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The TiO_2/Ta Ratio as an Indicator of the Degree of Differentiation of Tin Granites

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Tin deposits in Eastern Marche (French Massif Central) and North of Viseu (Portugal) are associated with final stages of differentiation of granitoid magmatism. Fractional crystallization causes increase in Sn, W, Ta, Rb, Cs, F and Li, and decrease in Ti, La, U, Th, Ba etc. That trend is very clearly expressed by tantalum, strongly correlated with tin, and by titanium. Hence the TiO_2/Ta ratio is a good indicator of granitic melt differentiation. Its value gradually ranges from 4 900 in the less differentiated granodiorite to < 1 in the most differentiated granite from Marche area. That ratio could be a useful guide to suitable areas for tin exploration.

I. SEARCH FOR TIN DEPOSITS

Panning is a technique suitable for prospection of every type of tin-deposits, primary (veins, disseminations etc.) as well as secondary (placers).

Geophysical methods can be used for regional exploration, for example to indicate the general plan form of granitic batholiths and then to delineate areas likely for prospection (Bott et al., 1958, in Hosking, 1974). In some particular cases, geophysical surveys can even be used for prospection: e.g. airborne magnetism in case of deposits containing magnetite associated with cassiterite (Hosking, 1974), or refraction seismic methods in case of small placers and of placers directly related to the morphology of the bedrock (Thawisak Danusawad, 1969).

The geochemical prospection applied to soil or rock samples is widely considered to be a method convenient to tin exploration. This method holds advantage to be useful in areas without streams, where panning is then not suitable (Sa-Ngob Kaewbaidhoon, 1969). Tin content is analyzed in any case, and in addition other elements considered to be geochemical indicators, useful at least locally: Cu, Zn, Mo (Hosking, 1965), Bi, As, Li, Rb, Be, F (Tischendorf, 1973, 1977).
A comprehensive geochemical comparison of "specialized", "precursors" and "normal" granites of various tin regions in the world was given by Tischendorf (1977), who suggests that stannigene granites could be characterized by the following anomalous averages of trace elements: 30 ± 20 ppm Sn, 220 ± 120 ppm or 400 ± 200 ppm Li, 550 ± 200 ppm Rb, 13 ± 6 ppm Be, 3 700 ± 1 500 ppm F.

For tin (and W, Be, Ta....) deposits related to granitic intrusives important guides for exploration, at a regional

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Table 1. Ratios proposed as indicators of tin granitoids

Authors	Ratio	Rocks or minerals	Range of values
Tischendorf et al (1972)	Mg/Ti	Normal granites	40
		Specialized granites	10 - 0.3
Beus and Sitnin (1968)	Mg/Li	Barren granites	270 ± 80
		Ore-bearing granites	75 ± 30
Beus and Sitnin (1968)	Zr/Sn	Barren granites	76 ± 20
		Ore-bearing granites	30 ± 10
Tischendorf (1977)	K/Rb	Normal granites	> 100 (max. 300)
		Specialized granites	< 100 (min. 20)
Beus and Grigorian (1975)	K/Rb	Normal granites	170
		Granites related to mineralization	130
Taylor et al (1956)	K/Rb	Differentiated granites and pegmatites	< 144
Taylor and Heier (1960)	Ba/Rb	Feldspars from augen gneiss	20.6
		Feldspars from pegmatite	6.06
		Feldspars from mineralized pegmatite of economic size	1.29
Shmakin (1973)	Rb/Ba	K-feldspars from muscovite pegmatites	0.276
		K-feldspars from rare-metal pegmatites	23.2
		Biotite from muscovite pegmatites	0.99
		Biotite from rare-metal pegmatites	62
		Muscovite from muscovite pegmatites	0.321
		Muscovite from rare-metal pegmatites	1928
Ahrens (1964)	Rb/Tl	Granites	200
		Pegmatites	115
		Biotite from granites	230
		Lepidolite from granites	140

scale, depend on lithology: special types of rocks (greisens, albitites....) characterized by hydrothermal alterations and metasomatism. Geochemical evolution of some elements in these special rocks and, generally speaking, in the granitic rocks allows to improve the lithologic guides. The chemical elements whose concentration widely ranges either during magmatic evolution or during hydrothermal and metasomatic processes are considered to be relevant exploration indicators: e.g. Li and Rb increase, Ba and Sr obviously decrease in the course of magmatic evolution (Groves and McCarthy, 1978). Commonly, the geochemical indicators are ratios between two elements either in rocks or in minerals. These ratios involve two chemical elements varying in a very different way, or even inversely: Mg/Ti, Mg/Li, Zr/Sn, K/Rb, Rb/Ba, Rb/Tl (Table 1). For pegmatites, Ginzburg (1960) proposes several indicator ratios increasing in the course of development of the pegmatitic process: (Nb + Ta)/Ti, Ta/Nb, Mn/Fe, Rb/K, Hf/Zr, $\Sigma(Y)/\Sigma(Ce)$, Ga/Al. These ratios were not included in table 1 for lack of values. A new ratio (TiO_2/Ta) is proposed here as a very accurate indicator of magmatic differentiation.

II. THE TiO_2/Ta RATIO

The magmatic evolution was recently compared in three composite batholiths bearing tin or tungsten mineralizations (M. Boissavy-Vinau, 1979; M. Boissavy-vinau et al., 1979): the eastern Marche with a Sn, Li, W, Be mineralized albitic cusp of leucogranite (Montebras, Allier, Massif Central); the NW end of the Margeride with the wolframite lodes of Enguialès and Leucamp; the North Viseu district (Beira Alta, Portugal) with the cassiterite pegmatite of Lagares.

97 rock samples representative of the main granitic facies have been analyzed for the following elements: major element oxides by quantometry (C.R.P.G., Nancy), 23 trace elements (Sn, W, Ta, RE, U, Th, Zr, Hf, Ba, Sr, Cr, Co, Ni, Sc, Sb, As, Cs, Rb) by neutron activation (Lab. Pierre Süe, CEN Saclay), F and Li by flame spectrophotometry and fluorimetry (Lab. de Géologie Appliquée, Paris).

The general outline of the petrographic and geochemical evolution is very similar in the two tin areas.

1. There are two successive fractionated suites, whose different stages are represented by eight to ten granitoid facies.

2. The evolution of granitic magma, involving a fractional crystallization process, is very advanced.

3. In the final stage of the magmatic evolution, tin is more concentrated than tungsten.

Continued fractional crystallization in the rest melts causes enrichment in the following elements: Sn, W, Ta, Rb, Cs, F and Li and on the other hand impoverishment in: Ti, U, Th, Hf, Ba, Sr, Zr, Ni, Co, Sc, RE.

Two elements are closely representative of that double trend: titanium and tantalum. Hence their ratio is a good indicator for the evolution degree of granitic magma differentiation. A clear positive correlation between tantalum and tin is evidenced (Fig. 1).

Because the studied tin deposits are related with the most differentiated granitoids, then the TiO_2/Ta ratio can be proposed as a regional guide for selecting suitable areas for detailed investigation.

The use of this ratio as an indicator of magmatic differentiation degree presents several advantages.

1. Late hydrothermal processes that affect the most fractionated granites leach some elements as rubidium or lithium. Consequently the range of values for ratios usually proposed as geochemical indicators Mg/Li, Ba/Rb, K/Rb, is not strictly significant of the magmatic processes. On the other hand tantalum and titanium are stable during these post magmatic alteration processes.

2. Ti and Ta are progressively fractionated all along the magmatic differentiation.

3. Their ratio varies conspicuously along the magmatic differentiation: in the Marche area it ranges from 4 900 in the earliest granitic facies to 1 in the final tin mineralized albitic granite (Table 2).

Such a range of values is much wider than for other ratios previously proposed (Table 1), and hence the TiO_2/Ta ratio is a very suitable geochemical indicator.

Table 2. Evolution of TiO_2 and Ta contents in the Marche area's granitic complex

	Lithology	N° of samples	Mean contents TiO_2 %	Mean contents Ta ppm	TiO_2/Ta (ppm) (ppm)
First suite	Guéret granodiorite	2	0.71	1.45	4896
	Chanon granite C1	5	0.32	2.4	1333
	Chanon granite C2	5	0.22	2.2	1000
	Jalèches granite	4	0.17	4.6	370
	Toulx granite	4	0.057	10.07	57
Second suite	Saint Silvain and Grand Roche granites	6	0.10	13.96	71.6
	Montebras microgranite	2	0.07	27.5	25.4
	Montebras albitic granite	2	0.02	211.5	0.94

Guéret: granodiorite with oriented structure - Chanon: biotite rich cordierite porphyritic granite; muscovite very rare in C1 facies, more abundant in C2 facies - Jalèches: K-feldspars rich two micas granite, free of albitization - Toulx: albite, tourmaline and two micas granite.

St-Silvain and Grand Roche: albitized two micas granite, muscovite rich - Montebras cusp microgranite with phenocryts of K-feldspars, quartz, muscovite and altered biotite - Montebras cusp albitic granite: intergrowths of lath-shaped albite crystals and muscovite flakes, interstitial microcline, late crystallized quartz, cassiterite, topaz, tantalite-columbite.

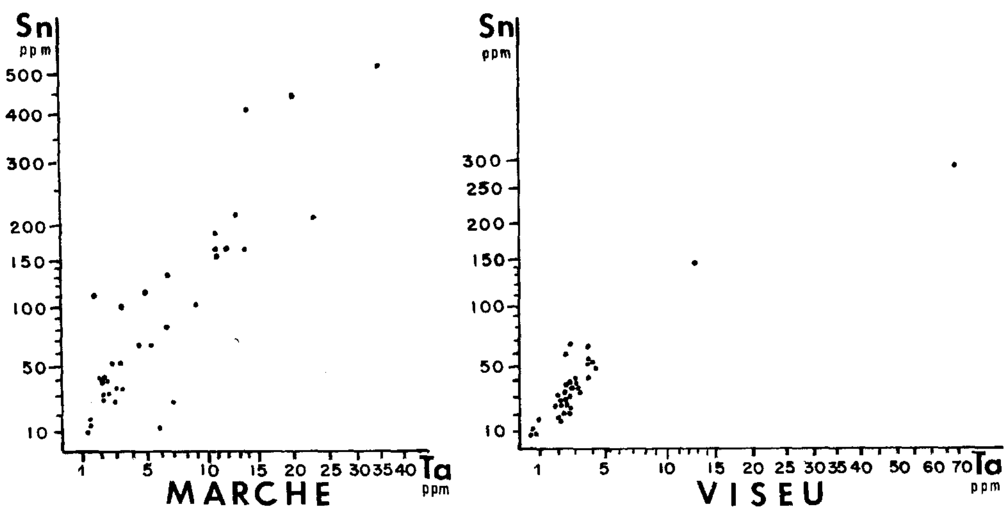

Fig. 1. Sn vs Ta plot of analyzed samples

4. Neutron activation is the most useful analytic method for weak traces of tin and tantalum (about 1 ppm). The tantalum analysis offers the advantage to be faster than the tin analysis which involves a chemical extraction.

Two other analytic methods can be used for traces of tantalum: colorimetry (> 10 ppm) and X-ray fluorescence spectrometry (>30 ppm). Their detection limits are low enough for analysis of differentiated granites (see table 2) and then these methods could be more suitable than neutron activation for exploration purposes.

In conclusion, it appears that the Ti_2O/Ta ratio is a specially suitable indicator of magmatic evolution by fractional crystallization, and in our opinion it could eventually be a reliable tool for assessing the tin potential of granitoids. These results concern two tin areas: the Marche and the North Viseu districts. Is it relevant to extend it to other tin granitic complexes? Actually, we cannot answer this question because of - lack of comparisons with other tin provinces or districts, - lack of general data about the geochemical properties of tantalum in granitic melts.

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