Sb deposit association: Sb-W-Zn-Cu-As

In this region the Hg content is high throughout.

However, when considering these reports within the framework of this thesis, it is difficult to determine whether these 'assemblages' are based on predominance or whether unmentioned elements are actually absent.

North Guangxi cassiterite ores are of interest, in that they are associated with basic igneous rocks of an ophiolite suite and contain the mafic elements Cu-Ni-Cr-Co-Sc, while being depleted in the acid components Li-Be-Ga. (Peng Daliang, 1988: Guo Wenkui, 1988).

The metalliferous zones described by Veeraburus and Japakasetr, (1967), Figure 212C, are:

a) Eastern Zone.

b) Northern Zone
   1. Chiang Rai sub-zone
   2. Median sub-zone
   3. Western sub-zone

c) Western and Peninsular Zone.
Figure 212C. Metalliferous Zones in Thailand. (Veeraburus and Japakasetr, 1967).
These roughly correspond to Hutchison and Taylor's regions and the mineral deposits documented by Scholla (1981), although the divisions between Veeraburus and Japakasetr's zones, sub-zones and provinces are somewhat nebulous.

According to Veeraburus and Japakasetr, metal deposits tend to be associated with certain types of igneous intrusions. For instance copper, lead, zinc and antimony mineralisation tend to be related to andesitic rocks, whereas tin tends to be related to biotite granites. This is better described in the tectonic framework of Hutchison (1988) and others, as discussed above.

In the Eastern Zone, deposits of copper, lead, zinc, antimony, iron, gold and manganese are characteristic of Chantaburi, Rayong, Chachoengsao, Prachin, Petchabun and Loei Provinces. Only minor occurrences of tin and molybdenum are reported. This zone has also been referred to as the Copper Province and corresponds with Scholla's reports on mineral occurrences in the north-south volcanogenic belt of central Thailand.

The Chiang Rai region of the Northern Zone, including Uttaradit, is noted for its copper mineralisation with minor gold, manganese lead and zinc.

The Median sub-zone incorporates the rich antimony, lead, zinc, copper, manganese, gold and tin deposits of Chiang Rai, Lamphun, Lampang, Phrae and Tak Provinces.

In the western sub-zone the tin-tungsten mineralisation dominates with minor occurrences of lead, zinc, antimony and manganese.

The Western and Peninsular Zone corresponds to the Thai Tin Belt and contains Sn- and W-rich granites. Lead, silver, zinc, manganese and antimony are found in marginal areas.

Antimony provinces are locally related to granite or andesite contacts with limestone and occur in the Chiang
Hutchison and Taylor (1978) recognised three metallogenic provinces on a wider scale, Figure 212D:

1. Peripheral Island Arc Cu-Ag-Pb
2. Mesozoic Sundaland Core Sn-(W-Sb)
3. Cratonic China W-Sb-(Sn-Hg)

Veeraburus and Japakasetr's zones are confined to the second of these.

Similarly there are significant differences between the Malaysian Eastern [Sn, W, Fe, Au, Cu, Pb, Zn, Ag] and Western [Sn, W, Ta, Nb] Belts recorded by Cobbing (1988). The distribution of Sn-Nb-Ta in relation to the belts is shown in Figure 212E.

The regional definition of ore sources has particular significance for the metallurgy of poorly mineralised areas such as Laos, Cambodia and the West Borneo basement.

Of a more local significance is the relationship between mineralogical assemblage, metal association and ore type of the primary tin deposits (Hutchison and Taylor, 1978). In the Southeast Asian Tin Belt, Sn-W mineralisation predominates with the the usual associations of Fe, Au, Pb, Zn, Sb, Hg, Ba and F. There is a wide diversity of primary tin mineralisation types, including pegmatites and aplites +/- Nb, Ta; Fe-rich skarns; vein and replacement deposits with varied mineralogy and greisen deposits with alteration mineralogy. For example, Sn-W and Sn-Cu only occur in the Malaysian East Coast Belt and Billiton, whereas Sn-Ca and Sn-Cu-Pb-Sb characterises the Thai Border, Kinta Valley and Kuala Lumpur fields. Sn-Li-Ta is scarce, except in the Phuket-Phangnga area. Tin ore from Gejiu (Kochiou) in Yunnan always contains Pb. The Gejiu ores are polymetallic cassiterite-sulphides like others of south China (Cao Xianguang, 1988; Peng Chengdian and Cheng Shuxi, 1988) characterised by Sn-Cu-Bi-As-Ag-Cd-Pb-Be-Mo-In.
Figure 212D. Major S.E. Asian Structural Zones. (after Hutchison and Taylor, 1978).
Figure 212E. Tin-Niobium-Tantalum Occurrences in Malaysia. (Praditwan, 1988).
In 1978, Goosens described the Shan-Tenasserim Metallogenic Province with its extensions into Thailand and Yunnan. He described it as an ancient mobile belt consisting of a tectonised carbonate platform intruded by granites. He recognised various metal associations in this region which are given as follows:

Table 221.

**Major component + Associated elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>Associated Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>+Ba</td>
</tr>
<tr>
<td>Ba</td>
<td>+Pb, Cu</td>
</tr>
<tr>
<td>Be</td>
<td>+Bi</td>
</tr>
<tr>
<td>Pb</td>
<td>+Zn, Ag, Cu, Au</td>
</tr>
<tr>
<td>Pb</td>
<td>+Ba</td>
</tr>
<tr>
<td>Pb</td>
<td>+Zn, Ag, Cu, Sb, Ni, Co, Ba, Cd</td>
</tr>
<tr>
<td>Cu</td>
<td>+Au</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>+Mo</td>
</tr>
<tr>
<td>Cu</td>
<td>+Ba, Zn</td>
</tr>
<tr>
<td>Cu</td>
<td>+Pb, As, Ag, Au, Sb, Fe</td>
</tr>
<tr>
<td>F</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>+As</td>
</tr>
<tr>
<td>Au</td>
<td>+As</td>
</tr>
<tr>
<td>Fe</td>
<td>+Cu</td>
</tr>
<tr>
<td>Fe</td>
<td>+Mn</td>
</tr>
<tr>
<td>Fe</td>
<td>+Ba</td>
</tr>
<tr>
<td>Fe</td>
<td>+Pb, Cu</td>
</tr>
<tr>
<td>Fe</td>
<td>+U</td>
</tr>
<tr>
<td>Mn</td>
<td>+Co</td>
</tr>
<tr>
<td>Hg</td>
<td>+Pb, Ag</td>
</tr>
<tr>
<td>REE</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>+REE</td>
</tr>
<tr>
<td>Sn</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td></td>
</tr>
<tr>
<td>Sn-W</td>
<td></td>
</tr>
<tr>
<td>Sn-W</td>
<td>+Mn, As</td>
</tr>
<tr>
<td>Sn-W</td>
<td>+Bi, Mo</td>
</tr>
<tr>
<td>Sn-W</td>
<td>+Pb, Cu, As</td>
</tr>
<tr>
<td>Sn-W</td>
<td>+Cu, Mo, REE, U, Bi, F</td>
</tr>
</tbody>
</table>

51
Major component [Associated elements]
Sn-W[+Be]
Sn-W[+Cu]
Sn[+Pt]
Sn[+REE]
W[+Sb,Bi,Mo]
W[+Cu]
Zn
Zn[+Cu]

Generally, this classification can be applied to the Thai Tin Belt although Nb and Ta should also be considered in Thailand.

Some of the documented associations in Southeast Asia are as follows:

Table 212B.

<table>
<thead>
<tr>
<th>Region</th>
<th>Association</th>
</tr>
</thead>
<tbody>
<tr>
<td>South China, general</td>
<td>Sn-W-Hg-Sb</td>
</tr>
<tr>
<td>China Sn/W Belt, East, general</td>
<td>W dominant</td>
</tr>
<tr>
<td>China Sn/W Belt, West, general</td>
<td>Sn dominant</td>
</tr>
<tr>
<td>SE Asia Island Arc</td>
<td>Cu-Ag-Pb</td>
</tr>
<tr>
<td>China, N of Red River 1</td>
<td>W-Sn-Hg</td>
</tr>
<tr>
<td>China, N of Red River 2</td>
<td>Sb-Sn-Hg</td>
</tr>
<tr>
<td>Malaysia East Belt, general</td>
<td>Sn-W-Fe-Au-Cu-Pb-Zn-Ag</td>
</tr>
<tr>
<td>Malaysia East Belt 1</td>
<td>Sn-W</td>
</tr>
<tr>
<td>Malaysia East Belt 2</td>
<td>Sn-Cu only</td>
</tr>
<tr>
<td>Malaysia West Belt, general</td>
<td>Sn-W-Ta-Nb</td>
</tr>
<tr>
<td>Malaysia West Belt 1</td>
<td>Sn-Ca</td>
</tr>
<tr>
<td>Malaysia West Belt 2</td>
<td>Sn-Cu-Pb-Sb</td>
</tr>
<tr>
<td>North Guangxi, mafics</td>
<td>Cu-Ni-Cr-Co-Sc-Sn</td>
</tr>
<tr>
<td>South Guangxi, veins 1</td>
<td>W</td>
</tr>
<tr>
<td>South Guangxi, veins 2</td>
<td>W-Sn</td>
</tr>
<tr>
<td>South Hunan, skarns, sulph. 1</td>
<td>W-Sn</td>
</tr>
<tr>
<td>South Hunan, skarns, sulph. 2</td>
<td>Sn</td>
</tr>
<tr>
<td>South China, pegmatites</td>
<td>Li-Be-Nb-Ta-REE</td>
</tr>
<tr>
<td>South China, skarns 1</td>
<td>W-Sn</td>
</tr>
<tr>
<td>South China, skarns 2</td>
<td>Fe-Sn</td>
</tr>
<tr>
<td>South China, polymetallic</td>
<td>Sn-Pb-Zn-Sb-Cu</td>
</tr>
</tbody>
</table>

52
<table>
<thead>
<tr>
<th>Region</th>
<th>Association</th>
</tr>
</thead>
<tbody>
<tr>
<td>South China, Manchang, polymet.</td>
<td>Sn-Pb-Zn-Sb-As</td>
</tr>
<tr>
<td>South China, Dachang, polymet.</td>
<td>Sn-Cu-Zn-W-Sb-As-Ag</td>
</tr>
<tr>
<td>South China, Dachang, Cass-sulph.</td>
<td>Pb-Zn-Sb-Sn-As</td>
</tr>
<tr>
<td>South China, Dachang, Zn/Cu zone</td>
<td>Zn-Cu-Sn-W-As-Sb</td>
</tr>
<tr>
<td>South China, Dachang, W/Sb zone</td>
<td>Sb-W-Zn-Cu-As</td>
</tr>
<tr>
<td>South China, Furongchang, poly.</td>
<td>Pb-Zn-Sb-Sn-As-Hg</td>
</tr>
<tr>
<td>South China, Furongchang, zone A</td>
<td>Sn-Hg</td>
</tr>
<tr>
<td>South China, Furongchang, zone B</td>
<td>Hg</td>
</tr>
<tr>
<td>South China, Gejiu, polymet.</td>
<td>Sn-Cu-Bi-As-Ag-Cd-Pb-Be-Mo-In</td>
</tr>
<tr>
<td>Phuket/Phangnga, pegs.</td>
<td>Sn-Li-Ta</td>
</tr>
<tr>
<td>Arakan-Chin Belt, Burma</td>
<td>Cr-Ni-Pt-Cu-Fe</td>
</tr>
<tr>
<td>NE Burma</td>
<td>Cr-Cu-Au-Pb-Mo-Fe-Mn-Zn</td>
</tr>
<tr>
<td>Shan-Tenasserim</td>
<td>Ag-Pb-Mn-Sn-W-Zn-Ba-Cu-Sb-Fe</td>
</tr>
</tbody>
</table>

Variations are undoubtedly more widespread than is apparent from the literature, but the metallurgical significance, as a whole, of the chemistry of the West Thai Tin Belt should be emphasised.

**Deposit Zonation.**

Individual lodes show little indication of primary zoning but there is some indication of regional zoning (Park, 1955; Rundquist, 1974, 1977, 1982; Varlamoff, 1974), demonstrated at Kinta, Malaya (Hosking 1969) and in the Chinese deposits. Tungsten occurrences at Kinta are close to the granite contact, with lead and zinc in the sedimentary basin away from the contact. Zoning in the Dachang ore deposits is described by Yang et al. (1988) and Liu et al. (1988) and in the Gejiu ores by Cao (1988).

The complexity of zonal variations is illustrated by the examples from the research of other authors, in Malaysia, China and Australia, shown in Figures 212F-H.

Vertical zonation within the ore deposits is also described and should be considered, (Figure 212I). A long-exploited
Figure 212F. Metal Zones in the Kinta Valley, Malaysia. (Hosking, 1969).

Figure 212G. Schematic of Regional Mineralisation Zones in the Dachang Ore Belt, S. China. (Chen Yuchuan et al., 1988).
Figure 212H. Mineralisation in the Herberton Tin field, Australia, Showing Zoning. (Taylor, 1979).
<table>
<thead>
<tr>
<th>Contactor position</th>
<th>Core-containing strata</th>
<th>Alteration type</th>
<th>Zonation of mineralizations</th>
<th>Mineralizing element associations</th>
<th>Ore-controlling structure</th>
<th>Form and mode of occurrence of orebody</th>
<th>Major mineral associations</th>
<th>Ore-forming temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Silicification and pyritization</td>
<td>Mercury mineralization zone</td>
<td>Hg</td>
<td>Interstratified displacement zone, fractures, and fissures</td>
<td>Stratabound produced mainly by replacement, fissure- filling-type veins (5)</td>
<td>Chalcopyrite–pyrite–quartz</td>
<td>120–200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Skarnization zone represented essentially by diopside– garnet– garnet–rhomboide–, and vesuvianite–skarns</td>
<td>Skarn–stage zinc and copper mineralization zone</td>
<td>Zn and Cu (sometimes with Sn and W)</td>
<td>Exosomatic and alteration of the granite terrains zone</td>
<td>Metasomatic stratified orebodies (1)</td>
<td>Marmatite–pyrochlore–chalcopyrite (cassiterite)</td>
<td>137–203</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-feldspathization on the top of the granite terrain with local potassium feldspar pegmatoid plagioclase</td>
<td>Early–stage biotite–granite</td>
<td>W and Sh (sometimes with Au)</td>
<td>Fracture–fissure zone</td>
<td>Fissure–filling veins and fracture–fissure veins (1) intersecting (1) and (2) orebodies</td>
<td>Scheelite–fluorite; wolframite–antimonite–quartz</td>
<td>275–314</td>
</tr>
</tbody>
</table>

**Figure 212I. Vertical Zonation of Mineralisation in The Biotite–Granite of the Dachang Tinfield, South China.** (Chen Yuchuan et al., 1988)
orebody will yield a different geochemical profile for samples taken from the lower levels today, than would be obtained from the upper levels worked in prehistory. Similarly, when considering trace element profiles related to genetic types of deposit, vertical zonation can affect the profiles if levels of erosion are significantly different.

Zoning within tinfields is of marginal use, except when attempting to determine which ores within a tinfield were being used for metal production. It may however, be of use where a production site is located at the ore source.

**Deposits Other Than Tin.**

Deposit Maps for this section are presented in Appendix 6.

**Copper and Lead/Zinc.**

Copper production in Southeast Asia is mainly from porphyry copper deposits and Kuroko-type volcanogenic sulphides (Scholla, 1981), although skarns and gossans are known. Porphyry coppers are restricted to south China and Indonesia with very minor occurrences in Nan and Loei Provinces, Thailand.

The main copper producing area of Thailand is a N-S belt from Nan and Loei in the north to Chachoengsao in the south (Scholla, 1981). The Khao Kaeo deposit at Tak and another, north of Song Toh, at Sangkhla Buri are small Pb-Zn-Cu sulphide deposits. The major Cu-Pb-Zn producer of the region is Bawdwin Mine in Burma. Furthermore, Bawdwin is the only Burmese copper producer although 45 copper prospects are recorded (Goosens, 1978).

Lead/zinc deposits tend to be restricted to the Ordovician volcanics found near Loei, Phrae, Tak, Kanchanaburi, Petchabun and between Mae Hong Song and Mai Sariang in Thailand and Sakar, Ulu Lebir and Bukit Ibom in Malaysia.
Both Bawdwin and Bawsaing Mines in Burma are large lead producers and were mined in prehistory (Goosens, 1978). The Chinese extracted silver from the ores in both places.

Bawdwin Mine, Burma is the biggest zinc producer where sphalerite occurs with argentiferous galena. Sphalerite also exists with galena at Phaungdaw. There are two Smithsonite deposits in Burma, at Sagyin and Lough Keng, which are similar to the Tak deposits (Goosens, 1978).

Barite.

Barite is associated with many of the lead deposits of Thailand but major producing regions are Lampang and Phrae, North Loei, Ratburi to Phetburi and between Surat Thani and Nakhon Si Thammarat. Unlike lead, barite is produced in peninsular Thailand near Krabi and Songkhla (Scholla, 1981). The associations of Ba-Pb and Pb-alone may be of possible interest.

Massive barite bodies are of little interest to this research as barite contamination of bronze is only likely to occur from a Ba-bearing metal ore. However barite is widely distributed in the Middle Ordovician limestones which host the lead deposits in Thailand and Burma. The major barite mining district of Burma is at Maymio near Mandalay, southern Shan State and the nearby Bawsaing district where the ore is associated with argentiferous galena. Numerous small-scale mines existed here before modern mining (Goosens, 1978).

Bismuth.

Bismuth occurs, as both the native metal and the sulphide, with the tin and tungsten minerals of the Tenasserim region. It is most common in the Tavoy district of Burma.

Antimony and Mercury.

Antimony occurrences seem to be restricted to Upper
Palaeozoic sedimentary facies and occur in the same geologic environment in both Thailand and Burma i.e. the Eastern Highland Belt (Goosens, 1978). They are fault-related quartz-stibnite veins east of the Shan scarp (Hutchison 1983).

Antimony is largely associated with the barite-producing regions and also at Chiang Mai, Chiang Rai, Lampang, Phrae and Surat Thani. It is also found in association with the lead deposits along Thailand's western border. Antimony is commonly associated with regions of hydrothermal activity, characterised by hot springs. Although minor Sb occurrences are scattered through northeast Burma and northwest Thailand, large deposits are restricted to those specifically mentioned above (Scholla, 1981). However, these cannot be considered comparable to the major Sb-producing region of south China.

There are over thirty antimony occurrences in Burma, of which the most northern is Bawdwin Mine. Here the antimony occurs in boulangerite, bournonite, pyrargyrite and tetrahedrite and, like most Burmese orebodies, occurs as veins or lenses. The southernmost occurrence in Burma is at Thabyu [lat. 15°31' N] while in Thailand antimony occurs as far south as lat. 8° N.

In only two instances is antimony associated with tungsten in Burma.

Even more than antimony, mercury is restricted to south China with a limited production region at Raub in Malaysia. (Hutchison and Taylor, 1979).

**Chromite.**

There are only two documented chromite-producing mines in Thailand. One is situated in a remote region in the South; southwest of Narathiwat and northwest of Sungei Ko Lok. The other was at Tha Pa in Uttaradit Province.
In Burma, all reported chromite deposits occur in the ophiolite belt of the Arakan-Chin Range of western Burma and its extensions. However, although copper is also produced from the ultramafics, it is perhaps more likely that chromium in bronze is derived from rutile, associated with porphyry coppers.

Gold.

Details of gold production are varied, depending on whether the report is dealing with primary deposits or alluvials or both. Like antimony, a gold producing region exists across south China with major Au-Sb mines at Toh Moh on the Thai-Malay border and Raub in Malaysia. Au-Ag and Au-Ag-Te-Se production is restricted to the islands (Hutchison and Taylor, 1979). The Au/Sb mineralisation, often with associated Hg, occurs in a narrow zone which corresponds to the Permo-Triassic sediments and volcanics on the east side of the Main Range in Malaysia. The ores are hydrothermal replacements and fissure fillings, located in zones of compressional faulting. The mineralisation consists of quartz, gold, pyrite, arsenopyrite, stibnite, scheelite, chalcopyrite and cerussite.

Gold production is scattered through the region but the production areas are usually very limited in extent: Chiang Rai and Wang Chin in the northwest; the Nam Som region in the northeast; Uthai Thani, Prachinburi and Rayong; Bang Saphan on the Kra Isthmus and Sungei Ko Lok on the Malay border.

In Burma, gold production is very small scale although widespread. Larger scale modern mining occurred in the upper reaches of the Irrawaddy until 1918. Indigenous gold washing is confined to placers and may be associated with platinum where the rivers drain the Arakan-Chin Range.

Zircons.

Zircons are only mined north of Prachuap Khiri Khan
although they occur as a minor constituent of several tin deposits. However, zircons do not generally occur in the ore concentrates. Their small size allows them to pass through the sieves into the lanchut.

**Tungsten.**

Tungsten, both in the form of wolframite and scheelite, is found in scattered occurrences in the tin belt along Thailand's western border. The main tungsten region is the Kanchanaburi/Tavoy region also, intermittently, southward into Malaysia, although there are some occurrences around Chiang Mai. In Chiang Mai, the tungsten occurs as scheelite associated with cassiterite, in quartz veins in granite. Kanchanaburi Province is characterised by wolframite in quartz veins cutting granite or schist.

Tungsten mineralisation is characterised by two types of primary deposit:-

1. Ore-bearing pegmatites associated with hydrothermal activity. Such as the quartz-wolframite-[cassiterite] occurrences found at Mae Sariang, Kanchanaburi Province and Prachuap Khiri Khan Province.

2. Metasomatic mineralised zones and ore veins of scheelite found at Doi Mok, Chiang Rai Province.

Hutchison and Taylor (1979) differentiate between Sn-W, Sn-only and W-only regions and show the only major W-only region to be southeast China although much of the Tin Belt produces W from the tin deposits. However, they also show the Kochiu in Yunnan, Phuket, Phangnga, Nakhon si Thammarat fields in Thailand and the Kinta, Kuala Lumpur, Pahang, Bankha and Billiton fields of Malaysia and Indonesia as tin-only producers. It must be borne in mind that much of this documentation indicates production rather than occurrence of a metal.

In Burma, tin and tungsten occur together. Most deposits
are mined for both cassiterite and wolframite but even those which are described as tin-only contain tungsten. The major mining district is Tenasserim and the western part of the Shan States where tungsten progressively increases towards the north. A more comprehensive account of tin-tungsten in Burma is given by Goosens (1978).

Uranium.

The Khorat Plateau of northeast Thailand has been the centre of uranium exploration in the country; it being analagous to the Colorado Plateau of USA. A uranium-copper deposit was discovered at Phu Wieng, Khon Kaen although indications of uranium were found in several areas of the Plateau; including Nakhon Ratchasima, Loei, Chaiyaphum, Nong Khai and Petchabun Provinces. Anomalous uranium is apparent in geochemical surveys in Uthai Thani and east of Bangkok. However, U/Th in samples is derived from REE minerals.

2.2 TIN GEOLOGY

2.2.1 TYPES OF TIN DEPOSIT

Tin Provinces

Globally, Tin Provinces are generally considered to be major tin producing regions of the world where numerous deposits are spatially and geologically related e.g. Southeast Asia, N.W. Europe [Cornwall/Brittany/Portugal], Nigeria and Rhondonia, Brazil. Regions where tin deposits do occur but are exploited on a small scale i.e. where the occurrences are widely scattered such as N. America, India, Turkey, etc., are not considered Provinces. In the definition of a Province the perspective of scale is important (Schuiling 1967a,b) and variations in the scale used can reveal 'sub-provinces' within the main area. Specifically, the Southeast Asian Tin Belt is considered a Province extending from S. China to Indonesia. It can however, also be considered a series of adjacent zones,
especially in Malaysia where the east and west tin zones are geographically isolated and display different characteristics. (Taylor, 1979; Hosking, 1969; Cobbing, 1988).

Taylor classified the Southeast Asian Tin Belt, with some reservations, as General Environment 1:-

"Tin deposits associated with granitoids which a show close spatial and temporal relationship with a major period of orogeny, i.e. folding, fracturing and uplift. Granitoid emplacement predominantly post major folding, i.e. late stage and controlled by major fracture-suture zones. Designated ;- FOLD BELT TYPE"

Subdivision (d):-


Intermediate to large scale intrusive complexes. Massifs- batholiths generally contain small number of individual plutons. Differentiation sequences are often well established between phases, and a relatively passive intrusion environment is suggested. Geochemically specialised granites are common, and often form minor phase end members of a granodiorite-granite sequence.

Predominantly granites, granodiorites with minor alaskites, leucogranites and other specialised intrusives. Plutonic textures prevail. Aplites and pegmatites common."

This environment is very much the domain of the 'greisen association' (Figure 221A) and also the quartz-cassiterite-wolframite veins of Southeast Asia. While the massive greisens and major quartz veins are economically dominant, the environment in Southeast Asia contains numerous 'non-
Figure 221A. The Greisen Environment. (Taylor, 1979).
economic vein swarms and stockworks. Major deposits such as Mawchi in Burma and the Pemali greisens, Indonesia are rare occurrences. Minor swarms and stockworks however, are an abundant primary source of alluvial cassiterite, which lends itself to small scale primitive mining in antiquity.

**Tectonic Environments**

Plate tectonics have also been used to classify tin provinces but lack of global information leads one to treat such classifications tentatively. However parts of the southeast asian Province fit the following tectonic environments and are shown in Figure 211C above:-

1. Above shallow-dipping Benioff zones with adjacent Sialic components - East Malaysia, West Thailand/Phuket (Mitchell 1977),

2. Continent-continent collisions - Central Belt Malaysia.

However, as there are many equivalent tectonic environments which are devoid of tin deposits, some doubt is cast on the usefulness of this classification for identifying tin sources. While the mechanisms of tin batholith generation and the complexities of mantle-crust interaction and hydrothermal influences undoubtedly have a significant bearing on tin generation and the mineralogy/geochemistry of tin deposits, they are as yet, too little understood to be more than mentioned in this work.

Within the mineralogical and environmental classifications mentioned above, there are the specific types of tin deposits present in Southeast Asia which are significant as sources of secondary alluvials or weathered primaries accessible to early miners.

Excellent descriptions and discussions on the types of primary mineralisation in Cornwall are given by Hosking (1962, 1969) but these are not totally applicable to
Southeast Asia. Manning's (1986) paper on the contrasting styles in the two regions is however a useful guideline to some of the variations.

The Classification of Tin Deposits

The wide range of morphological and mineralogical variations within tin deposits makes it impossible to achieve a satisfactory, comprehensive classification. Past classifications have been based on a single aspect of the deposits, such as mineralogy, which give little insight into the structural or genetic characteristics and even less into the relationships between deposits.

In 1968 S.S. Smirnov classified tin deposits mineralogically into three main types of stanniferous assemblages:

1. stanniferous pegmatites
2. quartz-cassiterites
3. cassiterites rich in sulphides and/or ferruginous silicates

There is however, only a brief mention of secondary alluvial deposits.

Other classifications include such categories as granite pegmatites, pneumatolytic-hydrothermal, contact metamorphic or skarn, sub-volcanic, fumarolic, greisens, schorl cassiterites, quartz-feldspar veins, aplites and disseminations. These classifications tend to overlap in their groupings and can be difficult to correlate. Hosking's classifications, as presented in Appendix 7, are preferred.

Differentiation between the various primary cassiterite deposits is of paramount importance in this work. At the same time it must be realised that most tin mining in early Southeast Asia was concerned with the secondary placer deposits derived from these sources. As a specific group
the alluvial deposits are rather neglected, although there are variations between them, both morphological and mineralogical, which can be used for classification. Differences between the placer deposits are usually the result of a combination of differing primary source mineralogy and the mechanisms of concentration. The latter, both in the concentration and the depositional phases, is closely linked to the morphology of the terrain. On a global basis, climate is also a factor but within Southeast Asia the climatic variation is not sufficiently varied to be of significance.

Hosking (1974) provided a working classification of southeast asian tin deposits, as well as a good general classification. As Southeast Asia, as a whole, has not been studied as comprehensively as is required for this work, it has been necessary to rely on general classifications describing deposits in different tin fields. Where the analysis of tin samples implies the presence of minerals not described in the southeast asian classifications and hence a genetic type of deposits probably of little significance in Southeast Asia, the only recourse has been to consider the data from other geographic contexts.

Hosking (1965) also pioneered the technique of using a pictorial diagram to place the types of deposit in their correct geological setting. This usefully illustrates the relationship between the structure, mineralogy and environment of the sources. It then becomes apparent that certain environments favour specific types of deposit. The concept of Tin Provinces is discussed above in the context of environments, as opposed to Metalliferous Regions.

However certain metal associations can be related to certain genetic types of deposit:-
Table 212A.
Mineral and Metal Associations of the Southeast Asian Tin Deposits.
(Hutchison and Taylor 1978)

<table>
<thead>
<tr>
<th>Mineralogical Assocn.</th>
<th>Metal Assocn.</th>
<th>Ore Type.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cas.-pyrrhotit-mag.</td>
<td>Sn-Fe</td>
<td></td>
</tr>
<tr>
<td>Bed/skarn</td>
<td>Sn-Ca</td>
<td>Skarn</td>
</tr>
<tr>
<td>Cass.-chlorite</td>
<td>Sn-Cu</td>
<td>Maj. vein</td>
</tr>
<tr>
<td>Cass.-malayite-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>varlamoffite</td>
<td>Sn-Ca</td>
<td></td>
</tr>
<tr>
<td>Cass.-stannite-</td>
<td>Sn-Cu-Pb-Sb</td>
<td>Xenotherm</td>
</tr>
<tr>
<td>complex sulphides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cass.-lepidolite</td>
<td>Sn-Li-Ta</td>
<td>Pegmatite</td>
</tr>
<tr>
<td>Cass.-wolframite</td>
<td>Sn-W</td>
<td>Veinswarm</td>
</tr>
<tr>
<td>Cass.-columbite</td>
<td>Sn-Nb(Ta)</td>
<td>Pegmatite</td>
</tr>
<tr>
<td>Cass.-arsenopyrite-</td>
<td>Sn-As-Fe</td>
<td>Stockwork</td>
</tr>
<tr>
<td>pyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cass.-galena</td>
<td>Sn-Pb-Ag</td>
<td>?</td>
</tr>
<tr>
<td>Cass.-ilmenite-</td>
<td>Sn-Fe-Ti-Zr-Ce-Yt</td>
<td>Alluvials</td>
</tr>
<tr>
<td>zircon-rutile</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It must be recognised that the above is concerned with major element association and that trace elements are also included in the major minerals.

Pegmatites.

The term pegmatite in the context of this study refers only to complex pegmatites of granitic composition, consisting primarily of quartz, K-feldspar and muscovite. The literature on S.W. England differentiates between true pegmatites which are generally poorly mineralised and hydrothermal Sn-W fissure veins. In Thailand however, much of the Sn-W mineralisation is described as pegmatitic but the term is used loosely. The literature on thai deposits tends to include many greisen-bordered veins, veinswarms etc. as pegmatites and in a literature survey it is difficult to distinguish the true pegmatites (Bradford, 1961).
It has been said that the list of minerals from a complex pegmatite reads like a page from the index to Dana's Textbook of Mineralogy and that as many as 100 accessory minerals have been listed, many of which are rich in Li, B, F, Nb, Ta Th, U, and REE's. A good petrographic description of pegmatites is given by Middlemist (1985). Complex pegmatites are the result of igneous processes rather than recrystallisation or palingenesis. They contain diagnostic elements such as Ta, Nb, Be, Li, Cs, U, Ce, La, Th, and Y. Sulphides are widely distributed but in small amounts. Nearly all pegmatites are zoned which, in the context of ancient mining is important, as ancient miners did not mine surplus rock of no value to them.

Pegmatites may also be the result of more than one phase of volatile injection and have multiple cores. The unzoned lithium pegmatites, in the Phuket-Phangnga region of peninsular Thailand, are interesting in that while the region as a whole is rich in Ta/Nb-bearing cassiterite deposits, the cassiterite in these pegmatites does not appear to be. Hosking (1988) suggests that the tin mineralisation of these pegmatites is a later hydrothermal introduction into the earlier pegmatite system. In this case the trace element profile of the cassiterite from these pegmatites will be different from its hosts, and its analysis will not truly reflect the ore used in bronzes.

'Pseudo-pegmatites', which should be described as vein swarms (Hosking, 1969) are mined at Pelepah Kanan, Johore and Serendah, Malaya.

Pegmatites are mined in various parts of the Tin Belt, often in conjunction with pegmatite-derived alluvials e.g. Katthu Valley, Phuket Province; Shone Mine, Surat Thani Province; Patoe, Chumporn Province; Takua Pa and Phangnga Provinces; (Puwakool, S. 1980) Samoeng, Chiang Mai Province; Ulu Kerling, Malaysia.
Veins and Stockworks.

Tin-bearing veins and stockworks above granite cupolas have been mined at Pilok, Thailand and elsewhere. Generally the granite has been kaolinised, allowing the cassiterite to be easily extracted by hydraulicking. Alluvial and eluvial deposits associated with the stockworks have also been worked and would have been accessible to early miners. Quartz-cassiterite veins have been mined at Ron Pibul, Khao Khiam and Sichon, Nakhon Si Thammarat Province

Greisens.

Much of the literature refers simply to greisen-bordered veins, which can be misleading when considering the lenticular or massive greisen-style tin systems with sheeted mineralisation (Pollard et al., 1988). However, while greisen deposits as primary tin sources tend to fairly low grade, the alluvials derived from them can be an important source of cassiterite.

Greisenisation as described above, has been comprehensively documented by Scherba (1970) and it should be noted that he included skarns and amphibolitisation under the hydrothermal classification of greisen. The opinion was that different rock alteration and mineralisation simply reflect the differing responses of the variety of country rocks to the ingress of hydrothermal fluids. It is an important source of stanniferous deposits in Thailand and the mineralogical accessories serve to differentiate these sources from those of ungreisenised deposits. Greisenisation is the result of hydrothermal alteration [albitisation and microclinisation] in the apical zones of granite batholiths with the decomposition of feldspars and biotite and the formation of topaz and ore minerals containing Li, Be, W, Sn, Mo and Bi (Taylor 1979). Greisen-bordered veins have contributed to the tin alluvials of Kinta and Indonesia, among others.
Skarns.

Skarns are variously referred to as hydrothermal metamorphic or pyrometasomatic (Lindgren, 1905, 1922; Evans, 1980), igneous metamorphic, contact metamorphic or contact metasomatic (Jensen and Bateman, 1979). They occur in various environments and therefore have varied elemental associations. Einaudi et al. (1981) and Einaudi and Burt (1982) wrote extensively on skarn deposits.

The primary requisite for skarn formation is the close proximity of a calcareous or magnesian rock such as limestone or dolomite alongside tin granites. Three types of skarn may be considered relevant here: the Be-(Sn-W) skarns, the Sn, Sn-W skarns and the Mo-Sn skarns. The main features of these are listed by Edwards and Atkinson (1986).

Skarns have received less attention in the literature of Southeast Asia than other forms of deposit but in the Southeast Asian Tin Belt both W and Sn/W skarns are represented. The South China polymetallic belt includes these and the Sn-Mo-Bi skarns and the Malaysian tin skarns are noteworthy. However, tin skarns generally have a grade of <1% and much Sn is included in silicates such as hornblende [6577ppm], garnet [1525ppm], muscovite, vesuvianite, epidote, magnetite, pyroxene etc. (Nekrasov, 1971; Liu Yingjun et al. 1983; Guo Wenkui, 1988). Economically only secondary derivatives of skarns are considered viable ores.

Greisenisation frequently accompanies Sn/W skarn formation resulting in cassiterite-sulphide deposits. This tends to result in some confusion in the literature as to which type of mineral deposit is meant. The Bukit Besi deposits are usually described as skarns, but Hosking (1973a) believes this to be misleading as they are not hosted by calc-silicate hornfels. Furthermore, Sn-mineralisation was introduced by fluids along fault zones. In his view therefore, these deposits are hydrothermal and metasomatic.
The Fe and Sn may be derived from different sources i.e. diorites and granites respectively.


**Altered Primary and Secondary Deposits.**

Although numerous types of primary tin deposits occur in Thailand, only some were readily workable by early miners. These were the weathered or altered primary deposits and the secondary alluvial, colluvial and eluvial deposits. Aranyakanon's work (1980) serves to illustrate the variety of cassiterite deposits which could have been exploited in antiquity.

a) Altered Granites with Cassiterite.

Altered granite zones may occur in the upper or marginal regions of an orogen where there has been significant erosion, especially in the upper part of granite cupolas, contact zones or any zone of weakness where penetration of volatile materials is greatest.

The pneumatolytic alteration, by fluorine, boron and H$_2$O, of a tin-bearing porphyritic biotite granite results in tourmalinisation, muscovitisation, albitisation, kaolinisation and silicification.

The tin deposit at Haad Som Pan, Ranong Province is characteristic of this type of alteration and also shows other features which may be significant in this type of deposit:

1) The manganese contents of all manganiferous minerals is very high.
2) Anatase, monazite, zircon, xenotime, fluorite and gilbertite are more widely distributed. (Aranyakanon, 1969)
Altered granitic hosts of cassiterite occur at Haad Som Pan, Bang Non and Thungkha in Ranong, as well as Kurod, Takua Pa. At Klong Nokhook/Kapong in Takua Pa cassiterite is associated with wolframite as well as Ta/Nb minerals. Mines operate in weathered granite in the Bang Song area of Surat Thani and in Huai Yot. At the Namom and Thung Kamin mines in Haad Yai, Songkhla there is associated uranium. Pa-pane mine in Yala works quartz veins in altered granite and deposits occur at Chae Hom in Lampang.

However, while Aranyakanon (op cit.) notes these occurrences of altered granites, and they have notable differences, it is apparent that the low grade of the ores [SnO2 < 15%] and the fine grain size of the cassiterite would not make them attractive to early miners.

b) Placers, Eluvial and Alluvial.
In the past, eluvial deposits were mined in preference to others because they were unusually rich, accessible and uniform in grade, compared to alluvial deposits where the high grades are concentrated in the lowest levels, but the underlying primary deposit was often left untouched. As a result few eluvial deposits remain to be mined today or survive later exploitation of the underlying primary.

An interesting eluvial/colluvial deposit is currently being mined at the Mae Boh Kaew deposit at Samoeng in Chiang Mai and there are also some in Patoe and Paksong in Chumporn where the underlying pegmatites are high grade. The Haad Som Pan, Thungkha and Bang Pra regions already mentioned were originally rich eluvials but now mining concentrates on the altered granites below. Another, recently discovered, eluvial occurs in Sichon district at Klong Thaleek in Nakhon Si Thammarat. Recent discoveries of eluvials are worth noting, from an archaeological point of view, as they may retain indications of earlier mining.

Alluvial tin deposits have always been the major source of tin in Thailand and occur as channel deposits [current or buried], and deltaic or beach deposits. The grade of
Alluvial deposits vary considerably and therefore whether they were worked in the past would depend on their viability at the time. Changing economic trends tend to favour the preservation of archaeological evidence in this type of deposit. Some alluvials are concentrated in geologic traps which act as collecting structures for the cassiterite. Often these are lines of faulting such as at Song Kwae and Pilok in Kanchanaburi, or limestone pavement as at Kinta in Malaya. Furthermore, the further an alluvial is from its source the poorer the grade, such as the Pak Long basin in Tha Sala, Nakhon Si Thammarat. Later erosion and remobilisation has concentrated the material in recent stream channels, but generally the deposit is considered unworkable by modern standards (Aranyakanon, 1980).

Alluvial placers were probably the most important sources of cassiterite in the 1st and 2nd millennia BC. These sources are varied in their geomorphological location and therefore required different techniques for exploitation. In mountainous regions residual deposits are generally created close to the primary source with seasonal action reworking and transporting these to form channel deposits in the gullies and streams of the mountain ranges. These deposits may not be large but they can be high grade. Furthermore some hill channel deposits cover fault traps forming large, rich deposits, such as those at Pilok, Kanchanaburi. Archaeologically, the disadvantages of many of these deposits is their inaccessibility in remote, scarcely populated, mountain regions and the greater hydraulic skill required to exploit them.

Of greater interest to archaeologists are the basin deposits, of similar provenance but accumulated on the basin floors and in the foothills. Some may also be coastal or deltaic. These deposits are often more accessible and require less skill to work. Basins which are close to the contact zone of the parent and country rock often give high tin values. When bowl-shaped, surrounded by high hills such as the Katthu Basin, Phuket, they can be exceptionally large and rich.
In the north west of the Tin Belt, river terrace deposits are more common, such as those at Wiang Pa Pao, Chiang Rai Province and in Lampang, Chiang Mai and Mae Hong Song Provinces.

Other interesting alluvial occurrences recorded by Aranyakanon (op. cit.) are the doline and cave deposits where limestone borders the stanniferous granite. Alluvial tin has been deposited in the caves and dolines as a result of underground streams. Such deposits are noted from Kanchanadit, Surat Thani Province and Pak Long, Tha Sala, Nakhon Si Thammarat Province. In Perlis, Malaysia, most of the underground mines are, in fact, cave workings where Sn concentrates are recovered from the alluvium in underground streams (Tham Weng Sek, 1988).

Placers are the most important source of tin ore in Southeast Asia but the hardest to classify geochemically and mineralogically, owing to their derivation from different and multiple primary sources.

Macdonald's (1983) classification of placers is one of the simplest and is illustrated in Tables 221A and B and Figure 221A.

Table 221A. Provenances of Some Placers Containg Tin and REE Mineral Species modified from Macdonald (1983).

1. Granitoid terrains and related pegmatites and greisens:
   Major: cassiterite, monazite, zircon, rutile and gold.
   Minor: wolframite, K-feldspar, quartz, topaz, beryl, spodumene, petalite, tourmaline, tantalite, columbite, monazite, fluorite, sphene.

2. Syenitic rocks and related pegmatites:
   Major: zircon, REE-minerals including uranium- and thorium-bearing species.
   Minor: ilmenite, magnetite, fluorite, pyroboles, K-feldspar, apatite, feldspathoids, zircon.
3. Contact metamorphic aureoles-skarns:
   Major: scheelite, rutile, occasional corundum.
   Minor: diopside, grossularite, diopside, calcite, basic
   plagioclase, epidote.

4. High-grade metamorphic terrain:
   Major: gold, rutile, zircon, gemstones.
   Minor: kyanite, pyroboles, quartz, sillimanite,
   almandine, feldspars, apatite.

Table 221B. Classification of Tin-bearing Placers modified
from Macdonald (1983).

<table>
<thead>
<tr>
<th>Environment</th>
<th>Sub-Environment</th>
<th>Product</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continental</td>
<td>Eluvial.</td>
<td>Au, Pt, Sn, WO₃, Ta, Nb, gemstones.</td>
<td>Percolating waters, heat wind, rain.</td>
</tr>
<tr>
<td></td>
<td>Colluvial.</td>
<td>- &quot; -</td>
<td>Surface creep, wind, rain, frost, elutriation.</td>
</tr>
<tr>
<td></td>
<td>Fluvial.</td>
<td>Au, Pt, Sn</td>
<td>Flowing streams.</td>
</tr>
<tr>
<td></td>
<td>Dessert.</td>
<td>Au, Pt, Sn, WO₃, Ta, Nb, gemstones.</td>
<td>Wind with minor stream flow, heat and frost.</td>
</tr>
<tr>
<td>Transitional</td>
<td>Strandline.</td>
<td>Ti, Zr, Fe, ReO, Au, Pt, Sn.</td>
<td>Waves, wind currents, tides.</td>
</tr>
<tr>
<td>Marine</td>
<td>Drowned placers</td>
<td>Au, Pt, Sn, diamonds, Ti, Zr, Fe, ReO.</td>
<td>Eustatic, isostatic, tectonic movements.</td>
</tr>
</tbody>
</table>
The characteristic mineralogy of a primary source is modified in a resulting placer as light minerals have been removed. Further beneficiation, prior to smelting, also reduces accessory components containing characteristic elements. However, beneficiation in prehistory was confined to hand picking the ore and heavy mineral separation resulting in a higher concentration of magnetic minerals in the early smelts.

2.2.2 GEOCHEMISTRY OF TIN

Previous Research.

Tin deposits are associated with highly differentiated granitic rocks. This relationship is explained by the decreasing affinity of Sn for Ca, Mg, Na and K, so that high-alkali granite melts cannot assimilate the tin and it is therefore available for redistribution by hydrothermal solutions (Burton, 1969; Rattigan 1960; Sutton 1963). Furthermore, repeated plutonic or orogenic events recycle and reconcentrate the tin mineralisation while adding more. The Yunnan-Thai-Malay Orogen appears to have undergone such enrichment to create one of the richest tin provinces in the world. (Burton, 1969)

Burton further noted that, in NW Malaysia, primary tin deposits showed a preference for calcareous hosts and
suggested that tin might be arrested by its affinity for calcium. He remarks that the majority of tin fields in the Malay-Thai peninsula contain limestone (Kinta, Perlis, Phangnga, Ron Phibun). It is difficult to decide whether he is referring to the primary sources here or to alluvials on limestone basement.

Schneider et al. (1978) have correlated the trace element distribution in Bolivian cassiterites with the geotectonic position of their deposits. Their study, using quantitative data expressed as intensity ratios, showed that the grouping of tin deposits according to geotectonic units is reflected in the characteristic trends of trace element distribution.

Although the levels of trace elements in tin ores have been researched in this century, much of the earlier work was carried out by the Russians using analytical techniques only offering detection limits greater than 100 ppm. In many instances, only qualitative data were obtainable which served to establish the link between the levels of trace elements with types of deposit. Using DC arc spectrography, Borovick and Gotman (1939) determined Nb, Ta, Be, Cu, Zn, Bi, Sn, Sb, Pb, Zr, Hf, Mo, V, W, In, Ge, Ga, Na, Ca, Cr, Al, Te, Mn, Ti and Si in 27 specimens of cassiterites from USSR tin deposits of differing genetic type. The data showed that cassiterites from pegmatites were readily distinguishable from cassiterites from other sources. However, the analyses did not provide sufficient information to differentiate other types of deposit. Of all the elements investigated, considerable data are available on Nb and Ta which have similar valences and ionic radii to Sn⁴⁺. It was found that both Nb and Ta concentrations were at a maximum in pegmatitic cassiterites (Dudykina, 1959; Borisenko and Lizunov, 1959; Steveson and Taylor, 1973). Levels of Nb and Ta were low in quartz-sulphide deposits (Steveson and Taylor, 1973). Based on the variation of Nb in cassiterites from different environments, Stumfl (1963) classified cassiterites of unknown origins.
The levels of In can be indicative of cassiterite types. Dudykina (1959) showed that cassiterite from cassiterite-sulphide deposits contained 210ppm In. Steveson and Taylor (1973) gave average indium contents as 13ppm for pegmatites, 158ppm for greisen and 30-108ppm for other genetic types. This does however, suggest that quantitative analytical results are somewhat subjective.

Elements Pb, As, Sb, Mo, In, Ag and Bi are generally at a maximum in the lower temperature sulphide cassiterite deposits and a minimum in the high temperature pegmatite types (Dudykina, 1959). Other elements which have been investigated include Zr, Hf, Sc, Ti, W, V and U. Some of these were reported to vary according to ore type and may have genetic significance.

In the past, very few elements have been established as diagnostically useful, although the literature is full of hints that certain elements may be significant. The major problem, until now, has been the unavailability of analytical techniques capable of providing quantitative analyses with high sensitivity and selectivity on a multi-element basis. In addition isotope ratios are considered potentially useful in furnishing information on different catagories of tin ores.

More recently, Traub and Moh (1978) analysed the trace elements in asian tin 'ores'. Their analyses are still confined however, to cassiterite and other tin species from the ores rather than the whole concentrate. They concluded that Nb, Ta, Zr, Hf, Al, Mg, Zn and, to a lesser extent, Fe, Mn and Cd, all seem to be characteristic of the high temperature pegmatitic/pneumatolytic and sometimes the greisen deposits. These trace elements decrease with the temperature of formation of the deposit, reaching a minimum in the hydrothermal lodes. Ag was only traceable in the high temperature cassiterites. With respect to V, W, Ti, Cu, In and Bi, the individual chemical environment rather than the temperature of formation seems to be the key factor.
Diagnostic Elements in Cassiterite Concentrates.

Of the 38 elements analysed, Nb, Ta, Zr, W, Mn, Ga, Ni, Hf, Fe, Ti, Ag, Cu, Cr, Sc, Ge and In have been recorded in cassiterite itself. In addition Ba, Pb, U, Ce, Y, Zn, Mo, Dy, Yb, Nd, Pr, Co, Bi, Hg, Sb, Cd, Sm, Th and La are contributed to the concentrates by other heavy minerals (Brooks, 1962). There is however, no record of Lu or Eu in cassiterite concentrates nor are these elements recorded in REE species (Henderson, 1984). These elements are recorded in allanite, a common mineral in tin-barren granites. However, Lu/Eu anomalies observed coincide with Th/REE anomalies in the ores.

The Rare Earth Elements (Lanthanides).

Generally REE's are concentrated in accessory minerals in rocks, rather than the major rock-forming minerals (Henderson, 1984). The amount of REE's reflects the composition of the host rock, rather than that of the primary ore deposit. As the host rock composition reflects the type of accessory minerals present the concentration of heavy, REE-bearing minerals along with the cassiterite may be diagnostic. Ore derived from a primary deposit will not show the REE enhancement that an ore derived from alluvials will show, as the concentration process is absent in the former.

Similarly, the accumulation of REE's in the ore concentrate, and hence the metal, is confined to those elements that occur in heavy minerals.

Only a selection of the REE's are considered here although it may be possible to consider the range of variation in REE concentrations as a separate study. A variety of granitic rocks can be produced by melting a variety of sources and, as long as these were tin-bearing, a regional pattern of REE concentration might be produced for the tin ores. It has also been suggested that partitioning of HREE's [Gd-Lu, yttrium group] and LREE's [La-Eu, cerium
group] may occur during igneous or metamorphic processes involving CO₂- or H₂O-rich fluids at certain pressures. Any process that affects the concentrations of these elements in a tin-bearing host rock will be, at least partially, reflected in the ore concentrates. A possible key mineral here would be the garnets. (Henderson, 1984) However a further study of this aspect of REE distributions is beyond the scope of this work.

The fractional crystallisation that results in the formation of pegmatites may also be instrumental in affecting LREE/HREE ratios.

When considering the REE concentration of tin ore deposits, as well as those of the base metals, it must be borne in mind that two processes are involved. Firstly, with alluvial deposits the primary consideration is the type of accessory minerals found with the tin ore which are derived from the host rock of the primary ore. Secondly if the ore source is a primary deposit the amount of REE contributed by the host rock is much reduced because a concentration mechanism has not been in operation. A greater influence on the REE distribution will be the effect of hydrothermal solutions on the ore itself and the host in the immediate vicinity of the ore. The REE distribution in hydrothermal solutions will be controlled by the partitioning of REE's between the solution and rock phases. Most sulphide and oxide ore minerals are not good hosts for REE's and concentrations are again determined by the non-sulphide gangue minerals. To date, the only reported ore mineral analyses have been for galenas from Colorado (Morgan and Wandless, 1980) where only La and Sm were detected [<1ppb]. Conversely analysis shows that an appreciable amount of REE's appears to be present in the carbonates associated with Pb/Zn deposits. The highest concentration [2500ppm] came from German deposits, while those from Missouri and Colorado had low concentrations [<25ppm]. The range of lead concentrations appears to be wide and therefore the sample size in this work must be considered insufficient for conclusions to be drawn. Unfortunately there are no data
concerning the concentrations of REE's in other types of ore deposit, therefore it would be premature to conclude that high REE concentration in bronze is specifically due to the lead component.

Niobium and Tantalum.

Niobium and tantalum are considered together because of their relationship as end members of the columbite-tantalite group minerals \((\text{Fe,Mn})(\text{Ta,Nb})_2\text{O}_6\). These minerals may occur as components of a tin ore deposit, especially the pegmatites or pegmatite-derived alluvials, or as inclusions within the cassiterite.

Niobium and tantalum have both been used to determine the type of source deposit. Cassiterites analysed contained up to 5% \(\text{Nb}_2\text{O}_5\) and 3% \(\text{Ta}_2\text{O}_5\) (Taylor, 1979).

The two elements, Ta and Nb, have a definite genetic and regional significance in Southeast Asia, which has been noted by several researchers (Pryor and Wrobel, 1951; Hutchison, 1978; Hosking, 1981). It was also noted by Hosking (1981) that Ta-Nb species occur in pegmatite/aplite bodies and sometimes greisen-bordered veins. In other words their concentrations are highest in the early-formed deposits. Furthermore, the earliest cassiterite contains the highest concentration of Nb/Ta. It is therefore relevant to note that geochemical characteristics are often related to time of formation rather than location.

Hutchison (1978) recorded that the cassiterite of Burma and North Thailand contained no Ta; that of South Thailand, high Ta with a Ta:Nb ratio of 2:1; Yala cassiterite, no Ta and that of Bujong Valley, Kedah very high Ta. In the Kinta Valley, Ta occurred in alluvials derived from the Main Range but not in that from the Kledang Range while the Kampar district contained high Ta but it decreased southward. There was no Ta in cassiterites from Nam Putain, Laos and offshore deposits in Thailand contained much higher concentrations than onshore.
Tungsten and Titanium.

It is generally believed that the W content of cassiterites reflects the environment of the deposit rather than genetic type and is therefore considered more useful as a regional indicator. Schneider et al. (1978) however, showed that the W/Sn intensity ratios varied significantly with the geotectonic group of the deposit.

According to Taylor (1979), titanium behaves in a similar way to tungsten.

Indium.

Indium has been used as a genetic indicator but it is also a trace element in galena, sphalerite and chalcopyrite. There are several other problems associated with the use of In as an indicator, including the suggestion that Sn$^{115}$ decays to In$^{115}$. (Taylor, 1979)

Scandium.

Scandium has also been considered diagnostic. According to Borisenko and Lizunov (1959), maximum Sc contents are in the region of 2000ppm Sc$_2$O$_3$ in greisen deposits but very low or absent in pegmatites or sulphide-cassiterite deposits. All Sc-bearing cassiterites contain Nb, Ta, W, Zr but not all Nb-bearing cassiterites contain Sc. Other researchers however, (Dudykina, 1959; Stumpfl, 1963; Nikulin, 1967) agree that Sc contents are highest in the pegmatites and greisens. Scandium however, is only of genetic significance if the cassiterite contains this element and not all pegmatites do so. Dudykina (1959) suggested that scandium was characteristic of magmatic and pneumatolytic processes rather than hydrothermal. Steveson and Taylor (1973) do not support these early conclusions and they found that Sc contents were highest in the sulphide cassiterites. Taylor (op. cit.) reports many unsubstantiated results concerning the behavior of scandium.
Zirconium.

Dudykina (1959) considered zirconium to be a dependable diagnostic element with definite genetic significance which may also be related to the hafnium content. Schneider et al. (1978) demonstrated its significance as an indicator of geotectonic groups. Moller and Dulski (1983) also showed that the Zr/Hf ratio varies with the degree of differentiation of the cassiterite source and that at least two types of deposit could be distinguished. They conclude that this ratio could be used to determine the primary source of placer cassiterite.

Lithium.

Although Li was not included in the current analyses, it should perhaps be considered in general studies of Thai archaeometallurgy. Some parts of Thailand, notably the Phangnga region, are characterised by cassiterite-bearing, lepidolite pegmatites (Garson et al., 1969). Although a cassiterite concentrate from these areas would be unlikely to contribute any high Li content to its products, the presence of lepidolite at a smelting site would indicate the origin of the ore.

Gallium.

Schneider et al. (1978) considered the Ga content to be a significant genetic indicator when expressed as an intensity ratio Ga/Sn.

Other Elements.

Vanadium may be a potential indicator. As may be the chalcophile elements Pb, As, Sb, Mo, Ag, Bi and also Ga and Be (Taylor, 1979).
Diagnostic Elements in the Study of Tin Bronzes.

Although a number of researchers have proposed that certain trace elements are of genetic significance in the study of tin deposits, the degree and type of diagnostic ability investigated by previous researchers is not necessarily relevant to this particular study.

Concentration data for individual trace elements from previous studies, provide a useful guideline as to which elements may be diagnostic. This study is concerned with the tin concentrates as they would have been added to the furnace and only qualitative data are applicable to ore concentrates and metals. The relative abundance of a particular element may be noteworthy but it appears unlikely that such variations can be considered useful for the purpose of this research. The variations are seldom large enough and may only be applied to single cassiterites. The presence or absence of certain groups of elements may be more diagnostic than those of individual elements.

Rapp (1977) did some preliminary studies on diagnostic elements in tin ore and their response to smelting. However, his paper lacks detail and no significant conclusions can be drawn.

In Chapter 3 the contribution of certain trace elements, from the alloy components, is established. These elements are:

<table>
<thead>
<tr>
<th>TIN</th>
<th>LEAD</th>
<th>COPPER</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Pb bronzes</td>
<td>Low Pb bronzes</td>
<td>High Pb bronzes</td>
</tr>
<tr>
<td>Sc</td>
<td>Hf</td>
<td>Co</td>
</tr>
<tr>
<td>Y</td>
<td>Ta</td>
<td>Ag</td>
</tr>
<tr>
<td>Zr</td>
<td>Au</td>
<td>Cd</td>
</tr>
<tr>
<td>Nb</td>
<td>Th</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>Nd</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

85
Previous trace element studies of copper ores indicate that Ag [<0.01%], As [<0.1%], Bi [<0.1%], Fe [>10%, Mn [<0.01%], Mo [<0.001%], Ni [<0.001%], Pb [<0.01%], Sb [<0.001%] and Zn [<0.1%] can occur but generally the concentrations are significantly less than these maxima (Edwards and Charles, 1982).

Therefore only these elements and some others of regional interest are considered in the following sections.

**Elements and their Mineralogical Association**

The mineralogical components of types of tin deposit are reflected in the trace element analyses. Some relevant accessory minerals are tabulated below:

**Table 222A.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>TiO₂</td>
<td></td>
</tr>
<tr>
<td>Baddeleyite</td>
<td>Zr(Hf)O₂</td>
<td>with anatase, rutile.</td>
</tr>
<tr>
<td>Barite</td>
<td>Ba(Sr)SO₄</td>
<td></td>
</tr>
<tr>
<td>Bismuthinite</td>
<td>Bi₂S₃</td>
<td></td>
</tr>
<tr>
<td>Chromite</td>
<td>FeCr₂O₄</td>
<td>with Cu</td>
</tr>
<tr>
<td>Columbite/Tantalite</td>
<td>(Fe,Mn)(Nb,Ta)₂O₆</td>
<td></td>
</tr>
<tr>
<td>Crocoite</td>
<td>PbCrO₄</td>
<td>with Pb</td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td></td>
</tr>
<tr>
<td>Ilmenite</td>
<td>FeTiO₃</td>
<td></td>
</tr>
<tr>
<td>Leucoxene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS₂</td>
<td></td>
</tr>
<tr>
<td>Monazite</td>
<td>(La,Ce,Dy,Nd,Th)PO₄</td>
<td></td>
</tr>
<tr>
<td>Powellite</td>
<td>CaMo(W)O₄</td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td></td>
</tr>
<tr>
<td>Scheelite</td>
<td>Ca(Mo)WO₄</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td></td>
</tr>
<tr>
<td>Stephanite</td>
<td>Ag₅SbS₄</td>
<td></td>
</tr>
<tr>
<td>Stibnite</td>
<td>Sb₂S₄</td>
<td></td>
</tr>
<tr>
<td>Tetrahedrite/Tennantite</td>
<td>(Cu,Fe)₁₂(Sb,As)₄S₁₃</td>
<td></td>
</tr>
<tr>
<td>Wolframite</td>
<td>(Fe,Mn)WO₄</td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Composition</td>
<td>Note</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------</td>
<td>-----------------------------------------------------------</td>
</tr>
<tr>
<td>Xenotime</td>
<td>(Y,Ce,Th)PO₄</td>
<td></td>
</tr>
<tr>
<td>Zircon</td>
<td>Zr(Hf)SiO₄</td>
<td></td>
</tr>
</tbody>
</table>

This list does not include the major Pb-Zn-Ag ore minerals which are listed elsewhere (Dana, 1939). Neither does it include: minerals which do not contribute diagnostic elements; silicates or borates of relevant elements (except Zircon); major ore constituents.

A comprehensive list of minerals is given by Dana (1939) and Ramdohr (1980).

Whereas the tin deposits of Thailand are generally characterised by a definite mineralogical assemblage typical of tin deposits throughout the world, certain types of deposit and certain regions show significant variations from the norm.

Mineralogical analysis of Thai tin deposits relies heavily on previous reports. Unfortunately, many of these reports are incomplete insofar as they do not always give a comprehensive list of minerals present. In some cases they list only major constituents and in others only the heavy minerals associated with cassiterite. If a light mineral is only an accessory constituent it is unlikely to occur in a heavy mineral concentrate in sufficient amounts to contribute trace elements to a bronze. On the other hand a light mineral which is a major constituent of the ore does need to be taken into account.

It should perhaps be mentioned here that, besides the minerals containing essential tin (cassiterite, stannite etc.), there are other mineralogical species which can contribute a significant amount of tin to any analysis (Hosking, 1981). Such minerals include:

**Skarn silicates:**
- Andradite garnet, Langkawi Islands, Indonesia - 2% Sn
- Pinyok, Thailand - 3% Sn
Iron oxides:
The Fe oxide ores of Bukit Besi, Trengganu are stanniferous.

Ta-Nb Minerals:
Tantalite/columbite can contain Sn, as can niobian rutile. The Nb-rutile from Takua Pa, Thailand contains Sn - 12.7%, (Na,Ta)\(_2\)O\(_5\) - 17.5% and TiO\(_2\) - 52%.

Localities which have significant mineralogical variations are discussed individually below.

2.2.3 TIN REGIONS RELEVANT TO SOUTHEAST ASIA

South China.

Chinese tin deposits occur as both primary and placer types, with the former predominating and the latter concentrated in the in the South China Tin Province. Chen and Wang (1988) recognise four primary tin metallogenic regions (Figure 212A above):-

1. The South China Fold System
2. The Daxingangling Fold System
3. The Jilin-Heilungjiang Fold System
4. The Sanjiang Fold System.

South China Fold System.

This is the main tin-producing region today, including the Gejiu and Dachang tin mines of southeast Yunnan and west Guangxi. The Gejiu tin deposits are mainly sulphide-cassiterite skarns in the granite-limestone contact and contain Sn, Cu, Pb, Zn and W with Mo, Bi, Be, In, Ag, As, S and F. Veins and stockworks occur with cassiterite-tourmaline veinlets and greisens. Dachang records Sn, Fe, Zn, Pb, W, As, Cu and Sb.
In addition to those mentioned, there are Ta-Nb cassiterite deposits, greisens and Sn-W quartz veins.

The central and eastern parts of the region, from Guangxi to the Guangdong volcanics, Fengdishan tin ores (Yu Zhunggi, 1988) and the coastal tin zone contain sulphide- cassiterite, Sn-W quartz veins, greisens, Sn-W skarns, Sn-Cu skarns, Fe-Sn skarns and pegmatites [Sn-Ta-Nb]. Associated metals are W, Bi, Mo, Ta, Nb, Cu, Pb, Zn. Porphyritic-type tin deposits have also been found.

Daxinganling and Jilin-Heilungjiang Fold System.

Sulphide-cassiterite and magnetite-cassiterite skarns occur in this region of north China, with minor greisens. The deposits however, are unlikely to influence southeast asian metallurgy.

Sanjiang Fold System.

This is described as a new tin province, occupying Sichuan and west Yunnan and joining the Thai Tin Belt. Significantly it coincides with the middle and upper reaches of the Mekong, Salween and Jinsha [Yangtze] rivers. Northwest Yunnan contains Sn-W polymetallic sulphide deposits, while west Sichuan is characterised by cassiterite and cassiterite-polymetallic skarns. The area west of the Mekong is dominated by tourmaline-quartz cassiterite deposits. The western most part of Yunnan seems to be analogous to the North Thailand Migmatite Province with a Sn-Cu-Pb-Zn assemblage with Ag, W and As.

Although this province is described as 'new', implying that it is the result of recent exploration attempts, there is no information to say whether or not tin could have been exploited here in antiquity. The existence of tin-polymetallics and its location on the important trade routes suggest that it might have been influential in the formative period of bronze metallurgy.
Shi Lin et al. (1988) describe the tin deposits of west Yunnan as small dispersed cassiterite-quartz and greisen veins resulting from hydrothermal alteration along a mylonite zone and genetically related to the epizonal anatetic granites. He describes the deposits as predominantly greisen/cassiterite-sulphides with quartz-tourmaline-cassiterite veins; Sn-polymetallic skarns; pegmatites with cassiterite-topaz-microlite-columbite-beryl etc. and cassiterite-rare metal disseminations with Li-muscovite-columbite-ilmenorutile-tapiolite-microlite.

Similarly the deposits of the Yunlong Tin Belt, west Yunnan are high in sulphides with the assemblage cassiterite-arsenopyrite-pyrrhotite-pyrite-chalcopyrite-scheelite-bismuthinite-sphalerite-galena (Zou Shu et al. 1988).

India.

On a global map of tin producing regions, India always appears to be tin-barren. This is not, in fact, so. Tin deposits in India are few, small and scattered but some have been the source of tin for indigenous smelting operations (Mukerjee and Rai, 1978).

Most of the deposits appear to be associated with pegmatites and later metasomatism, including greisenisation (Mukerjee and Rai, 1978). There are also associated alluvials. It is the opinion of these authors that there may be considerably more cassiterite mineralisation at depth. If so, anywhere where tectonic events or erosion have exposed the deeper levels of the deposits, cassiterite would be available.

Figure 223A shows the known tin deposits of India.

In the Sikkim Himalaya, tin-tungsten deposits occur. The mineralisation consists of cassiterite, ferberite, scheelite, pyrite, arsenopyrite, chalcopyrite, molybdenite and bismuth. Secondary mineralisation includes tungstite and hydrotungstite, malachite, azurite, chalcocite,
Figure 223A. (Mukerjee and Rai, 1978).

goethite, lepidocrocite and covellite.

**South Thailand.**

The South Thai Tin Belt is here defined as peninsular Thailand, south of Phetburi Province.

Major tin fields in this region are located in Phuket Province. Here the Katthu Valley produces cassiterite from pegmatites and pegmatite-derived alluvials, characterised by Sn-Ta-Nb and Sn-Li-F-W-Ta-Nb-REE assemblages (Gocht and Pluhar, 1982), with Zr and Ti present as accessories (Praditwan, J. 1985). Similar trace element and mineralogical characteristics were recorded for the Phangnga and Trang regions.

Chao Fah Mine, Phuket reworks an alluvial deposit in the river valley, which was previously back-filled with tailings. (Gocht, W. 1985) It is only economically viable in modern terms because modern techniques allow the extraction of the very fine cassiterite. Under these circumstances the mineralogy is likely to be the same as the original deposit although the ore grade is lower.

At Pinyok, South Thailand, a large stanniferous skarn consists essentially of cassiterite, galena, pyrite, arsenopyrite, chalcopyrite, magnetite, secondary limonite, grossular, andradite, quartz and diopside (Kaewbaidhoun and Aranyakanon, 1961). The cassiterite occurs as a fine grained aggregate with Fe-oxide in a matrix of calc-silicates that also contain chalcopyrite, bismuthinite and cobaltite.

**North Thailand.**

The Nam Mae Lao Valley, Chiang Rai contains major W mineralisation with Sn and is mentioned here as an anomaly. Gebert (1988) concluded that these sediment- and amphibolite-hosted Sn/W deposits were not epigenetic replacement deposits related to Triassic granites but are
Figure 223C. Map of the Pilok Tin-Tungsten Mineralised Field. (Mahawat, 1988).
instead Palaeozoic volcanogenic exhalites related to basic, island arc volcanism. The Mae Chedi scheelite-cassiterite deposits in amphibolite contain cassiterite, scheelite, wolframite, pyrite, bismuthite and sulphosalts. Antimony is characteristic of the Tha Ko scheelite deposit.

Central Thailand.

The Pilok district, Kanchanaburi, shown in Figure 223C, is one of the most productive Sn/W regions of Thailand and extends into Burma as the Tavoy Sn/W district. The mineralisation is related to Jurassic-Cretaceous granitoids with aplites and pegmatites. Two types of cassiterite-wolframite deposits occur; veins and skarns. These can be further subdivided into three vein-types and two skarn-types (Mahawat, 1988). The region therefore illustrates some of the genetic and mineralogical differences which can occur in a small area.

The ore veins are all quartz-type while the quartz-feldspar and pegmatite veins are barren. In the massive quartz veins, wolframite predominates while the microveinlets are almost exclusively cassiterite-bearing. In the shear zone the veins contain molybdenite, scheelite, pyrite, bismuthinite, arsenopyrite, galena, fluorite, cassiterite and wolframite.

The Etong-Epu field [I-Pu] consists of massive quartz-veins and stockworks of microveinlets. The latter occur in albitised, greisenised and chloritised leucogranites and are confined to the granite cusps, whereas the massive ore veins are distributed in the granite-country rock contact.

Phapare field [Pha Pae] consists of veinlets in greisenised granite. Ore-bearing quartz veins infill fault and shear zones. The stockwork ore is wholly cassiterite but the veins in the fault and shear zones contain cassiterite-wolframite-scheelite-molybdenite-pyrite-chalcopyrite-bismuthinite-arsenopyrite-fluorite.
The cassiterite-dominant veinlets are concentrated in the granite cusps, whereas the tungsten-dominant massive quartz-veins are randomly distributed. The skarn-type deposits are confined to the contact between the greisenised two-mica granite and the calcareous host.

Praditwan (1985) compared the mineralogies of Sn-Nb-Ta deposits in north, central and south Thailand and found that the basic mineralogy is very similar throughout although Nb was more common in the rutile from the north [Omkoi]. Similarly, scheelite was not present in south Thailand but wolframite was not present in the Kanchanaburi deposit [Patana Mine]. However the south Thailand deposits appeared to show a significant sulphide component.

**West Malaysia.**

The mineralisation of Malaysia is briefly considered here because, although malaysian tin is unlikely to have been imported into Thailand, it may have reached the coastal trade. Furthermore, there is considerably more information available on regional and genetic variations in the tin deposits of Malaysia than Thailand. It has therefore, often been necessary to apply malaysian findings to similar situations in Thailand.

Tin mineralisation in West Malaysia is related to the S-type granites and occurs as hydrothermal veining, Sn-Skarns, pegmatites/aplites with minor cassiterite-sulphide deposits. Deposits of pneumatolytic-hydrothermal origin predominate and are accompanied by greisenisation. Veins and stockwork greisens have muscovite-tourmaline and quartz-topaz assemblages represented in the Kuala Lumpur and Ulu Langat tinfields; Ulu Selangor/Pahang Border region; Kinta Valley and Klian Intan, Perak. The Kinta fields contain cassiterite, scheelite, wolframite, stannite, columbite/tantalite, galena and stibnite from hydrothermal sources but also arsenopyrite, pyrite, pyrrhotite, molybdenite, bornite and tremolite from stanniferous skarns. The Klian Intan stanniferous
stockworks contain cassiterite, tourmaline, pyrite, galena, sphalerite, arsenopyrite, pyromorphite and bismuthinite. (Chu Ling Heng et al. 1988). Uranium occurs in the veins of Ulu Selangor.

The magnesian skarn of Leong Sin Nam Pipe at Meglembu is characterised by cassiterite, arsenopyrite, pyrite, stannite, jamesonite and tennantite.

The Beatrice Pipe, Selibin occurs in Limestone and consists largely of tremolite. The associated ore minerals are arsenopyrite, cassiterite and chalcopyrite with some stannite, bornite and pyrrhotite. All the limestone-hosted pipes in Malaysia consist of cassiterite and sulphides (Hosking, 1969).

Stanniferous aplites and pegmatites are usually small but cassiterite-topaz aplites have been mined at Gunung Bakau and Toh Kiri in the Kinta Valley. Pegmatites are exploited at Ulu Kerling, Selangor and Ulu Petai, Perak but the best known are those of Gunung Jerai, Kedah including their secondary placers at Semiling and Bedong, and Bakri, Johore. These are characterised by columbite and monazite with Ti/Fe-oxides at Gunung Jerai.

The Klappa Kampit mining field at Billiton consists of stratabound stanniferous veins. The typically skarn-type deposits contain cassiterite and sulphides in the main lode.

Hosking (1981), in his research into pleochroism in cassiterites, noted that the Malaysian West Coast Belt was characterised by early phase pegmatites and greisens but that the East Coast Belt consisted of later hydrothermal mineralisation and was therefore deficient in Ta/Nb species.

This is confirmed by Praditwan (1985) who states Nb/Ta species are confined to the West Belt pegmatites and their derived secondaries. According to Wan Fad Tuah (1982), the
Pegmatitic tin deposits can be described as: 1. Columbite-tantalite-rich pegmatitic deposits found at Bakri and Semiling, which have a complex mineralogy and 2. Columbite-tantalite-poor deposits with very limited mineralogy such as the Taiping, Chenderiang, South Kinta and Kuala Lumpur deposits.

Kinta Valley.

The Kinta Valley Tinfield (Figure 223D), Perak is considered here because it is one of the best documented ancient mining regions of Southeast Asia. It is situated between two granite ranges: the Main Range on the east and the Kledang Range on the west. It is 36 miles long from north to south and the valley floor is 12 miles wide. The substrate is a limestone pavement incorporating both primary cassiterite deposits and secondary alluvials. The limestone pavement consists of deeply eroded limestone pinnacles between which the alluvial cassiterite is trapped. Much of the cassiterite has been extracted by 'fossicking' i.e. individuals or small groups who get the ore from pockets between the pinnacles. Siputeh has good examples of this type of mining although ore is won from this terrain throughout the region between Ipoh and Menglembu.

Pegmatites and aplites are mined in the valley including the topaz-aplite at Gunong Bakau and Toh Kiri, Ulu Petai and Gopeng Consolidated Mine.

At the same time, primary cassiterite 'pipes' are mined here and veins are exploited within the Kledang Range, at surface and underground. Big opencast mines operate in the weathered schists of the valley and have done for many centuries. The variety of tin deposits in the Kinta Valley inevitably gave rise to numerous mining methods and the region serves as a microcosm of primitive technology for Southeast Asia. Malay, Chinese and European methods coexist and although the intensive methods of the Chinese and Europeans have devastated the landscape to a greater extent.
Figure 223D. Major Primary Deposits of the Kinta Valley. (Chu Ling Heng et al., 1988).
and more rapidly than the earlier indigenous methods, the continuous small scale mining over centuries in prehistory can be equally devastating in such great tinfields with their almost inexhaustible ore deposits.

It was initially believed that the ore from the big tinfields would be difficult to fingerprint because of the variety cassiterite sources. It now appears that these complex mixed ores, for the same reason, may have very distinctive trace element profiles.

The central zone comprises schists, phyllite and limestone. Figure 223D shows some of the occurrences of primary tin mineralisation. The vein swarms at Tekka occur in both the granite and schist and have a complex mineralogy containing W, Nb, Ta, Pb and Sb (Chu Ling Heng et al., 1988).

The stanniferous sulphide skarn at Leong Sin Nam Pipe, Menglembu is dolomite-hosted and contains As, Pb, Zn and Sb. The Lahat Pipe is similar. These "pipes" are all irregular, chimney-shaped, hydrothermal skarns deposits. They are fissure-fillings or metasomatic replacements of limestones.

The Ulu Petai workings at Kinta illustrate some of the problems of tin mining high in the mountains, such as the scarcity of water. At Ulu Petai the supply is scanty and output much reduced as a consequence. The presence of metallic sulphides also requires that the ore be roasted so that the impurities [now oxides] can be removed by washing.

In some places e.g. the Beatrice Pipe, Menglembu, the sulphide ore is close to the surface and percolating groundwater has already partially oxidised the sulphides.

East Malaysia.

East Malaysia contains both S- and I-type granites although tin deposits are restricted to S-type. Hydrothermal veins and stanniferous skarns predominate with several Sn-Fe
skarns also present. Two types of deposit rare in Malaysia are the tin-polymetallic sulphide of Manson's Lode, Kelantan consisting of Pb/Zn sulphides with pyrite and pyrrhotite and minor cassiterite, chalcopyrite, stannite, arsenopyrite, gold and argentite and secondly the 'Cornish-type' lodes of Sungei Lembing, Pahang.

The occurrence of various genetic types of cassiterite deposit in Malaysia is summarised in Figures 223E and 223F.
Figure 223E. Distribution of Major Stanniferous Hydrothermal Veins, Pegmatites and Aplites in Malaysia. (Chu Ling Heng et al., 1988).
Figure 223F. Distribution of Tin-Bearing Skarns in Malaysia. (Chu Ling Heng et al. 1988).
Plate 2. The ICP-MS Plasma Impinging on the Sampling Cone.
3.1 INSTRUMENTATION.

It is not the purpose of this chapter to discuss the development of Inductively Coupled Plasma Source Mass Spectrometry [ICP-MS] nor determine the future trends of the instrumentation. The aim is to evaluate the technique, its advantages and problems, from the point of view of the relative laymen, who wish to use the method in their research.

3.1.1 ICP-MS.

Discussion of Methods.

For the purpose of this discussion ICP-MS refers to inductively coupled plasma mass spectrometry, ICP-ES is used to refer to inductively coupled plasma optical or atomic emission spectrometry and ICP-S is a general term for all methods.

When comparing spectroscopic techniques, at least five capability factors must be taken into account:–

1. Scope of application.
2. Ease of sample preparation.
4. Reproducibility of results.
5. Accuracy.

However, a comprehensive evaluation of the relative merits of analytical methods is rarely possible and is beyond the scope of this work. Comparisons are especially difficult where a new technique such as ICP-MS is used for new applications and is to be compared with established analytical methods. Little comparative data has, so far, been published for ICP-MS although ICP-ES is well reported in the literature. Unlike ICP-ES, where the plasma is used as an excitation source, ICP-MS uses the plasma as a highly
efficient ionisation source. Instead of measuring the characteristic radiation emitted by atoms and ions, as in ICP-ES, ICP-MS extracts ionised species from the plasma, into the quadrupole mass analyser.

There are several analytical techniques which could claim to compete with ICP-S for general archaeological applications, of which Atomic Absorption Spectrometry [AAS] and X-ray Fluorescence [XRF] are especially well established in both geological and archaeological fields. However, the major problem with XRF is that calibrations have either to be carried out against assumed concentrations in the material or quantification must rely on the availability of standards. This can be difficult with an unknown suite of trace elements at the concentrations in ppm or below, dealt with in this work. In many respects ICP-S and AAS complement each other as analytical methods and for the routine analysis of a few elements AAS is more cost effective (Ramsey and Thompson, 1982). However for large numbers of elements at varied concentrations the wide dynamic range of ICP-S is a considerable advantage and the simultaneous analysis of a wide range of elements more efficient. A further advantage of ICP-MS, is the isotopic ability which allows elemental analysis on a selection of isotopic peaks where interference may affect elemental peaks of ICP-ES and AAS. It also allows isotopic ratio determinations. Not only are these useful as interference checks but they can also be used in Isotope Dilution Analysis [IDMS]. This is currently one of the most accurate and precise methods of quantification (Longerich, 1989). Isotope ratio measurements can also be applied to the partitioning of trace elements during melting and to the tracking and locating of ore deposits; both of which are applicable to archaeometallurgy. Although the precision with which most isotope ratios can be determined [~1-3% 2σ] does not rival thermal ionisation techniques [TIMS], the rapid throughput of ICP-MS is more suited to survey work. ICP-MS also uses far smaller volumes of sample solution than AAS for a wider range of elemental analyses.
The literature at present, generally compares ICP-MS with one or two other methods for particular uses. Denoyer et al. (1989) state that, for precious metals, ICP-MS exhibits some of the lowest detection limits available [<1 ng/g]. These are commonly 2-3 orders of magnitude lower than for ICP-ES and equal or better than Graphite Furnace-AAS [GFAAS] and Instrumental Neutron Activation Analysis [INAA]. Lichte et al. (1987) and Date and Hutchison (1987) discussed the problems of ICP-MS instrumentation for REE work but even since then, significant improvements have been made. Similarly, Balaram (1989) reported that ICP-MS compared favourably with IDMS, INAA and ICP-ES for REE determination, with precisions better than 3% RSD for most elements. Moreover, ICP-MS is capable of REE determination to chondrite levels without preconcentration.

Longerich et al. (1987) used ICP-MS to analyse trace elements in archaeological native silver artefacts. Comparing the method with AAS and Spark Source Mass Spectrometry (SS-MS), they concluded that the small sample size and rapid generation of multi-element data had advantages over AAS. Furthermore, SS-MS had data quantification problems due to variations in element volatility.

ICP-ES and XRF however, are comparable techniques (Thompson and Walsh, 1983; Potts, 1987) where one is superior in some respects, such as sensitivity, this can be partially offset by the second's advantages in other respects.

Neither neutron activation nor mass spectrometry are directly comparable to ICP-ES. Although Roelandts (1988) compares ICP-ES with NAA for REE work he only concludes that they are both good but different. However, a variety of methods may be used to supplement ICP-S methods for specific elements.
In ICP-MS, an inductively coupled plasma is used as a source of ions and the mass spectrum is measured using a quadrupole mass filter. The technique therefore combines the freedom from matrix interferences of the ICP with the good signal-to-background ratios obtainable by mass spectrometry. The range of elements that can be determined by ICP-S is very large, probably greater than any comparable method of analysis, and certainly no simultaneous method exists at present that can be considered as comparable. In theory all elements in the periodic table can be measured with the exception of the plasma gas, usually argon. In practice, a complete scan of useful information is not always possible.

The sampling probe designed by Alan Gray is the key to the success of ICP-MS. The instrumentation and its evolution are described in several papers (Date and Gray, 1981, 1983; Gray and Date, 1983; Date, 1983). Ions pass through the orifice of the sampling cone into the pumped chamber containing the ion lens, which directs them through another aperture into the mass spectrometer (Figure 311A). The mass spectrum is then obtained in the normal way with a multichannel analyser which readily resolves peaks, one mass number apart down to zero background. Samples, in liquid form, are generally introduced into the plasma by a conventional crossflow nebuliser. In the earlier prototypes, boundary layer sampling was used where, with a small aperture [7μm] the ions were sampled from the area of maximum ionisation in the tail flame. In crossing the boundary layer of cooler gas, formed over the sampling cone however, many metal oxides and hydroxides could be formed [MO+, MOH+] as well as singly charged ions [M+]. Pinch discharge, resulting from increasing the aperture diameter, resulted in serious degradation in instrument operation. However, while boundary layer sampling offers good signal-to-background ratios, achieving detection limits lower by a factor of 10 than continuum sampling, it has a serious disadvantage. During the re-equilibration of
the plasma gases in the boundary layer, ions collide with the plasma gas species resulting in the formation of ion-molecular species. These not only confuse the mass spectrum but also make the boundary layer very sensitive to matrix effects. The effects and disadvantages of boundary layer sampling have been investigated by Houk et al. (1980). Current instrumentation uses continuum sampling where the sampling aperture is increased to allow the plasma gases to punch their way through the boundary layer which otherwise covers the sampling orifice. Pinch discharge is avoided when the sampling aperture is increased to 1.0mm, by keeping the area behind the sampling orifice at a relatively low vacuum ["1 torr]. The size of the ion beam passing into the mass spectrometer is then controlled by the skimmer, with an aperture of 0.7mm. The skimmer is placed 7mm behind the sampling orifice. Therefore, the interference effects which occurred while the plasma gas cooled in the boundary layer are removed. The current BGS equipment used in this research is described by Date and Hutchison (1987) and Date et al. (1988).

Formation of metal ions, as mentioned above, does occur but doubly charged ions are rare and restricted to elements that have low second ionisation potentials. The major background peaks arise from species of Ar, O, N, H. The method produces a high quality spectrum and isotope ratios compare very closely with with those of conventional thermal evaporation techniques but, because the ion source is external to the spectrometer, many samples can be examined in quick succession (Thompson and Walsh, op. cit.), requiring about 7 mins per sample. Detection limits are normally in the region of 0.1µg/l but may be lower. This is 1-2 orders of magnitude lower than can be obtained by ICP-ES. Calibration curves are often almost linear for several orders of magnitude above the detection limit. However, if the solution concentration is too high (>1µg/ml) condensation in the cool boundary layer causes blockage of the aperture and gives rise to non-linearity. Continuum sampling with a 400µm aperture reduces these problems but requires an extra pumped pressure stage.
Detection limits are commonly lower than for ICP-ES. Over 40 elements can be detected below 0.09μg/l and a further 25 below 0.9μg/l. The detection limits at parts per trillion levels are made possible by the high ionisation efficiency of the ICP source and the low signal-to-background ratios typical of ICP-MS at amu above 80. The rapid scanning quadrupole mass spectrometer is used for ion separation, making ICP-MS a rapid measurement technique, able to scan across the periodic table in milliseconds. In addition to the high sensitivity, ICP-MS provides a wide linear dynamic range of 5-6 orders of magnitude. According to Potts (1987), this allows combinations of elements, such as As, Sb, Se, Te, Cu, Ni, Zn, Pb, Bi, Au, Hg etc., to be analysed from a single sample solution, when they would normally require several analytical techniques. In practice, there are optimum instrument operating conditions for different elements and a wide range of elements can only be determined under compromise conditions. A further advantage is that all elements within a specified mass range can be determined without specifying precise instrument conditions for each.

As mentioned above, typical ICP-MS spectra are considerably less complex than ICP emission spectra. This results in easy interpretation and reduces the chances for spectral interferences, especially when analysing complex matrices (Figures 312A-G).

The advantages of ICP-MS in geological applications therefore, include high sensitivity [particularly for heavy elements], simple spectra [even for complex matrices] and rapid isotope ratio capability. However ICP-MS does undoubtedly suffer from a number of matrix effects in addition to those found with sample introduction to any ICP source. These need to be recognised and include:

1. Interface effects - the inability of the ICP-MS interface to tolerate high levels of solids.
2. Polyatomic ion interferences - characteristic of the medium used for sample dissolution and/or the

110
Figure 312B. Expanded Spectrum of BND-1101 Showing Tin Peaks.

Figure 312C. Expanded Spectrum of BND-1101 Showing Barium and Lanthanides.
Figure 312D. Expanded Spectrum of BND-1101 Showing Silver, Tin and Barium/REE Peaks.

Figure 312E. Spectrum of BND-1101, Reduced Vertical Scale to Show Tin Peaks.
Figure 312F. Spectrum of BND-1101 Showing Iron/Manganese Peaks.

Figure 312G. Expanded Spectrum of BND-1101 Showing Lead/Bismuth Peaks.
sample matrix.
3. Matrix enhancement and/or suppression.
4. Isobaric overlap - two or more isotopes with the same m:z ratio.

To reduce these effects the level of salt in solution is generally limited to 0.1%. The polyatomic ion interferences characteristic of different acid media are recognised (Date, Cheung and Stuart, 1986; Gray, 1986). Frequently new sample dissolution techniques need to be developed for ICP-MS, as the acids commonly used for the dissolution of geological matrices, hydrochloric and perchloric, can pose serious polyatomic ion interference problems. These problems are discussed in more detail below.

**Lead Isotopes by ICP-MS.**

By using a quadrupole mass spectrometer for lead isotope analysis, precision of the order of +/- 0.1% for the 207Pb/206Pb ratio can be reached. For natural samples the precision is more likely to be +/- 0.3% (Gulson, 1986). Combining ICP with the quadrupole mass spectrometer achieves a precision of +/- 0.2% for the 206Pb/204Pb ratio. The precision is so far limited by uncertain fractionation and non-linear transmission of the ion beam in the quadrupole lens system. Furthermore, the lens system gives rounded rather than the flat-topped peaks which, according to Gulson (op. cit.), are essential for precise isotope ratio measurements. Cheung (Pers. comm.) disputes this statement for modern ICP-MS instrumentation. If the peaks are well resolved and symmetrical about the mean, the shape is irrelevant. It is the counting statistics that govern the precision of isotope ratio determinations. 204Pb is the least abundant isotope, therefore ratioing against this will be less precise than ratioing against comparably sized peaks. In current sophisticated VG software, it is possible to predetermine the time spent on each isotope peak, minimising imprecision due to counting statistics.
Date and Cheung (1987) examined the use of ICP-MS for Pb-isotope ratio determination. They acknowledged the problem of mass fractionation and agreed with Longerich et al. (1987) that mass discrimination varies with the instrument operating conditions. However, internal standardisation using thallium improved the response. They concluded that ICP-MS offered a rapid technique to define broad groupings, with the added advantage of simultaneous multi-element trace determination.

The advantages of ICP-MS for lead isotope work are therefore:

1. High throughput.
2. No tedious chemical separations for lead.
3. Combined element content determination and isotopic analysis.

In the analysis of bronze and alluvial ores, the mixing of leads from different sources confuses lead isotope analysis. However, Figure 312H shows that isotope ratios of bronzes of similar provenance will still group them together.

3.2 ANALYTICAL PROCEDURE

3.2.1 BASIC PROBLEMS.

Contamination of Reagents.

All reagents used were of AristaR quality and the analysis of blanks showed very minor contamination in most cases. The exceptions tended to be lead and copper. Data analysis was performed on blank-subtracted data.

Contamination is however, a major problem at this level of sensitivity in analysis. Samples and standards were prepared immediately prior to analysis and any short term storage of sample solutions was in Teflon bottles at low temperatures. All containers were thoroughly cleaned in
acid and deionised water and glassware was soaked in 10% 
HNO₃ for several days before use. All reasonable 
precautions were taken against contamination.

**Preparation Methods.**

In order to obtain useful analytical information for 
characterising tin ores, it is important to ensure that the 
characteristic elements are not removed or added during 
sample preparation.

Cassiterite SnO₂⁺ is a refractory mineral, known for its 
resistance to dissolution and it was necessary to devise a 
total decomposition method which was also compatible with 
the instrumentation.

Although in some analytical work, acid dissolution may be 
adequate and the weight of the residue subtracted from the 
sample weight, total dissolution is preferred. Residues may 
not be representative of the original sample and sample 
subtraction followed by extrapolation of data will 
introduce errors. In this work therefore, it was felt that 
if total dissolution could be achieved it would be 
preferable.

ICP-MS is known to have little tolerance to high solid 
content solutions. As a rule total solid content of less 
than 100mg per 100ml of solution is preferred in order to 
minimise the interface effects due to condensation of solid 
around the orifice. Therefore acid decomposition of the 
sample is preferred.

Cassiterite is notoriously difficult to dissolve in mineral 
acids. Common methods of cassiterite dissolution are given 
by Block (1979) and Thibault (1908). Hydrofluoric acid does 
not decompose cassiterite and nitric acid reacts to form 
metastannic acid which is resistant to chemical 
dissolution. At high temperature and pressure hydrochloric 
acid will decompose cassiterite with only a limited degree 
of success. The aim was to dissolve as many of the minerals
in the ore concentrates as would be likely to yield trace components during the smelting process but at the same time to avoid introducing contaminants from numerous reagents or removing elements during sample preparation. Four methods of sample preparation were considered, each with its own problems. These were:-

1. Reduction of cassiterite to the metal using hydrogen prior to acid dissolution.
2. Fusion with ammonium iodide to remove the tin prior to acid dissolution.
3. Lithium metaborate fusions followed by a clean-up stage using ion exchange.
4. Reduction to metal using CO₂ and a lime flux prior to acid dissolution.

Lithium metaborate is normally used as a fluxing agent during the dissolution of cassiterite. However large quantities of added salt cause depression of the analyte signal intensity, signal drift and clogging of the sampler orifice. Therefore, removal of excess salts is necessary prior to analysis. Too many unknown factors were involved in using ion exchange resins for it to be acceptable in this research. Similarly, although boron can be volatilised as methyl borate, procedures for the removal of lithium are time consuming. Kantipuly and Westland (1988) reported using potassium tetraborate as a fluxing agent. The advantage of this is that potassium can easily be removed as the perchlorate without co-precipitation of REE's. However precipitation of other analytes or its use with cassiterite concentrates is unrecorded.

For the purpose of this study the ammonium iodide fusion method was considered the optimum. Ammonium iodide is used for extracting tin from cassiterites according to the reaction:

\[
\text{SnO}_2 + 4\text{NH}_4\text{I} \rightarrow \text{SnI}_4 + 4\text{NH}_3 + 2\text{H}_2\text{O}.
\]

As the tin iodide sublimes, the removal of the tin matrix results in a much cleaner solution and the reduction of tin interferences on the rare earth element peaks. Details of
Analysis of the results of various methods of preparation shows that the formation of volatile hydrides and/or iodides can affect the quantitative results. On the whole, ammonium iodide fusions appear to suffer greater losses of some elements as compared with hydrogen reduction methods.

On the other hand, the advantage of ammonium iodide fusions is the removal of the tin matrix. In ICP-MS the numerous tin matrix isotopes produce an abundance of isobaric and polyatomic ion interferences. Tin argides are excluded from discussion, as there is no evidence for their formation in the spectra.

The analysis of results of the carbon reduction method highlighted the near impossibility of meaningful comparisons between methods.

Concentrations of many elements were significantly increased in this method and suspicion falls on the charcoal as the major contaminant. It also casts doubt on the validity of comparison of trace elements in ores and smelted materials, especially in archaeometallurgical analysis.

**Polyatomic and Isobaric Overlap.**

This is a major problem in the interpretation of ICP-MS spectra and numerical data.

The work of several researchers (Tan and Horlick, 1986, 1987; Vaughan and Horlick, 1986, 1987; Date et al., 1987; Lichte et al., 1987) has led to an understanding of spectral interferences which allows them to be anticipated and corrections made. This, together with recent advances in computerised methods of forecasting spectral interferences, promises to significantly reduce the interpretation problems for the layman.

However, in addition to those interferences listed in the
<table>
<thead>
<tr>
<th>Tin isotope</th>
<th>Abundance</th>
<th>Isobaric overlaps</th>
<th>SnH⁺</th>
<th>SnO⁺</th>
<th>SnOH⁺</th>
<th>SnO₂⁺</th>
<th>SnAr⁺</th>
<th>Sn⁺</th>
<th>Sn³⁵Cl⁺</th>
<th>Sn³⁷Cl⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>1.0</td>
<td>Cd, In</td>
<td>113</td>
<td>128</td>
<td>129</td>
<td>144</td>
<td>152</td>
<td>147</td>
<td>149</td>
<td>149</td>
</tr>
<tr>
<td>114</td>
<td>0.65</td>
<td>Cd</td>
<td>115</td>
<td>130</td>
<td>131</td>
<td>146</td>
<td>154</td>
<td>149</td>
<td>151</td>
<td>151</td>
</tr>
<tr>
<td>115</td>
<td>0.35</td>
<td>In</td>
<td>116</td>
<td>132</td>
<td>132</td>
<td>147</td>
<td>155</td>
<td>150</td>
<td>152</td>
<td>152</td>
</tr>
<tr>
<td>116</td>
<td>14.4</td>
<td>Cd</td>
<td></td>
<td></td>
<td>133</td>
<td>148</td>
<td>156</td>
<td>151</td>
<td>153</td>
<td>153</td>
</tr>
<tr>
<td>117</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
<td>134</td>
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<td>157</td>
<td>152</td>
<td>154</td>
<td>154</td>
</tr>
<tr>
<td>118</td>
<td>24.1</td>
<td></td>
<td></td>
<td></td>
<td>134</td>
<td>150</td>
<td>158</td>
<td>153</td>
<td>155</td>
<td>155</td>
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<td>119</td>
<td>8.6</td>
<td></td>
<td></td>
<td></td>
<td>135</td>
<td>151</td>
<td>159</td>
<td>154</td>
<td>156</td>
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<td>120</td>
<td>32.8</td>
<td></td>
<td></td>
<td></td>
<td>136</td>
<td>152</td>
<td>160</td>
<td>155</td>
<td>157</td>
<td>157</td>
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<tr>
<td>122</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
<td>137</td>
<td>154</td>
<td>162</td>
<td>157</td>
<td>159</td>
<td>159</td>
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<tr>
<td>124</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
<td>138</td>
<td>156</td>
<td>164</td>
<td>159</td>
<td>161</td>
<td>161</td>
</tr>
</tbody>
</table>

Table 321A. Isobaric and Polyatomic Ion Interferences for Tin in HCl Acid Medium.
<table>
<thead>
<tr>
<th>M</th>
<th>MH⁺</th>
<th>MO⁺</th>
<th>MOH⁺</th>
<th>M^{35}Cl⁺</th>
<th>M^{37}Cl⁺</th>
<th>Mar⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti⁺</td>
<td>TiH⁺</td>
<td>TiO⁺</td>
<td>TiOH⁺</td>
<td>Ti^{35}Cl⁺</td>
<td>Ti^{37}Cl⁺</td>
<td>TiAr⁺</td>
</tr>
<tr>
<td>46</td>
<td>47</td>
<td>62  - Ni</td>
<td>63  - Cu</td>
<td>81</td>
<td>83</td>
<td>86  - Sr</td>
</tr>
<tr>
<td>47</td>
<td>48</td>
<td>63  - Cu</td>
<td>64  - Zn</td>
<td>82</td>
<td>84</td>
<td>87  - Rb, Sr</td>
</tr>
<tr>
<td>48</td>
<td>49</td>
<td>64  - Zn</td>
<td>65  - Cu</td>
<td>83</td>
<td>85  - Rb</td>
<td>88  - Sr</td>
</tr>
<tr>
<td>49</td>
<td>50  - Cr</td>
<td>65  - Cu</td>
<td>66  - Zn</td>
<td>84  - Sr</td>
<td>86  - Sr</td>
<td>89  - Y</td>
</tr>
<tr>
<td>50</td>
<td>51  - V</td>
<td>66  - Zn</td>
<td>67  - Zn</td>
<td>85  - Rb</td>
<td>87  - Rb, Sr</td>
<td>90  - Zr</td>
</tr>
<tr>
<td>Mn⁺</td>
<td>MnH⁺</td>
<td>MnO⁺</td>
<td>MnOH⁺</td>
<td>Mn^{35}Cl⁺</td>
<td>Mn^{37}Cl⁺</td>
<td>MnAr⁺</td>
</tr>
<tr>
<td>55</td>
<td>56  - Fe</td>
<td>71</td>
<td>72</td>
<td>90</td>
<td>92</td>
<td>95</td>
</tr>
<tr>
<td>Nb⁺</td>
<td>NbH⁺</td>
<td>NbO⁺</td>
<td>NbOH⁺</td>
<td>Nb^{35}Cl⁺</td>
<td>Nb^{37}Cl⁺</td>
<td>NbAr⁺</td>
</tr>
<tr>
<td>93</td>
<td>94</td>
<td>109 - Ag⁺</td>
<td>110 - Cd</td>
<td>128 - Te</td>
<td>130 - Te</td>
<td>133 - Cs</td>
</tr>
<tr>
<td>Ta⁺</td>
<td>TaH⁺</td>
<td>TaO⁺</td>
<td>TaOH⁺</td>
<td>Ta^{35}Cl⁺</td>
<td>Ta^{37}Cl⁺</td>
<td>TaAr⁺</td>
</tr>
<tr>
<td>181</td>
<td>182 - W</td>
<td>197 - Au</td>
<td>188</td>
<td>216</td>
<td>218</td>
<td>221</td>
</tr>
</tbody>
</table>

Table 321B. Polyatomic Ion Interferences Arising from Minor Elements in Cassiterite.
Table 321C. Equivalent Concentration Data for 500ppm Tin Polyatomic Ion Interferences

<table>
<thead>
<tr>
<th>Polyatomic Ion Interferences</th>
<th>Eq. Conc. ng/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{124}\text{Sn}^{16}O^+$</td>
<td>$^{140}\text{Ce}^+$ - 3.94</td>
</tr>
<tr>
<td>$^{122}\text{Sn}^{16}O^+\text{H}^+$</td>
<td>$^{139}\text{La}^+$ - 2.05</td>
</tr>
<tr>
<td>$^{124}\text{Sn}^{16}O^+\text{H}^+$</td>
<td>$^{141}\text{Pr}^+$ - 2.90</td>
</tr>
<tr>
<td>$^{119}\text{Sn}^{16}O_2^+/^{116}\text{Sn}^{35}\text{Cl}^+$</td>
<td>$^{151}\text{Eu}^+$ - 0.85</td>
</tr>
<tr>
<td>$^{118}\text{Sn}^{35}\text{Cl}^+/^{116}\text{Sn}^{37}\text{Cl}^+$</td>
<td>$^{153}\text{Eu}^+$ - 2.01</td>
</tr>
<tr>
<td>$^{122}\text{Sn}^{37}\text{Cl}^+$</td>
<td>$^{159}\text{Tb}^+$ - 0.45</td>
</tr>
</tbody>
</table>
Figure 321A. ICP-MS Spectrum of an Aqueous Tin Solution at 500ng/ml
Illustrating the Occurrence of Tin-related Polyatomic Interferences.
Figure 321B. ICP-MS Spectrum for 1 µg/ml Ta Indicating the Presence of TaO+ on Au at 197 amu.
$^{93}\text{Nb}^+$ (823,933 counts sec$^{-1}$)  $^{93}\text{Nb}^{16}_2^+ (4,083$ counts sec$^{-1}$)

125X scale expansion

$^{93}\text{Nb}^{16}_2^+$

Figure 321C. ICP-MS Spectrum for 1 µg/ml Nb Indicating the Presence of NbO+ Interference on Ag at 109 amu.
above works, many interference effects encountered during this research were due to the copper and tin matrices. The interference effects of Fe, Mn, Ar, Ca, Ba, Ti, Ga and Ge on each other are noted by Date et al. (1987). The copper matrix of the bronzes was found to cause few problems but the numerous tin isotopes of the ores resulted in considerable interference on the REE peaks. The major isobaric and polyatomic ion interferences for tin in HCl acid medium are given in Table 321A. Those arising from minor elements in cassiterite ores in Table 321B.

The most significant isobaric overlaps are 114Sn+ on 114Cd+ and 115Sn+ on 115In+. Therefore the determination of these elements is difficult without the removal of the tin matrix. For antimony, inadequate resolution from the tin isotopes presents a more serious problem than interference due to SnH+. For a solution containing 500ppm tin, the equivalent concentration data for some of the tin polyatomic ion interferences for Ce, La, Pr, Eu is given in Table 321C. This is also illustrated by the spectrum shown in Figure 321A. It is feasible to negate the polyatomic contributions by simple blank subtraction, providing that the degree of interference remains reasonably constant and that the REE concentrations are significantly greater than those of the blank.

It is also necessary to allow for other isobaric overlaps and polyatomic ion interferences due to high levels of other constituents such as Ti, Mn, Nb and Ta as shown in Table 321D. The most notable is the formation of 181TaO+ on monoisotopic gold at mass 197. Investigation shows that for 1ng/ml Ta solution, the TaO+ peak produced is equivalent to 33.8ppb of Au (Figure 321B). Thus the quantitative determination of gold is problematical. Similarly, NbO+ overlaps with 109Ag+ (Figure 321C) but in this case the alternative 107Ag+ is available for quantification but silver isotope ratio variations cannot be investigated.

Few doubly ionised species were observed of any
Partitioning of Trace Elements.

The use of comparative trace element analyses of metals and ores for provenancing ore sources in antiquity is seriously hampered by the lack of understanding of how various elements behave during smelting. This is compounded when considering alloyed metals in which the various components may have undergone separate smelting before being combined. Tylecote et al. (1977) did some work on partitioning during copper smelting and Rapp (1977) on losses during tin smelting but little is known about the behavior of trace elements during tin smelting. For this reason quantitative analytical data is of little value. Therefore, although quantitative data was obtained on all samples only qualitative data is used in interpreting the evidence.

Alloying.

It is apparent that the use of trace elements for provenancing is complicated when considering alloys such as bronze, which may be two-component [Cu/Sn] or three-component [Cu/Sn/Pb], with variations using Bi, Sb, As. While the tin ores have the widest variation in geochemistry, the number of trace elements which can be used is significantly reduced by the subtraction of those which may be introduced by the copper or lead components. It is therefore worthwhile analysing for as many viable elements as possible, hence the use of a technique capable of rapid simultaneous multi-element analysis of virtually the entire spectrum.

Recycling of Metal.

Exact correlation of metal artefact with ore source is only possible in the rarest of circumstances. According to Tylecote (1970) the ore must be an unmixed primary ore but
in the case of alluvial tin deposits this is not necessarily so. As long as the alluvial source has a distinctive trace element profile it is possible to locate it. However the same trace element profile may be obtained from a metal derived from ores from more than one source or recycled and mixed metals. While any degree of recycling or mixing of metal confuses the results, if a distinctive element is present at least one of the ore sources can be located.

**Fluxes and Charcoal.**

The use of fluxes is another major problem, especially where binary and ternary alloys are being considered. In such instances as many as three different fluxes may be involved. However the use of a flux in the primary smelt of alluvial cassiterite is unusual although a lime flux may be used in slag smelting. Flux contamination is most likely from the copper component.

Lime fluxes may introduce trace elements which are easily adsorbed onto clay minerals and iron oxides will introduce those with an affinity for Fe/Mn species [Ba, Cu, Co, Cr, Ni, Sr, Ti, V, Sc]. The contamination of smelting products through both fluxes and charcoal is difficult to establish. However, Kabata-Pendias and Pendias (1984) correlated much data on trace elements in soils and plants.

The availability of a trace element for uptake by vegetation depends on its solubility in the weathering environment, the pH/Eh conditions and its ability to form organo-metallic compounds. However, a trace element is not present in the vegetation unless it is also present in the local geochemical environment. Furthermore, significant enrichment of trace elements in vegetation is almost always related to mineral deposits or contamination due to mining and smelting. Therefore, local smelting of ores will not significantly alter the relevant trace element profile of the metal. However, alloy components are frequently
produced at different locations and transported for remelting at an alloying site. Alloying, as a crucible process, should not introduce further contamination. The individual trace element profiles [TEP] will still reflect their respective geochemistries.

Of the trace elements considered diagnostic in this work, all reflect the local geochemical environment when present in the vegetation. Zr and Cd are only slightly mobile and are rarely transported beyond the roots of plants. Au is toxic and plants perish at an early stage. Nb and Ta have no known effect on vegetation but Li is readily available to plants and reflects the local geochemistry. The geochemistry of environmental cobalt is complex but it is known to have an affinity for Fe/Mn. However, it should be noted that significant sources of Co pollution are related to non-ferrous metal smelters.

3.2.2 SAMPLE PREPARATION

**Cassiterite and Tin.**

Teflon PFA dissolution pressure vessels were cleaned with 5 ml of HNO₃ and 5 ml of HF at 150° C for 2 h and glassware was soaked in 10% v/v HNO₃ for several days before use. Samples were dried at 105° C for 6 h and AristaR grade reagents used for sample dissolution.

200mg of finely ground, dry cassiterite concentrate was reground with 1g of dry ammonium iodide and heated slowly, to dull red heat, in an open silica crucible over a bunsen burner until no more fumes were evolved. The residue was reground with a further 1g of ammonium iodide and the process repeated.

The residue was transferred to Teflon PFA dissolution bombs, 3ml of conc. HCl and 2ml of 40% HF added and left on a hot plate at 120° for 6 hours. After cooling the lids were removed and the sides of the vessel washed down with deionised water. The solution was evaporated to incipient
dryness. 1ml of HCl was added and the process repeated before 2ml HCl were added and diluted with deionised water. The solutions were warmed, filtered and made up to 100ml with deionised water. The average weight loss after fusion was 61% for the concentrates and 14.7% for the middlings fraction.

Any residues of the dissolution procedure were collected and analysed by X-ray diffraction at Birkbeck College. The residues consisted of a little undisolved cassiterite and, in some samples, tungstic ochre which was formed during dissolution procedures.

3.3 ANALYTICAL RESULTS

3.3.1 DESCRIPTION OF SAMPLES.

Tin Samples

CBSN-2
Cassiterite concentrate from Khao Khieu, Chonburi.

A fine-grained cassiterite from stream and beach sand alluvials. Some hydrothermal mineralisation is present in the region. The mineralisation is associated with Triassic-Jurassic granites which intrude quartzite, limestone and shale.

KBSN-3
Cassiterite concentrate from Amphoe Muang, Kanchanaburi.

Mineralisation is associated with Cretaceous-Tertiary biotite granites intruding palaeozoic slates, quartzite and limestone. Mining is predominantly from placers derived from veins and pegmatites.

PHSN-4
Cassiterite concentrate from Katthu Valley, Phuket Island.

The mineralisation is associated with numerous small
pegmatites and associated stringers and stockworks in the
contact zone of the biotite granites.

PHSN-5
Cassiterite concentrate from Phuket, not Katthu Valley.

The mineralisation is found in pegmatites, stockworks and
stringers with their associated alluvials related to the
Cretaceous tertiary granites.

CPSN-6
Cassiterite concentrate from Patoe, Chumporn.

Cassiterite is derived from pegmatites, hydrothermal lodes
and greisens and their associated alluvials.

KBSN-10
Cassiterite ore from Pha Pae, Pilok Mine, Thong Pha Phum,
Kanchanaburi.

Pegmatite dykes and cassiterite-wolframite quartz veins cut
the weathered granite and slates. The veins [E-W] in the
granite are predominantly cassiterite with some gold. The
N-S veins in the country rock are pegmatitic with
wolframite-scheelite-cassiterite.

KBSN-13
Cassiterite concentrate from Lum-I-Zoo Mine, Tambon Nong
Ree, Bo Phloy, Kanchanaburi.

KBSN-14
Middlings fraction from Lum-I-Zoo Mine, Tambon Nong Ree, Bo
Phloy, Kanchanaburi.

CMSN-26
Cassiterite ore from Ban Bo Kaew deposit, Samoeng Mine,
Chiang Mai.

A cassiterite-scheelite deposit genetically associated with
mesozoic-tertiary granite dykes and their contact with the
palaeozoic limestones. The contact consists of hard calc-silicate rocks cut by numerous quartz cassiterite veins. A softer weathered shear zone is mined, along with pegmatites and alluvials.

SPSN-27
Cassiterite ore from Khao Kamoi/ Khao Krachai, Amphoe Dan Chiang, Suphanburi.

The cassiterite quartz veins are associated with a porphyritic hornblende-biotite granite of Triassic age which intrudes gneisses, schists and marbles.

CRSN-28
Cassiterite ore from Mai Chedi Mine, Amphoe Wang Pa Poe, Chiang Rai.

A Triassic, porphyritic, biotite granite intrudes the palaeozoic metasediments. The granite is heavily weathered and basic rocks also exist within the area. Both are cut by quartz veins containing schorl, cassiterite and scheelite. Placers, stringers and stockworks are mined.

RBSN-29
Cassiterite ore from Takua Pit Thong Mine, Ratchaburi.

A rare skarn-type cassiterite-sulphide-magnetite deposit at the contact of the Upper Cretaceous granite with marble and calc-silicate hornfels, in a sheared zone in the granite.

LUSN-30
Cassiterite concentrate from Thung Luang Mine, Amphoe Serm Ngam, Lumpang.

TKSN-31
Cassiterite concentrate from Huai Luang, Amphoe Tha Song Yang, Tak.

Pegmatites with Nb/Ta and cassiterite quartz veins are
associated with the Triassic granites.

**PHSN-32**
Cassiterite concentrate from Chao Fah Mine, Phuket Island.

The cassiterite is derived from pegmatites and alluvials.

**PHSN-33**
Cassiterite concentrate from Chiang Talae Mine, Phuket Island.

Alluvials, possibly reworked.

**PHSN0—34**
Offshore concentrate from Seatran Mining, Phuket.

**TPSNO—18**
Offshore cassiterite concentrate from Ban Nam Kem Dredging Co., Takua Pa.

**TPSNO—18a**
Middlings fraction, offshore, from Ban Nam Kem Dredging Co., Takua Pa.

**NTSN-19**
Cassiterite concentrate from Nakhorn Si Thammarat.

Hydrothermal lodes and greisens, skarns and pegmatites with their alluvials are related to the Khao Luang batholith of biotite-muscovite granite. This Cretaceous-Tertiary granite intrudes palaeozoic quartzites, limestones, slates and phyllites.

**PHSN-20**
Cassiterite concentrate from Phuket Island.

**KBSN-21**
Cassiterite concentrate with sulphides from Preeya Mine, Kanchanaburi.
Cassiterite concentrate from Phuket Island.

Cassiterite concentrate from Ban Rai, Uthai Thani.

Pegmatite dykes in association with Nb/Ta are related to the Triassic hornblende granite.

Cassiterite concentrate from Wang Pa Poe, Chiang Rai.

Concentrate from Ranong.
Alluvial placers and pegmatites.

Concentrate from Song Mine, Thap Sa Kae, Prachuap Khiri Khan.

The tinfield is surrounded on three sides by biotite-muscovite granites and on the fourth by Upper Palaeozoic metasediments. The cassiterite is derived from pegmatite dykes.

Middlings fraction from Song Mine, Thap Sa Kae, Prachuap Khiri Khan.

Offshore cassiterite concentrate from Kobchai Tin Dredging Co. Ranong.

Cassiterite concentrate from Huai Yod, Trang.

This is a primary tin deposit associated with small biotite-muscovite granite stocks. Disseminated cassiterite occurs in altered granite and hydrothermal veins exist.
SKSN-7
Cassiterite concentrate from Khao Kho Hong, Amphoe Hat Yai, Songkhla.

The small stocks of Cretaceous-Tertiary, biotite-muscovite granite intrude Triassic conglomerates, shales and sandstones as well as Permian limestones and Silo-Devonian quartzites. Tin mineralisation is in the contact zones. The Na-Thawi placers are derived from hydrothermal cassiterite quartz veins and greisens.

KKSN-11
Cassiterite/gold concentrate, panned sample, from Muang Khun Play Mine, Tambon Rong Thong, Bang Saphan District, Prachuap Khiri Khan.

The alluvial cassiterite is extracted from a basal conglomerate overlying schists.

KBSN-16
Cassiterite/W concentrate from I-Pu Mine, Tambon Huai Hai Sok, Pilok Mine, Thong Pha Phum, Kanchanaburi.

The cornish samples were donated by Truro Museum, courtesy of Mr. R. Penhallurick. Details of cornish deposits are extracted from Dines (1956).

CWSNI-34
Tin Ingot from Chun Castle, Morvah, Cornwall.

CWSN-36
Cassiterite with gold ore from Carnon Valley, Cornwall.

Alluvials, some possibly reworked, derived from the St. Day area with some gold recorded. The tin lies within river mud with granite and quartz tourmaline fragments as well as organic remains.

CWSN-38
Cassiterite ore from Porth, St. Blazey, Par, Cornwall.
Stanniferous beach sands derived from the St. Austell granite. The streamworks existed at the river mouth and extended below high water level.

**CWSN-39**
Cassiterite concentrate from Fair and Honest Streamwork, Luxulyan, Cornwall.

Tin-bearing gravels with granite/schorl containing some gold. Layers consist of sand/silt interspersed with peat.

**CWSN-41**
Cassiterite concentrate from Goss Moor, Cornwall.

Alluvials derived from the St. Austell granite to the south and the mineralised high ground of Castle-an-Dinas and Belowda Beacon to the north. They are high in uranium and may contain fragments of micaceous and tourmalinised killas and elvan.

**CWSN-43**
Wood Tin from Cornwall.

**CWSN-44**
Cassiterite concentrate with wolframite from Vincent Mine, Altarnun, Cornwall.

Cassiterite and wolframite in quartz veins, some with minor greisenisation. Cassiterite is associated with arsenopyrite, pyrite and chalcopyrite. The alluvials have also been worked.

**CWSN-45**
Alluvial cassiterite from Gale Farm, N. Bickington, Dartmoor, Devon.

Surface workings of the tin lode in metamorphosed Culm. Copper was also produced and the region was exploited for manganese. Probably polymetallic sulphide lodes.
CWSN-46
Cassiterite concentrate from St. Erth Valley, Cornwall.

Most mines were copper producers with some lead/zinc and silver. The environment is predominantly killas with some greenstones and elvan dykes. The probable source of this sample is either Mellanear or Wheal Alfred.

CWSN-33
Cassiterite/tourmaline ore from Imperial Lode, Goonbarrow, Cornwall.

This is a quartz-tourmaline lode in kaolinised granite with some gold.

Copper Samples

All copper metal samples from Lopburi.

The Lopburi copper deposits are part of the same volcanogenic belt as the Phu Lon deposits, notable for the porphyry-type copper deposits of Permo-Triassic age.

Three prehistoric copper production sites have been excavated by the Thailand Archaemetalurgy Project [TAP] (Pigott and Natapintu, 1988). At Non Pa Wai, in the Khao Wong Prachan Valley, excavation revealed a 2-phase deposit. The earlier phase consisted of a habitation and cemetery site and included the grave of what has been identified as a metal worker, complete with ceramic bivalve moulds. The later phase included ores, slag, smelting crucible fragments in large quantities and 2 unique classes of casting moulds. Evidence of habitation included animal bone, ceramics, stone adzes and bracelets. At present a later 1st millennium BC date has been proposed for the later phase.

Bronze Samples

Details of these samples are taken from Rajpitak (1983).
Corroded fragment of D-shaped, solid section bracelet. Ban Chiang Culture, unknown site.

Samples from Non Chai.

The site is situated at Amphoe Muang, Khon Kaen Province and was surveyed by Charoenwongsa (Charoenwongsa and Bayard, 1983). It is situated in the upper reaches of the Chi River valley and was a large site for General Period B. Higham (1989) states that Kijngam identified a number of items suggesting widespread aquatic resources. Possibly the site was occupied in the late 1st millennium BC (Higham, 1989) and iron slag, although present, was not abundant until c. 200BC.

Six cultural layers were recorded and finds included shards, human bones, iron fragments, bronze artefacts, glass beads, clay mould fragments for the lost wax casting of bells and sandstone moulds for for piece mould casting of bronze axes.

123 bronze fragments, mainly ornamental, were found and 2 shouldered adzes.

Suggested dates are 1566-1813 BP. For the lowest levels c. 1500BC.

1. NC-1112 [Lab. No. Rajpitak 1912B]
Fragment of circular section bracelet from Ban Chiang culture site, Non Chai, probably Iron Age.

Samples from Tham Ong Bah.

Ong Bah Cave is located in the hills between the Menam Kwae Noi and Menam Kwae Yai in Amphoe Sri Sawat, Kanchanaburi Province. The cave was visited by Mr. Chin You-Di of the National Museum, Bangkok in 1957 and by the Thai-Danish Prehistoric Expeditions of 1960-62 and 1965-66. Much of the cave deposit was disturbed by later human activity but
several interment phases were recognised (Sorensen, 1979). The 3 pairs of kettledrums were thought to be related to the boat coffin burials although, strictly speaking, they were stray in the deposit. All the bronzes were associated with these burials and iron was also present. The bronze drums were considered by Sorensen (op.cit.) to have been old when buried and to span at least 2 centuries. His opinion, based on RC dates, is that the drums can be dated to the 2nd half of the first millennium BC [500 - 0BC].

1. OB-1113 [Lab. No. Rajpitak 1915B].
Fragment of kettledrum from Tham Ong Bah.

2. OB-1100.
Part of bronze drum from Tham Ong Bah.

Samples from Kok Makamtao.

Situated at Tambon Don Ka, Amphoe Ban Pae, Ratchburi Province, this site was surveyed by Son Daeng-i et of the Thai Fine Arts Department in 1978 (Rajpitak, 1983). There are no details of the site available but animal and human bones were found; ornaments and stone bracelets of chlorite schist as well as pottery.

1. RB-1114 [Lab. No. Rajpitak 1305].
Very corroded, complete circular section ring from Kok Makamtao, uncertain age.

Miscellaneous Samples.

1. BCC-1115 [Lab. No. Rajpitak 1911].
Corroded circular section bracelet; Ban Chiang culture.

2. BY-1116 [Lab. No. Rajpitak 1902G].
Corroded container rim fragment; Ban Yang, Nakhon Pathom.

Samples from Ban Na Di.

The site is situated in Tambon Phang-Ngu, Amphoe Nong Han,
Udon Thani Province, Northeast Thailand. (Rajpitak, 1983). It was investigated by Higham and Kijngam who discovered occupational and burial material southwest of Ban Chiang. The site revealed 59 inhumation burials including grave goods approximating Ban Chiang Phases III and IV. Also found were complete vessels not paralleled in the Ban Chiang assemblage.

The bronze was locally cast. The site revealed bivalve mould fragments, perhaps partially smelted ore bronze casting furnaces, crucibles, bronze arrowheads, bangles and chisels. The furnaces yielded in situ charcoal.

Iron was discovered at the level equivalent of Ban Chiang Phase IV. There were also in situ hearths and charcoal-sealed pits. The bronze was dated as in use in the period 1500 BC - 600 AD.


Samples from Ban Don Ta Phet.

The burial site of Ban Don Ta Phet is situated in Phanom Thuan District, Kanchanaburi Province, approximately 25 mi east of the Kwae River. Excavations were undertaken by the Thai Fine Arts Department [FAD] in 1975-76 and by the Institute of Archaeology and FAD in 1980-81 and 1984-85.

Bronze containers, bracelets and figurines were found among the grave goods. The containers, described by Rajpitak and Seeley (1979), are a high tin bronze containing up to 23% Sn and showing affinities with finds at Taxila, India. Glover (1989) notes that similar bronze containers have been recorded elsewhere: in the tin gravels of west Malaysia, Tham Ong Bah and at tin mining sites at Khao Jamook, Suen Peung District, Ratchaburi (Glover, 1990, pers. comm.). Rajpitak (1983) also noted their existence at Khok Khon, Sakhon Nakhon and also at Ban Chiang and Ban Na Di (Seeley and Rajpitak, 1984). The dating of the various
high tin bronzes ranges from 300 BC - 300 AD and are again associated with iron artefacts.

1. **BDTP-11X**
   Engraved bronze from Ban Don Tha Phet.

2. **BDTP-1103 [Lab. No. Rajpitak P33]**.
   Very corroded fragment of a container rim from Ban Don Tha Phet.

3. **BDTP-1104 [Lab. No. Rajpitak P61]**.
   Fragment of container, rim only, of waisted beaker shape from Ban Don Tha Phet.

4. **BDTP-1105 [Lab. No. Rajpitak P43]**.
   Base/lid of container with conical boss at centre, very hard, from Ban Don Tha Phet.

5. **BDTP-1106 [Lab. No. Rajpitak P31]**.
   Rim of thin bowl from Ban Don Tha Phet.

   Fragment of container with surface erosion from Ban Don Tha Phet.

7. **BDTP-1108 [Lab. No. Rajpitak P18]**.
   Ring fragment from Ban Don Tha Phet.

**Lead Samples**

All samples from Song Toh Mine are courtesy of Metalgesellschaft AG and KEMCO Mining. The ingots from the Chonburi wrecks are courtesy of Khun Vidhya Intakhosi, FAD.

**PTPB-1**
Sulphide ore from Kong La, Pattalung. Courtesy of Dr. Visuth Pisuta-Arnond, Chulalongkhorn University.

**PRPB-2**
Sulphide ore from Wang Chin, Phrae. Courtesy of Dr. Visuth
Pisuta-Arnond.

**KBPP-4**
Fine-grained sulphide ore from Song Toh, Kanchanaburi.

**TKPB-5**
Sulphide ore from Pha Daeng, Tak. Courtesy of BP Minerals.

**KBPP-6**
Sulphide ore C (Metallgesellschaft AG) from Song Toh, Kanchanaburi.

**I-7**
Conical lead ingot of unknown provenance. Courtesy of A. Bennett.

**KBSTI-8**
Conical lead ingot from Song Toh, Kanchanaburi.

**PWI-9**
Pattaya wreck ingot.

**S3WI-10i**
Sichang 3 wreck ingot, complete.

**S3WI-10m**
Sichang 3 wreck ingot, metal only.

**S3WI-10c**
Sichang 3 wreck ingot, corrosion products.

**STPBO-11**
Lead oxide ingot from Song Toh, Kanchanaburi.

**KBSTI-12**
Conical lead ingot from Song Toh, Kanchanaburi.

**KBSTI-13m**
Conical lead ingot from Song Toh, recent smelting experiments. Courtesy of Dr. G. Pedall and son.
3.3.2. STATISTICAL PROCEDURES.

Two statistical methods were considered for the analysis of multivariate data. These were Cluster Analysis and Principal Components Analysis, both of which were available as software packages for the computer.

The data consisted of 92 samples analysed for 39 elements and 75 isotopes. The isotopic data was treated differently to the elemental data.

The elemental results were analysed for relationships both as a whole and as groups comprising tin, lead, bronze, copper, copper with bronze and metals [ie smelted material rather than ore].
Using statistical packages has serious shortcomings in that the data is fed into the computer and a result is generated with no information as to various stages in the procedure. Anomalies within the data produced final results which, while accurate in themselves, were totally inaccurate as an interpretation of the data as a whole.

It was therefore considered largely impractical to use complex computer statistics at present, as it requires the undivided attention of a statistician to produce accurate results. Instead the data were treated to simpler methods which could be analysed at each stage to confirm the validity of the results.

The data were weighted according to their concentration in relation to other elements and other samples and the results, numbered 1 to 10, colour coded to produce an "anomalies map" of elemental concentrations.

The anomalies maps highlight significant elements, as unusual high or low concentrations, both within sample and between samples. Furthermore, this method picks out the areas which cause problems in the statistical packages.

Where a particular element has an unusually high concentration compared with other elements, the results are biased so that all other data in the same set are relegated to insignificance, thereby producing inaccurate, or at least misleading, results. Manganese, lead, titanium and iron/nickel are particularly liable to do this and where it occurs, these elements can be removed from the data allowing the remainder to regain their relevance.

Elemental ratio patterns are also shown by this method to indicate areas for further study and samples which are consistently high or low in most trace elements or groups of trace elements can also be picked out.

Anomalies maps can also be rearranged to highlight anomalies or similarities in geographical region or type of
sample. The weighted data are sorted to group certain factors such as geographical location, type of deposit, ingots, ores, concentrates and so forth. Any element showing a relationship to any grouping shows up as a colour coded cluster.

Isotopic data was analysed to discover any anomalies which might warrant further study.

The meaningful presentation of such complex data can be problematical. Some of the alternatives available, generated by computer packages, are illustrated in Figures 332A-G. Figure 332A shows the problem of 'masking' by the copper component in the sample from Ratchaburi. Figure 332B shows the same data when this sample is removed. However, although this change in the scaling factor allows the comparison of the remainder, it would be misleading to consider the Lumpang sample anomalous to any great extent. The only real Cu-anomaly is the Ratchaburi sample. This emphasises the way in which computer-manipulated data can be misinterpreted.

Similarly, the computer software allocates the vertical scale according to the data it is processing at the time. If the number of samples is great, it is necessary to split the data into 2 graphs. Therefore an anomaly occurring only in the first batch will reduce the scale generated, to accommodate it. The second graph, lacking the anomaly, is produced on an expanded scale and direct comparison, between the 2 graphs, is not immediately possible.

3.3.3 THE USE OF LEAD ISOTOPES.

In geology, the most common way of presenting lead isotope data, is the $^{207}\text{Pb}/^{204}\text{Pb}$ v. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. Here the uranogenic lead isotopes $^{206}\text{Pb}$ and $^{207}\text{Pb}$ are compared as ratios with the invariant, non-radiogenic $^{204}\text{Pb}$ isotope. This plot reflects the changes in the U-Pb system of the material. However, this type of plot is sensitive to measurement errors due to the low abundance of $^{204}\text{Pb}$. 

147
Cu, Pb and Zn in Thai tin [1]

Figure 332A.

Anomaly RB removed

Figure 332B.
Cu, Pb and Zn in Thai Tin [2]

**Figure 332C.**
samples 16-end

Cu, Pb and Zn in Thai Tin [2]

**Figure 332D.**
samples 16-end
Pb and Zn in Bronze

Figure 332E.

Pb and Zn in Bronze
Log. Chart

Figure 332F.
Figure 332G. 
Bronzes
Fractionation effects are also increased as the lighter 204Pb isotopes are preferentially removed during measurement in the mass spectrometer. The benefit of these ratios, on the other hand, is that only the U-Pb system is involved.

208Pb/204Pb v. 206Pb/204Pb thorogenic plots are also used when variations in the U-Th system are considered useful. These however, suffer the same disadvantages as the uranogenic plots.

In archaeology, the conventional method of presenting data is the 208Pb/206Pb v. 207Pb/206Pb diagram which, as it does not use 204Pb, can sometimes be used to discern very fine-scale isotopic variations.

There is some dispute as to which type of diagram is of most use for any particular type of work but figure 333A (Gulson, 1986) compares the various methods. Archaeological interpretations rely heavily on groupings and these diagrams show that while generally, the groups remain constant from one plot to another, one sample [Woodlawn] changes its group.

The theory of isotopic signatures of mineral deposits rests on the idea that all ore deposits, of a certain type, within a district have a common origin and that samples from the same deposit are isotopically homogeneous. Since the early days of mass spectrometry, a deposit has been considered homogeneous if the standard deviation for the 206Pb/204Pb ratio were +/- 0.3-0.5% and, even with the increased sensitivity of modern mass spectrometers, this has not changed much. However, new high precision mass spectrometry has shown that some orebodies, previously considered homogeneous, do exhibit variations in isotopic composition of up to 0.3% (Gulson, op. cit.).

Regional isotopic heterogeneity is particularly noticeable in carbonate-hosted Pb/Zn deposits such as those at Song Toh, Thailand; Laurion, Greece and the Mississippi Valley,
Figure 333A. Variations in Lead Isotope Plots. (after Gulson, 1986).

Uranium-derived lead isotope data from selected massive sulfide occurrences plotted on conventional $^{206}$Pb-based diagrams (B) compared with the $^{206}$Pb-based diagram (A).

Thorium-derived lead isotope data from selected massive sulfide occurrences plotted on conventional $^{208}$Pb-based diagrams (D) compared with the $^{206}$Pb-based diagram (A).
USA. In the latter, there are variations, not only between deposits but also within them and even in single crystals of galena. Isotopic variations in the 206Pb/204Pb ratios have been recorded of up to 2%. While geographic or even regional isotopic variations may be significant in archaeological work, deposit variations can throw considerable doubt on archaeological interpretation.

Therefore, in theory, the regional variability and local homogeneity of Pb isotopes should permit archaeometallurgical provenancing. In practice, the results must be considered inconclusive unless sufficient data are available on 'within-deposit' isotopic heterogeneity and the effects of remobilised lead on the isotopic signature. Otherwise interpretation of the data can only be considered in terms of probabilities.

For this reason, although some lead isotope data are presented, considerably more background data is advisable before even attempting an interpretation.

3.3.4. ICP-MS SPECTRA

The simplicity and clarity of ICP-MS-generated spectra have been mentioned above. These attributes, together with the flexibility of the software in manipulating the spectra, has been a great asset to this work. The spectra are no more than a guide to points of interest and a check on the performance of the instrument, as no normalisation factors have yet been applied. However, Figures 334Aa and 334Ab show part of the spectra for the samples from Nakhon Sri Thammarat and one of the Phuket concentrates. They graphically illustrate the Pb anomaly in the latter. One of the advantages of scanning the spectra is that it provides a backcheck. A spectral anomaly negates the possibility of a numerical error during later data processing. The spectrum here supports the Pb-anomaly in this particular deposit.

Figures 334Ba and 334Bb show the full spectra of the same 2
Figure 334Aa. Tin Sample from Nakhon Sri Thammarat.

Figure 334Ab. Tin Concentrate from Phuket Showing Pb Anomaly.
Figure 334Ca. Lanthanide Spectrum for Cassiterite-Sulphide Deposit.

Figure 334Cb. Lanthanide Spectrum for Phuket Alluvials.
samples and show, not only the Pb anomaly, in the region of m:z 204-208, but also the increased U/Th at m:z 232 and 238. There is also an increased response to the lanthanides: m:z 139-175. This characterises the pegmatite/greisen-derived alluvials, even after processing. However, in contrast to this, Figures 334Ca and 334Cb show the lanthanide spectra for ore from a sulphide-bearing deposit in Kanchanaburi and a Phuket alluvial concentrate. It is apparent that the REE component is significantly greater prior to modern processing techniques. This highlights the importance of differentiating between ores and concentrates when interpreting analytical data.

Figures 334Da and 334Db show the difference between the concentrate and middlings fractions of the same ore. Fe, REE, Zn and Cu are all much reduced in the concentrate. Interference on the Ge peak at m:z 70 is probably the result of FeO+ and Ce++ activity.

Figures 334Ea and 334Eb show the significant difference between the profile of the Katthu Valley alluvials, Phuket and that of another Phuket alluvial. Both are concentrates but the Katthu sample has the characteristic complexity of the bigger alluvial basins.

Figures 334F-I illustrate the possibilities of simple visual scanning of the tin spectra. Similarly figures 334Ja-d show variations between four lead sulphide ores from Thailand. Figures 334Ka-d illustrate variations between two Pb ingots and the PbO ingot from Song Toh. Figures 334La-d show the differences between the whole Pb ingot and its pure metal and corrosion products. Only quantitative differences are apparent. The latter two are magnified vertically with respect to the former.

Figures 334Ma and 334Mb compare the profiles of a high-Pb and a low-Pb bronze from Ban Don Ta Phet. The profile of the Ban Na Di bronze is illustrated in detail above (Figures 312A-F).
Figure 334Da. Concentrate Fraction of Takua Pa Ore

Fe

Zr

ClCl
Ce++
Ge

Ar dimer

Figure 334Db. Middlings Fraction of Takua Pa Concentrate.

Zn

Fe
Figure 334Ea. Spectrum of Ore Sample from Phuket, not Katthu.

Figure 334Eb. Spectrum of Ore Sample from Katthu, Phuket.
Figure 334Fa. Nakhon Sri Thammarat

Figure 334Fb. Uthai Thani

Figure 334Fc. Chiang Mai

Figure 334Fd. Phuket
Figure 334Ja. Lead Sulphide Ore, Song Toh, Kanchanaburi.

Figure 334Jb. Lead Sulphide Ore, Pha Daeng, Tak.
Figure 334Jc. Lead Ore, Kong La, Pattalung.

Figure 334Jd. Lead Ore, Phrae.
Figure 334Ka. Lead Ingot of Unknown Origin.

Figure 334Kb. Lead Oxide (PbO) Ingot from Song Toh, Kanchanaburi.
Figure 334Kc. Lead Ingot of Unknown Origin. Mass Range 45-70.

Figure 334Kd. Lead Ingot from Sichang 3 Wreck, Chonburi. Mass Range 45-70.
Figure 334La. Lead Ingot, Sichang 3 Wreck, Metal.

Figure 334Lb. Lead Ingot, Sichang 3 Wreck.
3.3.5. ANALYTICAL RESULTS

**Key to Figures in This Section.**

The following abbreviations are used in all figures. Repeats of the code indicate different samples from the same region, not duplicated samples.

- CB  Chonburi
- KB  Kanchanaburi
- PH  Phuket
- CP  Chumporn
- CM  Chiang Mai
- SP  Suphanburi
- CR  Chiang Rai
- RB  Ratburi
- LU  Lumpang
- TK  Tak
- TP  Takua Pa
- NT  Nakhon Si Thammarat
- UT  Uthai Thani
- RN  Ranong
- KK  Prachuap Khiri Khan
- TR  Trang
- SK  Songkhla
- CW  Cornwall
- O  Offshore Sample
- a  Middlings Fraction
- BCC  Ban Chiang Culture
- NC  Non Chai
- OB  Ong Bah
- BY  Banyang
- BND  Ban Na Di
- BDTP  Ban Don Ta Phet
- KK  Kok Khon
- NNT  Non Nok Tha

**FIGURE CAPTIONS**

*Figure 335A.*

1. Chumporn, conc.
2. Phuket, Katthu
5. Takua Pa, offshore, mids.
6. Chonburi
7. Phuket, Chiang Talae
8. Kanchanaburi, Amphoe Muan

Figure 335B.
1. Chonburi
2. Kanchanaburi, Lum-I-Zoo, conc.
4. Phuket, Chao Fah
5. Phuket, Katthu
6. Prachuap Khiri Khan, Sn/Au conc.
7. Cornwall, wood tin
8. Chiang Mai, Samoeng
9. Ranong, offshore
10. Takua Pa, conc.
11. Prachuap Khiri Khan, mids.
12. Uthai Thani

Figure 335E.
1. Chumporn
2. Phuket, Katthu
3. Chonburi
4. Takua Pa, offshore, mids.
5. Phuket, Chiang Talae
6. Prachuap Khiri Khan, Sn/Au conc.
7. Phuket, Chao Fah
8. Kanchanaburi, Lum-I-Zoo, conc.

Figure 335F.
1. Chonburi
2. Kanchanaburi, Lum-I-Zoo, mids.
4. Phuket, Chao Fah
5. Cornwall, wood tin
6. Phuket, Katthu
7. Prachuap Khiri Khan, Sn/Au conc.
8. Phuket, Chiang Talae
9. Kanchanaburi, Amphoe Muan

Figures 335G, 335H, 335J, 335K, 335L, 335M, 335N.
1. Chonburi
2. Kanchanaburi, Amphoe Muang
3. Phuket, Katthu
4. Phuket, not Katthu
5. Chumporn
6. Kanchanaburi, Pilok, Pha Pae
8. Kanchanaburi, Lum-I-Zoo, mids.
9. Chiang Mai, Samoeng
10. Suphanburi
11. Chiang rai
12. Ratburi
13. Lumpang
14. Tak
15. Phuket, Chao Fah
16. Phuket, Chiang Talae
17. Phuket, offshore
18. Takua Pa, offshore, conc.
19. Takua pa, offshore, mids.
20. Nakhorn Si Thammarat
21. Phuket
22. Kanchanaburi, sulphides
23. Phuket
24. Uthai Thani
25. Chiang Mai
26. Ranong
27. Prachuap Khiri Khan, conc.
28. Prachuap Khiri Khan, mids.
29. Ranong, offshore
30. Trang
31. Songkhla
32. Prachuap Khiri Khan, Sn/Au conc.
33. Kanchanaburi, Pilok, I-Pu
34. Cornwall, ingot
35-43. Cornwall

174
Figure 3351.
1. Takua Pa, mids.
2. Cornwall
4. Cornwall
5. Phuket, Katthu
7. Kanchanaburi, Amphoe Muang
8. Kanchanaburi, sulphides

Figure 3350.
1. Sonkhla
2. Ranong, offshore
3. Kanchanaburi, Pilok, I-Pu
4. Cornwall
5. Ratburi
6. Ranong
7. Prachuap Khiri, Khan, Sn/Au conc.
8. Uthai Thani
10. Cornwall

Figure 335P.
1. Chumporn
2. Prachuap Khiri Khan, Sn/Au conc.
3. Prachuap Khiri Khan, conc.
5. Phuket, Chiang Talae
7. Phuket, Chao Fah
8. Chonburi

Figure 335Q.
1. BDTP-1107
2. BDTP-1108
3. BDTP-11x
4. BDTP-1104
5. BND-1101
6. BDTP-1106
Introduction.

The southeast asian bronzes can be categorised as either two- or three-component alloys i.e. copper-tin or copper-lead-tin. Therefore trace elements can be contributed by any or all of these components. This study is primarily concerned with those trace elements contributed by tin and so those introduced from other sources must be eliminated. 39 elements were analysed and of these only 6 [Sc, Y, Zr, Nb, Ce and W] may be considered as originating in the tin. A further 5 [Hf, Ta, Au, Th and Nd] can be said to originate with the tin component in low lead bronzes. In general however, high Ta in bronze equates with high Nb rather than high Pb (Figure 335E). Therefore the Ta is most likely to be related to the tin content. The concentrations of all these 11 elements are variable in the tin samples and may therefore be considered diagnostic elements, characteristic of the tin ore source. However, in this study the Hf and Nd concentrations do not vary sufficiently for any conclusions to be drawn. Zr however, appears to have a geographic significance. It is absent
Zr:Nb in Tin

Figure 335A.
Geographical distribution of Zr, Nb
Figure 335B: Geographical distribution of Ti, Ta

Ti: Ta in Tin

Ti (Thousands) + Sn Cornwall

Ta (Thousands)
Ti:Zr
Geographical Variations.

Figure 335C.
Tin samples
Figure 335F.
Tin samples
from the cornish samples but present in significant amounts in southeast asian samples. Figures 335A-G show geographic groupings using Zr, Ta, Nb, Ti in various combinations. Cornish samples are low in all these elements compared with thai samples and may be easily identified from the plots.

Elements characteristic of the copper component of the bronze are cobalt, with silver and cadmium contents only applicable to the low lead bronzes. Of these only cobalt has sufficient variation in concentration to be regarded as diagnostically useful for copper provenance.

Ytterbium, lutetium and indium appear to be introduced from the lead component and concentrations seem to be consistent for all lead samples.

Finally, the remaining elements which are contributed by all three components can only be considered useful if their geographical location is restricted. Its presence in a bronze therefore implies that the source of at least one component can be located. If this source is far removed from the location of the bronze the implications for trade are obvious. Unfortunately few elements are so geographically zoned.

It can of course be inferred from the start that a bronze, or its components, from a non-metalliferous region must have been transported.

**Copper Samples.**

There are 4 groupings of copper samples based on a particular significant high-element component:

1. Those with tin.
2. Those with silver.
3. Those with lead.
4. Those with cobalt.

Alternatively they may be grouped as those without these
elements. These variations probably reflect zonation within the copper deposit and differing smelting practices.

Only one copper sample has significant zinc, Cu1005, possibly originating in a Cu-Pb-Zn sulphide deposit.

Although there is a fair range of element combinations among the copper samples Cu1000 has an anomalously low trace element profile with the exception of cobalt which is anomalously high.

Both cobalt and chromium appear to be components of the copper and are also restricted in occurrence. Chromium may suggest an origin in the copper deposits of an ultramafic environment, one of which exists in S.E. Thailand but is more likely to represent a high Cr component of accessory minerals and lateritic iron.

**Lead Samples.**

These samples consist of lead ores and lead ingots.

The lead sulphide ores all contain significant copper although that from Phrae has the highest content. Surprisingly the lead ingot of unknown origin also contains a high copper content. The lead ingots from the Chonburi wrecks and the Song Toh ingots contain very little copper. It is the opinion of the geologist at Song Toh (Pedall pers. comm) that the ancient smelters were not using the sulphide ore but the high silver cerussites. This is borne out by the copper contents. It also implies that the unknown ingot was produced using a sulphide ore and may not be of the same provenance as the other ingots.

The sulphide ores are higher in silver than the cerussites but presumably less easily obtained than the carbonates. Not all the galenas analysed however, are silver rich. Therefore if lead ingots were generally a by-product of the silver production then the regions where they were produced are limited in number.
The only ingot with significant tantalum was that manufactured at Song Toh by the mine geologist, using the cerussite ore. The only other high-Ta sample is the Song Toh cerussite.

Cadmium is restricted to the sulphide ores and chromium and molybdenum to vein ores not carbonate-hosted lead deposits.

REE's are richest in the oxidised ores but appear to be removed by smelting.

The lead ingots have the same profiles as the Song Toh carbonate ores with the exception of the Sichang 3 wreck ingot which is unmatched.

The unknown ingot has a high Bi anomaly which corresponds with only one of the Song Toh ingots but also corresponds with one of the Song Toh sulphide ores, allowing for the fact that Bi appears to be enhanced during smelting. This implies that one of the Song Toh ingots was produced, at least partially, from a sulphide ore. It is also the Song Toh sulphide which is highest in silver. This would no doubt have been the first choice after the easily smelted, but lower Ag, carbonates.

The Pattaya wreck ingot appears to retain its silver.

The modern ingot produced at Song Toh does have significant differences in its profile compared with other Song Toh ingots.

The red lead Pb₃O₄ from Song Toh smelting site has a noticeably Ba anomaly with a high Zr and Ti content which corresponds only with the carbonate ore found at the smelting site. The other local smithsonites and cerussites do not correspond.

The sulphide ores are all characterised by similar elements but not the ingot elements.
The cornish galena has an anomaly profile of high Cr, Co, Mo and W which is identical to that of the sulphide ore from Phrae. Similarly, the Irish galena has a profile anomaly of Sb and Ag, identical with that of the Kong La sulphide. This implies a genetic similarity rather than a geographic. The sample from Tak is anomalously low in Sb. The sulphide ore profiles are as follows:

Phrae - Zn, Cu, Fe, Cr, Mo, Co, W  
Kong La - Ag, Sb  
Song Toh 1 - Cd, Sb  
Tak - Mn, Y, Nd, Sm, Eu, Dy, Yb, Lu, low Sb  
Song Toh 2 - Cd, Sb

Sulphide ores may have a characteristic element e.g. Chromium in Cornwall, Cobalt in Wangchin and Silver and Antimony in Kong La and Ireland.

It is apparent therefore, that the lead ores from different regions will contribute different trace elements to a bronze. No hard-and-fast rule can be applied. It emphasises the need for a database of geochemical information or at least a study of the local ore sources for any archaeological site.

**Tin Samples.**

Significant elements appear to be tantalum, titanium, zirconium, REE's, tungsten, niobium, copper, barium, lead and gold.

Comparison of the analytical data for the tin ingot and the ores show that there are certain depletions and enhancements. These may be due to smelting or to deterioration of the metal over the centuries.

Depletions are noticeable in Ti, Zr, Nb, Hf and W. But Bi, Sb and In are enhanced.
High Thorium Tin Sources.
Thorium anomalies occur in concentrates from Kanchanaburi Province but unconcentrated ore does not show this anomaly. Similarly, offshore concentrates from Takua Pa and Ranong are also high in thorium while Phuket samples are not, with the exception of Katthu.

High Yttrium Tin Sources
Yttrium is characteristically high in offshore samples and onshore Ranong concentrates and the Katthu sample. It is also apparent in the middlings fractions from Kanchanaburi Province.

High cerium is also apparent in these samples.

High Tungsten Tin Sources
Kanchanaburi tin is high in tungsten as are those from Chiang Mai and Chiang Rai in northwest Thailand. Katthu is again anomalous in this respect.

High Gold Tin Sources
Cassiterite samples from Chumporn, Chonburi, Prachuap Khiri Khan and Phuket are all high gold samples. This corresponds with the gold-producing regions of the country except Phuket which is high in tantalum and may therefore be producing a TaO+ interference. Figure 335P however, implies that masking of high-Au samples by TaO+ interference is insignificant.

Categorisation of Tin Sources.
The complexity of the trace element profiles suggests that absolute categorisation is not feasible. However, even with a small sample group, certain anomalies can be identified which isolate some deposits.

High REE concentrations characterise the Kanchanaburi deposits and the Ranong, Takua Pa and Katthu alluvials. They are slightly higher in the offshore alluvials from Phuket but do not, in general, characterise the onshore Phuket mines.
Figure 335P.
Test for TaO+ in high-Au samples.
Within the REE identified group, only the samples from Katthu and Amphoe Muang, Kanchanaburi show Eu anomalies, the latter being further identified by high Zr.

All Phuket, Chonburi and Prachuap Khiri Khan samples show Au anomalies, except for an unlocated Phuket concentrate which has the only, but very significant, Pb anomaly instead. This probably represents a genetic difference. Similarly, the Co-bearing Phuket sample may represent a different genesis.

Only Ratchaburi shows a significant Cu-Fe-Mn-Cr anomaly (Figure 3350) although Cr is present at both Samoeng, Chiang Mai and offshore Takua Pa. Fe and Ba identify the Songkhla deposit and Ba, Suphanburi. W is apparent at Katthu, Ranong and Kanchanaburi as well as Samoeng and Mae Chedi in the north. However, Ta/Nb is present in the Katthu and non-sulphide Kanchanaburi deposits but not in the north. Samoeng is characterised by its Mo content. Sb is only present in peninsular Thailand.

Some samples stand out as anomalous in many respects and may be treated as 'anomalous sources', ie their TEP's isolate them from the general background of deposits. Katthu, Phuket; Lum-I-Zu, Kanchanaburi and Takua Pit Thong, Ratchaburi fall into this category (eg Figure 3351). Often the big onshore and offshore alluvials of peninsular Thailand are also anomalous in this respect. Other deposits, such as Lumpang and Chiang Talae, Phuket are recognisable by significant anomalies in Ag and Pb respectively. Reported anomalies in Co and Cr are harder to evaluate as there can be significant variation in the background concentration, depending on the local lithologies. The anomalous occurrences have been based on the reported background for granite environments.

It is therefore apparent that the number of variables available for categorising tin ores is considerable. The possibilities require to be ordered in the form of a
Figure 3350.

Represents anomalous Fe, Mn, Ce
leadarch
208:206, 207:206

Figure 335I.
Pb isotope ratios, Sn only

Tin Samples
'Twenty Questions' decision tree (Figure 335, encl.) and computerisation of the variables on this basis is simple.

The characterisation of the tin deposits is possible, on a greater number of trace elements than can be used to provenance the tin in bronzes. Therefore the use of the above database and characterisation program provides several source options for the bronze profiles. This is also a result of the lack of background data and too small a sample group. However, the additional elements used to categorise tin deposits will undoubtedly assist the provenancing of tin metal from archaeological sites.

Figures 335J-N show graphically some more of the anomalies mentioned. Graphical representation using ICP-MS spectra has been discussed and illustrated above.

**Bronze Samples.**

The samples BDTP-1104, BDTP-1107, BDTP-1103, BDTP-1106 are low lead bronzes and bronzes BCC-1111, BDTP-1105, BDTP-11x and BY-1116 are medium lead bronzes.

Little can be concluded from bronzes with no elemental anomalies.

In general, the significant elements for diagnostic anomalies of bronzes are W, Sc, Y, Ce, Hf, Ta, Au, Th, Co, Sb, and REE's as a group.

Elements contributed by:-

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</tr>
<tr>
<td>W</td>
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</table>

191
Tin Samples 3
element profile

Figure 335G.
Tin Samples 3
element profile

Figure 335H.
Figure 335K.
Tin Samples 2

Element Profile Figure 335L.
Tin Samples 2

Element profile

Figure 335N.
Notes on Some Elements.

Element profiles are shown in Figures 335R-W.

Silver.
High silver contents occur in BDTP-1104, BDTP-1105, BDTP-1106 and BDTP-1108.

Tungsten-Chromium-Cerium.
This grouping links the sample BND-1101 with the engraved bronze BDTP-11x. Cerium however is also high in 3 other BDTP samples, BDTP-1104, BDTP-1106 and BDTP-1108 and is related not only to the type of source but also to the processing of the ore.

Chromium is high in BDTP-1107 although it is apparent in all BDTP bronzes. The most likely source is a rutile-bearing deposit. All the Kanchanaburi tin deposits show significant Ti in the middlings fraction but in antiquity it would remain in the concentrates. Geographically, Cr is not a good indicator but does imply poor processing.

Lead-Bismuth.
This is characteristic of the Tham Ong Bah drums and the bronze from Ratchaburi. In the drums, the Bi content is sufficiently high to be considered significant, either metallurgically or as an indication of ore source.

Thorium.
Only significant in sample BDTP-1101, this may be related to specific source of high-U REE mineral species.

Cobalt.
Only significant in the engraved bronze BDTP-11x and may be derived from the Lopburi copper.

Antimony.
Very high antimony characterises sample BND-1101 but significant Sb occurs in 3 BDTP samples. Both groups imply large amounts of Sb which is available in Ratchaburi and in
northwest Thailand. Chinese Sb may be indicated if high Sb is linked with high Hg and Au.

Lanthanum and Barium.
These two link BND-1101 with BDTP-1104 and BDTP-1106.

Rare Earth Elements [REE's].
Generally, these are related to poorly processed, pegmatite/greisen-derived alluvials.

All the BDTP bronzes have a recognisable REE profile. This implies an alluvial tin source with significant monazite/xenotime present. However, BDTP-1106, a thin, high-tin bronze bowl, described by Rajpitak and Seeley (1979) is anomalously high in REE's. There is also a noticeable REE anomaly in the profile of BDTP-11X, an engraved bronze. BDTP-1106 has the highest tin content of the bronzes analysed and there is the expected direct relationship between tin content and REE content (Figure 335Q).

While one might be inclined to infer that BDTP-1106 and BDTP-11X belonged to a single group of bronzes with characteristic high REE profiles, this is contradicted by the W content. BDTP-11X has a high W profile while BDTP-1106 has an anomalously low W content. Although within-deposit W variations cannot be ruled out such inhomogeneity should be minimised in alluvial deposits. The tin ores therefore may have different sources. They are again linked by the Nb contents to a source region containing Nb/Ta-bearing minerals. This conclusion is supported by the Ta profiles.

The sources of tin involved here are:-
1. Pegmatite derived alluvials with a significant monazite/xenotime content.
2. A Nb/Ta bearing source region.
3. One W-bearing source region.

Comparing BDTP-11X and BDTP-1106, it is apparent that both
contain Ba which is available in the Ratchaburi deposits. The W in BDTP-11X is probably derived from the Kanchanaburi/Tavoy region which is the nearest W-producing region. This bronze is also high in Mo and although Mo is apparent in the Lopburi copper it is not high enough to account for the concentration in this bronze. Mo is however, present in some of the Kanchanaburi tin deposits. The Co, Cd and silver contents are consistent with a source of copper from Lopburi.

All the BDTP bronzes contain significant Sb which is available in Ratchaburi but the degree of Sb perhaps suggests a deliberate use of this element?

In some respects, these two bronzes have an affinity with the Ratchaburi bronze, RB-1114 and the Ban Na Di bronze, BND-1101. Both these are easily recognisable from their anomalous profiles.

The bronzes as a whole can easily be separated into two groups: 1. Those from Ban Don Ta Phet and 2. All others. A sub-group can also be distinguished, consisting of the Ratchaburi, Tham Ong Bah and BDTP-1108 bronzes. The major factor however, linking these latter bronze profiles is the high Pb content.

It appears that the BDTP bronzes contain constituents from different localities. The ores used to produce them are not the same. This has several possible interpretations:

1. That they were produced in different periods when ore sources had changed.
2. They were produced from different ores but within the same period.
3. That recycled metals from different sources were used.

However, with regard to point 1., Ban Don Tha Phet is a single period site which may only have required a single ore source.
The Ratchaburi bronze, RB-1114, is highly anomalous. The moderate REE profile and the high Ga and Ge contents being most significant. The high Zn and Bi components suggest a polymetallic source for, at least one of the alloy components. As was discussed above, the Ge/Ga anomalies are most likely to represent high Fe and Mn contents, as would be present in a skarn/gossan deposit. The Takua Pit Thong deposit in Ratchaburi Province is noteworthy as a polymetallic tin-magnetite sulphide deposit. Its characteristics are quite capable of producing the anomalies in RB-1114.

The 2 different fragments of drums from Ong Bah are characterised by their lead and bismuth contents.

The bronze from Ban Na Di, BND-1101, is unique in its very high antimony content and its titanium and chromium contents. It is also unique in its tungsten and thorium contents. Tungsten is only of any real significance in tin from certain locations or in lead from tin deposits.

Significant data appear from analyses of bronzes but conclusions are limited to those samples that show anomalies which either group them together or clearly differentiate them. Some elements can be related to different components in the bronze and some serve to identify a locality or type of ore source.

Summary of The Bronzes

The data indicate that 3 groups of bronzes are apparent:

1. The Ban Don Ta Phet Bronzes
2. The Tham Ong Bah Drums
3. All other bronzes

The Tham Ong Bah drums [2 samples] differ from all other bronzes in their high Bi content (Figure 335R). The Bi content appears to be unusually high with respect to the Pb content suggesting that high Bi is a characteristic of a lead deposit containing significant Bi species. The Bi
contents do not achieve the percentages required to indicate a deliberate metallurgical use but they are sufficiently anomalous to suggest that this type of ore source was of interest to the metallurgist. This would be of special interest if high Bi is characteristic of this group of artefacts as a whole. In all other respects the bronzes are very pure. Much care has gone into their manufacture. Although the samples have the same chemistry they are not identical but they are so pure that little can be concluded from their trace element profiles [TEP].

Tentatively it may be possible to infer that the Pb in these drums did not come from the same source as the Pb in BDTP-1108. Their purity allies them to the Khorat Plateau bronzes. These are also low in trace elements, although their profiles show the characteristic elements of pegmatite/greisen-derived alluvials. Care has been taken in the processing of the ores. The elements which do occur are those characteristic of heavy concentrates: W, Ba and Au. In other words, careful processing has successfully eliminated all but a few surplus heavy minerals.

The Ban Don Ta Phet bronzes on the other hand, are impure. Their element profiles imply hasty processing of the tin ores leaving quantities of REE species, W and Nb/Ta (Figures 335S,T). Furthermore, the combinations of elements could imply two tin sources. The elements are compatible with Ratchaburi and the W-producing region of Kanchanaburi as the sources, as well as Lopburi as the copper source. The implications are for a large demand for tin and mass production of bronze.

Therefore differences between the bronzes occur in three categories: processing and metallurgical techniques, regional variation in ore sources and genetic variation in ore sources. Within these categories, the following groups can be identified:-

1. Processing and Metallurgical Techniques.
   a) High purity tin used in sophisticated alloys.
      [Ong Bah, Ban Na Di].
b) High purity tin used with simple alloys.  
    [Khorat Plateau].

c) Poor quality tin with sophisticated alloys.  
    [Ban Don Ta Phet].

2. Regional Ore Variations.
   a) Ores containing W.  
      [Ban Na Di, Banyang, Ban Don Ta Phet].
   b) Ores containing Sb.  
      [Ban Na Di].
   c) Ores containing Nb/Ta.  
      [Banyang, BDP-1106].
   d) Ores containing Ba.  
      [Ban Na Di, Ban Don Ta Phet].
   e) Ores containing Au.  
      [Ratchaburi, Banyang].

   a) Ores with Sc, pegmatites.  
      [Ban Na Di].
   b) Ores with REE and Th.  
      [Ban Na Di].
   c) Ores with REE without Th.  
      [Ban Don Tha Phet].
   d) Ores with Fe, Mn, Zn, Ti, Ta, Au, skarns.  
      [Ratchaburi].
Pb and Bi in Bronzes

Figure 335R.
Ba, REE in Bronze

Samples

Ba and Lanthanides

Ba, La, Ce, Sm

Figure 335S.
W, Cr, Ce in Bronze

Figure 335T.
Figure: 335U.
Copper and bronze
Ta:Bi

Bi (Thousands)

Figure 335V.

Bronze and copper
4.1 TRADE AND ECONOMICS: THE PRESENT AND THE PAST

4.1.1 THE SOCIO-CULTURAL CONTEXT IN BRIEF

It is not within the scope of this thesis to review the archaeological data on Southeast Asia. Some of the most recent references are cited in the text and others listed in the bibliography. Some of the possible socio-cultural interpretations, as they are currently being discussed, are mentioned here with modern theories on the social and cultural implications of small scale mining.

The investigation of trade and, specifically the metals trade in prehistory can at best, only be speculative. Modern anthropological studies of primitive exchange in Southeast Asia by Hutterer (1987), Sahlins (1986) and Torrence (1986) among others, can shed some light on tribal society and intertribal relations. However in Southeast Asia during the bronze age, the degree of political cohesion between tribal groups and the level of social organisation remains unknown.

One of the main problems is the lack of a coherent chronology for Southeast Asia as a whole. Within-site chronologies indicate the phases of bronze introduction, whether as imported introductions or in situ metallurgy. These cannot however, always be correlated with other sites, except tentatively or where there is widespread social reorganisation. Figures 411A, B show some of the major archaeological sites in Southeast Asia.

Radiocarbon dates are frequently disputed where doubts are cast on stratigraphic provenance of charcoal fragments. (Higham, 1983) has mentioned the problems of using charcoal from a region of known fire climax ecology and White (1988) discusses the problems arising from the use of contained charcoal hearths within raised habitations. White (op. cit.) also mentions the documented use of charcoal/live
FIGURE 411A. Location Map of Some Important Sites Showing Settlements in Relation to Map 412A.

(after Higham, 1989).
coals in mortuary rites, thereby lending credence to the stratigraphic context of dated charcoal from burials.

From the discussions of southeast asian bronze chronology, basically two scenarios have been developed amid much controversy. The first, according to Higham (1988), suggests that the chronology for the presence of bronze in northeast Thailand, as presented by Bayard (1987), Solheim (1983) and White (1988), from the evidence at Non Nok Tha and Ban Chiang (Figure 411D), is wrong. These authors placed the advent of bronze-working in northeast Thailand at <2500BC, 3000-2500BC and <2100BC respectively. Higham (1988) however, disputes the mortuary evidence and suggests that the timespan of the mortuary sequence should be reduced to bring the advent of bronze-working to c. 1500BC and in line with that of the Red River and lower Mekong regions. He argues that it is more likely than that the first scenario [Bayard's] would imply that bronze-working was confined to the Khorat Plateau for 500-1000 years prior to its appearance elsewhere. The disputed mortuary sequence, if reinterpreted, would equally well support the second scenario in which, at c. 1500BC there was a rapid spread of bronze technology throughout Southeast Asia along pre-existing exchange networks. Bayard (1988) argues that Higham is basing the failure of metallurgy to spread to the south Thailand estuarine sites prior to this on the absence of bronze at Khok Phanom Di. However, 99.7% of this site remains unexcavated. Furthermore, the absence of bronze in a mortuary context may reflect the mortuary ritual rather than the lack of the metal.

Non Nok Tha has clear affiliations with both Ban Chiang and Ban Na Di but Solheim's (1983) view places bronze at Non Nok Tha nearly a millennium earlier than at Ban Chiang. It is apparent from the evidence at Ban Na Di, some 22km southwest of Ban Chiang (Higham, 1986) that bronze was being melted between 1500BC and 200AD. However, it also appears that the metals were obtained either as ready-made bronze or as copper and tin ingots. These were then remelted and cast into a variety of objects. Furthermore,
<table>
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Figure 411E. Chronological Relationships. (Higham, 1989).
Figure 411C. Location of the Copper Mining District of Lopburi and Khao Wong Prachan. (Higham, 1989).

Figure 411D. Important Sites of The Northern Khorat Plateau. (Higham, 1989).
the variety of objects, ornaments and tools, and the different alloys used (Rajpitak and Seeley, 1984), hint at a society well accustomed to bronze metallurgy. Apparently however, Ban Na Di was settled after the first appearance of bronze at Ban Chiang (Higham, 1988). Two C14 dates from basal Ban Na Di contexts establish cire perdue casting to c. 1700-800BC, with establishment of bronze-working at Ban Chiang Hian, in the Chi Valley c. 1100-800BC (Chantaratiyakarn, 1984). The latter site, excavated by A. Kijngam, is a moated settlement of the middle Chi valley, and all layers yielded bronze (Higham, 1983). The initial occupation was dated to the end of the second millennium BC and the appearance of iron to 600-300BC.

The other site on the Khorat Plateau considered here is Non Chai. This large site, ascribed to General Period B (Figure 411E), in the upper Chi Valley was believed to be occupied between 300BC and 200AD when iron was already in use (Charoenwongsa and Bayard, 1983). Pottery from Non Chai parallels that of Ban Na Di Level 5 (Higham, 1983). According to Charoenwongsa, the dates of 400BC-200AD refer to the later settlement excavated and, while iron slag was present throughout, it did not become abundant until the first two centuries BC. The pottery is distinctive and noticeably different from Ban Chiang Hian styles. Ban Chiang Hian pottery from the site may represent trade goods.

According to Higham (1988), the stratigraphy at both Ban Na Di and Ban Chiang indicate a major cultural dislocation occurring c. 500BC. Standard low-tin bronze was replaced by varied alloys. These alloys were manufactured into ornaments rather than weapons. In General Period B, bronze was used for axes and spears. At much the same time as this metallurgical change, both mortuary ritual and exchange patterns change with the loss of shell ornament and the advent of glass beads and iron smelting.

Ban Chiang bronze tradition equates with Ban Na Di Levels 8-6 (Wheeler and Maddin, 1976) with the exception of the
socketted spearhead. Similarly, this tradition is supplanted during the sequence by the advent of high-tin bronze and iron-working.

Higham (1986, 1988) has suggested that, at the end of General Period B, the autonomous villages of the region already had a social ranking system. Population expansion may have resulted in increased settlement of areas suitable for rice cultivation. Pottery styles support the concept of autonomous villages although an exchange network extended into the hills for metals/minerals and to the coast for shell. Towards perhaps the end of the first millennium BC, there was a trend towards the moated settlements in the Chi and Mun Valleys draining the Khorat Plateau. One of these, Ban Chiang Hian, incorporates a double moat, reservoir and possibly ramparts. All of these suggest the development of a high degree of social organisation, efficient hydroengineering and possibly a need for defence. Ban Chiang Hian, at 38ha, significantly exceeds the size of other known moated settlements. Furthermore, the sequence indicates a social change where Ban Chiang style red-on-buff pottery was superceded by plainer ware and water buffalo and iron appear. Higham (1986) believes that the disparate size of moated sites such as Ban Chiang Hian, Phimai, Non Chai and Non Dua, compared with surrounding areas, departs from the idea of village autonomy and indicates the emergence of centralisation. This could provide the sophisticated social organisation capable of providing water for a large population in the dry season. Furthermore, Moore (1986) considered the distribution of moated sites and noted that not all are clustered along the rice-growing margins of the flood plain. Some may be situated to take advantage of local iron ore deposits for smelting.

There is however, no evidence to suggest that the moated settlements are related to even the later phase of copper mining at Phu Lon on the Mekong River in Non Khai Province (Plate 3). This important mining site appears to have been exploited by at least the mid second millennium BC (Pigott
Plate 3. General View of the Phu Lon Copper Mining District.
(Piggot, 1988.)
and Natapintu, 1988) and continued to be worked intermittently, throughout the first millennium BC. Both copper and bronze appear to have been produced here although little metal has been found on site. The presence of a low-tin bronze [6.91%Sn] at a copper mining site (Pigott, 1988) implies the importation of tin from elsewhere. The most convenient tin source would be the Laos deposits or those of the Thai Tin Belt between Chiang Rai and Nan. The latter are also close to the Mekong River. The high antimony content of the analysed bronze also suggests an antimony-rich source. This occurs in the Chiang Rai region but unfortunately little comparative data is available for the Laos deposits. However, high-antimony bronzes are by no means the norm and, to date, characterise the Ban Na Di and Ban Don Ta Phet bronzes.

Other relevant copper mining sites which should be mentioned are those of the Khao Wong Prachan Valley in Lopburi Province (Figure 411C). Here the sites of Non Pa Wai and Nil Kam Haeng are important copper producing sites. The local ores are extensively mined and small standardised copper ingots apparently mass produced (Pigott and Natapintu, 1988; Bennett, 1986, 1988). Tentative dating has suggested a first millennium date for the habitation and exploitation of the site, extending into the iron-using period. Again, the occurrence of mass production and, what appears to be, the production of copper metal alone well into the bronze/iron eras is significant.

The copper mining and smelting sites of Thailand such as Phu Lon and the Lopburi sites of Tha Kae, Lopburi Artillery Centre, Wat Tung Singto, Huai Yai, Non Mak La, Non Pa Wai, Nil Kam Haeng and others have been adequately described by Bennett (1986, 1989), Natapintu (1984, 1987), Pigott (1984, 1985, 1988), Pigott and Natapintu (1988), Pigott, Natapintu and Theetiparivatra (1985) Maleipan (1979) and others. However, it is unfortunate that the literature on southeast asian smelting sites does not always differentiate clearly between those producing copper alone, copper and bronze or bronze alone. These factors are extremely pertinent to the
interpretation of the early metals industry. Bennett (1989) has pointed out the complexities of interpreting the chronological relationship between the copper-producing periods of southeast Asian prehistory and the bronze- and iron-using. She notes that at Ban Chiang and Non Nok Tha, a neolithic culture preceded the appearance of bronze with no intervening copper or experimental bronze phases. However, she also mentions that high-arsenic bronze prills in slag from Non Mak La might indicate experimentation with arsenical bronze (Bennett, 1986). It is significant that such evidence suggests the introduction into Thailand of metallurgical skills rather than local development. Furthermore, indications of specialised metal production for export to bronze-producing sites must be noted in any attempt at economic interpretation.

It therefore emerges that, by the mid second millennium BC, the societies of Southeast Asia were socially complex with a ranked structure displaying status with exotic artefacts, including bronze (Bayard, n.d.; Higham, 1989). Interlinking trade networks between the highlands and coastal settlements already existed along major waterways. By the first millennium BC regions of development are apparent in the Red River Valley, Khorat Plateau, Lower Mekong Valley and Tongle Sap Plains and in the Chao Phrya Depression. By 500BC Higham has indicated change from village autonomy to strategic centralisation. Craft specialisation with mass production of metal, a high degree of social organisation and population expansion are implied, concommitant with a possible need for defended sites and the appearance of iron. Non Nok Tha was abandoned and Ban Na Di reoccupied. Standardised low-tin bronze was replaced by specialised bronze of great sophistication (Stech and Maddin, 1967; Rajpitak, 1983; Rajpitak and Seeley, 1979; Pham Minh Huyen et al. 1987). Even at ametallic sites such as Khok Phanom Di, changes in mortuary ritual appear to reflect the general social upheaval.

In this context then, tin trade economics are considered.
4.1.2 GEOLOGICAL AND GEOGRAPHICAL INFLUENCES ON POLITICO-
ECONOMIC STRUCTURE.

It has fairly been noted that mineral production is
influenced by geologic conditions and therefore market
analysis needs to be conducted by mineral economists with
good geological knowledge (Gocht et al., 1988). Any
analysis of early metals trading economics must necessarily
incorporate the available archaeological data, as outlined
above, as well as the strategic position of metal-working
centres in relation to the topography and geology.

It is recognised, in the context of this thesis, that any
scenario presented on the basis of the mechanics and
economics of metals trading in general and studies of
modern small-scale mining in particular is purely
speculative. However, archaeological interpretation of
early mining and metals trading should incorporate the
viewpoint from within this industry. While the
archaeological and analytical data to date do not
contradict the scenarios discussed, it is also apparent
that the data would also support various other
interpretations and only further research will clarify the
situation. Therefore, in spite of these limitations, the
early southeast asian metals industry is considered from
the point of view of mineral economics and their possible
influence on archaeological and anthropological
interpretation.

The major features of southeast asian geography which need
to be considered are given below, based on Higham (1989),
(Figure 412A).

**The Red River Valley, Bac Bo**

The latter half of the second millennium BC saw widespread
use of bronze tools containing 20% Sn, implying advanced
metallurgical skills in the Dong Dau Culture which
culminated in the fine bronzes of the Dong Son Culture in
the late first millennium BC. Strategically situated, the
FIGURE 412A. Geographical Regions of Southeast Asia. (after Harlan, 1989).
estuarine settlements were capable of dominating coastal trade with Vietnam and Southeast China. The Red River could provide access to the Gejiu/Dachang polymetallic tin fields as well as the cultures of the Yunnan Plains. Access across the Annamite Mountains to the Khorat Plateau would have been possible.

The Southeast Asian Tin Belt

This was a sparsely populated highland region, extending from Yunnan to the Tin Islands of Indonesia and incorporating, west Thailand, east Burma and Malaysia. Its rich and varied tin deposits were available for exploitation by various cultures and are the basis for tin ore provenancing.

The Chao Phraya-Paklong Depression

This fertile plain and major waterway is bounded to the west by the Thai Tin Belt and to the east by the copper-producing regions of the Permo-Triassic Volcanogenic Belt. The region therefore had access to both copper and tin and could influence trade to the northeast and the Gulf of Siam.

The Tonle Sap Plains and Mekong River

Estuarine settlements could be influential in controlling coastal trade. The Mekong River was a major arterial route serving the Khorat Plateau but could only be a major influence on the tin trade if the Mekong Delta settlements controlled a major market.

The Khorat Plateau

This is a fertile agricultural region which is also largely ametallic. The societies had a sophisticated culture prior to the introduction of bronze and were therefore in a position to take advantage of the burgeoning metal market. They had access to the copper deposits of Loei and Lopburi.

224
and trade networks capable of importing tin. The Khorat Plateau was better able to dominate the trade along the Upper Mekong than the Mekong Delta settlements. Tin or tin-bronze could be traded northeast from the Khorat Plateau and would be a major supplier to this region and the Red River Valley if the South China tinfields failed. The Khorat Plateau could also supply tin to the metal-deficient regions to the southeast.

**The Sichuan-Yunnan Region**

Largely occupied by the Dian Culture, this region controlled the upper reaches of the Irrawaddy, Salween, Mekong, Brahmaputra, Yangtze and Red Rivers. The region was capable of influencing cultural/technological dispersion throughout Southeast Asia. The east-west flowing Yangtze provided access to the Shang state of the Central Plain in the second and first millennia BC where 10% Sn bronze was used for weaponry (Watson, 1984). Shang influence at this time however, did not appear to extend south of the Yangtze or into the Dian cultural sphere. The region's influence on southeast asian bronze culture is hinted at by the sophisticated metallurgy of early [700-400 BC] bronze drums from Wanjiaba and Dabona on the Mekong-Yangtze watershed. Westward expansion of the Zhou in c. 500-300BC, into Dian territory may have influenced the metals economy of Southeast Asia.

It is therefore apparent that certain cultural/geographic regions of Southeast Asia are theoretically capable of controlling ore sources and/or trade and communications. These factors, which influence the development of metals trade are discussed more fully below.

4.1.3. TRADING ECONOMY

**Bronze Production and Trade**

The advent of bronze in Thailand, as discussed above, at least implies the introduction of basic technology from
elsewhere. This being so, there is little reason to suppose that metal production initially influenced the basic social organisation of a culture where the necessary infrastructure already existed. Existing organised communities were undoubtedly able to take advantage of the demand for a new commodity but the long term socio-cultural effects of economic change may have been more far reaching.

The development of a metal production economy is a natural advance on a metal goods trading economy if the goods in question acquire a high enough social value. In general it is the rule that there is a search for raw materials to fit an available technology and not to develop technology for the available raw materials (Villas-Boas, 1988). However, awareness of technology and even domestic implementation may exist for a considerable time before demand is sufficient to promote large scale exploitation of raw materials. Furthermore, increased long distance trade is the result of local need for goods and ideas rather than of foreign need to export (Hutterer, 1987).

This work attempts to consider mineral markets and exchange within the archaeological framework discussed above. That is, a sophisticated bronze-using, tribal structure developing into hierarchical, centralised polities in the period from the early-mid second millennium BC to c. 500BC. The analysis necessarily departs from conventional economics to incorporate anthropological economics in which socio-cultural traditions are frequently more influential than crude commercialism.

In prehistory the reasons for trade were usually socially complex and largely unfathomable to modern economic thinking. While trade implies an exchange or dispersal of goods, in the form of 'reciprocity', it does not necessarily incorporate commercial profit. Economic trade tends to involve redistribution rather than simple exchange (Kennedy, 1987). Social status, wealth and inter-tribal harmony were all factors. Therefore the value of commodities and trade agreements could be determined by
tact and diplomacy within the socio-cultural framework rather than by economics. Where differential social status depends on the extent of the individual's trade network or the amount of trade he can generate, advancement depends on expanding the trade network or increasing the volume of trade with existing partners (Sahlins, 1972). In both instances the market is stimulated to further production.

Tribal structure fosters inter- and intra-tribal exchange in metal goods both for use and as indications of status, whether for cementing tribal relationships or materialistic dealings. However, the organisation required to control and intensify production is a function of internalisation resulting from centralisation.

"Reciprocity" to cement inter-tribal relations developed into commercial exchange but an unfortunate fact of primitive exchange is the indeterminacy of rates. Furthermore, the rate of exchange tends to vary with distance from the source of supply. Similarly, modern concepts of competition seem to have been absent (Sahlins, op. cit.). Exchange in tribal societies may be on a direct need-for-need basis, along a linked chain of social groups, between two sources of goods. The goods from each source are transferred along the chain by a series of exchanges and the rate of exchange varies en route. Alternatively, a group deficient in trade goods or raw materials may trade for commodities for redistribution to several neighbouring societies. This development of Phoenician-like Middlemen, generating wealth through trade is crucial to the evolution of a trading economy. Such trading groups are usually centrally located but lacking in commodity resources. Their technical means of production and exchange are imported for redistribution either in form [raw metal] or transformed [bronze goods]. Typically such traders are the wealthiest social groups in the region. This prosperity is the dividend of trade, amassed from the neighbouring societies who, themselves better endowed with raw materials, nevertheless indulge in commerce rather than production (Sahlins, op.cit.). This principle is most

227
relevant to Southeast Asia because, where mine or smelter production is exported prior to treatment, the economic benefits are lost to the country of origin (Molalapata, 1988) and indications of wealth generated by tin production may occur far from the Tin Belt.

In a well developed metal-using economy, the easy negotiability of the commodities results in a regionally extended metal market. In the bronze age, this generalised market incorporates several smaller markets:

1. The market for ores, Cu, Sn.
2. The market for concentrates, Cu, Sn.
3. The market for raw metals, Cu, Sn.
4. The market for finished bronze.

These markets can differ in their geographical location, size, wealth generated, number of participants and socio-cultural framework. This study is primarily concerned with home produced bronze in Thailand and the technology of production. Therefore foreign imports of bronze are not considered.

In Southeast Asia the markets for ores and concentrates are confined to the mining sites themselves or very close to them. Indeed the evidence suggests that smelted raw metal is produced near the mining sites for redistribution. Therefore these markets are limited to the Thai Tin Belt and the copper-producing regions of central Thailand.

Several tin mining sites have been identified in Ratchaburi Province and throughout the Tin Belt but, in the absence of any chronological detail, cannot be considered relevant to this discussion. However, reports of Ban Don Tha Phet-type bronzes at Huai Suan Plu (Bennett, pers. comm.) should be noted. Other occurrences of tin such as at Ob Luang, Chiang Mai, close to the Mekong are also of interest.

Depending upon demands of the local economy, the output of
small mines may be absorbed locally. Only the introduction of Middlemen seeking sources of supply for profit, provide incentives for local overproduction. The scale of mining at Phu Lon and Lopburi indicate over-production. Demand for ore can reach the point where there is no domestic use and the miners have no conception of the ultimate use of the ore (King, 1989). The geologic controls of copper production and the spatial occurrence of the workings, suggest an oligopolistic market, whereas the widespread occurrence of small tin mines imply a more competitive tin market. In any socio-cultural context the difference in market structure for different minerals should be considered.

Transport of run-of-mine was extremely limited but the standardised production of metal ingots, evidenced at Khao Wong Prachan Valley implies widespread trade in metal.

The market for finished bronze is however, a major, wealth-creating market in Southeast Asia. Communities, with no local ore reserves, can "buy" their raw materials from the other sources, manufacture high quality, high value bronze goods for shipment to a variety of destinations.

While there is not necessarily any definite division between these Markets or divisions may vary from region to region there are definite economic and social effects on the communities involved.

It has been hinted above that the real profits of the prehistoric metal industry in Southeast Asia, were reaped by hypothetical Middlemen. These people without raw materials, were nevertheless shrewd enough to take advantage of and possibly monopolise the production of high value bronzes.

In order to maximise the profit on any commodity, it is necessary to monopolise the source. However, on a local scale in Southeast Asia this is virtually impossible. The Tin Belt is vast and the commodity widespread. If one
postulates that the source of tin were monopolised, then it is necessary to believe in social and political organisation on a large scale. The benefits of controlling the source must be weighed against the cost of protecting it. Where the commodity is as widespread as tin in Southeast Asia, the centres of tin production would have been in a constant state of flux. On the other hand, it is possible to envisage temporary control of a limited source area. Such limited monopolisation would arise if there were competition in demand but would result in loss of profit and abandonment of the source. This would evidence itself in numerous small sites in the Tin Belt with a short lifespan and rapid abandonment. It is admittedly, an unlikely and indeed, unnecessary scenario. Monopolisation was more likely to occur in the copper markets. The Thai bronze industry could have been well controlled by monopolisation of only one market.

Prior to the advent of commercial traders, small scale mining begins and continues for long periods, in the absence of any significant external influences (Robertson, 1988) and may take place in a state of harmonious equilibrium with little social impact. Social disturbance is caused by the expansion initiated by commercial Middlemen. Sudden expansion in an agricultural community can result in the subordination of subsistence agriculture to the lure of "profit" from mineral production. If this happens, the society is subject to total collapse if the market falls, with the resultant abandonment of villages. Similarly this tends to generate a social sub-group specialising in mineral production i.e. miners and smelters.

Societies which develop a high level of mining technology and a mineral-based economy expand only if they maintain control over the sources. The appearance of commercial Middlemen, exploiting production, results in a rapid decline in local living standards and the removal of metallurgical innovation and artistry to the cultural centres of the Middlemen.
Similarly, the interdependence between the Middlemen and the suppliers of raw materials, creates an unstable economic situation, especially where long distance trade is involved. If the trading society collapses then the dependant mining society follows suite. If social upheavals along the trade route disrupt commerce between traders and suppliers, the latter collapse. More importantly, a technological innovation such as the appearance of iron in a bronze dependant economy will reduce the value of bronze to the extent that that total collapse or wholesale re-evaluation of the economy must occur.

The above scenarios are undoubtedly hypothetical but are based on what can and does occur in primitive communities involved in mining. If similar events occurred in Southeast Asia in prehistory then the archaeological record should provide some evidence for them.

Tin Mining in the Historical Period

Although tin mining and processing technology in early prehistory is largely unknown, some conclusions may be drawn from the general methods used prior to industrialisation.

The exploitation of tin deposits in antiquity depends on a number of factors:

1. Geographical location, the availability of markets.
2. Accessiblity: deposits must occur at or close to the surface.
3. Climatic conditions.
4. Workability: minerals must be identifiable and easily extractable.
5. Availability of water.

However, if these conditions are satisfied, to place early tin mining in its proper context, it is necessary to be able to:

1. - identify the different types of tin mining site
2. - determine, as far as possible, the social milieu in which mining was occurring.

The Identification of Sites

Two of the main problems with locating ancient mining sites in Thailand are the nature of the terrain, ie jungle (Plate 4), which can make it virtually impossible to locate a site which has been abandoned for any length of time, and the climate. Mining however, does leave scars on the landscape which can survive for centuries, if later mining does not obliterate them. At the same time the obvious place to look for ancient mining sites is at a modern mine and close collaboration with mining companies is imperative. Mines where there are indications of ore at surface should be a primary target. Modern mining companies or their local personnel usually know if their deposit has been worked in antiquity and may have collected artefacts. Very often exploration has been conducted on old workings as these are generally indicative of the high grade ore (Metallgesellschaft AG, pers. comm.).

Another factor which affects the landscape in mining areas is the geomorphological degradation by climate owing to the influence of miners (Plate 6). Especially in regions of high seasonal rainfall and tropical forest like Southeast Asia, the long term effects of disturbance can be significant. Dense vegetation such as rainforest intercepts rain and protects the soil from erosion, but if that cover is removed or reduced by mining [or farming] activity, degradation occurs by splash erosion and runoff (Tricart and Cailleux, 1965). The result of this can be twofold. Firstly, possible mining sites may be targeted because erosion and rill formation have prevented regeneration of forest on a site but secondly, evidence of mining activity in the form of waste heaps may be obliterated as splash erosion levels the surface again. The latter is an important mechanism of destruction at alluvial mining sites where the fine sands and gravels, which constitute the waste, are easily washed away by rain. However, mining
sites where the virgin forest has been removed may also be revegetated by a totally different flora from that of the surrounding forest. The secondary flora may consist of species more capable of maintaining a foothold on eroded and shifting substrails or species tolerant of high metal contents. The tree ferns at Song Toh, Kanchanaburi Province are an example (Plate 7) (Pedall, pers. comm.).

Alluvial tin mining often works and reworks the same deposits with the result that the earliest workings are generally destroyed but a rich and easily accessible deposit near ancient trade routes or habitation sites may have been worked from ancient times.

The Working of Different Tin Deposits

Alluvial tin mining leaves a different set of scars on the landscape to lode working and open pitting. The main working not only is at surface and generally shallow but also works rich deposits associated with water. This means that there is not the large removal of gangue along with the ore to create large scars on the surface and that flowing water has probably destroyed much of the detail. Characteristic scars are however apparent and are best discussed by looking at the current situation in Thailand.

Pilok, Kachanaburi

At Pilok, in the mountains on the burmese border, both vein/stockwork and alluvial cassiterite are worked from weathered granites. The cassiterite is coarse-grained and easily picked by hand. Although the modern mining company works three mine faces with monitors there are a number of contract workers using palongs and dulangs in the area.

There are also some small independant mines, usually illegal and operated by three or four Burmese with a monitor and palong. The small operators are constrained by climatic variations, as their monitors are maintained by pressure generated by head of water, not pumps. This is
provided by a reservoir some 30 m above the face and slurry is fed into the palongs, about 2 m in length, for gravity concentration. The reservoir water can also be used directly to feed the palongs in a stream gully. This was the method used before the introduction of hydraulic monitors. In most cases where monitors have been introduced, using head of water pressure, they have simply superseded the usual ground and box sluicing methods of an earlier age (Plate 5). The principle is the same: i.e. to use a flow of water to wash ore from bedrock into a sluice.

In the wet season, the contract workers at Pilok wash the sands and friable granite in the stream beds using dulangs and palongs. Hush gullies [ground sluicing] are also apparent on the slopes. Hush gullies are formed when a reservoir of water is released downslope, to remove overburden and wash out the ore. They are combined with ground sluices into which the ore is washed. Further details of mining methods are given in Appendix 8. During the dry season, water is led from the reservoirs for dulang washing and the miners drive short adits (Plate 8) into the granite to extract ore for washing. The adits are just large enough for a man to enter with a pole to break the ore and a basket to carry it. They slope downwards and inwards for about 10 m and are unsupported and remarkably unstable (Figure A9.4). These primary ore mining areas are characterised by the adits, with a small rock crushing area at their entrances, where the ore is partially crushed and hand-sorted to minimise the transport of gangue to the washing site. Heaps of rock rubble occur which are not easily degraded and may remain for centuries to identify the site.

Klong Thom, Bang Saphan, Prachuap Khiri Khan

This is a mountainous region where gold and cassiterite are panned from alluvial deposits along the river valleys, by family groups. The ore-bearing strata are basal conglomerates overlying a schist at a depth of about 10-15m. The local miners dig shafts to bedrock (Plate 9) and
Plate 4. An Overgrown Mining Region, Kanchanaburi Province.
Plate 5. Simple Palong into which Ore Slurry is Washed, Kanchanaburi.

Plate 6. Abandoned Tin Mining District Showing lack of Revegetation.
Plate 7. Tree Ferns on Land Contaminated by Heavy Metals.
Plate 8. Small Mining Adits at Pilok, Kanchanaburi Province.
carry the ore in baskets to the river where it is panned to concentrate gold and cassiterite (Plate 10). All the family are engaged in this operation, men, women and children in family groups. The jungle around the village is riddled with shafts, both in use and abandoned. Many of these have been sunk below the water table and can only have been in use in the dry season. According to the locals, mining had been practised in this way for many generations.

The shafts are sunk through soft alluvials and the waste heaped around the site. Over a period of time the shafts collapse and the waste heaps are washed away, leaving a mild hummock/hollow terrain which could easily be overlooked (Plate 11).

The Peninsular Coast

At Ranong, Chumporn, Takua Pa, Phangnga and Phuket, onshore and offshore alluvials are worked and have been exploited for many centuries. These are coastal and alluvial plain workings and, a head of water being unavailable, surface alluvials are worked by panners (Plate 13), some with box sluices. Buried alluvials are raised to the surface for concentration resulting in the formation of ponds and swamps over the mining area (Plate 12). Unlike similar mining in mountainous areas, the characteristic discarded boulders are largely absent.

The offshore dredging is the largest producer of tin-in-concentrates today but although it may seem to be outside the scope of ancient miners, this may not necessarily be so. Local miners in Ranong say that it has been the practise for generations for locals to 'fish' for tin from small boats. They throw a bucket, attached to a rope, overboard and effectively dredge for alluvial cassiterite. This process developed from working beach sands and following the deposit offshore. The method may be of considerable antiquity, especially as a major market would have been along the coasts, easily accessible to coastal
Plate 9. Simple Mining Shafts, Prachuap Khiri Khan, Province.

Plate 10. Washing Ore, Prachuap Khiri Khan Province.
traders. The only evidence of such ancient working however, is likely to be smelting sites.

Ban Bo Kaeo, Samoeng, Chiang Mai

This lies in the mountainous region of northwest Thailand. The primary deposit consists of coarse cassiterite and scheelite in a sheared, soft, weathered matrix. This lies at the head of a valley and associated pegmatites are mined as well as the derived alluvials in the plains at the foot of the valley.

The mines, though commercially operated, are worked by contract workers in family groups, mostly from the hill tribes. The hilly nature of the terrain at the top end of the valley and the multitude of deep stream channels allow water to be used to the best advantage and large reservoirs are built at the top of the mountain above the mine for use in the dry season, as at Pilok. Some of the streams are dammed at strategic places for sluicing and to provide a source of water for hushing (Plate 14). In other places the soft ore-bearing rock is broken from the faces by means of long poles. In falling it is broken up and the miners can shovel it into a handy palong, often raised, in which the ore is concentrated (Plate 15). Very often the outflow from the palong is being worked by children with dulangs to recover the finer material (Plate 18).

Smaller palongs are built in the stream beds themselves [box sluices and ground sluices] (Plate 17) where the alluvials in the stream banks are exploited. The ore-bearing sands and gravels are shovelled into the palong and the stream is allowed to flow through to wash the ore from the gangue. Panners also operate in the stream beds.

On the alluvial flats below the valley, families work the tailings from upstream by panning. They also dig shafts to reach the buried alluvials (Plate 16). These shafts are
Plate 11 Hummocky Terrain in a Kanchanaburi Mining District

Plate 12 Alluvial Mining Region on Coastal Plain, Ranong
Plate 13. Small-Scale Alluvial Mining, Phangnga.
about 1m in diameter and are similar to those at Klong Thong except that, at the bottom [about 10m], the miners drive out in all directions for about another 10m to extract the orebearing strata (Figure A9.3). This they carry out in baskets to be washed by the dulang operators in the streams. As the streams dry up the ore is washed in small ponds, excavated in the mudflats, to which water can if necessary be piped or carried. Bamboo pipes are still much in evidence (Plate 19).

When looking for indications of what might remain for centuries to indicate ancient mining sites Samoeng is a useful guide. Hush gullies leave noticeable features which remain and are indeed enhanced over the years, into broader, straight gullies down mountainsides. Tin streams, which have been intensively worked by panners and palong operators, are artificially deepened and new streams made by diverting water for use by other miners until the area becomes a network of stream channels which bear little resemblance to Nature's handiwork. Furthermore, as the miners dig gravel for their pans or palongs, they extract the larger rocks and pile them out of the way to create stone-lined gullies (Plate 20). Sometimes they build stone retaining walls in this way to guide ore slurry into the palongs. Either way this feature should be readily identifiable in ancient tin mining sites of this kind.

On the alluvial flats however, although there may be 200 or more panners operating at any time, producing up to 3 kg ore/person daily, no evidence remains from one season to the next.

Song Toh, Kanchanaburi

At Song Toh the paired shafts are sunk through the lateritic soils and remain fairly stable though much overgrown and may be easily identified by anyone careless enough to fall down them.
Plate 15. Miners Breaking Ore to be Shovelled into Raised Palong, Chiang Mai Province.
Plate 16. Old Mining Shaft, Samoeng, Chiang Mai Province.

Plate 17. Simple Palong, Samoeng, Chiang Mai Province.
Plate 18. Small Boy Working the Outflow of a Raised Palong.
Summary

It is therefore important when discussing ancient mining sites in Thailand to emphasise that even when concentrating on tin mining sites there are a number of factors operating and no one set of characteristics can be said to represent all tin mining sites in Southeast Asia. It is most necessary to be aware of the differences and the reasons for these differences. To describe the geomorphological effects of only one type of mining site would be unforgivably misleading.

Historical Information on Social Contexts

Mining

Quite apart from modern observation of current mining practice in underdeveloped regions, the literature of colonial mining provides observational records of ancient practices.

Many southeast asian tin mines, ancient and modern, have been worked by chinese labour and it may therefore be said that it is difficult to establish what is local technology and what is chinese import. It has been noted however, that the chinese did not establish any great presence in the mining industry of Southeast Asia until the 16th century. The early timbered shafts at Song Toh Lead Mines have been dated to the eleventh century (Busse, pers. comm.). Furthermore, the Chinese tended to use labour intensive methods employing coolie labour to work the large lombong, or open pit, mines. The Thais and Malays worked small family mines.

Prior to the arrival of large numbers of chinese, tin mining in Malaysia was a small-scale, disorganised affair. The malay miners were also actively engaged in agriculture and it was therefore the constant supply of landless chinese labour, dependant on wage employment that allowed the tin industry to modernise and expand in the 18th
In their spare time Malays panned for tin in streams and in virgin fields the dulang washer could earn a comfortable income. Considerably more in fact than earned by a labourer in a tin mine. Another popular method of malay mining, which required more organisation, was lampan or sluicing. In its more primitive forms this method involved digging a ditch or race in a stream bed into which the ore was shovelled (Appendix 8). Lampan mining could only be used to exploit rich stream deposits in hilly terrain where sufficient water power was available but could not be used to tap the richer ore at bedrock (Hughes, 1949; Smith, 1980-82).

In order to reach the deeper ores pits were sunk but at deeper levels drainage became a problem. In the upper parts of the plains and the foothills the ore was usually close to the surface and the pits, or ludang mines, seldom more than a couple of metres deep so that a bucket was usually adequate to keep the pit dry. Drainage became more of a problem in the deeper, tebok mines. The walls needed some support and some mechanical method was required to lift the soil because of the small workforce. A typical tebok mine would have a workforce of about 6 men working a pit about 17' sq and 13' deep. The pit walls were supported by a rough wooden framework and the ore and water lifted by the kait ayer and kait raga respectively. The kait raga was a simple balance pole with a bucket at one end which could lift water from the bottom of the mine and empty it into a shute leading away from the pit. The kait ayer operated on the same principle but had a basket instead of a bucket, and was capable of swinging in a horizontal arc to deposit the ore at a distance.

These malay mines were slightly different from similar pits found in the Lahat hills which were about 8' in diameter and 20' deep. In Pahang [Selinsing] there were derelict mines with remnants of galleries, stopes and shaft, the
construction of which was said to require more mechanical
skill than the Malays possessed. These mines, and others
found in Kinta, were ascribed to the Thais and called
'Lombong Siam' by the locals. Whatever the truth, the malay
knowledge of drainage was insufficient to allow them to
exploit any but the driest of deposits and any increase in
rainfall or seepage effectively halted operations. The
result of this was that the Malays concentrated their
efforts on the foothills and could not exploit the rich
deposits of the alluvial plains. The Thais however, were
excellent hydroengineers, as were the Mon-Khmer, and
developed efficient drainage systems enabling them to
exploit the richest deposits.

The malay mines were considered very inefficient and as
backward as their technical knowledge. Manpower was short
and therefore the deadwork could not be kept in advance of
production. Mining could not start each day until the mine
had been drained of accumulated water and even then someone
had to work the kait raga and kait ayer all day. This
inefficiency of the drainage system meant that the mines
had to be abandoned in the rainy season which was when the
smelting was done.

There is little evidence in Southeast Asia that large scale
exploration for ores occurred by shaft sinking and
exploration galleries were seldom constructed. Shafts were
sunk on lode and the galleries followed the ore. The
central organisation required to coordinate the
construction of exploration drives was lacking.

This picture of southeast asian mining indicates a
fragmented mining economy with, especially in Malaysia, a
casual attitude to commercial expansion which probably
existed from early prehistory to the 2nd millennium AD
expansion. The Thais seem to have been more commercially
orientated and technologically sophisticated, possibly as a
result of external pressure to export. Malaysia was less
influenced by demand from China but possibly more subject
to demand from later arab expansions.
Chinese tin mining in Bangkha probably improved on the local mining method of digging shallow pits. Chinese methods in Yunnan developed to reach the tin lodes and J. Crawfurd, writing in 1820, observed that, in Bangkha, the miners sank a narrow cylindrical shaft, capable of admitting one person, until they reached the ore-bearing strata. They then followed the strata which 'often fall upon them'. Without drainage, these mines were restricted to naturally drained slopes. The method however, is identical to that observed near Chiang Mai today, by the Karen hill people.

In Larut, the Chinese abandoned ditches in favour of the lanchut in about 1850. This implies that, in terms of prehistory, the use of the lanchut may not be a technological factor.

In antiquity, Malaysia was regarded as a source of gold. This was derived largely from the hornblende granites, diorites and volcanics of the Central Belt. It is also found in smaller quantities with the tin of the Western Belt. However, gold in Malaysia and South Thailand is widely scattered and, although mined on a small scale in the past, it is not mined by modern methods except at Raub. Some small mines existed in Perak and Kelantan and it was sometimes produced as a by-product of the tin mines. Before modern mining at Raub, there was said to exist a malay mine known as the 'Raub Hole'. This was a water-filled open pit into which the Malays dived for gold (Scrivenor, 1928).

Any mining region would contain abundant small workings, producing minimal output but providing a small income between paddy seasons. Generally the malay miner produced sufficient for his needs and no more. The Chinese, on the other hand, were interested in profits. The Malays believed that the Chinese knew everything about mining but, prior to the advent of european miners, much of their equipment was simple adaptations of agricultural tools: the water wheel and the iron shod rice pounder for crushing ore. Similarly their knowledge of minerals was extremely limited and
costly mistakes were often made. Records contain accounts of garnets mistakenly concentrated by Chinese under the impression it was tin ore. Haematite was similarly misidentified as cassiterite. Malay miners were not renowned for their mineralogical or metallurgical expertise. They referred to ore as 'bijeh' [seeds] and regarded it as tin seed. They frequently tried to extract tin from a variety of minerals which had nothing to do with tin. The Malays described such minerals as 'unripe seed' or 'seed that cannot be cooked'.

The primitive mining equipment of the Malays and Chinese has the advantage of mobility over modern equipment. This allowed the smallest deposits to be worked for a short time and then the whole plant would be removed to another site.

The Chinese tended to use short palongs which allowed a certain amount of tin ore to escape in the tailings. Unfortunately this has meant that ancient mining sites became attractive to modern companies who rework the tailings. Any archaeological evidence is destroyed in the process. Even the Malay dulong washers would work the outflow of the palongs. While the Chinese were industrious miners they did little prospecting and relied more on the Pawangs [local witch doctor] or inspiration to locate ore.

In 1927 the itinerant Chinese miners produced more tin than the managed mines. The Chinese labour system closely paralleled the Cornish system in that they were 'hun' men [tributers], 'kong-si-kong' [wage earners] or 'nai-chang' [piece workers].

Almost no literature exists concerning pre-industrial tin mining in Thailand or her neighbouring states, with the exception of Malaysia. The observations of mining engineers and geologists in Malaysia at the turn of the century, such as J.B. Scrivenor (1928), do provide some insight into both mining methods and the local culture. It is therefore appropriate here to review primitive Malay mining culture as a framework for prehistoric mining culture in Southeast
Asia as a whole.

**Customs**

Malay mining was also riddled with superstition which could be costly as the Pawang, had to be paid as intercessor between the miners and unfriendly supernatural forces. The local Pawang collected large fees for locating tin ore or 'calling' it to the place where the Chinese or Malays wished to mine. Fortunately, as tin ore was widespread, the Pawang's few failures could be attributed to some violation which caused the tin to remove itself. He was apparently the prospector which suggests that the methods used to identify ore sources were semi-religious or at least the closely guarded secrets of certain individuals. The Pawang not only exacted payment for both these functions but also imposed fines for the breach of mining superstitions and collected 1 slab of tin per annum for every sluice box in use or the entire yield of one of the races. The organisation of the malay tin industry was based on custom and remained unchanged until the mid-19th century.

Both tin ore and gold were believed to be alive, capable of moving and having souls; the gold in the form of a deer and the tin of a buffalo. One of the most important precepts of early mining was that the ore should not be offended. Otherwise it would leave.

Prohibitions abounded. Some are obviously of recent provenance and the reasons for others only guessed at. Boots and umbrellas were forbidden in a mine, as were raw cotton, black coats, hides, earthenware, limes, coconut husks and weapons. Bathing, chopping wood, quarrelling and gambling were likewise prohibited and one of the strictest rules was that a miner must wear trousers. Furthermore they must be his own.

However, once the tin ore was won, the Pawang apparently had the monopoly on smelting.
The last observational reports on malay tin mining are dated circa 1920. By 1940, descriptions are limited to the 'new technology' (Hughes, 1949) of dredging etc. although some comments about chinese open cast methods still appear. Virtually no mention is made of malay methods.

SMELTING Sn

Malay smelting was a simple affair and was successful largely because the alluvial ores had none of the impurities associated with lode ores. These had been eradicated by the weathering process. The alluvial ores could be dressed by washing and reduced in simple shaft furnaces, in which charcoal acted as both fuel and reductant. In fact dulang washing was a method of recovering ore which had been mined and dressed by natural processes. The resulting concentrate could be 90% SnO₂. In the lampan mines, and also the ludang and tibok mines, the ore was dressed in three stages, first in the races, then in an eight foot palong (a sluice box made of a split tree and hollowed out) and finally in a pandei which was a smaller palong. The ore was then reduced in simple clay furnaces.

The malay clay furnace was charged with alternate layers of ore and charcoal and the blast was produced simply by blowing into the furnace along a bamboo pipe. The molten metal emerged from the lower end of the furnace and dropped into a receptacle below (Figure 413A).

An advance in the local malay methods of tin smelting occurred with the introduction, probably from Thailand, of a Siam furnace consisting of a low clay cylinder in which the blast was produced by a crude blowing apparatus made of bamboo pistons standing on end and worked by one man (Plate 21). The tin was ladled out into moulds making slabs about 2.75 lbs.

Another introduction, possibly from China, was an air furnace ie a shaft furnace worked by natural draught. This
Figure 413A. Malay Clay Furnace.

- 6ft -

2ft -

Crucible 2ft

5ft

1½ " Bamboo blast pipe.

Flote

Clay plug with small taphole

Cylindrical clay tuyere.
furnace was very popular but could only be used when a supply of good, dense charcoal was available. It produced a high quality tin for much less effort but eventually had to be abandoned as the Kampa [species unknown] tree from which the charcoal was produced was soon eradicated from the mining districts.

In construction the air furnace consists of a mass of kaolin rammed inside a casing made of bamboo or poles stuck in the ground and held together with hoops of rattan. Kaolin is specifically mentioned, perhaps merely because it was readily available at tin mining sites, rather than for any specific property. In some cases the rattan was replaced by hoop-iron. The draught is supplied by two clay tubes about 2 inches in diameter, clayed into a square opening at the back of the furnace. After construction, this crude apparatus is allowed to dry for some months.

Another type of furnace described as a primitive furnace consisted of a hole in the ground about 20" deep with a diameter of 14" and the blast was delivered through 1-2 pipes driven through the ground from a pair of bamboo pistons. In form these furnaces appear to be similar to the lead furnaces at Song Toh. A 4-5 hour shift would produce 20-24 lbs of tin (Figure A3.1).

There were many variations in the details of construction, dimensions and shapes of the furnaces used in different parts of the Malay Peninsula, depending on the quantity of ore and charcoal available and, apparently, on the fancy of the smelter.

Smelting practises varied from district to district but they all had one thing in common: they left very little trace, unlike lead smelting slags (Plate 22). In some places it was a continuous operation, if seasonal, but in others it was carried out intermittently as concentrate was accumulated. In Bankha smelting was only done at night and then only for four nights before allowing a day for repairs. Also the season was limited to a period starting
from November. Elsewhere blasting occurred all year but only at night and in some regions there was a communal furnace rented to the owner of the ore.

In the Islands, particularly Borneo, tin smelting was a late development, and the technology was apparently adapted from the local iron smelting technology. Nor was the slag ever resmelted.

The primary smelt resulted in a tin rich slag which was examined as it cooled from the furnace. If it contained unreduced oxide it was immediately returned to the furnace but the discarded slag could still contain as much as 20% Sn, much in the form of prills. It was intentional on the part of the smelters to produce a tin-rich slag as this resulted in a high quality tin metal and every so often a slag smelt would be performed in which all the primary slags would be resmelted for the tin. The slags were very often broken up and washed in the rivers as if they were tin ore and the heavy tin-rich portion re-smelted. The final slags were sold to slag smelters who extracted the remaining tin leaving a final slag of about 1% Sn. These practises serve to minimise the amount of slag left to be discovered by archaeologists as much is washed away in the streams as fine particles or has been resmelted so many times as to leave very little anyway and it has usually been broken up.

On the whole the Chinese were superior to the Malays when it came to smelting and the Malays preferred to sell ore to the Chinese rather than smelt it themselves. With the result that very little is known about pre-chinese smelting methods.

The Chinese probably introduced smelting to Bankha from whence it spread to other parts of the Malay Archipelago.

Within this general mining framework, or something very similar, tin mining was undertaken in prehistoric Southeast Asia. Furthermore, this industry must have been an integral
Plate 22. Lead Slags at Abandoned Mining/Smelting Site
Bo Ngam, Kanchanaburi Province.
part of the economic and social life of the bronze-using cultures.

Although historical information on pre-industrial mining and smelting is fragmentary and caution should be exercised when extrapolating into prehistory, some concept of social customs may be obtained. The picture of rural tin mining during the last century seems to imply a haphazard industry which does not seem to equate with complexities of the industry at the height of the bronze period. It is possible that the advent or generalised use of iron resulted in a steady decline in tin production and that the prehistoric industry was more sophisticated and better organised than in the later historical period. An alternative to this may be that the importance and value of bronze fluctuated after the advent of iron and been dependant on the location of ore sources. Bronze undoubtedly remained an important commodity in the iron age with new exploitation of tin deposits continuing although the trading structure may have changed to accommodate competition from iron. However, descriptions of early types of mine, smelting practices and furnaces can undoubtedly provide a guide to archaeological interpretation of sites and artefacts.
It is apparent from the preceding chapters that the geochemical variation of tin deposits in Southeast Asia is sufficiently wide to allow provenancing of tin on a regional basis. Supported by regional geochemical variations in the metallogensis as a whole therefore, some conclusions on the sources of tin used in the prehistoric bronze industry are possible. However, it would be unwise, at this stage, to make definite statements on ore sources. The complexity of small scale variations between deposits of similar type makes the local identification of mining regions difficult, without a considerably larger analytical database. The unusual genetic types of ore deposit are however, more easily identifiable from their TEP's, against a background of more common genetic types.

Similarly, although it was believed that alluvial tin deposits would be difficult to categorise, unless their primary source were known, it now appears that this is not so. The preliminary evidence suggests that small alluvial deposits retain the characteristics of their source and hence the regional trace element profile. The large alluvial tinfields such as the Katthu Valley, Phuket, which derive their cassiterite from a variety of sources, acquire a complex and largely unique TEP. The accessibility of these ores suggests that major tinfields such as the Gejiu ores of South China and the Kinta Valley ores of Malaysia would benefit from further study.

Furthermore, although there is a disturbing shortage of detailed geochemical and mineralogical information for Southeast Asia and South China as a whole, lithological and structural information is more readily available.

The examination of background data has resulted in an awareness of how the various types of geological information can be used to provenance ores. Although this
research has concerned itself primarily with the investigation of Trace Element Profiles for tin in ores and bronzes, it cannot fail to recognise the restrictions of such a limited approach. The relevance of other geological information is mentioned in the preceding chapters and appendices.

As in any exploration programme, much useful information can be obtained before commencing field studies. Chapter 2 indicates that the geological structure of Southeast Asia, defined by the tectonic history of the region, significantly limits the areas where certain ores may be found. It is therefore possible to predict where ores may occur in relation to archaeological sites, without necessitating expensive, reconnaissance programmes. In addition, provenancing would benefit if on-site investigation of early mining and smelting sites included increased attention to lithological and mineralogical detail. It has been shown above that both the mineralogy of the waste rock and the crystallographic details of cassiterite can be used to identify ore sources. The importance of such information should not be overlooked.

The geochemistry of Southeast Asia however, is obviously extremely complex and the trace element variations of the ores themselves dependant on:

1. Regional lithogeochemistry and tectonic history.
2. Genetic type of deposit.
3. Concentration processes.

This research shows that the possibilities for metal provenancing are far greater, with new analytical techniques, than has previously been considered. It has become apparent that a parochial approach to provenancing in Southeast Asia is limiting to the wider interpretations of the early metals industry; hence the attempt to correlate data from further afield than Thailand.

In spite of the limits to the available background
geochemical data mentioned, conclusions can be drawn, both on the sources of ore in antiquity and on the nature of the metals industry itself.

It should be emphasised that many difficulties exist in interpretations of this kind, not only in the deciphering of geochemical data but also in the recognition of the problems themselves. Much of the data lends itself to more than one interpretation and the resolution of these anomalies must await the results of further research. The behavior of trace elements during smelting, contamination by fluxes and charcoal and recycling or combining of metals may all confuse the interpretation of data.

These variables negate the effective use of quantitative data for identification of ore sources and the research has relied on qualitative data and the identification of trace element anomalies. In this respect Inductively Coupled Plasma Source Mass Spectrometry has proved invaluable. The high sensitivity of the technique allowed the presence of an element to be established and the rapid simultaneous determination of trace elements provided sufficient regional background data for areas of interest to be highlighted. Although analytical problems do occur, these are recognised and are not insurmountable. The recent advances in Laser Ablation ICP-MS, the increasing sensitivity for lead isotope work and the development of sophisticated software to identify and remove interference effects, combine to make this technique a promising addition to those already in use in archaeological science.

To date, the generation of large volumes of analytical data, subject to interference effects, has meant that complex statistical procedures have not been feasible. However, computer-aided analysis of the results has not only provided useful data but also identified the software needs of the future. Much of this software is currently either under development or already exists in a basic form although some adaption is required, of programs designed to handle geochemical data, for use with metal alloys.
ICP-MS is the most promising technique available. The amount of data generated rapidly is vital for the regional geochemical overview required. Areas of special interest can then be targetted for more detailed sampling and more sensitive isotopic analysis by alternative methods better suited to small sample batches where time is not a factor.

ICP-MS also produces elemental and isotopic spectra of very high quality, with little background interference and good peak resolution. The software enables the spectra to be manipulated such that any part may be examined in detail and compared with each other. The spectra are, in effect, characteristic TEP's of the samples analysed and were found to be reproducible in separate analyses.

It is therefore feasible that a library of TEP spectra, for qualitative comparison would supplement a large, numerical, analytical database. This would provide a rough guide to the trace elements present in any region or deposit and instant recognition of relevant elements. This flexibility of ICP-MS data is as much an advantage in this work as the rapid generation of the data itself.

The number of samples available to this project is not considered sufficient for many conclusions to be drawn with absolute certainty. However, in spite of the problems and limitations encountered, the data suggest that further work would allow a more definite response to the tentative conclusions drawn here.

The analyses have shown that some trace elements are of more use at present than others and also that their uses are varied. This however, does not imply that other elements are of no use, merely that research to date has been unable to determine the significance of their presence, absence and relative abundance.

Some elements; W, Sb, Hg, Ba, Bi, Au, Nb/Ta, may all be used as regional indicators when examining bronzes of unknown provenance. However, the same elements may be used
as local indicators where the production site of the bronze is known.

The genetic type of ore deposit cannot be determined on the basis of single element anomalies. Groups of elements however, may be indicative. The REE's, Cu/Zn and Fe/Mn may all be used tentatively to suggest types of deposit.

It is apparent that the isotopic ratios of some elements vary between deposits but the data is at present too limited and too complex to provide useful information as yet. Furthermore, the lack of research into the behaviour of isotopes during smelting limits the use of isotope ratios in provenancing bronzes.

It must be emphasised that few of the above elements are totally absent from cassiterite deposits and that only significant anomalies may be considered indicative. Furthermore, in a primary source, the occurrence of an indicator element such as W, may be localised within the deposit. However, alluvial sources are generally more homogeneous in this respect.

The processing of cassiterite ore also has a significant effect on the TEP of ores and bronze. It has been noted above that modern cassiterite concentrates lack the magnetic fraction of ancient ores, perhaps to the extent of removing a significant W, Fe or Ti anomaly. This danger can however, be negated by extracting samples prior to magnetic and high tension separation.

Panning by itself can be a very efficient means of concentration, especially when coupled with hand sorting. Careful concentration can remove a very high proportion of REE-containing species, leaving a concentrate contaminated only with other heavy minerals eg. Ba, Zn, Pb species. Therefore a TEP may reflect the genetic type of ore source, the geographic region and/or the efficiency of processing.

The TEP's of the bronzes, while suggesting that bronze
production sites are not necessarily near the mining sites, imply that trade in ores was not long distance. The TEP's for the Khorat Plateau bronzes are consistent with ores from northwest Thailand while those of the Kwae Valley/Chao Phrya bronzes are consistent with ores from Kanchanaburi, Ratchaburi and Tavoy.

The geochemical evidence presented supports the current views on southeast asian metallurgy. The early thai miners/metallurgists were producing a tin concentrate of considerable purity which was undoubtedly the result of skilled mineral processing. They later enhanced their metallurgical skills and experimented with various alloys, using Pb, Sn and Bi. A high degree of specialisation is apparent in the Tham Ong Bah drums where trace elements are so low as to have little value in provenancing.

The Ban Don Ta Phet bronzes, while showing alloying skills also indicate very poor mineral processing, possibly as the result of mass production.

The scenario supported here is that of an organised society in the early 1st millennium BC, which had developed a sophisticated mining and mineral processing industry, capable of supplying a bronze manufacturing industry with high quality tin. By the later 1st millennium BC, sophisticated alloys were being produced from high quality tin and, especially at Ban Don Ta Phet, there are indications of mass production, leading to the deterioration in the quality of tin produced owing to inadequate processing. Preliminary analysis of bronze from Non Nok Tha suggest that it falls into the category of early, high quality tin bronze.

Chapter 4 has presented an interpretation of how a primitive society can be influenced by basic mineral economics. While it is recognised that such hypotheses are difficult to support with hard archaeological evidence, it is felt that the archaeological/anthropological study of the early minerals/metals industry requires an
understanding of mineral economics. It has been argued that the metals trade is subject to the same market forces as any other commodity trade in prehistory. However, it has also been noted that metals production, trade and technology is more closely linked with aggression than other commodities. Increased production of metal weapons destabilises social structures and stimulates the metals industry to even greater production. Such social effects may be recognisable in the archaeological record as increased emphasis on metal for weapons rather than tools or decoration; possible changes in settlement patterns in the early bronze periods; perhaps the development of well-defended settlement sites and possibly major changes associated with the advent of iron.

A brief review of the records of pre-industrial mining society in Southeast Asia does indicate to the researcher the rather haphazard and custom-bound nature of early mining. Native southeast asian mining customs have undoubtedly been severely influenced since the 15th century by the Chinese and their technology. However, the picture of native mining in 19th century Malaysia shows a very fragmented system with little or no central organisation, even locally; subject to superstition and relying as much on luck as geological and technological know-how. At the same time, records of smelting practices imply a sophisticated knowledge of tin metallurgy calculated to produce the highest quality tin possible before producing lower quality tin from the slags.

It appears therefore, that, in the historical period, tin mining was the province of anyone with the inclination and spare time. It required some luck but not much specialised skill to produce a concentrate from an alluvial deposit.

Smelting tin ore on the other hand, was a skilled and specialised occupation and may have been a full time trade of certain families. However, the extrapolation of this information into the 1st millennium BC assumes that the same market forces existed. Three major events could have
radically affected the tin industry since the 1st millennium BC; the advent of iron; the influence of the Chinese; the demand for tin from the industrialised West. If the demand for tin in the bronze-using cultures of prehistory were great, then it is possible that early mining technology and organisation was very sophisticated and that there has since been a marked decline. It is equally possible however, that Malaysian mining has always been less sophisticated than that of the Thais and more northern cultural groups.

Pre-industrial mining lore and social customs associated with mining communities are complex and care must be taken when extrapolating into prehistory. However the production of tin was undoubtedly a major industry involving technological specialisation in mining, mineral processing and smelting. Nevertheless, centralised control appears unlikely and tin mining merely a widespread occupation of individuals. Tin smelting as a specialised trade may have existed with a sub-group specialising in slag smelting.

Primitive mining technology in Southeast Asia appears to have always been confined to techniques which are easily moved to other sites or easily built from scratch. Fixed installations and technology requiring a centralised 'plant' are not in evidence. Such technology is favoured by small-scale alluvial miners whose lifestyle is largely itinerant. They can work a small deposit for a few months and move on thereby leaving very little sign of their occupation. Under these circumstances the trace element profiles cannot normally be related to specific deposits but only to regions. The importance therefore, of the major producers; Kinta, Katthu, Gejiu etc. and unusual genetic types; Takua Pit Thong, with their characteristic TEP's is evident.

The data yielded by this study is, as yet, insufficient to support any new theories on the southeast asian metals industry nor the broader theories of trade and economics. However this evidence of sophisticated bronze on the Khorat
Plateau, the specialised production at Ban Don Ta Phet and the decline of tin mining technology tend to support the overall view of mineral economics expressed above.

In future, the correlation of ores and pure metals from archaeological sites should be attempted wherever possible. Alloying produces a chemical fingerprint of considerable complexity and a sophisticated statistical technique will be required to process the data. The additional information obtainable from the increasing amount of metal from archaeological sites, especially tin, would simplify the interpretation considerably.

However, while the specialised metallurgy of the Bronze Drums is more difficult to categorise and provenance, their wide distribution throughout Southeast Asia and their evolution of form, suggest that a comprehensive trace element study of this group of artefacts may yield significant data on trade. Similarly the bronzes characteristic of Ban Don Ta Phet are another group with wide distribution and a metallurgical evolution which would benefit from further study.

The interpretation of long distance trade in tin ore tin-bronze is limited by the complex regional tin geochemistry. The question of whether southeast asian tin was used in the manufacture of indian or chinese bronzes or indeed if it reached the Mediterranean is difficult to answer. The study of trace elements in tin and tin-bronze from these regions will help to establish the truth but simple comparison with southeast asian tin ore profiles is insufficient. Trace element studies are required of the other tin deposits available, however small. Although geochemical data on tin deposits outside the Tin Provinces e.g. India, is extremely limited, the accumulation of such data is simplified by the efficiency of ICP-MS for just such work.

This research has made apparent both the limitations and advantages of this approach to ore provenancing. Previous research on this subject has tended to concentrate on
acquiring a very specialised and limited set of data, the interpretation of which leads to the proving, or otherwise, of specific questions. This approach, using ICP-MS, is capable of providing data to answer many questions, not only on provenance but also on processing technology, social context and trade. Furthermore the same set of data may be used by different specialists throughout Southeast Asia and is not limited to a particular aspect of archaeometallurgy, mining region or archaeological site.

As geochemical data accumulates on tin ores, metal and bronze the picture will undoubtedly clarify and further diagnostic elements be identified for different regions. Indeed, with further work, the diagnostic elements listed above as characteristic of southeast asian deposits, may be enlarged.

It has not been the purpose of this thesis to provide details of ore sources in antiquity, although useful data has emerged. The work has however, achieved its purpose in establishing this method as an extremely useful tool for future archaeometallurgical research.
For archaeometallurgical purposes, a reduction method of sample preparation more closely duplicates the conditions prevailing in antiquity. The problem with hydrogen reduction is that it yields residues along with the metal bead. It is believed that the partitioning of trace elements during smelting, into metal and slag, should, to a large extent, be reflected in the partitioning between the metal bead and the powder residue yielded by this method. However, since reduction by hydrogen took place at ~500°C and by smelting at ~1100°C there might be significant differences in the products formed.

**Hydrogen Reduction.**

2g of finely ground cassiterite concentrate was reduced in a stream of hydrogen at 600°C. The weight loss on average was 19% for the concentrates and 4% for the middlings fractions.

The samples were than dissolved in acid as described in the ammonium iodide fusion method.

**Carbon Reduction**

1g of the sample was intimately mixed with 5g potassium carbonate, 5g sodium carbonate and 1g powdered carbon [assay coke]. This mixture was heated in a porcelain crucible in a muffle furnace at 900°C for 20-25 mins. The metal formed was refluxed. The melt was then cooled and the crucible and its contents leached with distilled water. Any metal residue was separated mechanically from siliceous matter and metal carbonate residue by decantation and hand picking.

The samples were dissolved in acid as previously described.
ICP-MS CONDITIONS

Standard Solutions for Calibration

Standard solutions at 10, 50 and 100 ppb in 2% v/v hydrochloric acid were prepared fresh from individual stock solutions at 100 µg/ml [prepared using Specpure Johnson Matthey reagents].

Instrument Operation

The second UK prototype ICP-MS instrument used in this work has been described in the literature [Date and Hutchison, 1987; Date et al. 1988] but the Canberra series 80 multi-channel scaler and its associated data storage and output devices were replaced by an IBM-XT data station using VG software for data acquisition. Raw data were processed using multidimensional spreadsheet and database programs.

Inductively coupled plasma: All argon plasma
  Forward power 1.25 kw
  Reflected power <5w
  Coolant 12.0 l/min
  Auxiliary 0.2 l/min
  Carrier 1.0 l/min

Jarrell Ash Crossflow Nebuliser
  Pressure 40 psi

Water-cooled Spray Chamber (University of Surrey)
  Ground strap from load coil to front of torch box.

Solution uptake rate (Gilson Minipuls 11) 0.8 ml/min
Distance from load coil to aperture 10mm
Distance from torch end to sampling aperture 5mm
Nickel sampling aperture, orifice diameter 1mm
Nickel skimmer aperture, orifice diameter 0.7mm
Aperture to skimmer separation 7mm

Optimisation: mass spectrometer parameters were adjusted to give fairly uniform response for mono-isotopic elements
over the mass range 23-240 m/z

Data acquisition:
VG IBM PC XT data station
2048 MCA channels
100 µsec dwell time
300 sweeps

2% hydrochloric acid aqueous blank solution and calibration standards were run at the start of the analysis cycle. A 50ppb calibration standard was run at regular intervals [every 2 samples] as a check for signal drift. During the analysis sequence, a washout period of 3-4 minutes using 5% v/v HCl was found to be satisfactory in reducing memory to background levels for most elements. External calibration incorporating 187 Re as the internal standard was used for calculating the concentrations. There was no matrix matching of the standards.

For the hydrogen and carbon reduced samples there was a gradual decrease in sensitivity with increasing analysis time. However, for the ammonium iodide fusion samples, the ion response remained stable over a period of 2.5 hours.

Two bronze reference standards were used to check the calibration:

1. CRM C54.06 Phosphor bronze (MBH Analytical Ltd.)
   Analysed by BNF Metals Technology Centre.

2. An archaeological tin bronze from Thailand analysed independantly by ICP-OES at University of London.
APPENDIX 3

LEAD AT SONG TOH

Lead in antiquity has been thoroughly discussed by Nriagu [1983] and leaded bronze in China by Bayard [1972], Chase and Ziebold [1978] and others. The importance of lead in southeast Asian metallurgy possibly lies, primarily, in the extraction of silver, especially in early mediaeval times. Although the main ore of lead, galena [PbS], contains about 86% Pb, it has been noted in several localities that the silver-rich cerussites [PbCO$_3$] have been preferentially exploited [Wertime 1973, Pedall pers. comm.]. Lack of mining technology may have restricted the use of the richer sulphide ores in favour of the various oxidised ores [cerussite, anglesite and the oxides], as the former tend to occur below the water table. It is however, necessary to separate types of lead mining enterprises into those exploitable and exploited for lead in antiquity and those exploited primarily for silver at a later period.

Extensive prehistoric lead/silver mining has occurred at Song Toh in Kanchanaburi Province and various artefacts have been uncovered by modern mining operations. Conical lead ingots are abundant, as well as extensive slag heaps and smelting furnaces which date from the Chinese mining operations. The paired shafts, which give the mine its name, are located on the ores richest in silver and are sunk only as far as the water table. Bamboo-lined shafts have been dated to 1100 AD [Busse pers. comm.]

SONG TOH, KANCHANABURI

Song Toh Mine is in Kanchanaburi Province, Thailand where exploration and mining of the lead/zinc/silver ores are based on the sites of ancient workings and the old shafts or Song Tohs are an infallible guide to the richest silver ore.

The ore body at Song Toh does not crop out at surface and
there was, for some time, some speculation as to how the ancient miners could have discovered the ore in the first place. Locally there are some plant indicators of high lead in the soil, namely Tree Ferns and a particular type of grass [species unknown]. Another possible indicator is the nature of the laterites above the ore deposit. There are two types of laterite: an allochthonous yellow laterite above an autochthonous buff laterite (both are not always present). The yellow laterite is always barren except for the occasional formation of secondary lead sulphides formed round organic matter. The buff laterite, on the other hand, contains carbonate ore and many artefacts. The carbonate ore may well have attracted the first miners. Timbered shafts dating from the first millenium A.D. (Plate 23) are known and the Song Tohs are sunk through 10-30 m of laterite to the cementation zone where the secondary enrichment of silver is greatest.

Another feature of this limestone terrain, which may have contributed to the early discovery and exploitation of this deposit, is dolines or sinkholes. These are common features in limestone country and are formed by cavern collapse and the dissolution of the limestone by percolating groundwaters and are often conical in shape, rather like a funnel into the earth (Plate 24), and may be tens of metres deep. One of these dolines is directly above the ancient workings at Song Toh Open Pit and it is the opinion of the local geologists that the early miners may have found traces of the deposit in the sinkholes which led them to explore further.

It is hard to say whether the paired shafts of the Song Tohs are mining shafts or exploration pits as they may be either or both. No one has investigated the bottoms of all the shafts to see if they strike ore.

The shafts are normally about a metre in diameter and occur in pairs, the two shafts being about 0.50-1.00 m apart. The shafts are connected at the bottom in a bell-shaped chamber (Figure A9.3) and this pairing was probably to assist