Tin granites, geochemical heritage, magmatic differentiation

By B. Lehmann, Berlin[*])

With 12 figures

Zusammenfassung

Metallogenetische Provinzen stehen nicht zwangsläufig mit einer spekulativen regionalen geochemischen Spezialisierung im Zusammenhang. Am Beispiel der Zinngranite wird ein Schema zur Quantifizierung der beiden Komponenten »geochemische Vererbung« und »magmatische Differentiation« vorgestellt. Geochemische Vererbung kann dabei auf den Bereich von maximal 5–10 ppm Sn eingegrenzt werden. Entscheidender Prozeß für die Bildung von Zinngraniten ist die magmatische Differentiation, wobei ein variabler Bulk-Zinn-Verteilungskoeffizient das mögliche Zinn-Potential bestimmt.

Abstract

Metallogenic provinces are not self-evident geochemical provinces. A scheme to quantify the processes of »geochemical heritage« and »magmatic differentiation« in the evolution of tin granites is presented. Geochemical heritage can be limited to a maximum contribution in the 5–10 ppm Sn range. The crucial process in the formation of tin granites is magmatic differentiation. A variable bulk Sn distribution coefficient controls the tin ore potential of granites.

Résumé

Les provinces métallogéniques ne correspondent pas nécessairement à des domaines à permanence géochimique. Prenant l'exemple des granites à étain, l'auteur présente un schéma qui quantifie les deux composants que sont »l'héritage géochimique« et la »différenciation magmatique«. L'héritage géochimique peut être limité à une contribution maximale de 5 à 10 ppm Sn. Le processus décisif dans la formation des granites à étain est la différenciation magmatique, au cours de laquelle le coefficient de répartition de Sn est variable et détermine le potentiel-métal du granite.

Краткое содержание

Металлогенетические провинции не обязательно связаны с региональной геохимической специализацией их. На примере оловосодержащих гранитов представлена схема для оценки, как "геохимической наследственности", так и "магматической дифференциации". Геохимическая наследственность оказывается ограничена пределами 5–10 ppm олова. Ведущим процессом при образовании оловосодержащего гранита является дифференциация магмы.

Introduction

Ore deposits of certain metals are clustered in relatively well defined geographical zones on earth. This observation led De Launay (1913) to the concept of metallogenic provinces. Often in these regions the province-specific metals have become concentrated into ore deposits at various times (»étagement temporel«; Routhier 1967).

At first glance it seems logical to interpret these observations in that the spatial and temporal relationships of ore deposits in metallogenic provinces are caused by a common geochemically anomalous reservoir. Schuiling (1967:540) postulates: »The concept of a metallogenic 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.« By this interpretation the neutral term of »metallogenic province« changes into the speculative concept of »geochemical provinces«, »regional geochemical specialization«, or »metal domains« (Routhier 1967; 1980).

In its most elaborate form this concept has become the »Unitarian metallogenic law« (Routhier 1980:46): »Les concentrations d'un métal prennent naissance à l'intersection d'un domaine métallique (en réalité un volume pouvant descendre jusqu'au manteau), porteur pendant de longues durées (cf. permanence et héritage) d'un ›potentiel métal‹ (c'est le métallotecte primordial) et d'autres métallotectes, jouant comme ›révélateurs‹ de ce potentiel.«

---

[*]) Author's address: Dr. Bernd Lehmann, Institut für Angewandte Geologie, Freie Universität Berlin, Wichernstraße 16, D-1000 Berlin 33

Tin granites

Some of the best examples of metallogenic provinces are the tin provinces, which form well-defined belts on a 100–1,000 km scale.

The »étagement temporel« in some of these provinces is very striking. A famous example is the Bolivian tin province where ore deposits associated with both Triassic tin granites and Tertiary tin granites and tin porphyries occur in the same area.

Generally, tin deposits are spatially and temporally related to magmatic rocks of granitic composition (mainly »tin granites«, in some cases »tin porphyries«). Tin granites display geochemical specialization, i.e. enrichment in a suite of characteristic trace elements (Sn, F, B, Rb, Cs, Li, . . .) and impoverishment in other trace elements (Ba, Sr, Zr, Ti, . . .). It is interesting to note that geochemical specialization and ore productivity of tin granites are directly related (Tischendorf 1969).

The geochemical specialization of tin granites can be understood in terms of two basic processes:

1. Geochemical heritage: The geochemical characteristics of tin granites are inherited from anomalous pre-grantitic source material.
2. Magmatic differentiation: During fractional crystallization a suite of elements with bulk solid-liquid distribution coefficients $K_D < 1$ becomes enriched, whereas other elements with $K_D > 1$ are impoverished in residual melts.

Both processes may be involved in the evolution of tin granites. There is general agreement that the trace element pattern of tin granites points to an important contribution by magmatic differentiation but it is often suggested that this process only enhances primary geochemical anomalies. The variation diagram of Figure 1 allows a quantification of the role of both processes.

The model

A perfect fractional crystallization process is described by Rayleigh fractionation (Rayleigh 1986):

$$c_{i_t} = c_{i_0} \cdot F^{K_{D_i} - 1} \tag{1}$$

whereby F = Mass ratio of residual melt M_t to initial total melt M_0

K_{D_i} = Bulk solid-liquid distribution coefficient of element i

c_{i_0} = Initial concentration of element i in melt M_0

c_{i_t} = Concentration of element i in residual melt M_t

The validity of equation (1) for a suite of rock samples can be verified by the presentation of geochemical data of elements with $K_D \neq 1$ in a log-log diagram.

Linear correlation of elements i and j in such a diagram follows from transformation of (1) into:

$$\log \frac{c_{i_t}}{c_{i_0}} = (K_{D_i} - 1) \cdot \log F \tag{2}$$

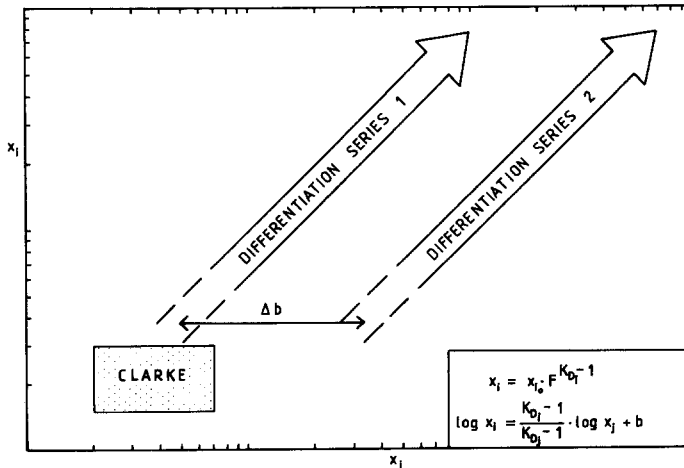$$\log \frac{c_{j_t}}{c_{j_0}} = (K_{D_j} - 1) \cdot \log F \tag{3}$$

Fig. 1. Quantification scheme for geochemical heritage in magmatic fractionation series (x_i = neutral fractionation indicator; x_j = element to be tested for geochemical heritage). For explanation see text.

The combination of (2) and (3) gives the linear equation for a log x/log y plane:

$$\log \frac{c_{i_t}}{c_{i_0}} \Big/ \log \frac{c_{j_t}}{c_{j_0}} = \frac{K_{D_i}-1}{K_{D_j}-1} = c \qquad (4)$$

The constant c corresponds to the slope m of the general linear equation:

$$\log c_{i_t} = m \cdot \log c_{j_t} + b \qquad (5)$$

The term b can be used as a measure of the component of geochemical heritage in magmatic differentiation suites (LEHMANN 1982) whereby Δ b is defined as the difference between the term b_1 of a normal fractionation line and b_2 of an anomalous fractionation line. A normal fractionation line would be one which can be traced back to an average rock composition field, whereas a fractionation line starting from a geochemically anomalous source would be shifted away by the amount of Δ b from such a reference field (Fig. 1).

It should be noted that complications of this simple picture may arise from different degrees of partial melting for different fractionation suites or from the fact that the bulk distribution coefficient K_{D_i} is treated here as a constant. However, this last assumption is not unreasonable in the case of tin granites whose major element chemistry is essentially near minimum melt composition.

The fractional crystallization pattern in a log-log diagram cannot be confused with possible mixing processes such as restite control (WHITE & CHAPPELL 1977) or assimilation of country rocks. The variable mixing of two end-member compositions in a log-log diagram results in hyperbolic mixing lines.

Results

Differentiation suites from tin and non-tin granites have been plotted in terms of a neutral fractionation indicator (x-axis) and the Sn content (y-axis) (Figs. 2–10). The Rb/Sr ratio and TiO_2 have been used as neutral fractionation indicators because these elements are readily available in routine geochemical analyses and therefore are often given in the literature. Other element combinations would of course be feasible as well.

In each diagram reference fields for average crustal, granite, and shale composition are plotted according to the data collection in RÖSLER & LANGE (1976). The shale reference field has been slightly enlarged towards lower Sn levels down to 4 ppm which corresponds to recent geochemical studies by TERASHIMA & ISHIHARA (1982) and LEHMANN et al. (1983). Only one variation diagram for each area is reproduced here for reasons of space, but the synoptic diagrams in Figs. 11 and 12 also show the second correlation line for each sample set. The correlation lines are mostly valid at a level of certainty of more than 99% (solid lines), the correlation lines of very little slope for the non-tin granites are valid at a 95% level (stippled lines). It follows from the diagrams in Figs. 2-10 that the data displayed can be interpreted in terms of fractionation although the main arguments for this finding are derived from other criteria discussed in the original papers.

The non-tin granites from the Cape Province/South Africa (KOLBE 1966) and from the Snowy Mountains/Australia (KOLBE & TAYLOR 1966) are plotted in Figs. 2 and 3. There is no distinct increase in Sn content during magmatic differentiation. The
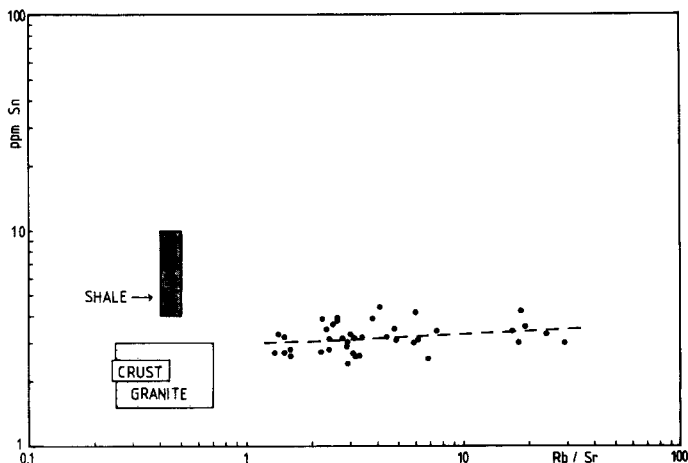

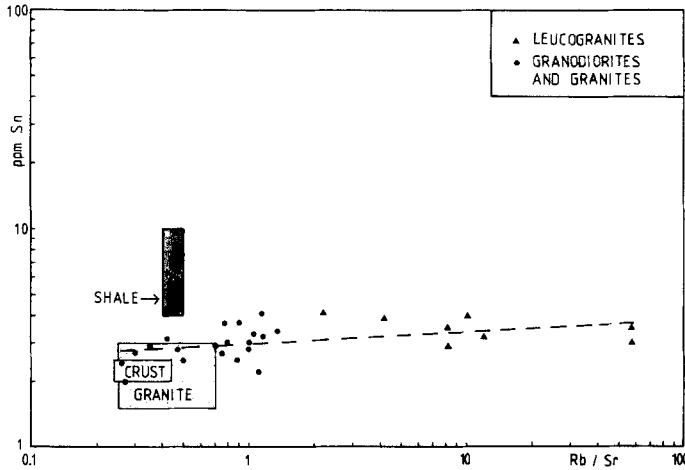Fig. 2. Granitic samples from the Cape Granite, South Africa (n = 40; r = 0.28). Data from KOLBE (1966).

Fig. 3. Granitic samples from the Snowy Mountains, N.S.W., Australia (n = 28; r = 0.44). Data from KOLBE & TAYLOR (1966).

correlation lines pass through the reference field for average granite.

Data from the Erzgebirge/GDR are plotted in Figure 4 (LANGE et al. 1972). The correlation line passes through the average shale field at the 5 ppm Sn level. A comparison with some data from the tin-barren granites of the neighbouring Thuringian Forest (BRÄUER 1970) shows the non-tin granite characteristics of Figs. 2 and 3.

Some data from the Triassic tin granites of northern Bolivia are shown in Figure 5 (LEHMANN 1979). The correlation line for primary magmatic rocks passes through the shale reference field at a 5 ppm Sn le-

Fig. 4. Granitic samples from the Erzgebirge, GDR (n = 11; means of 456 samples; r = –0.72). Data from LANGE et al. (1972). Crosses indicate mean values and minimum and maximum values for each sample group (RG = »Reliktgranite«; ÄG = »Ältere Granite«; ZG = »Zwischengranite«; JG = »Jüngere Granite«). Data for Thuringian Forest granites are from BRÄUER (1970).
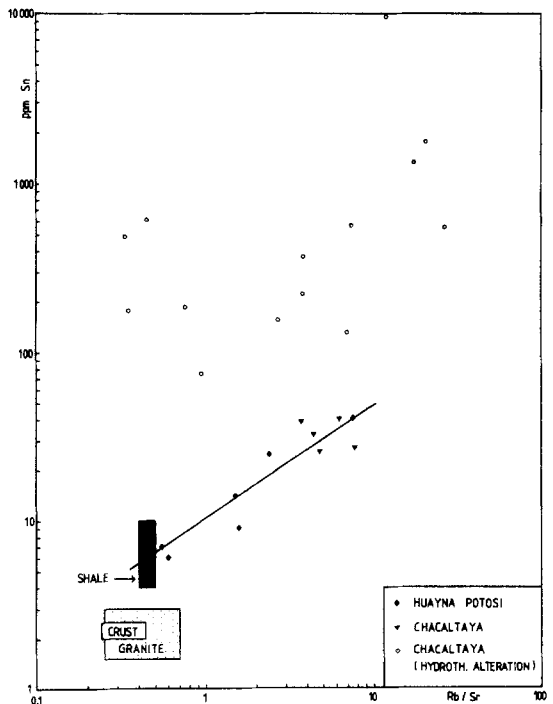

Fig. 5. Granitic samples from the Cordillera Real, Bolivia (n = 13; r = 0.94). Open circles indicate hydrothermally altered rocks from the same rock suite. Data from LEHMANN (1979).

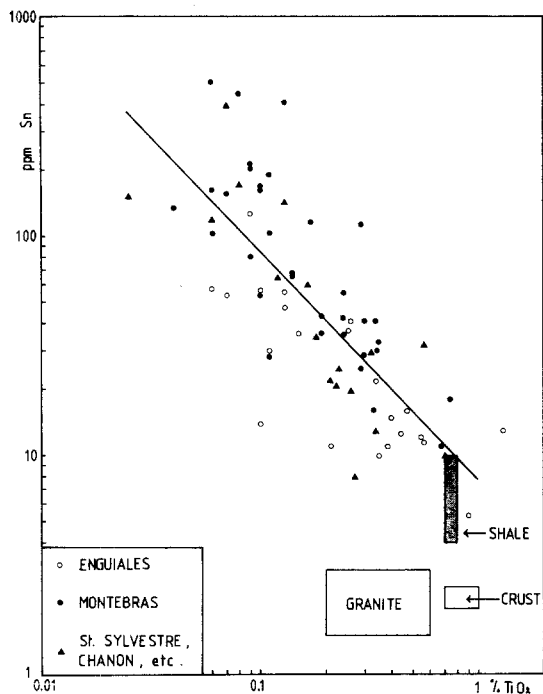Fig. 6. Granitic samples from the Massif Central, France (n = 73; r = −0.77). Data from BOISSAVY-VINAU (1979); BOIS-SAVY-VINAU & ROGER (1980); BURNOL (1978).

blastesis of fluorite, tourmaline, apatite, cassiterite, and siderite. The highest degree of alteration is shown in quartz-muscovite rocks (greisens) where the primary magmatic fabric is totally destroyed by heteroblastic-metasomatic transformations.

Data from the Massif Central/France are shown in Figure 6 (BOISSAVY-VINAU 1979; BOISSAVY-VINAU & ROGER 1980; BURNOL 1978). The least evolved members of this fractionation series are in the 3–10 ppm range. A similar behaviour is shown in Figure 7 for tin granites of Northern Portugal (NEIVA 1975, 1981; NORONHA 1982).

Tin granites from Thailand (ISHIHARA et al. 1980; NAKAPADUNGRAT et al. 1985) give correlation lines which can be interpreted as related to differentiation of average granitic material (Figs. 8 and 9). Hydrothermal alteration in the Takua Pa area/southern Thailand is characterized by a strong increase in Sn contents at a ± constant Rb/Sr ratio. The Triassic tin granites from the west coast of peninsular Malaysia (LIEW 1983) are the most evolved members of a fractionation line which would pass the shale reference field at a 5–10 ppm Sn level (Figure 10). Geochemically less evolved granitic rocks from this region have been analyzed by YEAP (1974) who found Sn contents of 4–5 ppm at Rb/Sr ratios of 1–3.

vel. Hydrothermally altered rocks from the same rock suite give a scatter distribution with distinctly high Sn values. The hydrothermal alteration is petrographically characterized by breakdown of plagioclase and biotite, muscovitisation, chloritisation,

Conclusions

The synoptic diagrams in Figs. 11 and 12 allow two basic conclusions:

1. The tin granite fractionation series are traceable back to the 4–10 ppm Sn range for relatively little-evolved members of the sample suites studied.
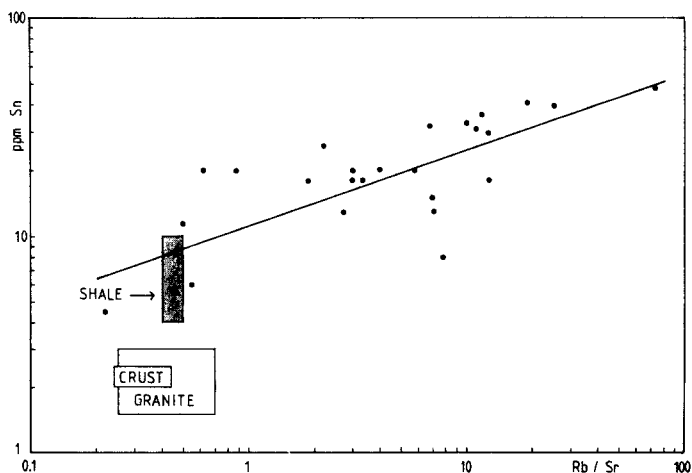

Fig. 7. Granitic samples from Northern Portugal tin granites (n = 24; r = 0.77). Data from NEIVA (1975, 1981); NORONHA (1982).
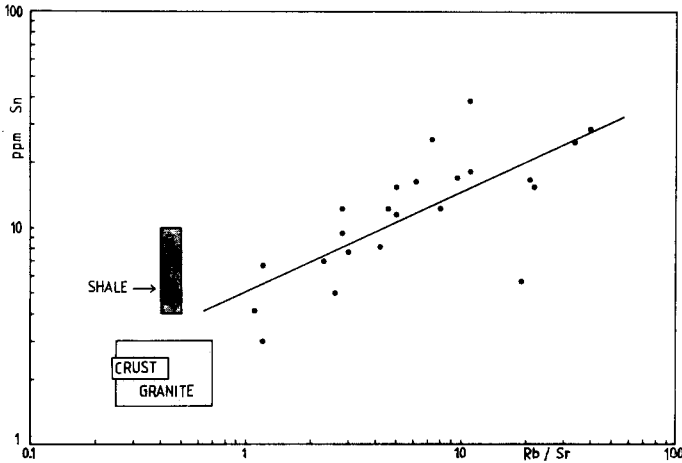
Fig. 8. Granitic samples from Thailand (n = 23; r = 0.73). Data from ISHIHARA et al. (1980).

This Sn range corresponds to average shale composition which may be a coincidence; but it should be noted that thick metasedimentary sequences (stratigraphic thicknesses around 10 km) are typical of tin provinces. The contribution of geochemical heritage in the sense of anomalous source rocks is limited to a maximum of 2-3 times enrichment compared to average crustal rocks. This possible regional geochemical specialization is relatively modest as compared to tin enrichment by magmatic differentiation, which may be tenfold and more. It is not evident why a possible but only slight regional geochemical specialization should critically control the formation of tin granites when the effectiveness of magmatic dif-
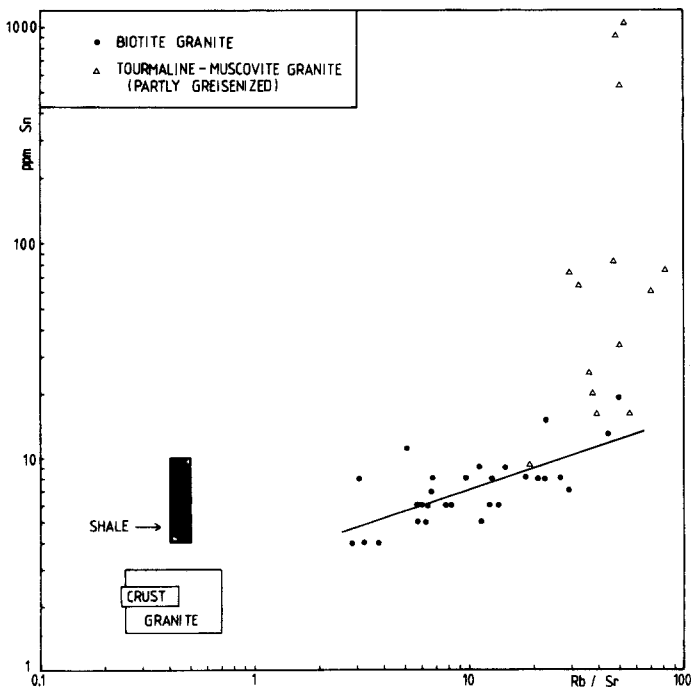

Fig. 9. Granitic samples from the Takua Pa tin granite, Southern Thailand (n = 29; r = 0.69). Open triangles are hydrothermally altered rocks. Data from NAKAPADUNGRAT et al. (1985).
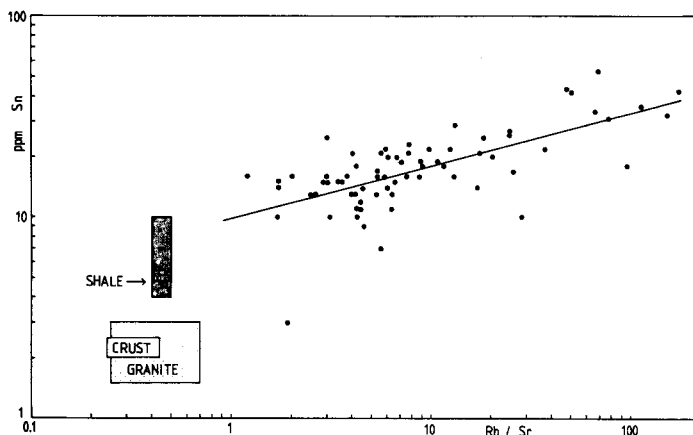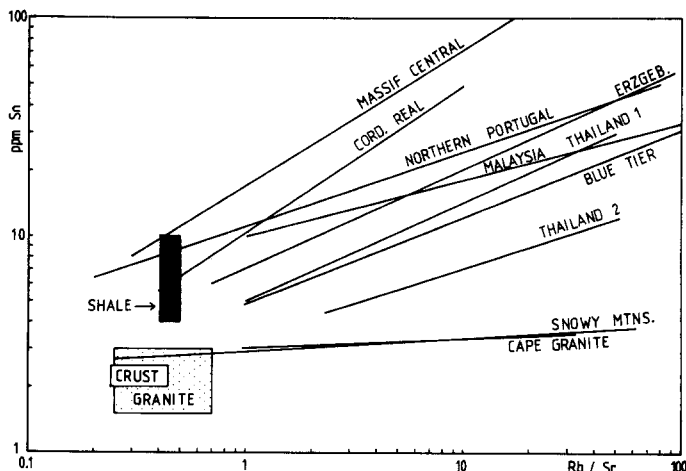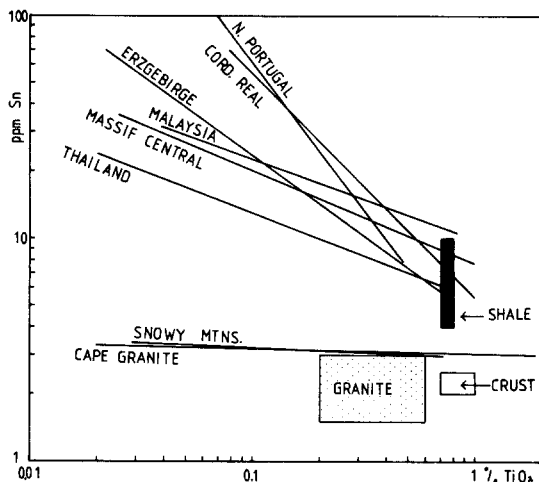
Fig. 10. Granitic samples from the West Coast tin province, Malaysia (n = 70; r = 0.68; all samples > 67% SiO$_2$). Data from LIEW (1983).

Figs. 11 and 12. Synoptic compilations of correlation lines from the sample suites of Figures 2–10. Crustal averages are from RÖSLER & LANGE (1976). In the Sn–Rb/Sr diagram an additional correlation line from the Blue Tier Batholith, Tasmania, Australia has been included (data from GROVES & MCCARTHY 1978).

ferentiation can easily balance initial chemical differences.

There is a possibility that tin granites are the most evolved phases of mantle-derived magmas. Current research in the Erzgebirge (SCHÜTZE et al. 1983; DAHM et al. 1985) and in Portugal (SCHERMERHORN this volume) point to very extensive fractionation lines. Under such an assumption the slightly tin-enriched earliest granitic phases are already the result of a long fractionation history. This process cannot be traced back by extrapolation of correlation lines in the scheme of Figure 1 because the drastic change in major element chemistry involved is accompanied by a non-linear variation of the bulk Sn distribution coefficient.

2. The slope of the correlation lines in Figs. 11 and 12 is variable. According to equation (4) this indicates a different bulk Sn distribution coefficient for different granite suites. It can be deduced that K_{DSn} for non-tin granites is ≤ 1, whereas for tin granites it is $\ll 1$. The reason for this variable bulk distribution coefficient is not well understood but it may depend on the Sn^{2+}/Sn^{4+} ratio in the melt which in turn is a function of f_{O2}. Under conditions of low oxygen fugacity in the melt (ilmenite-series granitoids of ISHIHARA 1977) tin may be in a predominantly bivalent state and would behave as an incompatible element whereas at high f_{O2} it may behave more compatibly (a reverse case of K_D-f_{O2} systematics has been demonstrated by TACKER & CANDELA 1985 for molybdenum).

In summary, a tin granite is formed by a prolonged fractionation history combined with a small Sn bulk distribution coefficient. Geochemical heritage plays only a minor or no role. The actual formation of tin deposits is, in addition, dependent on the release of a fluid phase and the associated release of mechanical energy which produces the permeability for effective hydrothermal circulation/mineralization.

Acknowledgements

References

BOISSAVY-VINAU, M. (1979): Processus géochimiques de concentrations liés à l'évolution de magmas granitiques. Applications aux filons à Sn-W du Massif Central et du Nord Portugal. – 220 p, unpubl. thesis, Université Paris VI.

BOISSAVY-VINAU, M. & ROGER, G. (1980): The TiO_2/Ta ratio as an indicator of the degree of differentiation of tin granites. – Mineral Deposita, 15, 231-236.

BRÄUER, H. (1970): Spurenelementgehalte in granitischen Gesteinen des Thüringer Waldes und des Erzgebirges. – Freiberger Forschungsh., C 259, 83–139.

BURNOL, L. (1978): Different types of leucogranites and classification of the types of mineralization associated with acid magmatism in the northwestern part of the French Massif Central. In: STEMPROK, M., BURNOL, L. & TISCHENDORF, G., Eds., Metallization associated with acid magmatism. – Vol. 3, 191–204, Praha (Czech. Geol. Survey).

DAHM, K.-P., GERSTENBERGER, H. & GEISSLER, M. (1985): Zum Problem der Granitgenese im Erzgebirge, DDR. – Z. geol. Wiss., 13, 545–557.

DE LAUNAY, L. (1913): Traité de métallogénie. Gîtes minéraux et métallifères. – 3 Vol., Paris (Ch. Béranger).

GROVES, D. I. & McCARTHY, T. S. (1978): Fractional crystallization and the origin of tin deposits in granitoids. – Mineral. Deposita, 13, 11–26.

ISHIHARA, S. (1977): The magnetite-series and ilmenite-series granitic rocks. – Mining Geology, 27, 293–305.

–, SAWATA, H., SHIBATA, K., TERASHIMA, S., ARRYKUL, S. & SATO, K. (1980): Granites and Sn-W deposits of peninsular Thailand. – Mining Geology, Spec. Issue 8, 223–241.

KOLBE, P. (1966): Geochemical investigation of the Cape Granite, South Africa. – Trans. Geol. Soc. S. Africa, 69, 161–199.

– & TAYLOR, S. R. (1966): Geochemical investigation of the granitic rocks of the Snowy Mountains area, New South Wales. – Journ. Geol. Soc. Australia, 13, 1–25.

LANGE, H., TISCHENDORF, G., PÄLCHEN, W., KLEMM, I. & OSSENKOPF, W. (1972): Fortschritte der Metallogenie im Erzgebirge. B. Zur Petrographie und Geochemie der Granite des Erzgebirges. – Geologie, 21, 457–489.

LEHMANN, B. (1979): Schichtgebundene Sn-Lagerstätten in der Cordillera Real, Bolivien. – Berliner Geowiss. Abh., A 14, 1–135.

– (1982): Metallogeny of tin: magmatic differentiation versus geochemical heritage. – Econ. Geol., 77, 50–59.

–, PETERSEN, U., SANTIVANEZ, R. & WINKELMANN, L. (1983): Tin and boron distribution in the Lower Paleozoic sequence of the Cordillera Real, Bolivia. – Unpubl. report to Intern. Union Geol. Sci., Research Developm. Program, 11 p.

LIEW, T. C. (1983): Petrogenesis of the peninsular Malaysian granitoid batholiths. – 291 p., unpubl. thesis, Australian National University.

NAKAPADUNGRAT, S., CHULACHARIT, T., MUNTHACHIT, Y., CHOTIGRAI, T. & SANGSILA, S. (1985): Geology of Sn-W granites in Takua Pa area, Southern Thailand. – Paper presented to Intern. Symposium Geology of Tin Deposits, Nanning, 35 p.

NEIVA, A. M. R. (1975): Geochemistry of coexisting aplites and pegmatites and of their minerals from central northern Portugal. – Chem. Geology, **16**, 153–177.

– (1981): Geochemistry of hybrid granitoid rocks and of their biotites from central northern Portugal and their petrogenesis. – Lithos, **14**, 149–163.

NORONHA, F. (1982): Rochas graníticas do triângulo Gerês-Barroso-Cabreira. Suas relações com mineralizações em Sn e W-Mo. – Publ. Mus. Lab. Mineral. Geol. Fac. Ciênc. Porto, **93**, 1–39.

RÖSLER, H. J. & LANGE, H. (1976): Geochemische Tabellen. – 2nd ed., Stuttgart (Enke).

RAYLEIGH, J. W. S. (1986): Theoretical considerations respecting the separation of gases by diffusion and similar processes. – Philos. Mag., **42**, 77–107.

ROUTHIER, P. (1967): Le modèle de la genèse. Quelques concepts fondamentaux en pétrologie et en métallogénie. Modèles de théories métallogéniques. – Chronique Mines Rech. Minières, **363**, 177–190.

– (1980): Qù sont les métaux pour l'avenir? Les provinces métalliques. Essai de métallogénie globale. – Mém. BRGM, **105**, 1–410.

SCHÜTZE, H., STIEHL, G., WETZEL, K., BEUGE, P., HABERLANDT, R., GERSTENBERGER, H., TISCHENDORF, G., WAND, U., MÜHLE, K., RÖSLER, H.-J., HERMICHEN, W.-L., GEISLER, M. & STRAUCH, G. (1983): Isotopen- und elementgeochemische sowie radiogeochronologische Aussagen zur Herkunft des Ehrenfriedersdorfer Granits. Ableitung erster Modellvorstellungen. – ZFI-Mitteilungen, **76**, 232–268, Leipzig.

SCHUILING, R. D. (1967): Tin belts on the continents around the Atlantic Ocean. – Econ. Geol., **62**, 540–550.

TACKER, R. C. & CANDELA, P. A. (1985): Experimental determination of crystal-melt partitioning of molybdenum in high-silica systems. – Geol. Soc. Am. Abstr. with Programs, Ann. Meet., p. 732.

TERASHIMA, S. & ISHIHARA, S. (1982): Tin abundance of some geosynclinal shales from Japan. – J. Japan. Assoc. Min. Petr. Econ. Geol., **77**, 1–6.

TISCHENDORF, G. (1969): Über die kausalen Beziehungen zwischen Granitoiden und endogenen Zinnlagerstätten. – Z. angew. Geol., **15**, 333–342.

WHITE, A. J. R. & CHAPPELL, B. W. (1977): Ultrametamorphism and granitoid genesis. – Tectonophysics, **43**, 7–22.

YEAP, C. H. (1974): Some trace element analyses of West Malaysian and Singapore granites. – Geol. Soc. Malaysia Newsletter, **47**, 1–6.