3 Magmatic Enrichment of Tin

The chances are small that an igneous rock presently exposed at the Earth's surface might be a true copy of the chemical inventory of its past magmatic state. Chemical interaction with a fluid phase during crystallization, cooling and at later stages is inevitable, and is the condition for any hydrothermal ore formation in association with igneous rocks, even though sample suites from igneous rocks often display a more or less extensively preserved magmatic distribution pattern which can be identified because of systematic trends between mineral phases or between individual rock portions. Linearly correlated log-log trace element distribution patterns in granitic fractionation suites, as discussed above, can be interpreted as a result of magmatic evolution and will be increasingly disintegrated into scatter patterns with increasing fluid overprint.

The dominantly magmatic (in a relative sense) distribution pattern of tin in granitic rock suites is shown in the following cases as a function of degree of fractionation. Titanium content and Rb/Sr ratio will be frequently used as an index of fractionation in these examples. Ti has compatible behaviour in granitic melts (although incompatible in mafic melts) and usually has little mobility under hydrothermal conditions. Rb and Sr are easily mobile, but can, however, remain fixed in incipient stages of hydrothermal alteration (low water/rock ratio) by microscopic to submicroscopic blastesis of sericite/muscovite or epidote/carbonate. Such a situation is indicated by a relatively undisturbed Rb-Sr pattern (linear log-log correlation) and systematic Rb/Sr variation complementary to TiO₂.

Zirconium is occasionally used as an additional indicator of fractionation. This element is present nearly exclusively in zircon. Correspondingly, Zr content in a melt is controlled by zircon solubility which is dependent on temperature and on melt composition as expressed by the parameter (Na+K+2Ca)/Al·Si (Watson and Harrison 1983). Zircon saturation in moderately peraluminous granitic melt is around 1250 ppm Zr at 1000 °C, and around 50 ppm Zr at 700°C. Accordingly, there is a tendency of Zr to become enriched in the melt at high temperature (partial melting and early magmatic evolution), which turns around towards lower temperatures. The change from incompatible to compatible behaviour, and the kinetic problem of metastable pre-magmatic zircon in some granites complicate the interpretation of Zr data in fractionation suites.
The following examples give tin distribution trends for granite suites from a few tin provinces only (Erzgebirge, Malaysia/Thailand, Nigeria). Further data in the framework of the same interpretative model are for the Central African tin province in Lehmann and Lavreau (1987, 1988), for Portugal in Neiva (1984), and for the Bushveld granites in Lehmann (1982), based on data in Lenthall and Hunter (1977). Systematic tin data on the Cornwall tin granites are not available. Some examples of granitic fractionation suites from areas with little or no tin mineralization are briefly discussed below (Nova Scotia, Cape/RSA, SE Australia). Further tin data on non-tin granites are in Biste (1979) for Sardegna, Italy, in Speer et al. (1989) for South Carolina, USA, and in Grohmann (1965) for Austria, among others.

3.1 Erzgebirge/Krusné Hory, Germany and Czechoslovakia

The Erzgebirge or Krusné Hory (German and Czech = ore mountains) is the birthplace of modern mining geology (Agricola 1546) and was long rated as a standard ore province. Silver mining in the Freiberg polymetallic veins started in 1168, and production of tin from placers near Krupka (Graupen) is even somewhat older. However, the historic Erzgebirge tin production is relatively small and corresponds to only about 15 % of the cumulated Cornwall tin output. The great scientific tradition of the Erzgebirge, together with detailed research and exploration work during the last 25 years, however, make it probably the best-studied tin province in the world. The present state of knowledge on the metallogenesis of the Erzgebirge is condensed in the compilation of Tischendorf (1989).

The Erzgebirge mountain region (Fig. 16) is part of the Saxothuringian zone of the European Variscan orogenic belt. It is a WSW-ENE-running fault block (120 x 45 km large) with a large negative gravimetric anomaly, consisting of a sequence of Proterozoic to Lower Paleozoic metamorphic rocks intruded by Variscan granitic rocks which at depth coalesce into the Erzgebirge batholith. The granitic magmatism is divided into an early Variscan cycle (orthogneisses) and a quantitatively dominating late-Variscan cycle (unfoliated granites). The post-kinematic late-Variscan granites are subdivided into two major granite suites, the Older Granites (OG) and the Younger Granites (YG) (Lange et al. 1972). Tin and tin-tungsten ore deposits are spatially associated with the YG suite only, and are located mainly in apical portions of small stocks and their immediate exocontact (Tischendorf...
Fig. 16. Generalized geological map of the Erzgebirge tin province (Baumann and Tischendorf 1976:298). 1 NW limit of Older Granite suite; 2 NW limit of Younger Granite suite; 3 areas with tin mineralization; 4 Erzgebirge fault zone (Ohre Graben); 5 axis of tin belt; 6 Older Granites; 7 Younger Granites; 8 depth contour of Erzgebirge batholith at 0 m NN et al. 1978; Stemprok 1987). Minor tungsten-molybdenum ore occurrences are associated with the OG suite.

Tin and tin-tungsten mineralization is of greisen type (Altenberg, Cinovec/ Zinnwald, Krásno/Schlaggenwald), of stockwork or sheeted-vein/vein type (Ehrenfriedersdorf, Geyer, Krupka/Graupen) and in breccia pipes (Seiffen, Sadisdorf, Gottesberg-Mühlleiten, Sachsenhöhe), with all phenotypes present in variable proportion in each individual ore system. Mineralization of skarn or sulphide replacement type has never been mined, but has a large tin potential (Pöhla, Zlaty Kopec, Halsbrücke). The largest active mine is Altenberg (short of being shut down) which produces 2200 mt Sn per year out of 1,200,000 mt of ore (Mosch and Becker 1985). The Ehrenfriedersdorf, Krásno and Cinovec tin mines produce currently about one tenth each of this figure.
Homogenization temperatures of fluid inclusions in cassiterite define a minimum temperature range of formation of 350-500 °C; pressures of formation are at ≤ 1 kbar. The ore solutions consist in an early stage of a low-salinity (2-3 wt% NaCl), high-CO$_2$ fluid phase and a coexisting high-salinity (ca. 35 wt% NaCl) fluid with magmatic stable isotope pattern, and become progressively more diluted by meteoric water during cooling over a period of several million years (Durisova et al. 1979; Thomas and Tischendorf 1987; Thomas and Leeder 1986).

Tin and tungsten ore formation is associated with extensive and widespread hydrothermal overprint, which in an early late-magmatic stage commences with pervasive blastesis of quartz, topaz and mica (muscovite and a variety of dark Li-bearing micas), microclinization and albition. The subsequent stage of greisen formation is increasingly more fracture-controlled and is accompanied by major metal deposition characterized by the mineral assemblage quartz-topaz-muscovite/zinnwaldite-cassiterite. The large bulk-mining centres of Altenberg (GDR) and Cinovec/Zinnwald (CSSR) with an ore tonnage of 50-100 x 10$^6$ mt each belong to this type (Cinovec: 0.2 % Sn, 0.035 % W, 0.35 % Li; Altenberg: 0.2-0.3 % Sn, 0.01 % W, 0.01 % Mo, 1 % F; Mosch and Becker 1985; Dasek pers. commun. 1988). Some ore fabrics of the greisen environment are shown in Fig. 17.

The schematic illustration of Fig. 18 demonstrates the zonal arrangement of the mineralogical associations in major types of tin deposits and their spatial relation with adjacent granitic intrusions (Baumann and Tischendorf 1976). The lower parts of the Erzgebirge tin ore systems (endocontacts) are dominated by the topaz-muscovite/zinnwaldite-cassiterite association in a

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Fig. 17 (next page). Some textural patterns of greisen-style tin ore of the Ehrenfriedersdorf and Altenberg tin ore deposits.

A Pervasive greisenization (quartz-topaz-mica mineral assemblage) with metasomatic layering in the Ehrenfriedersdorf YG 2 granite. The dark layers consist of Li-mica. Inclusion of greisenized YG 1 xenoclast near hammer (Ehrenfriedersdorf Mine, Sauberg section).

B K-feldspar megablasts with haloes of Li-bearing mica (dark) in greisenized YG 2 granite. Further blastesis of K-feldspar and quartz leads in apical contact zones to the formation of pegmatitic "stockscheider" zones. Length of photograph is about 1 m (Ehrenfriedersdorf Mine, Sauberg section).

C Stockwork/sheeted-vein mineralization in greisenized YG 2 microgranite ("Schnittmuster-Greisen"). Veinlets consist predominantly of Li-mica. Length of photograph is about 1.5 m (Altenberg Mine).
Fig. 18. The zonal arrangement of major morphologic-mineralogical types of tin mineralization in the Erzgebirge (Baumann and Tischendorf 1976:301). Stippled areas denote pervasive hydrothermal alteration and disseminated mineralization (grain boundary-controlled permeability) in conceptual opposition to fracture-focused fluid circulation and vein mineralization.

greisen environment. The exocontact zone has fracture-controlled mineralization which grades from a tourmaline-into a chlorite-dominated mineral association with an increasing amount of sulphide minerals (pyrite, arsenopyrite, chalcopyrite, bismuth, bismuthinite, stannite, etc.).

The OG suite consists of biotite monzogranites, the YG suite is composed of biotite syeno- to monzogranites with substantial amounts of sub-solidus muscovite. Each suite can be divided into a main intrusive phase and two additional successive intrusive phases (OG 1 → 2 → 3; YG 1 → 2 → 3). The main intrusive phase is distinguished by a coarse-grained porphyritic texture, the first additional phase is medium-grained, and the second additional granite phase is fine-grained. The quantitative proportions of the individual granite phases are approximately 60:30:10 according to outcrop dimensions in the western Erzgebirge (Tischendorf et al. 1987). In an intermediate temporal position in between the OG and YG suites occur locally so-called Intermediate Granites (IG 1 2) and Transitional Granites (OGt) with a distinct texture and composition.

The granitic intrusions appear to form a composite batholith at depth which underlies the entire Erzgebirge block (Watznauer 1954). The country rocks of the granite intrusions consist predominantly of Ordovician phyllites in the western part of the Erzgebirge, and of Proterozoic paragneisses ("Graugneis") in the eastern part. The erosion level in the western Erzgebirge is relatively
deep with an exposure of granitic rocks at a plutonic level, whereas the eastern Erzgebirge granites are exposed in most apical portions and at a subvolcanic level (Fig. 19). The eastern Erzgebirge granites and cataclasite-subvolcanic complexes are characterized by multiple episodes of large-scale fluid-explosive brecciation and concomitant greisenization in a caldera setting (Seltmann et al. 1990). Geological and thermobarometric data suggest for the Altenberg tin deposit a depth of formation of 1000-1500 m below the paleosurface, whereas the corresponding figures for the Ehrenfriedersdorf deposit are 2000 m, and for the Eibenstock deposit in the western Erzgebirge 4000 m (Thomas 1982).

The relative age positions of the individual granite phases are well documented by field relationships. There is, however, no plain radiometric evidence for age differences between the OG and YG suites. All granite intrusions appear to have an Upper Carboniferous age in the range of 300-320 Ma (Gerstenberger et al. 1984). Rb-Sr areal isochrons of the OG and YG suites are identical within the analytical error margins and define an age of $317 \pm 5$ Ma. Sr initial ratios are around 0.707 for the OG suite and only around 0.702 for the tin-bearing YG suite. On the basis of these values, a petrogenetic model has been put forward recently which derives the Erzgebirge batholith from mantle material, with a major degree of crustal contamination in the OG.

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Fig. 19. Structural setting and recent erosion level (broken lines) of Sn-(W) ore deposits of the Erzgebirge according to Seltmann et al. (1989, 1990). 1 Older Granites (OG suite); 2 Younger Granites (YG suite); 3 microgranite dykes; 4 breccia pipes
Fig. 20. Multi-element spectrum for major granite phases of the Erzgebirge (OG 1-2 Older Granites; YG 1-2 Younger Granites), normalized to average crustal element contents (CLARKE values) specified in the lowermost column (in ppm). (Tischendorf et al. 1987:227)

suite and less crustal input in the YG suite (Schütze et al. 1984; Gerstenberger et al. 1984; Stiehl 1985; Dahm et al. 1985). The exceptionally low Sr initial ratio of the YG suite may, however, result as well from postmagmatic rubidium metasomatism, which is a very widespread and typical phenomenon in the Erzgebirge tin granites and which has been shown to affect the intrusions up to several Ma after their solidification (Gerstenberger 1989). Such an explanation would allow an essentially identical lower crustal source for both OG and YG suites. First Nd isotope data from the Altenberg and Eibenstock tin granites with initial εNd values of 0.0 and -6.0, respectively (Gerstenberger 1989), point nevertheless to quantitatively variable involvement of mantle material in these rocks.

Based on numerous Rb-Sr and K-Ar ages and on field relations, the older concept of two major phases of granite magmatism in the time intervals of 340-310 (OG suite) and 305-280 Ma (YG suite) is still widely accepted, with tin mineralization associated with the end of the younger granite cycle (Lorenz and Schirm 1987; Stemprok 1986; Tischendorf et al. 1987). This concept is
compatible with the geological evolution in neighbouring Hercynian granite provinces (Fichtelgebirge, Black Forest and Vosges Mountains, Massif Central).

Both Older and Younger Granite suites have peraluminous composition, with mol. Al$_2$O$_3$/Na$_2$O+K$_2$O+CaO 1.06-1.11 for OG and 1.20-1.27 (muscovitization) for the YG suite. The entire granite sequence from OG1 to YG3 appears to be interlinked by systematic chemical enrichment and depletion patterns, i.e. successive enrichment in F, Cs, Li, Rb, Ta, Sn, W and complementary depletion in Ti, Fe, Mg, Ca, Co, Cr, Ni, V, Zr, Sc, Hf, Ba, Sr, REE (Figs. 20 and 21).

The trace element trends indicate a process of magmatic evolution predominantly controlled by fractional crystallization. The degree of fractionation F of the youngest granite phase of the OG suite has been estimated by Budzinski and Tischendorf (1985) as 0.1-0.2. The YG suite marks for some elements and isotope ratios a hiatus with the OG suite, and is also modified by fluid interaction, but its consistent and systematic element distribution pattern is in favour of an interpretation as the most evolved granite stage of a general late-Hercynian differentiation suite. The latest YG3 subintrusions consist of small alkalifeldspar aplogranite bodies which display an extreme degree of fractionation. Ti-Ta data from the Altenberg, Sadisdorf and Zinnwald alkalifeldspar aplogranite stocks (Just et al. 1987; Tischendorf
1989) define a range of 50-200 ppm Ti and 15-100 ppm Ta for both magmatic and hydrothermally overprinted (mineralized) rocks (Fig. 22). The immobile and incompatible nature of tantalum allows an estimate of the minimum

Fig. 22 (continued on next page). Ti-Zr, Sn-Ta and Ta-Ti variation diagrams for various granite units of the Erzgebirge. Data points are arithmetic means from the compilation of Tischendorf (1989). Correlation coefficient r for log[Ti]-log[Zr] is 0.86 (n=17), for log[Ta]-log[Sn] 0.88 (n=17), for log[Ti]-log[Ta] (n=23) -0.94.

NB 0-2 Niederbobritzsch massif (least-evolved part of OG suite); GP Granite porphyry of Altenberg-Frauenstein (OG suite); OG 1-3 Older Granites (Aue, Bergen, Schwarzenberg, Flaje, Kirchberg); OGt Transitional Granites (Bergen-type); IG 1-2 Intermediate Granites (Krinitzberg, Walfischkopf; xenoliths inside of YG suite); S 1-2 Schellerhau granites (early YG suite); YG 1-3 Younger Granites (Eibenstock-Nejdek, Schellerhau, Altenberg, Zinnwald, Sadisdorf, Sachsenhöhe, Greifenstein, Ehrenfriedersdorf, Geyer; Z Zinnwald alkalifeldspar aplogranite (latest subintrusion of YG suite). Data for Ti-Ta diagram include in addition (Just et al. 1987): Sa 1-2 Sadisdorf syeno- and monzogranite; A 1-3 Granite suite of the Altenberg ore deposit (analogous to YG 1-3 suite), with A 3 being an alkalifeldspar microgranite; A locates arithmetic mean of mineralized samples of greisenized granite unit A 2
degree of fractionation which gives $F = 0.01$ for most evolved rock portions (calculated from Eq. 9 in Chapter 2.2 with the limiting assumption of $\overline{D} \equiv 0$).

The distribution pattern of tin as a function of TiO$_2$, Zr and Rb/Sr is given in Fig. 23. According to our general model depicted in Fig. 6, the contents of titanium, zirconium and the Rb/Sr ratio are taken as three independent indicators of fractionation of granitic melt. The Erzgebirge granite suites follow essentially a tin enrichment pattern in accordance with a fractional crystallization model (linear correlation of trace elements in log-log space). The least evolved granite portions have tin contents of 5-6 ppm, tin levels which would be expected by partial melting of average crustal material. There are no indications of a regional geochemical specialization in tin previous to the large-scale action of magmatic fractionation in the Erzgebirge granite batholith.

The geological situation of the western Erzgebirge is very similar to the neighbouring Fichtelgebirge in eastern Bavaria. The trace element trends of the Fichtelgebirge granite suite look like the Erzgebirge trends, without, however, reaching the very high degree of fractionation typical for the tin-bearing granite phases of the Erzgebirge (Richter and Stettner 1979; Tischendorf et al. 1987) (Figs. 24 and 25). Differentiation suites for individual granite intrusions of the Fichtelgebirge are documented in Richter and Stettner (1979, 1987) and Richter (1984).

The late-orogenic Hercynian granites of the Black Forest and Vosges Mountains are similar to the Fichtelgebirge and Erzgebirge granites as well. Rb-Sr isochron data from the Black Forest and Vosges Mountains document an early-orogenic granite suite of 365-329 Ma in age, followed by post-orogenic biotite granites with 325-310 Ma and biotite-muscovite granites with 300-280 Ma (von Drach et al. 1974; Brewer and Lippolt 1974). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.708-0.730 suggest crustal source material. Fractional crystallization controls the magmatic evolution of at least the youngest and most evolved granite phases which reach locally (granites of Bärhalde and

Fig. 23 (next page). TiO$_2$-Sn, Rb/Sr-Sn and Zr-Sn variation diagrams for Erzgebirge granite phases (arithmetic means ± one standard deviation). Trace element data from Tischendorf et al. (1987). Correlation lines are statistically significant at a confidence level of >99 %. Reference fields for global averages of bulk and upper crust according to Taylor and McLennan (1985), shale data from Rössler and Lange (1976).
Fig. 24. Compositional trends of the Erzgebirge and Fichtelgebirge granite suites in the Sr-Ba-Rb triangle (Tischendorf et al. 1987:230). The data of the Fichtelgebirge granites are from Richter and Stettner (1979) and represent: R1 and R2 marginal facies; G1, G1R, G1S porphyritic granites of Weißenstadt-Marktleuthen, Reut and Selb; G2 "Randgranit"; G3 "Kerngranit"; G4 "Zinngranit". The YG suite of the Erzgebirge and the G4 granite of the Fichtelgebirge ("Zinngranit") are hydrothermally overprinted.

Sprollenhaus in the Black Forest) a relatively high degree of fractionation (Emmermann 1977). Tin data from Black Forest granites are not available, but mineralogical occurrences of cassiterite on fractures and in greisen bodies in the Sprollenhaus granite suggest a situation close to a tin granite.

3.2 Massif Central, France

The NW part of the French Massif Central hosts over an area of 150 x 50 km several small tin deposits which are associated with Hercynian granite intrusions. Tin mining in the Massif Central dates back to Roman times, but
Fig. 25. Sn-Zr variation diagram of the Fichtelgebirge granite suite (Richter and Stettner 1979:110; see explanation of granite types in this reference). The sample group G4 ("Zinngranit") represents the most fractionated granite phase of the Fichtelgebirge and is hydrothermally overprinted was, however, never important. There are several geochemical and petrographic studies in relation to exploration work for tin, tungsten and uranium which give whole-rock tin data (Aubert 1969; Ranchin 1970; Burnol 1974, 1978; Boissavy-Vinau 1979; Raimbault 1984).

Tin mineralization is of combined greisen and vein type (Montebras, Échassières, Blond, Saint-Sylvestre) and is bound to locally albitized alkalifeldspar granite stocks which have a Rb-Sr isochron age of 320-300 Ma with Sr initials of 0.707-0.712 (Burnol 1978; Duthou 1978). The high degree of fractionation of these rocks is documented in detail in the above studies. The tin distribution pattern of the granites is given in Fig. 26 as a function of TiO$_2$ and Rb/Sr. There is a statistically significant linear log-log correlation, in spite of petrographically distinct hydrothermal overprint, which reflects magmatic

Fig. 26 (next page). Tin distribution as a function of TiO$_2$ and Rb/Sr in granitic rocks of the French Massif Central. Data from Burnol (1978), Boissavy-Vinau (1979), Boissavy-Vinau and Roger (1980). Shale and crust reference compositions from Rösler and Lange (1976), and Taylor and McLennan (1985). The correlation lines are significant at a confidence level of >99.9% (TiO$_2$-Sn: $r=-0.77$, $n=73$; Rb/Sr-Sn: $r=0.82$, $n=55$)
fractionation, in accordance with other trace element data. The fact that this tin enrichment trend reaches up to 100-500 ppm Sn in strongly albitized and muscovitized rock portions indicates a little effective tin redistribution process during hydrothermal overprint, and explains the very limited tin mining potential of this area. The reason for the limited postmagmatic mobility of tin in the Massif Central may lie in the relatively oxidized state of the granites which are situated above the NNO buffer [Raimbault (1984) reports on accessory magnetite]. In contrast, such a situation is favorable for the mobility of uranium which is extensively leached from the granites and which is concentrated in several important ore deposits.

3.3 Cornwall

The Cornwall tin province is, according to both historical and current tin mining figures, the most important European tin producer (mine output in 1988: 3500 t Sn). The hydrothermal Sn-W-As-Fe-Cu-Pb-Zn-Ag-U mineralization in Cornwall is spatially associated with posttectonic Hercynian granites which intrude a 12-km-thick Upper Paleozoic low-grade metasedimentary flysch sequence with subordinate mafic volcanic intercalations (Holder and Leveridge 1986). There are five larger plutons (Dartmoor, Bodmin Moor, St. Austell, Carnmenellis, Land's End) and numerous smaller stocks and dykes which are, according to geophysical data, part of an inferred granite batholith about 250 km by 40 km in size. The total volume of the batholith is estimated at around 68,000 km³ (Willis-Richards and Jackson 1989).

The granitic plutons have Rb-Sr isochron ages of 280-290 Ma; granite porphyry magmatism extends to 270 Ma (Darbyshire and Shepherd 1985, 1988). Sr and Nd initials ($^{87}$Sr/$^{86}$Sr₂ = 0.709-0.717; $\varepsilon_{Nd}$ -4.5 to -7.2) correspond to the peraluminous S-type character of the granites and suggest, together with high $\delta^{18}$O values of 10.8-13.2, an anatectic origin from Proterozoic pelitic material which did not suffer an earlier high-grade metamorphic event (Darbyshire and Shepherd 1985, 1988; Floyd et al. 1983; Jackson et al. 1982). Fluid inclusion Rb-Sr isochron data define a main episode of tin mineralization around 270 Ma (Darbyshire and Shepherd 1985). K-Ar age data from polymetallic veins indicate continued low-temperature hydrothermal activity throughout the Mesozoic and Cenozoic (Halliday 1980; Jackson et al. 1982) which is commonly seen as a consequence of the high total content of heat-producing elements (average values for least altered
Cornubian granites are 11.3 ppm U and 19.1 ppm Th; Tammemagi and Smith 1975).

The predominant lithology of the composite batholith is K-feldspar megacrystic coarse-grained biotite granite (about 90% of outcrop area). It is intruded by fine-grained biotite and biotite-muscovite granite, and by volumetrically subordinate granite porphyry dikes (known as elvans). The granitic rocks are peraluminous (A/CNK = 1.1-1.4), have low magnetic susceptibility typical of ilmenite-series granitoids, and have a modal composition near the 1 kbar thermal minimum of the experimental granite system. Hydrothermal overprint is very widespread (albitization, microclinization, muscovitization, tourmalinization, kaolinization; Exley and
Fig. 28. Metal production of the Cornwall tin province as a function of vertical distance from granite contact. Diagram from Willis-Richards and Jackson (1989)

Stone 1982; Ball and Basham 1984; Charoy 1986). Immobile element patterns indicate pronounced fractionation trends (Ball and Basham 1984; Charoy 1986; Darbyshire and Shepherd 1985). The REE distribution patterns in Fig. 27 for granite phases with minor hydrothermal modification (incipient sericitization and chloritization of feldspars and biotite, respectively) imply strong feldspar fractionation, corroborated by correlation between SiO2, Rb, Rb/Sr and negative Eu anomaly (Darbyshire and Shepherd 1985). The increasing degree of hydrothermal overprint amplifies the magmatically established REE trends (Alderton et al. 1980).
Tin mineralization is mostly in the form of steeply dipping vein systems and sheeted vein swarms, and has a strong affinity for the granite contact. Fig. 28 shows the recorded historic mine output for a number of metals in relation to the vertical distance from the granite contact (Willis-Richards and Jackson 1989). Homogenization temperatures in fluid inclusions give a minimum temperature range for major cassiterite deposition of the order of 350-450°C with fluid salinities of 15-23 eq. wt% NaCl (Jackson et al. 1982).

Systematic studies on tin contents in the Cornwall tin granites have not been published. The data of Stone (1982) and Ball and Basham (1984) hint at tin enrichment with increasing degree of fractionation (Fig. 29). The highly evolved nature of the Cornubian granites is graphically summarized in Fig. 30.
Fig. 30. Trace element characteristics of Cornubian granites (n = 14) normalized to average granite composition as defined by Le Maitre (1976) and Abbey (1983). Diagram from Hall (1990).

The average tin content of the Cornubian granites is given as 14-36 ppm (Stone and Exley 1985), 7-20 ppm (Willis-Richards and Jackson 1989), and 23 ppm (Hall 1990).
3.4 Malaysia

The SE Asian tin belt is composed of three petrogenetic-chronologically distinct granite provinces (Fig. 31).

Fig. 31. Geographic distribution of granite provinces in the SE Asian tin belt according to Cobbing et al. (1986), and location of places mentioned in text.
Fig. 32. The composition of the Main Range and eastern province granites of Malaysia in the PEARCE diagram. Data from Cobbing et al. (1986)

1. The Main Range granite province which hosts the famous Malaysian tin fields near Kuala Lumpur and in the Kinta Valley and which is of minor economic importance in central and northern Thailand. The Main Range granites are peraluminous, S-type biotite granites and have Rb-Sr ages in the range 220-200 Ma with Sr initials of 0.716-0.751 (Liew and McCulloch 1985; Darbyshire 1988a). Their geotectonic position is posttectonic with respect to the pre-Permian folding of the Paleozoic country rocks, and is a result of either continental collision of several micro-terranes (Mitchell 1977; Beckinsale et al. 1979) or of intracontinental rifting (Helmcke 1985).

2. The eastern granite province is relatively poor in tin (the ratio of historic tin output of Main Range to eastern granite province in Malaysia is 19:1) and is composed of hornblende-biotite and biotite granites of Permo-Triassic age (265-230 Ma). The granites of the eastern province are chemically more
primitive compared to the Main Range granites, and classify as volcanic-arc granites in the sense of Pearce et al. (1984) (Figs. 32 and 33). The hornblende-bearing granites have I-type characteristics and their Sr initials are 0.705-0.710, whereas the biotite granites are closer to S-type and have Sr initials of 0.708-0.714 (Liew and McCulloch 1985). The same rock group occurs also in Thailand, where no tin is associated. The prolongation of the eastern granite province into Indonesia is uncertain. The granites of the Tin
Islands appear to represent both petrologically and chronologically a mixed population of Main Range and eastern province (Darbyshire 1988b; Cobbing et al. 1986).

3. The western granite province is restricted to western Thailand and Burma and is composed of Cretaceous-Tertiary granite intrusions in geotectonic relationship to the still active subduction of the Indian Plate below SE Asia. The intrusions consist of metaluminous hornblende-biotite granites (I-type) and peraluminous biotite granites (S-type) with ages of 95-50 Ma and Sr

Fig. 34. TiO$_2$-Sn and Rb/Sr-Sn (see next page) variation diagrams of Main Range and eastern province granites in Malaysia. (Data from Liew (1983); all samples >67 wt% SiO$_2$). Boxes with reference compositions according to data in Taylor and McLennan (1985) and Rösler and Lange (1976). Correlation for Main Range samples significant with confidence level of >99.9% (TiO$_2$-Sn: $r$=-0.63, n=68; Rb/Sr-Sn: $r$=0.68, n=70); samples of eastern granite province have log[Rb/Sr]-log[Sn] correlation with 99% confidence level ($r$=0.40, n=43), log[TiO$_2$]-log[Sn] with 80% ($r$=-0.22, n=43)
Fig. 34 (continued)
initials of 0.708-0.735 (Beckinsale 1979; Beckinsale et al. 1979; Nakapadung-rat et al. 1984b; Darbyshire 1988c; Darbyshire and Swainbank 1988). The large tin mining areas of Phuket and Phangna in southern Thailand, as well as the Burmese tin deposits, are associated with these Cretaceous-Tertiary biotite granite suites.

The tin distribution pattern of both Main Range and eastern province granites (East Coast) of peninsular Malaysia, based on data in Liew (1983), is compiled in Fig. 34. Both sample populations define statistically significant log[Rb/Sr]-log[Sn] and log[TiO$_2$]-log[Sn] correlation lines, in spite of considerable scatter. Part of this scatter is likely to be a result of hydrothermal overprint, particularly primary dispersion associated with the rich tin mineralization in the Main Range. Another part of this scatter derives from the proximity of tin levels in the eastern granite population near the analytical detection limit. However, the tin contents in both granite populations are distinctly different. Both correlation trends have a similar slope and, at a given Rb/Sr ratio or TiO$_2$ content, tin content of the Main Range samples is three to four times higher than in those from the East Coast.

The parallel displacement of the two tin enrichment trends suggests different source material and similar magmatic evolution for both rock groups. Their origin is constrained by initial Sr and Nd isotope data (Liew and McCulloch 1985; Darbyshire 1988a). The $\epsilon$Sr(T)-$\epsilon$Nd(T) diagram in Fig. 35 locates the different compositional fields of both Malaysian granite provinces. The Main Range granites are, in accordance with their mineralogical-geochemical characteristics, of crustal origin. Their source material is probably of Middle Proterozoic age (1700-1500 Ma) as recorded by U-Pb ages of inherited zircons and deduced from Nd model ages (Liew and Page 1985). The East Coast granites, on the other hand, have Sr and Nd initials which suggest the involvement of more primitive source material, in line with their petrochemical characteristics. Nd model ages give a range of 1400-1000 Ma (Liew and McCulloch 1985) and can be interpreted to indicate a mixing process between primitive mantle material and crust (Darbyshire, pers. commun. 1988). It follows from this model that the Main Range tin enrichment trend in Fig. 34 reflects the composition of the metasedimentary basement whereas the East Coast trend is a result of mantle plus basement melting. A linear extrapolation of the TiO$_2$-Sn variation pattern towards subgranitic composition is not permitted because of the increasingly compatible behaviour of titanium towards mafic composition.

It should be noted that the granite samples plotted in Figs. 32-34 are from the granitic main phases in Malaysia and not from those granite variants directly
Fig. 35. Initial Sr and Nd isotope composition of Malaysian granites from the Main Range (MWC) and eastern granite province (MEC) in comparison with other Phanerozoic continental margin granitic rocks. PR Peninsular Ranges; SN Sierra Nevada; AD Central Andean; LI Lachlan Foldbelt, I-type; LS Lachlan Foldbelt, S-type; BCO British Caledonian Older Granites; BCN British Caledonian Newer Granites; FH French Hercynian, Pyrenees; black line: mantle array; IA primitive island arc basalts. (Liew and McCulloch 1985:598)

associated with tin mineralization. As in all other tin provinces, the Main Range granites consist dominantly of K-feldspar porphyric medium- to coarse-grained biotite granite which forms large plutons/batholiths. These are locally cut by quantitatively subordinate, medium- to fine-grained subintrusions which are more or less hydrothermally overprinted and which consist of biotite-muscovite to muscovite-tourmaline granite. Tin mineralization is associated with these late muscovite-bearing granite phases.

3.5 Thailand

Tin deposits in Thailand are restricted to the western mountain range near the Burmese border and are associated with both Triassic Main Range granites and, economically more important, Cretaceous intrusions of the western
granite province (Fig. 31). Granitic rocks east of Bangkok, such as the Rayong pluton (Main Range type), and all Permo-Triassic intrusions further east, such as the Chanthaburi and Loei granites (eastern granite province) are tin-barren. They are, however, associated with some copper and molybdenum mineralization of porphyry type (Brown et al. 1951; Jacobson et al. 1969; Lehmann 1988a).

A regional petrographic-geochemical study in central and northern Thailand and in the Hermyingyi Mine (Burma) compared the following granite intrusions, located in Fig. 31:
1. Mae Sariang pluton (Triassic): K-feldspar megacrystic biotite-hornblende granite; metaluminous to weakly peraluminous (I-type); no tin mineralization.
2. Om Koi pluton (Triassic): K-feldspar megacrystic biotite and biotite-muscovite granite (sub-solidus muscovite); peraluminous (S-type); minor tin mineralization in associated pegmatite and hydrothermal systems (quartz-tourmaline-cassiterite-wolframite-muscovite-biotite-kaolin veins).
3. Mae Tom pluton (Cretaceous): K-feldspar megacrystic biotite granite; weakly peraluminous (I-type); no tin mineralization.
4. Loei intrusions (Permo-Carboniferous): a granitic suite with a wide range of compositions from hornblende quartz monzonites to hornblende-biotite granodiorites to biotite-hornblende granodiorites/granites and to biotite granites; metaluminous to weakly peraluminous (I-type); no tin, but copper porphyry mineralization.
5. Chanthaburi intrusions (Permo-Carboniferous): a suite of K-feldspar megacrystic biotite-hornblende granites to biotite granites; metaluminous to weakly peraluminous (I-type); no tin, but molybdenum porphyry mineralization.
6. Rayong pluton (Triassic): K-feldspar megacrystic biotite and biotite-muscovite granite (sub-solidus muscovite); peraluminous (S-type); $^{87}\text{Sr}/^{86}\text{Sr}=0.726$ (Nakapadungrat et al. 1984b); no tin mineralization.
7. Border Range granites (Pongkrathing, Pilok, Hermyingyi) (Cretaceous and early Tertiary): K-feldspar megacrystic biotite and biotite-muscovite granite (sub-solidus muscovite) with alkalifeldspar aplogranite subintrusions; peraluminous (S-type); Hermyingyi: $^{87}\text{Sr}/^{86}\text{Sr}=0.727$ (Lehmann and Mahawat 1989); tin mineralization of greisen, stockwork, vein and sulphide-replacement type associated chiefly with aplogranites and aplite-pegmatite systems.

All these granitic intrusions have a high emplacement level and are partly (eastern granite province) or completely (Main Range and western granite province) equilibrated with 1 ± 0.5 kbar minimum-melt conditions in the
Fig. 36. The composition (arithmetic means) of granite populations from Thailand, Burma and Indonesia (Tanjungpandan Pluton, Belitung Island) in the Pearce diagram. SYN-COLG syn-collisional granites, VAG volcanic-arc granites, WPG within-plate granites, according to the terminology of Pearce et al. 1984)

experimental Qz-Ab-Or-An-H₂O system. Systematic trace-element trends imply for all granite populations fractional crystallization as the dominant process controlling magmatic evolution. The tin-bearing alkalifeldspar aplogranites display an extreme degree of differentiation which has no petrological equivalent in the eastern granite province (Lehmann and Mahawat 1989).

Analogous to the situation in Malaysia, the granites of the Main Range and western province are located predominantly in the "syn-collision" reference field of the Pearce diagram, i.e. crustal source material, whereas the more primitive granitic rocks of the eastern province plot in the "volcanic-arc" reference field (Fig. 36). Included in Fig. 36 are the four main intrusive phases of the Tanjungpandan pluton from Belitung Island, Indonesia, which are
discussed later (Chap. 4.1). All granite populations in this figure are of posttectonic position with respect to the early Permian regional folding event, and are not foliated. The trend of increasing Rb and Y+Nb contents in the most evolved granite phases (along the "syn-collision"-"within-plate" division line in Fig. 36) is a result of intramagmatic fractionation and not of changing source rock composition as usually implied in the petrogenetic interpretation of such diagrams (Pearce et al. 1984).

The tin distribution pattern for these granite populations is given in Fig. 37 which compares average tin contents (arithmetic means ± one standard deviation) with degree of differentiation. The parameters used as indicators of differentiation are TiO$_2$, Rb/Sr and D.I. (normative Qz+Or+Ab, i.e. Thornton-Tuttle differentiation index). Tin mineralization is associated only with those

![Graph showing tin content as a function of D.I. and TiO$_2$ and Rb/Sr](graph.png)

Fig. 37. Tin content as a function of D.I. (normative Qz+Ab+Or, i.e. Thornton-Tuttle differentiation index), and of TiO$_2$ (wt%) and Rb/Sr (see next page) for several granite populations from Thailand and Burma. Important tin mineralization is associated with Hermyingyi and Pilok aplogranites. Global reference fields from Taylor and McLennan (1985)
Fig. 37 (continued)
rocks which have the most differentiated composition. These rocks plot on the most evolved part of a general tin enrichment trend which extrapolates back to average crustal composition. The highly fractionated Pilok aplogranite has a very large scatter in tin content which is a result of hydrothermal tin redistribution and which will be discussed in Chapter 4.

3.6 Nigeria

About ninety percent of the Nigerian tin production comes from placer deposits associated with greisens, albitization zones and vein swarms in apical portions of Jurassic biotite granite intrusions (Buchanan et al. 1971; MacLeod et al. 1971; Bowden and Kinnaird 1984). There is also a small amount of tin and tantalum produced from deeply weathered pegmatites of Middle-Cambrian age in a 400-km-long, SW-NE-aligned belt between Ife and Jos (Matheis and Caen-Vachette 1983).

The Mesozoic biotite granites are part of a petrologically extended ring-complex suite and occur locally along a more than 1000-km-large lineament zone which stretches from the Air Plateau in Niger in the north to the Jos Plateau in central Nigeria to the south. The ring complexes have dimensions in the 1- to 10-km range and consist of an often eroded superstructure of trachytic to rhyolitic rocks intruded by high-level alkalifeldspar-biotite granites and quartz syenites of metaluminous to peraluminous composition with variable mineralogy (hornblende, riebeckite, hedenbergite, fayalite, etc.). The age of this anorogenic magmatism decreases systematically towards the south, with an age of 164 ± 4 Ma in the Jos Plateau. This trend has been interpreted as related to a stationary thermal anomaly in the mantle (Sillitoe 1974; Breemen et al. 1975).

The ring complexes consist of composite A-type intrusions (Collins et al. 1982) which have trace element distribution patterns typical of fractional crystallization suites (diagnostic elements are particularly the least mobile elements Zr, Ti, Nb, Y). Tin mineralization is associated with most fractionated and peraluminous granite phases (Imeokparia 1980, 1984, 1986a,b; Olade 1980). Sr initials of biotite granites with little hydrothermal overprint are in the range 0.706-0.709 and indicate an origin from the lower crust or from mantle with crustal contamination. Most fractionated granite phases with hydrothermal overprint have Sr levels of a few ppm only (sensitivity against Sr
Fig. 38. Tin content as a function of Rb/Sr, TiO$_2$ (wt%) and Zr (ppm) in the Jurassic granite suites of the Kwandonkaya and Ganawuri ring complexes in central Nigeria (in both suites: hornblende-fayalite granite to biotite microgranite). The data are arithmetic means of individual granite units and represent 38 samples from Ganawuri and 108 samples from Kwandonkaya (Imeokparia 1984, 1986a). All correlation lines are statistically significant at a confidence level of >99% (log[TiO$_2$]-log[Sn]: $r$=0.83, $n$=11; log[Rb/Sr]-log[Sn]: $r$=0.92, $n$=11; log[Zr]-log[Sn]: $r$=-0.95, $n$=11)
exchange) and record heterogeneous $^{87}\text{Sr}/^{86}\text{Sr}_i$ values up to 0.752 (Breemen et al. 1975).

The tin distribution patterns for two tin-bearing granite suites from the central part of the Jos Plateau are shown in Fig. 38, based on data in Imeokparia (1984, 1986a). The linear correlation lines are in accordance with a magmatic evolution controlled by fractional crystallization; tin contents of least evolved granite samples are near Clarke values. The relatively high Zr contents result from the alkali-rich melt and high melt temperature (hypersolvus composition) which allow high zircon solubility (Bowden 1982; Watson and Harrison 1983).

![Geological outline of SW Nova Scotia and distribution of the Halifax (1), New Ross (2), and West Dalhousie (3) plutons mentioned in text. Tin prospects are located by solid triangles. (According to Smith and Turek 1976, and Smith et al. 1982)](image)

**Fig. 39.** Geological outline of SW Nova Scotia and distribution of the Halifax (1), New Ross (2), and West Dalhousie (3) plutons mentioned in text. Tin prospects are located by solid triangles. (According to Smith and Turek 1976, and Smith et al. 1982)

### 3.7 Nova Scotia, Canada

A large part of the Nova Scotia peninsula in eastern Canada is composed of Devonian granitic rocks which intrude a 12-km-thick, Lower Paleozoic volcano-sedimentary sequence in low-grade metamorphic facies (Fig. 39).
The largest intrusion in Nova Scotia is the South Mountain batholith, which is exposed over 6000 km$^2$. It consists of several little-mapped subintrusions with gradual contacts from peripheral biotite granodiorite towards biotite and biotite-muscovite granite in the central parts. The petrological and chemical zonation is explained by a process of in situ differentiation (Smith 1979; Smith and Turek 1976). There are similarities to the Blue Tier batholith in Tasmania, Australia (Groves and McCarthy 1978), which has, however, much more tin. Tin mineralization in the South Mountain batholith is restricted to several tin prospects in the New Ross pluton (Fig. 39).

The zoned plutons of the South Mountain batholith are 380-350 Ma old and have initial Sr isotope ratios of 0.708 ± 3. They have peraluminous composition (accessory cordierite and andalusite; 2-4 wt% normative corundum), contain abundant metasedimentary xenoliths, and satisfy the criteria for S-type granitic rocks (Chappell and White 1974). Their magmatic evolution is controlled by plagioclase and biotite fractionation (Smith 1979).

Figure 40 shows the tin distribution patterns for the three largest subplutons which are dominantly composed of biotite granite (Halifax, New Ross, West Dalhousie). Chemical data for individual samples are not published, but the arithmetic means for ten granite units demonstrate a tin enrichment trend very similar to that in the Erzgebirge. The high degree of fractionation of the Erzgebirge tin granites is, however, not attained, and only few samples from the weakly tin-bearing New Ross pluton can compare to the Younger Granites in the Erzgebirge.

3.8 Cape Granite, South Africa

The post- or anorogenic Cape batholith consists of several smaller granite plutons which form a 200-km-long, NW-SE-orientated belt near Capetown. The granites are around 600 Ma old and represent a differentiation suite with high intrusion level which goes from K-feldspar megacrystic coarse-grained

Fig. 40 (next page). Tin content of three plutons from the South Mountain batholith in Nova Scotia as a function of TiO$_2$ (wt%) and Rb/Sr. Data points are arithmetic means (horizontal and vertical bars for Halifax samples indicate one standard deviation) and are from Smith (1979) and Smith et al. (1982)
Fig. 40. For legend see previous page
biotite granite (main phase) to medium-grained biotite granite and to fine-grained biotite-muscovite and alkalifeldspar granite in peripheral subunits (Kolbe 1966). Hornblende, cordierite and titanite are accessory components in the coarse-grained granite phase, tourmaline is abundant in the medium- and fine-grained phases. There are several prospects with quartz-tourmaline-muscovite-cassiterite-pyrite-arsenopyrite veins in the endo- and exocontact of the granites (Malmesbury shale-quartzite sequence), and small tin placer deposits were sporadically mined prior to World War II (Thamm 1943; Hunter 1973). Disseminated molybdenite and breccia pipes with pyrite-molybdenite-scheelite in fluorite-bearing alkalifeldspar granite have been described by Scheepers and Schoch (1988).

Based on geochemical data, Kolbe (1966) and Kolbe and Taylor (1966b) interpreted the Cape granites as a comagmatic fractionation suite. The porphyritic main phase has a composition near average "low-Ca granite" (Turekian and Wedepohl 1961), the two younger granite phases display an advanced degree of fractional crystallization and are modified by fluid interaction and resultant loss of mobile elements (Kolbe 1966). Low normative corundum content (<1 wt%) and metaluminous to weakly peraluminous composition (mol. Al₂O₃/Na₂O+K₂O+CaO <1.1) in all granite phases point to an I-type origin; high Nb, Ga and Y contents in the alkalifeldspar granites are similar to those of anorogenic, within-plate granites (A-type). Biotite compositions from leucogranites indicate oxygen fugacities between the Ni-NiO and hematite-magnetite buffers (Scheepers and Schoch 1988), and Fe₂O₃/FeO rock ratios of ≥0.5 are indicative of a magnetite-series affiliation. Pervasive hydrothermal alteration under oxidizing conditions is accompanied by molybdenum and uranium redistribution (Th/U 10-20; Scheepers and Schoch 1988; Schoch and Scheepers 1990).

The tin distribution pattern of the Cape granite suite is shown in Fig. 41. The behaviour of tin is distinctly different from elements like Cs, Rb, Sr, Co, Ni, V and Ti, which display systematic enrichment and depletion trends (Kolbe 1966). The samples have a nearly constant tin content around 3 ppm and there is no significant dependence on degree of fractionation, i.e. coarse-grained main phase with 3 ppm Sn, medium-grained phase with 3.2 ppm Sn, and fine-grained phase with 3.4 ppm Sn. A similar situation is seen in the Snowy Mountains granites of SE Australia.
Fig. 41. Tin content as a function of TiO₂ (wt%) and Rb/Sr in the Cape granite suite, South Africa. (Data from Kolbe 1966)
3.9 Snowy Mountains, SE Australia

The approximately 200 x 100-km-large region of the Snowy Mountains in New South Wales, SW of Canberra, is part of the Lachlan Foldbelt and consists chiefly of Silurian granitic rocks intruded into low-grade clastic sediments (flysch) of Ordovician age. The granitic rocks are locally foliated, have discordant contacts and high intrusion level, and form a composite intrusion suite of tonalitic to leucogranitic composition. The chemical variation of the mainly granodioritic plutons has been interpreted by White and Chappell (1977, 1983) as a result of mixing of anatetic partial melts and of restitic material. The leucogranitic late phases with a composition near the low-pressure thermal minimum of the experimental Qz-Ab-Or-H₂O system are characterized by an advanced degree of fractional crystallization (Kolbe and Taylor 1966a,b) and have a less peraluminous (locally even metaluminous) composition compared to the granodioritic main phase. The leucogranites satisfy some I-type criteria, the biotite granodiorites are of S-type (White and Chappell 1977, 1983; Hine et al. 1978). Initial Sr and Nd isotope data of the S-type granitic rocks are in the range of 0.709-0.718 and εNd -6 to -10, respectively, and suggest a crustal origin from 1400 Ma old basement (Nd model age). For the I-type leucogranites, on the other hand, values of 87Sr/86Sr 0.705-0.712 and εNd(T) 0 to -9 document involvement of mantle material (Compston and Chappell 1979; McCulloch and Chappell 1982). The leucogranites of the Lachlan Foldbelt are classified as magnetite-series rocks (White and Chappell 1983).

Tin data for the Snowy Mountains granites are given in Kolbe and Taylor (1966a) and are plotted in Fig. 42. The samples are grouped into biotite granodiorite (S-type) and biotite leucogranite (I-type). The granodiorites occasionally have accessory cordierite and muscovite, rarely green hornblende, and correspond to average high-Ca granites (Turekian and Wedepohl 1961). The leucogranites have low Ca, Fe, Mg, Cr, Ni, Co, Cu, V, Zr, and Sr contents and are high in U, Rb, Cs (Kolbe and Taylor 1966a). Their Sn contents are, however, constant and range from 2-4 ppm. The absence of any tin enrichment in these rocks in spite of a high degree of differentiation, similar to the case of the Cape granite, is probably understandable as a consequence of conditions of high oxygen fugacity (magnetite-series granites) and of a low degree of alumina saturation (metaluminous to weakly peraluminous composition).
Fig. 42. Tin contents as a function of TiO$_2$ (wt%) and Rb/Sr in granitic rocks from the Snowy Mountains, Lachlan Foldbelt, Australia. Data from Kolbe and Taylor (1966a)