

# Anomalous Sn-rutiles in wall rocks of Bolivian tin deposits

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With 7 figures and 2 tables in the text

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**Abstract:** Heterogeneous Ti–Sn-accumulations (Sn-rutiles) have been detected in quartzitic wall rocks of Bolivian tin deposits by microprobe studies. Epitactic crystal growth by heteronucleation is suggested to explain their varying chemical composition. Transformation of sedimentary rutiles by hydrothermal-metasomatic fluids seems probable.

**Key words:** Rutile, Sn, quartzite, epitaxy, nucleation (hetero-), microprobe analysis; Bolivia.

**Auszug:** Bei Mikrosondenuntersuchungen an quarzitischen Nebengesteinen von bolivianischen Zinn-Lagerstätten wurden anomale Sn-Rutile festgestellt. Der stark schwankende Sn-Gehalt wird mit epitaktischem Kristall-Wachstum bei Hetero-Keimbildung erklärt. Hydrothermal-metasomatische Umwandlung von sedimentären Rutilen ist wahrscheinlich.

## Introduction

Rutile ( $\text{TiO}_2$ ) and cassiterite ( $\text{SnO}_2$ ) have the same lattice type ( $D_{4h}^{14}$ -group) with the same C-4 structure. Ionic radii of  $\text{Ti}^{4+}$  and  $\text{Sn}^{4+}$  differ only by about 5 % (Table 1).

Rutiles investigated up to now do not have any natural  $\text{SnO}_2$ -rich members (max. ca. 3 %  $\text{SnO}_2$ ) and  $\text{TiO}_2$  in the cassiterite lattice seems to be of minor importance in natural occurrences (about 0.5 %  $\text{TiO}_2$ ) (RAMDOHR, 1975). Miscibility experiments by LIETZ & NODOP (1955), NODOP (1956), and PADUROW (1956) showed complete isomorphism of the system  $\text{TiO}_2$ – $\text{SnO}_2$  at 1350 °C with a broad miscibility gap at temperatures below 1000 °C. These syntheses have been performed under dry conditions and do not simulate natural environmental conditions accurately.

Ionic substitution of  $\text{Sn}^{4+}$  and  $\text{Ti}^{4+}$  in a tin-titanite with 10 % Sn from the South African tin deposit of Arandis has been reported by RAMDOHR (1935).

In a survey of part of the Bolivian tin province we found in the wall rocks of tin deposits of the mining area of Milluni–Kellhuani–Kalauyo anomalous tin-rutiles of probably hydrothermal-metasomatic origin.

### Geologic situation

The tin deposits of Milluni, Kellhuani, Huallatani, and Kalauyo are situated in the Cordillera Real/Bolivia, and have been reviewed recently by SCHNEIDER & LEHMANN (1977). Besides the Sn-Zn vein of Milluni the

Table 1. Crystal-chemical affinity of Sn<sup>4+</sup> and Ti<sup>4+</sup>.

	Sn <sup>4+</sup>	Ti <sup>4+</sup>	Author
Ionic radius (Å)	0.71	0.68	AHRENS (1952)
	0.67	0.64	BELOV & BOKIY (1959) in WEDEPOHL (1970)
Coordination number	6	6	
Ionization potential (V)	40.74	43.24	AHRENS (1952)
Electronegativity (kcal/g atom)	235	260	POVARENENYKH (1955) in: WEDEPOHL (1970)
Lattice dimensions (Å)	cassiterite:	rutile:	RAMDOHR & STRUNZ (1967)
	a <sub>0</sub> :	4.59	
	c <sub>u</sub> :	2.96	

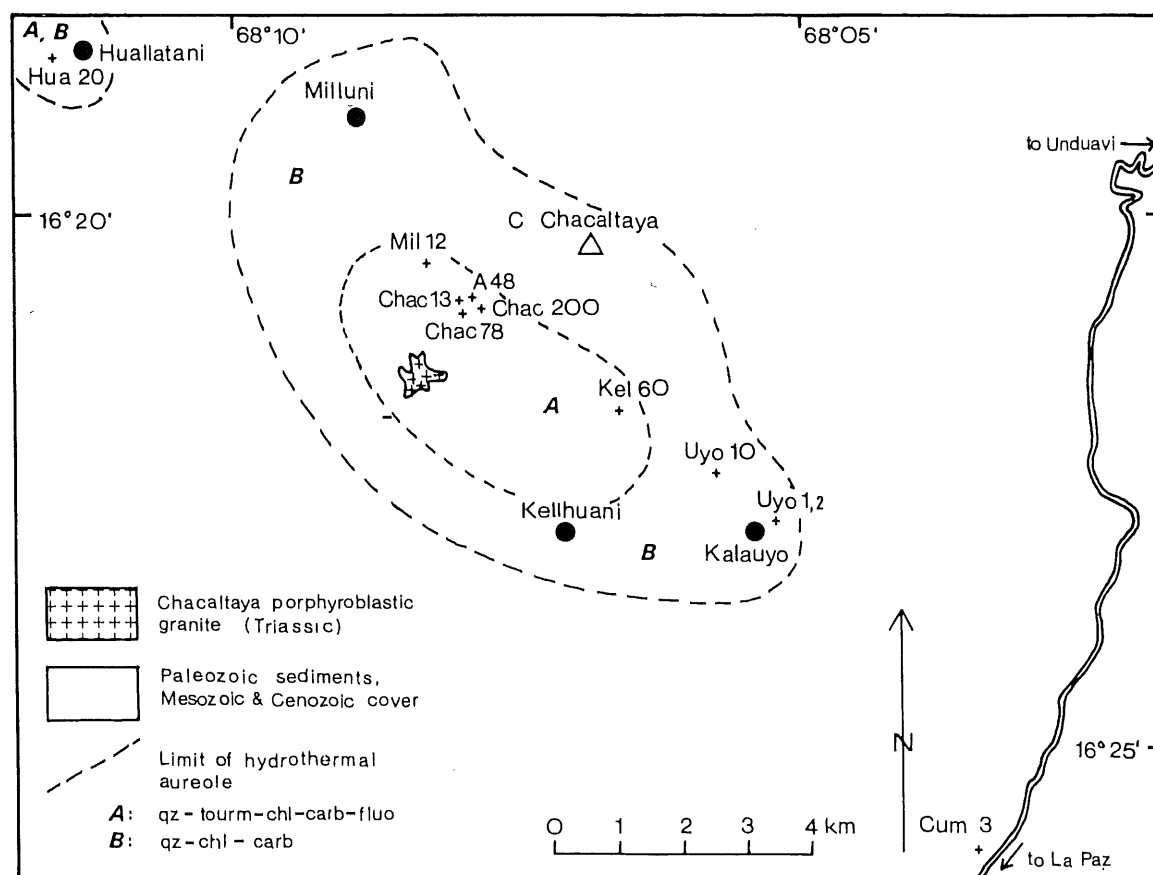
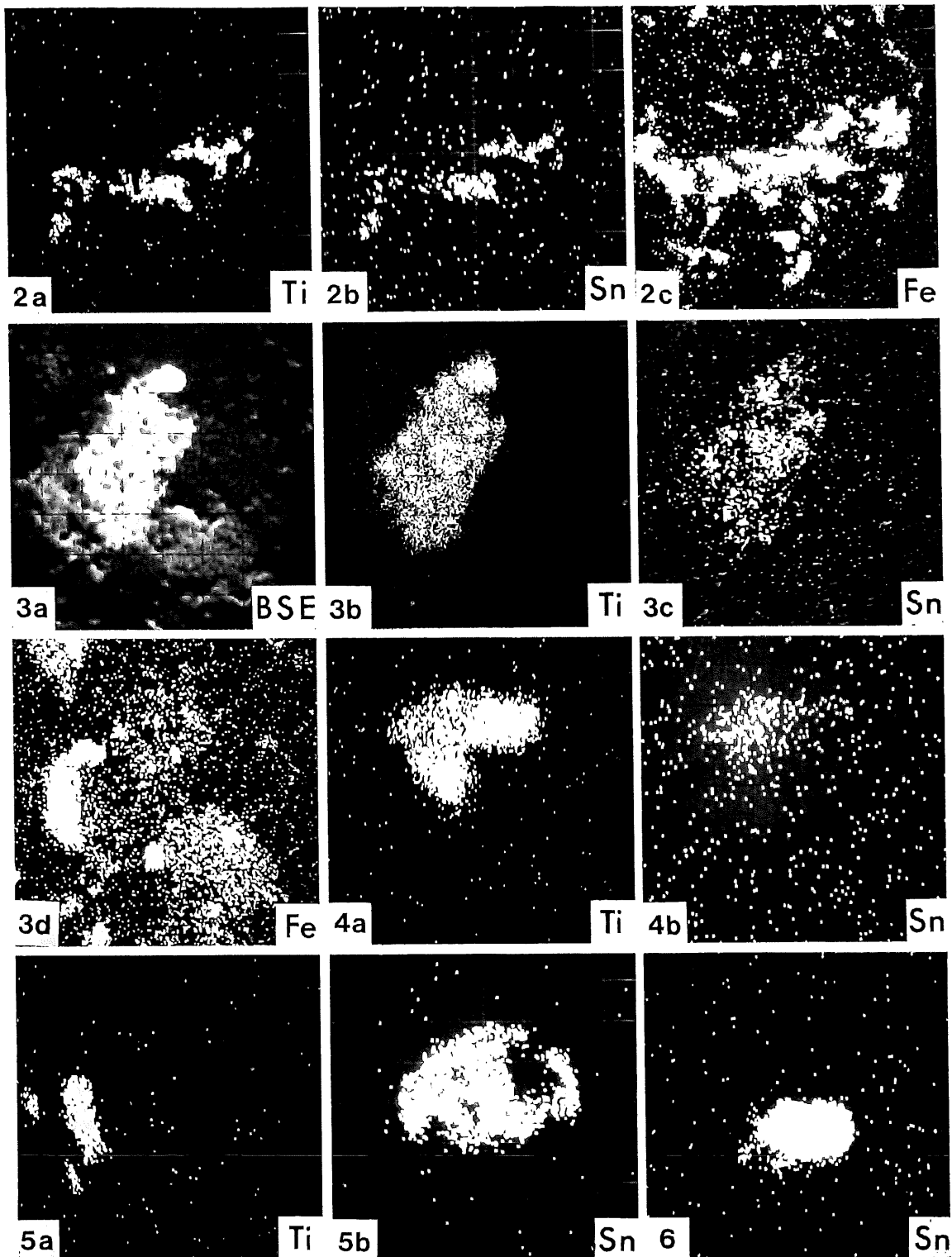


Fig. 1. Location of microprobe samples.



Figs. 2-7. Microprobe X-ray element distribution and back-scattered electron images (BSE). Magnification 230 $\times$ , except of Fig. 4 with 460 $\times$ .

2 a-c: Heterogeneous Ti-Sn accumulation (= Sn-rutiles); Chac-200.

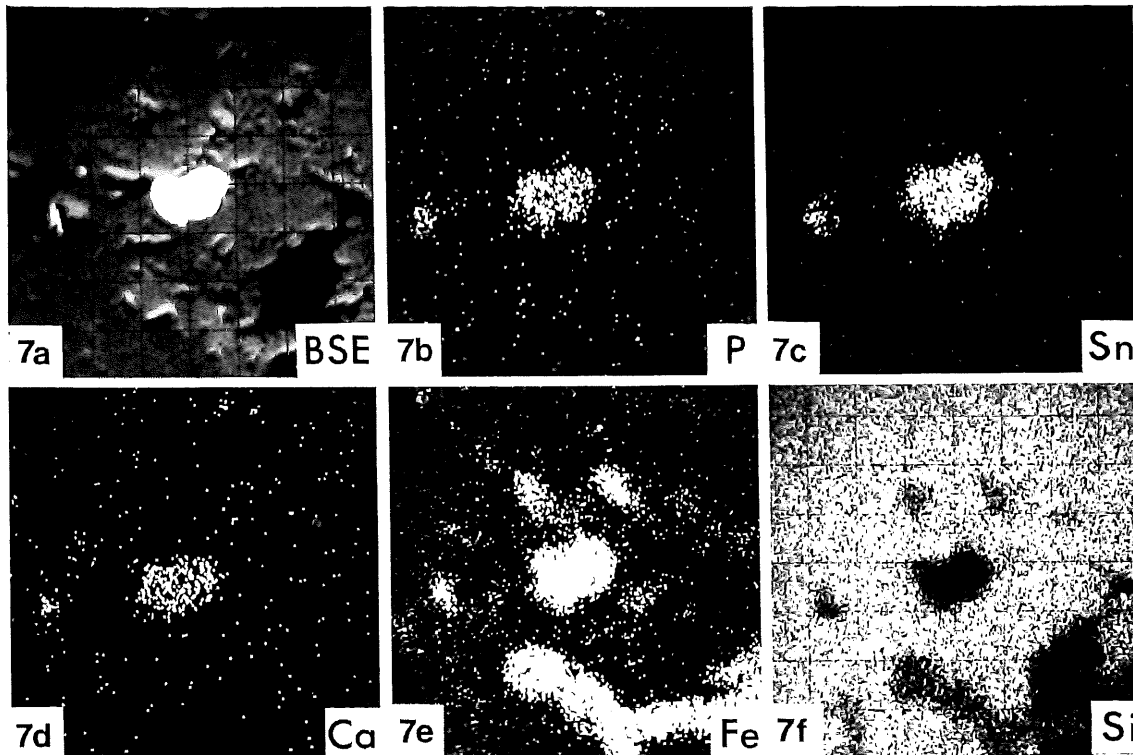
3 a-d: Granular Ti-Sn accumulation (= Sn-rutiles); Mil-12.

4 a-b: Oriented overgrowth of Ti-Sn accumulation on two rutile grains; Mil-12.

5 a-b: Oriented overgrowth of heterogeneous Sn-accumulation on rutile grain; Mil-12.

6: Cassiterite grain; Mil 12.

7 a-f: Sn-Fe-P-(Ca) particle (unknown mineral); Mil-12.



deposits exhibit stratiform character (mantos) and are bound to quartzitic layers of the Silurian Catavi Formation. Regional metamorphism is of very-low-grade to low-grade. Mineralization occurs predominantly in small joints and multidirectional fissures with whole rock bulk contents of up to more than 1% Sn. Disseminated tin contents are in the range of 100 ppm.

The deposits of Kalauyo, Kellhuani, and Milluni are located in a large hydrothermal aureole which is centered at the Chacaltaya granite porphyry (Fig. 1). Hydrothermal alteration has greisenized in part the granite stock, the aureole is characterized by tourmaline-chlorite-carbonate blastesis and sericitization. The geochemical distribution pattern in B, Sn, F, Rb/Sr, and Li shows the same halo characteristics (LEHMANN, in prep.).

The Huallatani deposit belongs to a second, smaller aureole with no magmatic rock outcropping.

The location of the 10 samples analysed is indicated in Fig. 1. The unaltered reference sample Cum-3 is a feldspar-bearing sandstone of very fine grain size. The other samples are of very fine sandstone to siltstone grain size and show distinct blastic fabric. Tourmaline and/or chlorite and carbonate porphyroblasts are superimposed on an equigranular quartz mosaic with mutual grain boundaries. Small heavy mineral layers of rounded zircon, opaques, and detrital tourmaline and rutile indicate relics of old planes of stratification. In the inner zone of the hydrothermal aureole fluorite and andalusite are common accessories.

Very small, disseminated granular aggregates of amoeboid shape display the optical characteristics of rutile or cassiterite with high index of refraction and high birefringence. Because of the tiny size of the particles ( $\mu$ -range) microprobe studies have been performed.

### Results of microprobe analysis

Analyses have been carried out using an ARL-EMX electron microprobe. In all samples of the hydrothermal aureole Sn-accumulations have been detected. Their particle size rarely reaches 10–20  $\mu$ , generally they are too small for microscopic investigation and present difficulties in microprobe study, too. From multi-element scanning diagrams and many spot analyses four types of Sn-accumulations can be distinguished:

1. **Ti-Sn-accumulations (= Sn-rutiles)** (Figs. 2 and 3). They are most abundant and of very irregular, amoeboid shape and heterogeneous internal structure. The Sn-content varies strongly and can amount to more than 50 weight-%. The average Sn-content is about 3 weight-%. The heterogeneity of the mineral aggregates makes the stoichiometric calculation of the mineral phases very difficult. As the sum of  $\text{TiO}_2 + \text{SnO}_2$  not always matches 100 % but may only yield 70 or 80 % in some cases, the presence of hydrate complexes is probable, a fact which is also indicated by the instability of the electron beam.
2. **Intergrowths of rutile with Ti-Sn or Sn-accumulations** (Figs. 4 and 5). Frequently Ti-Sn-accumulations of varying Ti/Sn ratio are associated with a pure rutile phase.
3. **Pure Sn-accumulations (= cassiterites)** (Fig. 6). This type is rare and forms larger homogeneous grains. The typical catholuminescence is visible.
4. **Sn-Fe-(Ca)-accumulations** (Fig. 7). Small amounts have been detected in sample Mil-12. Mineral composition is 56 %  $\text{SnO}_2$ , 19 % FeO, 28 %  $\text{P}_2\text{O}_5$  and 3 % CaO. The difference of summation to 100 % is due to the heterogeneity of the material and/or insufficiency of the reference standard. Because of the low Ca-content malayaite or other known Sn-minerals can be excluded.

Pure rutile occurrences are very rare especially in the samples from the inner hydrothermal aureole (Fig. 1, area A), but are more frequent in samples Uyo-1,2 and Uyo-10 from the outer field of the aureole (area B).

In Table 2 a comparison of microprobe and X-ray fluorescence analyses of Sn bulk contents is presented. The microprobe calculations are based on an average of 3 weight-% Sn in Ti-Sn-accumulations which constitute the majority of tin occurrences. Under this assumption the integration of all automatically registered tin accumulations (line scanning) corresponds fairly to the bulk analyses by XRF.

Table 2. Tin content in rock samples analysed; comparison of microprobe and X-ray fluorescence analysis.

Sample	Mineralized spots in microprobe section (% of total surface)	Integrated Sn-content by microprobe analysis (ppm Sn)	Bulk analysis by X-ray fluorescence analysis (ppm Sn)
A 48	0.55	130	125
Chac 13	0.4	95	138
Chac 78	0.7	165	69
Chac 200	0.6	142	142
Kel 60	0.8	189	246
Mil 12	0.3	71	352
Hua 20	0.2	47	10
Uyo 1,2	0.2	47	47
Uyo 10	0.5	118	208
Cum 3	0.0	0	6

### Interpretation of results

The main part of the circulating mineralizing solutions has been channelled by joints and fissures in the extremely competent quartzitic rocks. Here abundant vein cassiterite is formed by precipitation from concentrated fluids.

Compared with the bulk flow in the fracture system the penetration of the wall rock by Sn-bearing solutions is slow and hindered by low permeability of the rock (intergranular spaces). Hereby intensive chemical interaction of the aqueous phase with its mineralogic environment takes place. Various components of the penetrated host rock are corroded and dissolved by the chemically aggressive Sn-bearing solutions, among others sedimentary rutiles enriched in small heavy mineral layers.

The Ti-content of the solution may now easily surmount the Sn-content. At supersaturation undissolved submicroscopic fragments of rutile can nucleate the epitactic crystal growth of new hydrothermal rutile together with SnO<sub>2</sub>. As the surface of the heteronucleus (rutile) matches well with the cassiterite surface, the free enthalpy change of nucleation is smaller than in spontaneous, homogeneous nucleation. The matching between surfaces is predominantly a matter of agreement in lattice type and atomic distances which for the cassiterite-rutile series are very similar (Table 1). Heteronucleation in this case is energetically more favourable and may take place at lower Sn-supersaturation than at homogeneous nucleation. Therefore pure SnO<sub>2</sub> aggregates can be only rarely detected (Type 3; Fig. 6).

### Note to mechanism of nucleation

Before crystallization of a supersaturated solution can start, a free enthalpy barrier must be overcome which defines a critical size of particles to initiate crystal growth (concept of surface tension; vide f.i. NIELSEN, 1964). Nuclei consisting of a small, subcritical number of ions or molecules will dissolve completely, whereas if a critical nucleus size is reached, nucleation will induce crystal growth spontaneously. Nucleation rate is strongly dependent on the degree of supersaturation of the solution.

As a function of the Sn-concentration in the solution, rutiles of various Sn-contents can form (Type 1; Figs. 2 and 3) dependent on the previous reaction history of the solution with its environment.

Zoning of crystals reflecting solution chemistry at actual growth time should develop which, however, is beyond the resolution power of our microprobe equipment and may be in the order of several atomic layers.

If the mineralizing solution is poor locally in Ti a crystallographically preferred surface of a sedimentary rutile may act as matrix for nucleation of cassiterite which can display Sn-Ti-distributions of Type 2 (Fig. 5).

The degree of hydrothermal rutile conversion with metasomatic formation of Sn-rutiles is greatest in the inner field of the aureole of the Chacaltaya granite porphyry. A weaker influence of hydrothermal fluids is indicated by the greater number of unaltered rutiles in the Uyo-samples.

### Conclusions

Epitactic crystal growth by heteronucleation processes may best explain the wide range of composition of the rutiles analysed, reflecting local supply conditions of Sn/Ti of the mineralizing solutions.

The general observation of very low contents of Sn in many natural rutiles is predominantly due to the fact that there is a big gap of solubility between rutile and cassiterite. Only in environments where Ti and Sn are brought together in solution by different geochemical processes in major concentrations,  $\text{SnO}_2$ - $\text{TiO}_2$  phases can be expected. This requirement is complied with in the present case by the combination of sedimentary heavy mineral accumulations in sandstones with consequent hydrothermal-metasomatic alteration in relation to a tin-granite.

Another possibility of Sn-rutile generation is supposed to be the alteration of endogeneous rutile by greisenization within a tin-granite itself.

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