1 Introduction

1.1 General Metallogenic Concepts

Ore deposits are distributed unevenly on Earth and tend to cluster in specific large-scale zones for which de Launay (1913) introduced the term "metallogenic province". The observational background for this situation has been known since the earliest days of mining. Pliny the Elder (A.D. 23-79) states with reference to silver-bearing veins: "...ubicumque una inventa vena est, non procul invenitur alia". (Where a vein is found, there will be another one not far away).

Cotta (1859:236) establishes in one of the first textbooks on ore geology the principle: "Wo einmal eine Erzlagerstätte gefunden wurde, da kann man erwarten, unter analogen Verhältnissen auch mehrere derselben oder ähnlicher Art zu finden, denn die meisten von ihnen pflegen gesellig aufzutreten". (Where an ore deposit has been found, it can be expected to find others of similar type under analogous conditions, because most ore deposits tend to occur gregariously). This simple rule is of fundamental importance in exploration geology, condensed in the familiar saying "If you are hunting elephants, go to elephant country".

A further accentuation of the concept of "metallogenic provinces" is derived from the fact that the province-specific metals are sometimes repeatedly concentrated in the same area by different geological processes and at different times, a situation which has been characterized by Routhier (1967) by the notion of "étagement temporel" (temporal superposition). Examples for such situations are given in Routhier (1980).

The existence of metallogenic provinces, i.e., concentration of ore deposits with similar metal-mineral association on a regional scale, points to the control of ore-forming processes by the regional geological framework. The critical role of such large-scale factors is the subject of metallogenic studies. The broader regional approach offers an important supplement to the more usual detailed investigations of individual ore deposits. The focus on detailed relationships within individual ore deposits has yielded critical data about the ores and their genetic processes. The regional approach addresses the broader relationships that link deposits to one another and provides insights into the regional geological environment which causes locally extreme metal concentrations.

Broad-scale relationships are per se more complex than relationships on a local scale, which makes quantitative modelling difficult. On the other hand, the regional approach makes it possible to filter from the many individual observations those that are specific for the sum of the ore deposits in a given metallogenic province, and that can be regarded as critical factors for ore formation in general.

The observational background of each student of ore deposits is, of course, different. This may introduce a subjective factor into any judgement of a complex sum of individual observations. The acquisition of general principles from a large data set relies on extra-observational background knowledge and the partly intuitive notion of relevance, about which different people may have different ideas. This is the reason for the diversity in metallogenic concepts dealing with identical subjects.

The existence of metallogenic provinces has been interpreted by Schuiling (1967:540) as reflecting a regional geochemical anomaly: "The concept of a metallogenetic province implies the existence of large-scale chemical inhomogeneities in that part of the crust or the mantle from which the ore deposits ultimately were derived".

This statement extends the neutral notion of metallogenic province to the speculative concepts of geochemical province, regional geochemical specialization and metal domain (Routhier 1967). It has been developed by Routhier (1980:46) into the "basic theorem" of metallogeny: "The concentrations of a metal appear at the intersection of a metal domain (actually a volume capable of reaching down to the mantle), bearing during very long periods of time (permanency and heritage) a «metal potential» (that is the primordial metallotect), and of other metallotects, acting as revealers of this potential" (translation in Routhier 1983:42). The term "metallotect" has been defined by Laffitte et al. (1965:3) as "any geological feature or phenomenon associated with lithology, paleogeography, structure, geochemistry, etc. which has contributed to the formation of a mineral concentration" (translation in Routhier 1983:42).

Brimhall and Crerar (1987:235) give a more physicochemically defined concept of ore formation: "...chemical fractionation effects peculiar to fluid/fluid, fluid/rock, and fluid/solute interactions which efficiently extract ore elements from large source regions and quantitatively concentrate them in

relatively small physical domains which are preserved for geological periods of time. It is the potential for such repetitive chemical focussing in the vicinity of available sources of thermal energy that drives ore-forming systems to extreme values of reaction progress and fluid dominance. The attainment of end stages of chemical fractionation separates ores from the more common products of petrogenesis".

It is interesting to note that the basic concept of these modern metallogenic theories was put forward a very long time ago. Rößler (1700:5) states in one of the first compilations on ore deposits, referring to vein deposits which at that time were identical to ore deposits in general: "Das Ertz hat seinen Wachsthum aus den Gebürgen und Gestein. Weil aber das Gestein ein festes Corpus, so kan der Gang nicht allenthalben seine Nahrung so vollkömmlich zu sich ziehen, und die Würckung rechte statt finden, wo nicht Flötze, Fälle und Geschicke sich dabey befinden, oder andere Gänge übersetzen, welche alle das Gestein durchschneiden und öffnen". (Condensed translation: Ore has its growth from the rocks. Because rocks are solid, veins develop preferentially in those parts of rocks which have been transformed and opened by faulting).

Zimmermann (1746:105) explains: "Mineralien werden ordentlich im Gesteine erzeuget...Das Gesteine wird nur nach gewissen Strichen und Streifen, welche man Gänge nennet, in Ertzt verwandelt...Dergleichen Gänge, wenn wir sie genau betrachten, nichts anders als ein durchwittertes und mürbe gemachtes Gestein... vorstellet, und wir können sehr wahrscheinlich schliessen, daß dieser Gang vorher ebenfalls mit dem Gestein des gantzen Berges gleiches Wesens gewesen, durch ein auf denen Klüften eindringendes Saltz-Wesen aber also durchdrungen, in seinem Gewebe geändert, aufgeschlossen, und zur künftigen Ertzt-Erzeugung geschickt gemacht worden". (Condensed translation: Ore develops in orderly fashion in the rock. The rock is transformed into ore in certain zones which are called veins. These veins represent brittle and altered rock, and it can be concluded that veins originate from rock which has been transformed by salt fluids percolating on fissures).

Agricola (1546) had already stressed the importance of water in ore formation. His ideas, however, were firmly confined by the theory of the four elements of the Greek philosophers Empedocles and Plato, leaving little room for a chemical understanding of ore deposits.

1.2 The Example Tin

Tin provinces are one of the best examples of metallogenic provinces. They define belts on a 100- to 1000-km scale. Inside tin provinces, the association of tin ore deposits with granitic rocks has long been known (Werner 1791; Zimmermann 1808). Very early studies already emphasize the association of tin and quartz-rich rocks (Rößler 1700), which at that time could not be further detailed (i.e. the non-discrimination of sandstone and granite).

These oldest observations are clouded by theoretical concepts which relate ore formation to astronomy and climate, a result of the then still influential Aristotelian physics. Rößler (1700:19) remarks with respect to tin: "Dieses Metall hat seine Art gerne an kalten Orten" (This metal likes cold places); and Lehmann (1751:12) notes: "Das eintzige Zinn scheinet eine gemäßigte Gegend zu lieben, und es ist daher entweder gar nicht oder wenigstens sehr selten in denen kältern Nord-Ländern zu finden". (Tin appears to love moderate climates and is therefore never or at least rarely found in cold northern countries). Lehmann (1753:203) adds shrewdly: "Zinn ist gerne alleine". (Tin loves to be alone).

Humboldt (1823a) introduces the term "tin granite" as opposed to "normal granite" (in the first edition of his book on global comparative geology, written in French: "granite stannifère" versus "granite primitif").*1

A first comprehensive treatise on the ore geology of tin and at the same time the first scientific theory of magmatic-hydrothermal ore formation in general is given by Beaumont (1847), helped by the work of Daubrée (1841). Essential findings are:

^{*1} Humboldt fixes the notion of tin granite in a purely chronologic or stratigraphic sense, on the basis of the (erroneous) neptunistic concept that specific metal accumulations and specific rock types characterize specific geological epochs, i.e. different evolutionary stages of sea water (Werner 1791). This concept leads to the systematic theory on time-bound mineral deposits (Karsten 1806). The observation that tin deposits are not only confined to primitive granites ("Ur-Granit" as earliest precipitation from sea water; Goethe 1785) but occur also in the gneiss and mica schist of Gierczyn/Giehren in Silesia (Buch 1802) (see Chap. 5.2), with gneiss at the time generally accepted as the second-oldest rock formed from sea-water precipitation, led Humboldt (1823a,b) to the conclusion that tin-mineralized granites must represent a separate evolutionary stage in between the granite- and gneiss-forming epochs.

- 1. Tin ore deposits are associated with granites.
- 2. Tin ore deposits are located preferentially in apical portions of granites and their immediate country rocks. [Daubrée (1841) had already pointed to the fact that tin deposits in Cornwall, in the Bretagne and the Erzgebirge are always confined to a zone ≤500 m from the granite contact].
- Tin ore deposits are often associated with individual granite bodies pointing out of larger batholiths: "les roches stannifères sont souvent des masses détachées qui ont pointé en dehors des grandes masses granitiques" (Beaumont 1847:1302).
- 4. The tin ore host rocks are particularly rich in quartz, tourmaline and fluorine-bearing minerals.
- 5. Tin granites are anomalous in texture and composition: "des monstruités de granite" with a "caractère ultragranitique" (Beaumont 1847:1303).

Daubrée (1841) and Beaumont (1847) define tin granites as granitic rocks in which the metals of the "tin family" are particularly abundant, i.e. Sn, F, B, P, As, W, Mo, Fe. The typical kaolinization in tin granites is interpreted by Daubrée (1841) as a result of hydrothermal alteration by acid fluids. The formation of tin ore deposits is explained by Beaumont (1847) by the action of circulating fluids which leach the chemical components of the ore deposits from the wall rock. The possibility that water and other volatile components may depress the solidus of a granitic melt is discussed, and Beaumont (1847) speculates that tin granites possibly solidify at lower temperatures than normal granites.

The rule of the association of tin deposits with granitic rocks was first derived from European localities only. The validity of this assertion was extended by the statistical analysis of Ferguson and Bateman (1912) on a worldwide basis.

Cotta (1859:680) stressed the important fact that granite magmatism is only exceptionally accompanied by tin mineralization: "...man darf nicht, überall wo granitische Gesteine zu Tage treten, an ihren Grenzregionen auch Zinnerze erwarten, vielmehr ist die Zinnerzbegleitung für die Granite nur eine Ausnahme, während die Granitbegleitung für die Zinnerze eine Regel bildet". (Not everywhere where granitic rocks are found, can tin ore be expected in the contact zones. The occurrence of granitic rocks together with tin ore is an exception, whereas the occurrence of tin ore together with granitic rocks is a rule).

These early observations provide the basis for subsequent investigations which refine the geological-mineralogical-geochemical framework of tin deposits. Sandberger (1885) emphasizes the point that tin granites carry Li-

mica (protolithionite and zinnwaldite) with tin contents up to more than 1000 ppm. This aspect of chemical specialization is later developed by Barsukov (1957) on a systematic basis (see below).

A modern and detailed overview of the geology of tin ore deposits is given in Taylor (1979); shorter reviews of general aspects of tin ore formation are provided by Eugster (1985), Kwak (1987), Plimer (1987) and Strong (1988). The more important types of tin ore deposits are compiled in the models of Fig. 1. The ore deposit spectrum can be understood as consequence of a general magmatic-hydrothermal evolution which falls into two broader subjects discussed in detail below:

- 1. Granitic magmatism of specific petrogenetic type.
- 2. Associated hydrothermal activity, physically and chemically focussed by the local geological framework and by evolutionary permeability conditions.

All major types of tin ore deposits are associated with highly fractionated granitic rocks in a high-level environment (including the tin pegmatites in Central Africa and SE Asia). The geometric style of the ore deposits is a consequence of local conditions of permeability (tectonic-geological framework plus fluid evolution in the magmatic-hydrothermal system). Examples for these relationships will be given in Chaps. 3 and 4.

1.3 Spatial and Temporal Distribution of Tin Ore Deposits

The province character of tin ore deposits is particularly well developed. Zippe (1857:184) notes: "Das Zinnerz ist nur in sehr wenig Ländern einheimisch". (Tin is indigenous to very few countries). Only four well-defined regions account for 80 % of the cumulative historic tin mine output. These are (Table 1, Fig. 2):

Fig. 1 (next page). Schematic models of the major groups of primary tin ore deposits. After Taylor et al. 1985. 1 tin porphyries (examples: Llallagua and Chorolque, Bolivia; Yinyan, Guangdong, China); 2 skarns and carbonate/sulphide replacements (examples: Cleveland and Renison Bell, Tasmania, Australia; Dachang district, Guangxi, China); 3 veins and sheeted veins (examples: Chojlla, Bolivia; Geevor and Wheal Jane, Cornwall, England; Hermyingyi, Burma); 4 greisens (examples: Altenberg, East Germany; Cinovec, CSSR; Tikus, Indonesia) and pegmatites (examples: Manono, Zaire; Phuket district, Thailand)



- 1. The SE Asian tin belt (Burma, Thailand, Malaysia, Indonesia) with a 50 % share of the total world tin production.
- 2. The Bolivian tin belt (ca. 10 %).
- 3. The South China tin province (ca. 10 %).
- 4. The Cornwall tin province (ca. 10 %).



Fig. 2. Geographic distribution of major tin provinces. Area of black squares is proportional to cumulative tin production (data from Table 1)

More than 99 % of the historic tin production is from ore deposits directly or indirectly related to granitic rocks, i.e. granites and their volcanic and subvolcanic equivalents. A small quantity of tin is recovered as a by-product of mining of base-metal massive sulphide deposits. In such deposits, cassiterite is occasionally concentrated at high-temperature vent zones of the submarine-hydrothermal systems of both volcano-sedimentary sequences (such as Kidd Creek, Canada, or Neves Corvo, Portugal) and in clastic sedimentary sequences (such as Sullivan, Canada) (Mulligan 1975).

The economic significance of this mineralization style will increase with the inauguration of the new tin processing plant of the Neves Corvo copper-tin

Table 1 (next page). Cumulative tin production up to 1986 (in metric tonnes of metal content) and tin reserve base 1984-1986. Placer deposits are assigned to their primary source deposits

	Location	Production [x 1000 mt]	Reserves [x 1000 mt]
More than 1 Mio t Sn			
1. SE Asian Tin Belt 200-220 Ma 50-100 Ma	Malaysia Indonesia Thailand Thailand Burma	5200 2500 300 900	1200 1550 300 900 500
2. South China Tin Province 70-150 Ma	China	1500	1500
3. Bolivian Tin Belt 200-220 Ma 12-25 Ma	Bolivia Bolivia	250 2000	180 800
4. Cornwall Tin Province 270-290 Ma	England	2000	260
0.5-1 Mio t Sn			
5. W Australian Tin Fields 350-360 Ma 220-240 Ma	Tasmania Queensland	400 200	230 120
6. Central African Tin Provinc 950-1050 Ma	ce Zaire Rwanda Burundi/Uganda/Tanzania	450 80 40	200
7. Jos Plateau Tin Fields 540-565 Ma 160-170 Ma	Nigeria Nigeria	54 486	28 252
0.1-0.5 Mio t Sn			
8. Tin Fields in the Far East of 120-170 Ma 50-100 Ma	f the USSR USSR USSR	100 300	300 700
9. Erzgebirge Tin Province 280-305 Ma	Germany/CSSR	300	200
10. Rondônia and Amazona 1000/1500 Ma	s Tin Provinces Brazil	180	> 1000
11. Iberian Tin Province 280-300 Ma	Spain/Portugal	150	30
12. Bushveld Tin Province 1950-2000 Ma	RSA	115	150

Historical tin production data from Reyer (1881), MacAlister (1908), Beyschlag et al. (1910), ITRDC (1938), Ahlfeld (1958), Ahlfeld and Schneider-Scherbina (1964), ITC (1967), Fox (1969), and Metallgesellschaft (1965, 1976, 1989). Reserve data from Crowson (1984, 1986), Thormann and Drew (1988), Seltmann (1990)

mine in mid-1990, which is designed to produce 5000 t/y of tin in concentrate, i.e. 2.5 % of the world tin production. The Neves Corvo massive-sulphide ore deposit is located in the Upper Paleozoic Pyrite Belt of southern Portugal and Spain and has ore reserves of 27 Mio t with 8 wt% Cu, 1 wt% Zn, 0.2 wt% Pb, and 33 ppm Ag, of which 2.8 Mio t contain 2.6 wt% Sn (Carvalho 1986; Tin International 1989; Mining Journal 1990). The geology of this spectacular ore deposit is currently still little known.

The age distribution of tin ore deposits is strongly biased towards the Phanerozoic (Fig. 3). About 90 % of the historic tin production is related to primary tin ore deposits ≤300 Ma in age. This is a situation similar to and even more pronounced in molybdenum porphyries, copper porphyries and epithermal Au-Ag ore systems (Meyer 1985).

Such a pattern may result from an accelerating rate of ore formation towards the present, or, alternatively, from continuous reworking/destruction of ore deposits with a constant or variable rate of ore formation. It is evident that the survival rate of an ore deposit in a shallow environment, subjected to uplift and erosion, must be small (fast recycling rate) whereas an ore deposit formed at deep levels of the crust and/or with little uplift and erosion will have a high survival rate. The particularly ephemeral nature of oceanic crust with a half-life of around 60 Ma (including ore deposits within this crust) is shown in Fig. 3.

It is a feature common to both tin ore deposits and molybdenum and copper porphyries, as well as to epithermal ore systems, to be located in tectonic environments very sensitive to erosion. These environments include apical portions of shallow-level intrusions or generally, regions near the Earth's surface, that also experience active uplift in continental margins. The important control of level of erosion is demonstrated by the SE Asian tin province in which primary tin ore deposits are preserved only as relics and are mostly in an early state of erosional dispersion, i.e. in placer deposits. The age distribution of copper and Au-Ag deposits underlines this aspect. These metals are not only related to granitic magmatism in the general porphyry/uplift environment, such as is the case for tin, but are concentrated also in intra- and pericratonic depressions/basins (high survival rate) in which they occur in the Proterozoic (Cu-Pb-Zn-Ag-Au) and Archaean (Au).

The oldest tin ore deposits occur in the Kapvaal craton in southern Africa (Swaziland) in association with Archaean, intracratonic A-type granites (Hunter 1973; Trumbull and Morteani 1986). An intracratonic and anorogenic setting is typical of all major Precambrian tin provinces (Bushveld, Central Africa, Amazonas and Rondônia/Brazil), as opposed to the active margin



Fig. 3. Age distribution of tin deposits (historic tin production plus reserves: age refers to primary tin accumulation) compared to crustal growth curve (stippled pattern: Taylor and McLennan 1985; Jacobsen 1988) and age distribution of exposed continental crust and oceanic crust. The data for Precambrian crust exposed on land surfaces are from Hurlev and Rand (1969),adapted to the global ratio of Phanerozoic/Precambrian exposures of three (Blatt and Jones 1975). Phanerozoic data from Blatt and Jones (1975), data on oceanic crust from Sclater et al. (1981).

setting of most Phanerozoic tin provinces. A systematic treatment of the age relationship of major geotectonic environments has been given by Veizer and Jansen (1979, 1985). This approach arrives at average net rates of generation and destruction of global tectonic environments which can be compared to our data on the age distribution of tin ore deposits (Fig. 4). The metal distribution for tin ore deposits in active margin settings follows approximately



Fig. 4. Age distribution of tin ore deposits (historic production plus reserves; age refers to primary tin accumulation) in intracratonic (solid diamonds) and active margin settings (solid circles). Age domains of major continental geotectonic environments are from Veizer and Jansen (1985) and Veizer (1988)

an exponential pattern, similar to the age distribution of orogenic belts. The half-life (50th percentile) is between 100-200 Ma which implies a survival rate of tin deposits with an age of \geq 500 Ma of only 1 % in this setting. The intracratonic environment has a much larger survival rate with a half-life of 690-1800 Ma (Veizer and Jansen 1985), which explains the preservation of Precambrian tin accumulations in this environment.

The geotectonic stability of host environments seems to have generally a first-order control on the time distribution of ore deposits. The statistical investigation by Veizer et al. (1989) arrives at half-lifes for ore deposits in a cratonic setting of \geq 1700 Ma for mafic-ultramafic associations, \geq 1350 Ma for

metamorphic associations, and ca. 800 Ma for volcano-sedimentary associations. This contrasts with half-lifes of hydrothermal ore deposits in orogenic belts (95 ± 41 Ma) and of surficial deposits (a few Ma).

The long-term evolution of the Earth is a combination of both cyclic processes and superimposed unidirectional phenomena. Global chemical trends are a consequence of the crustal growth curve in Fig. 3. Although models of crustal growth differ widely for the early history of the Earth, there is a general consensus that a major portion of the present-day crust was generated until the Archaean/Proterozoic boundary. The early Archaean evolution appears to be dominated by partial melting of mantle material (i.e. basaltic system) with little intracrustal differentiation which would result in the enrichment of the crust relative to the mantle of strongly incompatible elements such as Ag, Pb, Mo, Ta, W, and to a lesser degree Au, Cu, Zn, Sn. Intracrustal melting (granodioritic system) can be expected to become increasingly important with an increase in crustal volume. The granodioritic melt system will result in a separation of the under these conditions compatible elements Au, Ag, Cu, (Zn) from the further incompatible elements Sn, W, Ta, Mo, Pb. Such an interpretation arises from the geochemical data in Table 2, which gives some reference values for major geotectonic units. Primitive mantle (whole mantle plus crust) is computed from analytical data on ultramafic inclusions in the upper mantle (primitive spinel- and garnet-Iherzolites), which are taken as being representative for the bulk mantle.

These general observations point to the importance of two metallogenetically critical factors for the formation of tin ore deposits: petrogenesis of tinbearing granitic rocks (degree of differentiation) and geotectonic position (probability of survival of hydrothermal systems). The following examples focus on the

Table 2. Mean contents of some metals in global geotectonic units of the $\ensuremath{\mathsf{Earth}}$

	Sn	W	Та	Мо	Cu	Pb	Zn	Au	Ag
Primitive mantle	0.6	0.02	0.04	0.06	28	0.12	48	0.5	2.9
Bulk crust	1.5	1.0	1.0	1.0	75	8	80	3.0	80
Lower crust	1.5	0.7	0.6	0.8	90	4	83	3.4	90
Upper crust	3.0	2.0	2.2	1.5	25	20	71	1.8	50

Data from Taylor and McLennan (1985), Wänke et al. (1984), Loss et al. (1989). Au and Ag in ppb, all other elements in ppm.

petrological-geochemical evolution of magmatic systems on a regional scale and the associated hydrothermal systems locally developed on this regional framework.

1.4 Global Geochemical Evolution of Tin

Metal enrichment to ore grade is the ultimate outgrowth of efficient largescale and long-term fractionation processes in a global context (Brimhall 1987). The geochemical evolution of tin and some other elements during the Earth's history is schematically depicted in Fig. 5. The element contents given are derived from analytical data on C1 chondrites, ultramafic nodules from the upper mantle, and on rocks from the continental crust. The bulk Earth composition is from a model calculation by Morgan and Anders (1980) and has a large error margin.

It is generally believed that Type 1 carbonaceous chondrites (C1) closely approximate the condensable fraction of primordial solar system material. The accretion of the Earth appears to have taken place heterogeneously from two chemically different end-member components as a function of oxygen fugacity and temperature (in turn dependent on distance from the centre of the primitive solar system), i.e. a highly reduced component in which all elements with volatilities higher than that of sodium were depleted relative to C1 during earlier cosmochemical fractionation, and a more oxidized component which had a composition close to C1 abundances (Wänke 1981).

Core segregation and ongoing accretion result in an element distribution pattern in the primitive mantle which is controlled by volatility (depletion in volatile elements/enrichment in refractory elements) and siderophility (preferential partitioning of siderophile*2 elements into the core), i.e. vapoursolid fractionation and metal-silicate fractionation. The volatility of tin

^{*2} The terms siderophile, chalcophile and lithophile describe those elements that preferentially enter metal, sulphide or silicate phases, respectively (Goldschmidt 1937). This classification is based primarily on the distribution of elements in these phases in meteorites. The behaviour of the elements in the solar nebula is controlled by their volatility (examples in parentheses): gaseous (H, C, N, O, noble gases), very volatile (Bi, Pb), volatile (Sn, Rb, Cs), moderately volatile (K, Mn), moderately refractory (V, Eu), refractory (Ca, Al, U, La) and super-refractory (W, Zr).

RESENT DAY ARTH			UPPER CRUST	2.5-5.5 ppm 2.0 ppm 2.2 ppm 1.5 ppm 0.0018 ppm 0.32
G	INTRACRUSTAL FRACTIONATIC	CRYSTAL-LIC FRACTIONAT	LOWER CRUST	1.5 ppm 0.7 ppm 0.6 ppm 0.8 ppm 0.0034 ppm 0.02
D EVOLV EARTH	CTIONATION	STAL-LIQUID CTIONATION	BULK CRUST	2.0 ppm 1.0 ppm 1.0 ppm 0.003 ppm 0.12
DIFFERENTIATE EARTH	AANTLE MAN ONATION FRAC	SILICATE CRY DNATION FRA	PRIMITIVE MANTLE	0.60 ppm 0.016 ppm 0.059 ppm 0.0005 ppm 0.028
rimitive Arth	CORE-N FRACTI-N FRACTI-N 4.5	NT METAL-9	BULK EARTH	0.39 ppm 0.18 ppm 0.023 ppm 2.35 ppm 0.032 ppm 0.032
сш	ACCRETION	REFRACTORY- VOLATILE ELEMEI FRACTIONATION	C1 CHONDRITES	1.79 ppm 0.092 ppm 0.014 ppm 0.218 ppm 0.295 ppm
SOLAR NEBULA		•		Sn W Mo Rb/Sr

Fig. 5. Fractionation pattern of tin and some other elements during the Earth's history. C1 data are from Anders and Grevesse (1989) and Loss et al. (1989). The bulk Earth data are from Morgan and Anders (1980) and are calculated assuming chemical equilibrium between mantle and core. Primitive mantle data are from Anderson (1983). Wänke et al. (1984) and Taylor and McLennan (1985), data on continental crust from Taylor and McLennan (1985)

(50% condensation temperature at 10⁻⁴ bar total pressure: 720 K) is distinctly different from the volatility of the ore-paragenetically related elements W, Mo, or Ta (50% condensation temperatures at 10⁻⁴ bar total pressure: >1400 K; Ringwood 1979:100). This results in a drastic decrease of tin content from ca. 1.8 ppm in condensed solar material (as seen in C1 chondrites; Loss et al. 1989) to ca. 0.4 ppm in bulk Earth and 0.6 ppm in primitive mantle (lithophile behaviour). The refractory and moderately siderophile elements W and Mo partition preferentially into the core, which leaves the primitive mantle depleted in these elements when compared to solar composition. However, as deduced from the abundances of siderophile elements in the mantle, general chemical equilibrium between the Earth's mantle and largely metallic core is not established, which is the reason for a large error margin for all bulk Earth chemical models (Newsom and Palme 1984; Wänke and Dreibus 1988). The refractory and lithophile Ta is affected neither by volatile depletion nor by substantial partitioning into the core, and during both cosmochemical and geochemical evolution follows a continuous enrichment trend.

Archaean crust formation by crystal-liquid fractionation of mantle material and dominance of intracrustal fractionation in the Phanerozoic lead to the present-day tin distribution with 1.5 ppm Sn in the lower crust and 2.5-5.5 ppm in the upper crust. The upper crustal range in tin contents is an artifact of analytical uncertainties which arise from conflicting data. The conventional value of 2.5 ppm Sn as compiled by Rösler and Lange (1976) has been revised to 5.5 ppm Sn by Taylor and McLennan (1983) on evidence based on spark-source mass spectrometry. However, this analytical method depends on theoretical sensitivity factors, and new data by a mass spectrometric isotope dilution technique (Loss et al. 1989) confirm the older data and suggest a systematic error by the factor of 1.5-2 in the data of Taylor and McLennan (1983, 1985). The best estimate for the upper crustal tin content is therefore around 3 ppm. The value of 2.32 ± 0.04 ppm Sn for international USGS rock standard BCR-1 (Loss et al. 1989) may be used to calibrate tin data from different laboratories.

It is interesting to note that long-term geochemical fractionation restores in the Earth's crust approximately that tin level which was present in the condensed solar starting material before the onset of cosmochemical fractionation. The same applies to the global fractionation pattern of molybdenum, whereas tantalum provides an example of a continuous cosmo-geochemical enrichment pattern.

1.5 Geochemical Specialization of Tin Granites

The petrological particularity of tin granites was noted very early by Beaumont (1847) on the edge between fact and intuition. The systematic geochemical campaigns in the USSR provided Barsukov (1956, 1957) with a data base to define the geochemical specialization of tin granites as opposed to non-tin granites based on whole rock tin content:

"The investigations carried out have established that granitic massifs not associated with tin ores, while not differing substantially in age or mineralogical composition from tin-bearing granites, do contain tin in amounts of 3-5 ppm, which is equivalent to the Clarke of tin. Massifs, carrying tin ores in varieties unaltered by postmagmatic or contactmetamorphic processes, contain tin in somewhat larger amount - four to five times the Clarke of tin or 16 to 30 ppm (usually 18-26 ppm). Consequently, in the case of tin-bearing granites we can speak of a specialization of the granitic magma from which a given intrusive rock has solidified. Tin-bearing granites are characterized by higher tin contents in those varieties that have not been altered by contact- or postmagmatic processes" (Barsukov 1957:41).

This simple but essential relationship provides the starting point for a qualitatively new period of research on tin deposits, which focusses on geochemical evolution paths in the granitic host environment. Systematic tin distribution patterns allow insight into the evolution of tin during both magmatic and hydrothermal stages and give direct information which is much more obliterated in the comparable environments of copper or molybdenum porphyries.

The geochemical tin specialization of tin granites is accompanied by characteristic enrichment and depletion patterns of other elements. Besides the often anomalously high boron and/or fluorine contents in tin-bearing systems (noted early on by Daubr,e 1841), tin granites, when compared to average granitic rocks, are enriched in lithophile elements such as Rb, Cs, Li, Th, U, Nb, Ta and W, and are depleted in elements which are compatible with the granitic main mineral components such as Sr, Eu, Ba, Ti, Co and Ni. Trace element patterns in tin granites as well as the petrochemical equilibration to their high intrusive level at 1 ± 1 kbar (minimum melt composition) point to the important role of fractional crystallization during the magmatic evolution. This situation does not easily allow the application of the usual petrogenetic-tectogenetic classification schemes which are based on source rock chemistry (Chappell and White 1974; Pearce et al. 1984; Brown et al. 1984; etc.).

The geochemical definition of tin granites by Barsukov (1957) based on tin levels is commonly used and mostly valid. A more general definition is preferred here which takes into account the occasionally drastic hydrothermal tin depletion in tin granites: tin granites are granitic rocks for which spatial, temporal and chemical relations point to a causal association with neighbouring tin deposits.

A definition of tin granites must inherently be arbitrary, because those granite phases immediately associated with tin mineralization are parts of much larger composite granitic intrusions of the same petrochemical suite. Granite plutons in tin provinces are circular or elliptical bodies (usually elongated along regional strike) ranging from a few km to several tens of km in diameter, with high intrusion level. They are often assembled in such close proximity that they coalesce or can reasonably be inferred to coalesce into batholiths of regional extent (in tin provinces, for example, the Cornubian batholith, the Erzgebirge batholith, the Main Range batholith in Malaysia, etc.).

In a generalized picture which is in accordance with most situations in tin provinces, the plutons consist dominantly of coarse- to medium-grained Kfeldspar megacrystic biotite monzogranite which is intruded by one or several later granite phases with a great textural variety. These subintrusions range from microgranites to granite porphyries and are often characterized by secondary magmatic textures (Cobbing et al. 1986; see Chap. 6.4). Such granite variants occur often in marginal or apical zones within plutons, but may also form the major outcrop area in particular situations with a high erosion level. They are geochemically more evolved than their parental granite host and are affected by processes of pervasive microbrecciation and fluid overprint. Hydrothermal tin-tungsten ore systems are centred on these late granite phases.