

correlated with photosynthetic capacity in *D. emarginata* [1] and other species of vascular epiphytes (Zotz, Stuntz, Schmidt, unpublished data) but also affects their in situ gas exchange. Photosynthesis in smaller plants seems to operate at lower c_i/c_a , leading to a higher instantaneous water use efficiency. This trend as revealed by differences in carbon isotope discrimination may be partly concealed by an apparent increase of Δ in smaller individuals due to relatively higher rates of nocturnal recycling of respiratory CO_2 .

The proximate mechanism behind the findings of size-related changes in PC and in Δ remains unknown. A lower photosynthetic capacity in smaller individuals could be a consequence of very low nutrient availability in the epiphytic habitat. Smaller individuals are usually also younger, and the possibility exists that these plants have not had enough time to obtain the necessary resources for higher rates of CO_2 fixation. On the other hand, our results show significantly lower Δ in smaller individuals, suggesting a stronger reduction of stomatal conductance than necessary to maintain a constant c_i/c_a ratio at different chloroplast demand, i.e., different PC. Zotz [1] suggested that the increase in PC in larger plants was the result of an adaptive strategy to the stronger drought stress experienced by smaller plants. By this line of reasoning, smaller plants may well obtain enough nutrients, but store a larger proportion in long-lived organs such as stems for later use in a then larger plant that is partially released from the effects of drought. Pertinent experiments are now underway to distinguish between the different possibilities. Independent of the mechanism, however, this study adds to the evidence that size is a relevant parameter in any physiological study with vascular epiphytes and has to be adequately addressed in future investigations.

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Magma Mixing in Bolivian Tin Porphyries

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Melt inclusions in quartz phenocrysts from Bolivian tin-porphyry systems have a highly fractionated rhyolitic composition, distinctly different from the rhyodacitic bulk rock. The melt-inclusion geochemistry (electron and proton microprobe analysis) points to mixing of a highly evolved rhyolitic melt with andesitic to basaltic melt portions in an upper crustal reservoir.

Such a mixing process can induce catastrophic volatile exsolution and may be the controlling factor not only in tin porphyries but also for the metallogeny of other porphyry systems.

Introduction

Most of the metals that form porphyry and granite-related hydrothermal ore deposits are probably derived from magmas [1], but the controlling processes in the magmatic evolution prior to large-scale volatile exsolution are little understood. Trace-element microanalysis in melt inclusions offers the potential to better understand the early evolution of magmatic-hydrothermal ore-forming systems. We

Electronic Supplementary Material

Table 1 and Table 2 (see our homepage at: <http://link.springer.de/journals/nawi>)

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Dedicated to Prof Hans-Jochen Schneider on the occasion of his 75th birthday

used proton-induced X-ray emission spectrometry (PIXE), supplemented by traditional electron microprobe analysis (EMPA), to study melt inclusions in quartz phenocrysts of major tin-porphyry systems in Bolivia.

The Central Andean Metal Province

The Bolivian tin belt is an important feature of the regional metallogenic pattern of the Central Andes, with the continentwide copper-porphyry belt to the west and the areally much more restricted subparallel tin belt about 300 km to the east [2]. The tin belt hosts a number of world-class porphyry deposits such as Llallagua (Sn), Cerro Rico de Potosi (Ag-Sn), Chorolque (Sn), and Tasna (Bi-Sn) [3]. Whereas the metallogeny of copper-porphyry belts is generally understood as a result of their convergent margin setting with subduction of oceanic lithosphere and partial melting of hydrated mantle-wedge material, the conceptual model for the metallogeny of tin is usually based on intracrustal melting and advanced degree of magmatic fractionation in high-silica systems [4]. An apparent exception are the Bolivian tin-porphyry systems which are associated with only moderately fractionated subvolcanic rocks of rhyodacitic composition.

Bulk-Rock Versus Melt-Inclusion Geochemistry

We studied the geochemistry of the tin-porphyry systems of Llallagua, Cerro Rico de Potosi, and Chorolque in central and southern Bolivia. These systems range in age from 21 to 14 Ma and consist of rhyodacitic stocks and breccias with pervasive hydrothermal overprint (mainly sericitization, silicification, and tourmalinization) [5, 6]. The igneous rocks are composed of fine- to coarse-grained phenocrysts of feldspars, biotite, and strongly corroded quartz, set in a fine-grained matrix. Phenocrysts share about 40–50% of the rock and are often broken to fine-grained fragments. The approximate primary phenocryst proportion is 35% quartz, 50% feldspars and 15% biotite. Tin mineralization occurs as disseminated

hydrothermal cassiterite and in quartz-tourmaline-cassiterite-sulfide veins [3–7].

The bulk-rock geochemistry of the porphyry systems defines a rhyodacitic to dacitic composition with moderate degree of fractionation (TiO_2 0.5–0.9 wt%, Zr 100–300 ppm, Ta 1–4 ppm; see Table 1; original data through <http://link.springer.de/journals/nawi>). Hydrothermal overprint has resulted in strong enrichment of B, Bi and Sn ($>100\times$ upper continental crust), and in moderate enrichment of Sb, Pb, Ag, As, Au, W ($10\text{--}100\times$ upper continental crust).

Silicate-melt inclusions occur both randomly distributed in their host-quartz crystals and aligned along crystal-growth zones (Fig. 1). Sizes range from a few up to 100 μm , with round to negative crystal shape (often hexagonal bipyramidal habit). Most melt inclusions consist of colorless to greenish glass with a shrinkage bubble, but some melt inclusions are opaque and recrystallized. The latter were rehomogenized in a tube furnace (850°C, 24 h). About 75 melt inclusions in magmatic quartz phenocrysts were studied by EMPA, and 31 by PIXE (Table 2; original data as electronic supplementary material, see address above).

The melt inclusions have peraluminous composition; alkali and silica contents define an alkali-rhyolitic to rhyolitic melt phase of high-K affinity. Major-element composition re-

flects that crystallization occurred after fractionation of plagioclase and mafic phases, and prior to or synchronous to formation of alkali feldspar. The trace-element composition of the melt inclusions is distinctly different from the bulk-rock geochemistry. Electron and proton microprobe data indicate a highly evolved melt with 0.03–0.12 wt% TiO_2 , 15–85 ppm Zr, 5–17 ppm Ta, 5–43 ppm Sn, and Rb/Sr up to 20. Low Nb/Ta and Zr/Hf ratios of 2–6 and 3–11, respectively, are typical of highly fractionated tin granites and rare-element enriched pegmatites. The melt-inclusion data align with the general fractionation trend of Tertiary felsic rocks of the Andean tin belt, and are similar to the Macusani lithophile-element enriched rhyolites, SE Peru, and to the most fractionated rocks in the Cordillera Quimsa Cruz tin granites of northern Bolivia (Fig. 2). The immobile-element bulk-rock data of the tin porphyries plot in between the upper-crust and bulk-crust reference points; the scatter distribution of the bulk-rock tin data reflects pervasive hydrothermal overprint.

Mixing and Ore Formation

The compositional gap between the highly evolved nature of the melt inclusions and the intermediate bulk-rock geochemistry cannot be explained by crystal-liquid fractionation in a closed system. The amount of phenocrysts in the tin porphyries ranges in between 40 and 50%, which allows only up to twofold enrichment of perfectly incompatible elements in a late-stage cogenetic melt phase. The correlation trends of Fig. 2 preclude any important influence of boundary-layer effects. The highly fractionated nature of the melt inclusions would require a phenocryst/melt ratio of >4 which appears unrealistically high. In addition, the melt inclusions occur in quartz phenocrysts with strong magmatic corrosion features arguing against late quartz crystallization. We therefore propose an explanation by mixing of a highly evolved silicic melt, containing quartz phenocrysts, with andesitic to basaltic melt fractions in an upper crustal reservoir. Tin mineralization and boron metasomatism

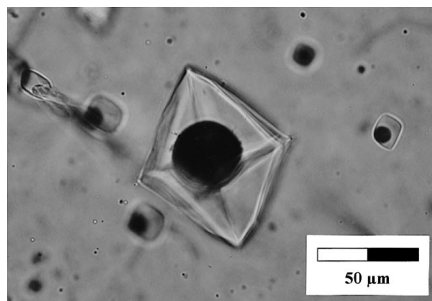
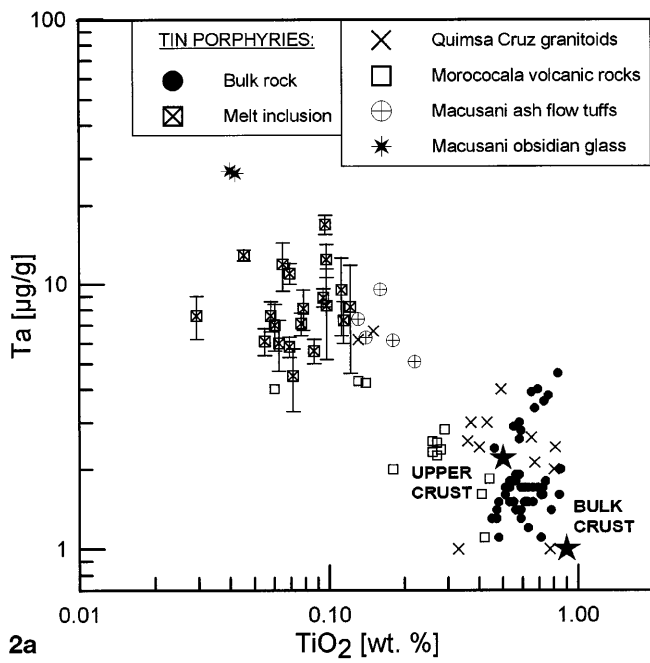
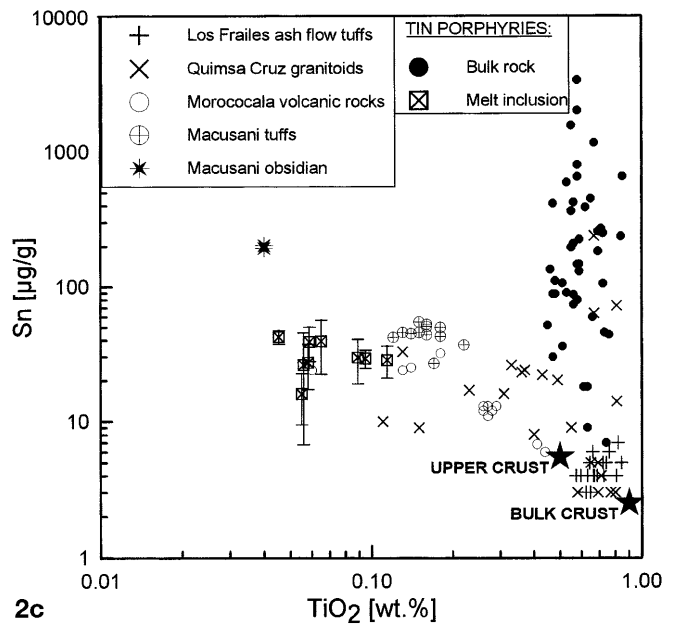


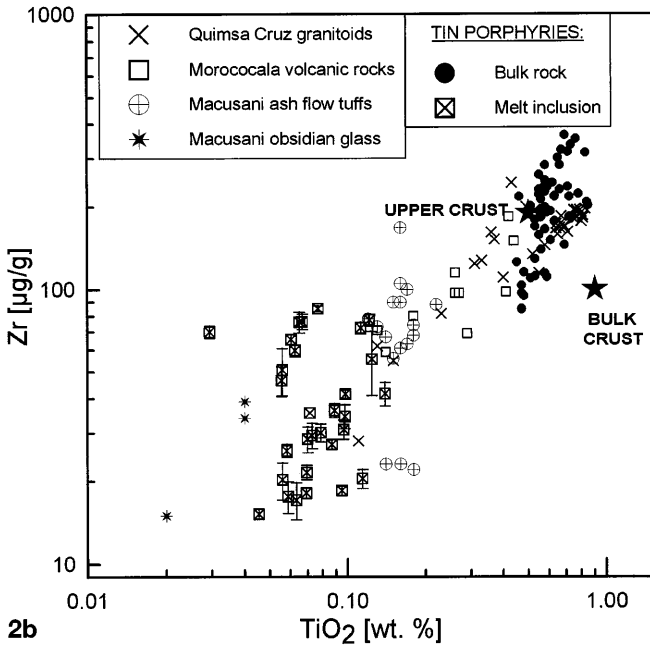
Fig. 1. Negative crystal-shaped melt inclusions with large shrinkage bubbles in quartz phenocryst from the Cerro Rico de Potosi tin porphyry (polished thick section P97-1x1i, plane polarized light). Microanalysis was performed on the glass fraction in melt inclusions. Trace-element data are therefore minima because volatile components may have unmixed into shrinkage bubble



2a



2c



2b

Fig.2a-c. Log-log variation plots for titanium versus tantalum, zirconium and tin in bulk-rock samples and melt inclusions. The fractionation trend of Tertiary magmatic rocks of the Andean tin belt is defined by the Lower Miocene granitoids of the Quimsa Cruz (unpublished data), the Upper Miocene Los Frailes (unpublished data) and Morococala volcanic fields [9], and the Mio-Pliocene Macusani ash flow tuffs and obsidian glasses [10–12]. Bulk-rock data by X-ray fluorescence spectrometry (Ti, Zr, Sn) and neutron activation analysis (Ta). Melt-inclusion data by proton-induced X-ray emission [8]. Error bars on melt-inclusion data, ± 1 SD; the error width of titanium data is within symbol size

appear to be related to fluid exsolution from this inferred highly fractionated melt reservoir which could explain the exceptional association of tin mineralization with an only moderately fractionated bulk-rock system. Given the amount of tin of about 2 million tons in ore plus geochemical halo in the Llallagua system [13], the largest tin ore deposit in the world, this high-silica melt reservoir would

need a volume of $\geq 320 \text{ km}^3$. The total melt volume would be on the order of $100\text{--}200 \text{ km}^3$ which is within the size range of medium-scale volcanoplutonic systems.

Mixing is also indicated by new neodymium isotope data from the Bolivian tin porphyries which range in ϵ_{Nd} from -5 to -10 [14]. The Lower Paleozoic country rocks and the Proterozoic basement have ϵ_{Nd} ranges of -8 to

-12 , and -11 to -14 , respectively [14]. These data suggest a largely intracrustal source but require some mantle input for the Bolivian tin porphyries.

The mixing process between mafic or andesitic melt and a high-silica melt may trigger a runaway mechanism of catastrophic volatile release and explosive venting in subvolcanic plutons [15, 16]. Large-scale vapor percola-

tion can effectively sequester ore metals, given the favorable confluence of a number of critical chemical parameters such as magma composition and oxidation state [17]. The punctuated evolution of devolatilizing composite magmatic systems may also be important in the evolution of the Chilean copper-molybdenum-gold porphyries for which Sr-Nd isotope data suggest magma mixing concomitant with hydrothermal breccia and ore formation [18].

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Hypogean life-style fuelled by oil

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Cave ecosystems are characterized by constant abiotic factors such as perpetual darkness, high humidity, and low temperature. The only fluctuating parameter is the food supply, which is derived mainly from allochthonous sources. The shrimp *Troglocaris anophthalmus* from the Planina cave in Slovenia is perfectly adapted to irregular food supply by possessing hundreds of oil-storing chambers which fill when food is available in excess. In a laboratory experiment we have now shown that the lipid reserves of these oleospheres are sufficient to fuel the metabolism of the shrimp for more than 2 years. We have further demonstrated that *Atyaephyra desmarestii*, a close epigeal relative without oleospheres,

can survive only 4 weeks without feeding. Therefore we conclude that the successful conquest of the Dinaric caves by *T. anophthalmus* was based on the evolution of oleospheres as a specific means to withstand long-term starvation.

Limitation and irregular supply of food is a major driving force for the evolution of cave animals (Vandel 1964; Barr 1968). According to the energy-economy hypothesis, the adaptation of troglobites to low energy includes a reduction in pigments and eyes, infrequent reproduction, small brood size, reduced metabolism and growth rates, and increased longevity (Poulson and White 1969; Howarth 1983). The shrimp *Troglocaris anophthalmus planinensis* Birstein from the Planina cave in Slovenia fits well into this scheme (Matjašič 1958; Juberthie-Jupeau 1972, 1975) but has developed

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