

Boron isotope composition of melt inclusions from porphyry systems of the Central Andes: a reconnaissance study

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ABSTRACT

Quartz-hosted melt inclusions from latite dykes of the Eocene El Salvador copper porphyry system in northern Chile display wide ranges in both boron concentration (15–155 p.p.m. B) and isotope composition ($\delta^{11}\text{B}$ –7 to +12‰; $n = 10$), likely reflecting slab-derived fluid input from seawater-altered oceanic crust. In contrast, the major Miocene tin-silver and tin porphyry systems in the Bolivian back-arc region (Cerro Rico de Potosí, Chorolque, Llallagua) have distinctly different melt inclusion compositions

with $\delta^{11}\text{B}$ of $-11.4 \pm 2.7\%$ ($n = 10$), and magmatic boron enrichment up to several hundred p.p.m. B. The 'seawater' signature in the El Salvador melt inclusions explains the oxidized mineral assemblage of the copper porphyry system, as opposed to the more reduced nature of the Bolivian tin porphyry systems, which reflect intracrustal melting of pelitic rocks.

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Introduction

The Central Andes hosts the world's largest copper (El Teniente and Chuquicamata, Chile), silver (Cerro Rico de Potosí, Bolivia) and tin (Llallagua, Bolivia) deposits, all of which are in porphyry systems that form part of the Cenozoic continental-margin magmatism of the Andes (Sillitoe, 1976, 1988). Both the regional metallogenic zoning, with tin-silver in a back-arc setting and copper more outboard, and the role of slab-related fluids in the generation of these systems remain poorly understood. Here we present boron concentration and first isotope data on melt inclusions from quartz phenocrysts from the large tin porphyry systems of Cerro Rico de Potosí, Chorolque and Llallagua in Bolivia, and the northern Chilean copper porphyry of El Salvador (Fig. 1). These porphyry systems have experienced pervasive hydrothermal alteration, such that melt inclusions in quartz phenocrysts preserve the only direct information on the magmatic history of fluid-mobile elements. Melt inclusions are small droplets of melt (now glassy or crystallized), which became trapped during the

growth of their host mineral, and micro-analysis of trace elements can provide important insight into igneous processes. Such studies on Central Andean porphyry systems were carried out by Dietrich *et al.* (2000), Campos *et al.* (2002) and Davidson *et al.* (2005). We here present the first boron isotope study applied to melt inclusions in porphyry systems. The isotope composition of boron eventually allows to trace the source of boron, and to enlarge the scale of understanding of magmatic-hydrothermal ore formation.

Geological background

The Central Andean tin belt in the Eastern Cordillera reaches from southern Peru through Bolivia to northern Argentina, and it consists of a folded and thrustured basement of Early Palaeozoic siliciclastic rocks with more than 10 km thickness (Sempere, 1995). Major tin deposits are associated with Miocene porphyries and their genetically related vein systems (Grant *et al.*, 1980). The general plate tectonic setting during the formation of the Bolivian tin deposits is characterized by a transition from flat slab to normal subduction at 25–15 Ma (James and Sacks, 1999). A particular feature of the tin belt is strongly peraluminous rhyodacitic ash-flow tuffs, which are both coeval

to and younger than the porphyries while all other Andean volcanic rocks are of metaluminous composition (Ericksen *et al.*, 1990; Morgan *et al.*, 1998).

The Central Andean copper porphyry province in northern Chile consists of several N-S trending sub-belts, which record a progressive eastward shift of the volcanic arc since the Early Jurassic by some 200 km. The giant copper porphyry systems of Chuquicamata, Escondida and El Salvador formed between 41 and 31 Ma and are related to a period of flat slab subduction with porphyry emplacement controlled by the more than 1000-km-long N-S trending Domeyko continental strike-slip fault (James and Sacks, 1999).

The subvolcanic dome of Cerro Rico de Potosí in southern Bolivia consists of 13.8-Ma-old dacitic to rhyodacitic rocks (Zartman and Cunningham, 1995) and hosts both the world's largest silver resource in its epithermal superstructure and a major tin resource in its deeper parts (Sillitoe *et al.*, 1975). Hydrothermal alteration and mineralization occurred within 0.3 Ma of dome emplacement (Cunningham *et al.*, 1996). Vuggy silica alteration on top is underlain by a high sulfidation lithocap with advanced argillic alteration and sericitization. The root of the system is dominated by pervasive tourmalinization

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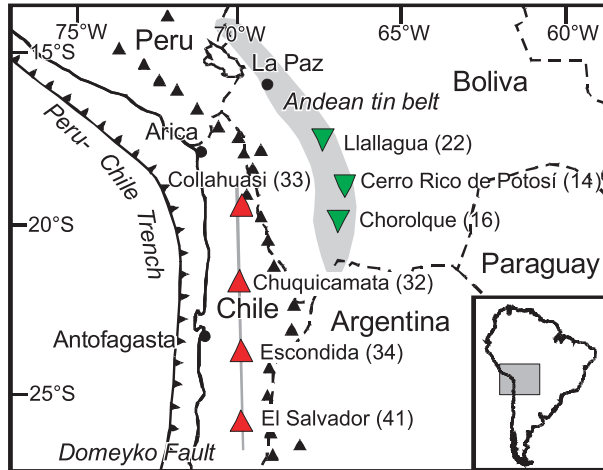


Fig. 1 Major copper and tin porphyry deposits in northern Chile and Bolivia. Green triangles: tin porphyry systems; red triangles: copper porphyry systems; small solid triangles: Recent volcanic chain. Intrusive ages in brackets (Ma).

with cassiterite-pyrite stockworks and veinlets.

Chorolque in southern Bolivia is a 16-Ma volcanic complex with a 1-km-diameter vent, which is surrounded by crystal- and pumice-rich rhyodacitic tuffs. The vent hosts a major breccia system (silicified volcanic and sedimentary clasts) with tin mineralization in veins and stockworks (Sillitoe *et al.*, 1975; Grant *et al.*, 1979, 1980). The hydrothermal system shows a concentric zonation from tourmalinization and silification in the centre to sericitization to distal propylitization in the pyroclastic rocks.

The giant tin porphyry system of Llallagua in central Bolivia is hosted by a rhyodacitic pipe-like intrusion or diatreme of which the volcanic superstructure has been eroded away. Sericite-tourmaline alteration is widespread. Stockworks and veins carry the hydrothermal assemblage of quartz-tourmaline-cassiterite-pyrrhotite/pyrite. K–Ar ages are around 22 Ma (Grant *et al.*, 1980), but the igneous system may be as old as 40 Ma (Kempe *et al.*, 2008).

The El Salvador copper porphyry system in northern Chile is one of the best studied porphyry systems (Gustafson and Hunt, 1975; Gustafson *et al.*, 2001). The multiphase magmatic evolution of El Salvador started with barren rhyolitic ignimbrites (~65–55 Ma) and rhyodacitic to rhyolitic domes (58–55 Ma (Cornejo *et al.*, 1997). A second magmatic cycle

(44–41 Ma) hosts the copper porphyry mineralization in a granodioritic porphyry sequence. Stockwork K-silicate alteration is widespread with the assemblage of K-feldspar-biotite-anhydrite-quartz and the ore assemblage of chalcopyrite-bornite-pyrite, followed by sericitic to intense argillic alteration. The late magmatic activity of the porphyry complex is represented by potassic and argillic

altered porphyry dykes (Latite dykes, 41 Ma) with pervasive weak copper mineralization.

The Bolivian tin porphyries have ϵ_{Nd} values of -5.3 to -10.7 (Lehmann *et al.*, 2000), and intrude a Palaeozoic sedimentary sequence with largely overlapping ϵ_{Nd} values of -8 to -12 (Miller and Harris, 1989; Basu *et al.*, 1990). Their rare-earth element distribution patterns, particularly for the Cerro Rico de Potosi system, are steep with a concave heavy REE pattern, which suggests a garnet-bearing source (Dietrich *et al.*, 2000), probably near the base of thickened continental crust. The El Salvador intrusive complex has ϵ_{Nd} values of $+2$ to $+4$ (Maksaev, 1990) and less fractionated REE patterns at lower REE levels, compared to the Bolivian tin porphyries (Dietrich, 1999).

Sample material

Magmatic quartz phenocrysts were either hand-picked from crushed bulk-rock samples or exposed by polishing from bulk-rock chips. The quartz-hosted melt inclusions studied have diameters between 10 and 100 μm with variable shapes. The inclusions from Cerro Rico de Potosi and Chorolque reveal a perfect nega-

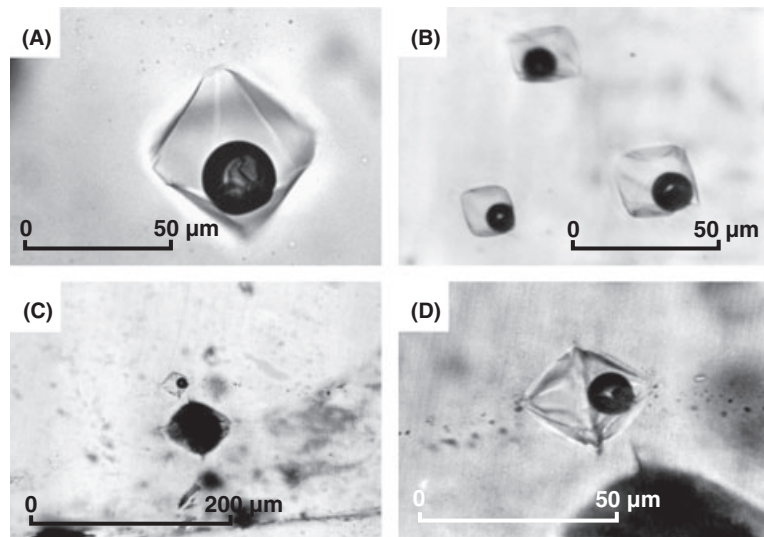


Fig. 2 Typical melt inclusions from the porphyry systems studied. A: Cerro Rico de Potosi, Bolivia: negative-crystal shape, glassy with vapour bubble; B: Llallagua, Bolivia: rounded to negative-crystal shape, glassy with vapour bubble. C and D (enlargement): El Salvador, Chile: Most melt inclusions in copper porphyry systems are opaque and affected by fluid overprint (see dark inclusion in C). Only some small inclusions are glassy with a vapour bubble.

Table 1 Geochemical and boron isotopic data of melt inclusions of Central Andean porphyry systems.

Sample number	SiO ₂ wt.%	TiO ₂ wt.%	Al ₂ O ₃ wt.%	ΣFeO wt.%	MnO wt.%	MgO wt.%	CaO wt.%	K ₂ O wt.%	Na ₂ O wt.%	P ₂ O ₅ wt.%	Total δ ¹¹ B ‰	δ ¹¹ B ‰	B p.p.m.	SIMS 1σ	SIMS 1σ	As p.p.m.	As 1σ	Rb p.p.m.	Rb 1σ	Sr p.p.m.	Sr 1σ	Zr p.p.m.	Zr 1σ	Nb p.p.m.	Nb 1σ	Ba p.p.m.	Ba 1σ	Yb p.p.m.	Yb 1σ							
																														EMPA PIXE	EMPA PIXE	EMPA PIXE	EMPA PIXE	EMPA PIXE	EMPA PIXE	EMPA PIXE
Llallagua																																				
L22-3	74.7	0.08	11.7	0.74	0.03	0.10	0.56	4.56	2.92	na	95.4	-5.8	-8.8	1.9	63	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na						
L24a-1	74.9	0.04	10.9	0.75	<0.03	0.11	0.56	4.06	2.55	0.11	94.0	-7.6	-10.6	1.1	83	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na						
L24a-2	74.9	0.10	13.2	0.79	0.04	0.15	0.74	4.89	2.22	0.29	97.3	na	na	106	17	1250	40	73	0.3	59	0.3	11	0.5	254	2	101	1	42	1.4	12	1	318	38	13	1.0	
L24a-3	76.2	0.09	10.3	0.67	0.04	0.11	0.60	3.83	2.20	0.08	94.1	na	na	47	6	1634	54	84	0.7	48	0.6	12	0.7	253	3	98	2	36	2.1	11	1	515	61	<3		
Chorlque																																				
C65a	68.9	0.06	16.1	0.47	0.04	0.04	1.06	6.51	2.34	0.09	95.7	-5.5	-8.5	0.6	75	64	1442	2	19	50	314	131	66	15	367	10	367	10	367	10	367	10	367	10		
Cerro Rico de Potosí																																				
P1	72.1	0.08	14.3	0.51	0.04	0.06	0.46	5.62	1.99	0.19	95.3	-9.3	-12.3	2.1	108	21	1634	89	37	38	463	104	41	25	363	11	363	11	363	11	363	11	363	11		
P2	76.3	0.08	14.9	0.79	0.05	na	0.70	6.54	na	0.22	99.6	-9.3	-12.3	0.9	245	19	2165	68	80	1.6	38	42	452	9	75	5	29	5.3	32	6	nd	18	3.6			
P4	78.0	0.07	14.4	0.60	0.04	na	0.57	5.69	na	0.25	99.6	-13.1	-16.1	1.0	316	25	1566	54	18	1.0	38	5.1	404	6	78	3	18	3.5	21	3	<252	14	2.4			
P5	76.2	0.09	15.3	0.88	0.05	na	0.64	5.93	na	0.02	99.1	-11.3	-14.3	0.8	306	28	2229	82	58	0.8	30	1.4	471	5	105	3	27	2.8	28	2	157	36	14	1.9		
P95-1a	74.0	0.05	13.0	0.28	0.03	<0.01	0.23	6.38	2.62	0.04	96.6	-4.4	-7.4	0.5	296	17	933	46	1	0.2	45	0.6	488	2	41	1	293	2.7	25	1	<47	6	0.8			
P95-1b	73.3	0.09	13.5	0.42	0.04	0.01	0.31	7.97	2.39	0.10	98.1	-8.0	-11.0	0.6	234	15	1390	38	4	0.2	45	0.4	510	1	49	1	19	0.7	24	1	86	22	11	0.8		
P97	71.8	0.05	14.1	0.55	0.04	0.06	0.25	6.01	0.74	0.21	93.8	-9.8	-12.8	0.8	576	45	590	27	2	0.2	46	0.3	85	0.5	637	2	11	1	15	0.6	29	1	<38	13	0.7	
El Salvador**																																				
E1	78.2	0.10	12.5	0.62	0.03	<0.40	0.79	4.76	na	na	97.0	14.7	11.7	2.2	74	6	641	60	2	0.4	32	0.6	26	1.2	122	2	147	3	55	3.5	7	2	507	36	18	2.2
E2	77.2	0.07	12.5	0.43	0.01	0.40	0.88	4.62	<3.04	<0.06	96.1	na	na	72	7	272	56	na	9	1.7	38	1.1	95	7	121	8	71	10.7	<21	564	50	18	6.5			
E3	75.5	0.07	11.9	0.40	0.02	0.63	0.68	4.04	<2.74	<0.04	93.2	1.1	-2.1	1.0	78	6	583	47	<1	20	0.5	18	1.0	84	2	103	2	45	2.8	6	1	661	27	13	1.8	
E4	71.0	0.08	12.1	0.33	0.03	0.51	0.74	4.69	4.57	<0.05	94.1	-1.0	-4.0	1.5	45	3	1587	54	1	0.5	54	0.7	33	1.9	203	3	159	3	48	3.4	<3	680	30	6	2.1	
E5	79.0	0.10	12.3	0.35	0.01	<0.22	0.83	4.45	<1.80	<0.03	97.1	0.8	-3.8	1.8	78	5	261	32	na	13	0.7	20	1.4	74	2	129	3	55	4.0	8	3	743	39	12	2.5	
E6	80.2	0.08	12.6	0.55	0.03	<3.67	0.99	4.99	na	0.10	99.5	5.3	2.3	1.6	155	12	550	38	3	0.5	24	0.7	25	1.1	110	3	125	3	51	4.3	7	2	260	35	7	2.2
E7	na	na	na	na	na	na	na	na	na	na	na	-1.7	-4.7	2.1	15	1	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	
E9	82.6	0.11	11.4	0.28	0.01	<0.44	1.01	4.24	na	<0.11	99.7	6.9	3.9	2.1	24	2	1308	85	2	9	1.0	<43	59	3	129	5	53	5.9	9	4	nd	<7	na	na		
E10a	na	na	na	na	na	na	na	na	na	na	na	9.2	6.2	1.5	35	9	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	
E10b	na	na	na	na	na	na	na	na	na	na	na	-4.0	-7.0	1.6	47	5	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	
E11	82.1	0.09	11.7	0.50	0.03	<4.40	0.79	4.75	na	<0.05	99.9	6.4	3.4	2.3	50	4	715	47	3	1.4	28	1.6	22	1.9	110	6	137	8	74	9.6	<18	635	51	14	4.9	

*SRM 612 standard corrected for instrumental mass fractionation of +3 per mil **All major elements for El Salvador sample population by PIXE.

Note that PIXE data on the major elements Si, Al, Fe, Ca and K are semi-quantitative only (error margin of 20–30%). Sample numbers: Capitalized letters and numbers refer to individual rock samples; (a) and (b) in samples P95-1 and E10 refer to individual melt inclusions within the same quartz phenocryst sample.

tive crystal shape and are commonly glass-clear with a shrinkage/vapour bubble (5–25% of the inclusion volume), whereas the inclusions from Llallagua and El Salvador have more rounded shapes and are mostly opaque. Some smaller melt inclusions ($\leq 20 \mu\text{m}$) are glassy and have a vapour bubble. We selected only those non-crystallized melt inclusions for analysis (Fig. 2). Experimental data on water and zircon solubility in felsic melts, applied to the composition of the melt inclusions, as well as the phenocryst nature of the host quartz with more than 50% groundmass of the bulk rock suggest a depth of entrapment of the melt inclusions, i.e. formation of the quartz phenocrysts corresponding to a pressure of more than 1 kb (Dietrich *et al.*, 2000).

The quartz phenocrysts in the shallow subvolcanic systems of Cerro Rico de Potosi and Chorolque are much less affected by fluid overprint than is the case for the quartz crystals from the diatreme environment of Llallagua. The deeper copper porphyry environment of El Salvador has closely spaced fluid inclusion trails across quartz phenocrysts, which have modified extensively the melt inclusion inventory. We intensively searched several Chilean copper porphyry systems (Los Pelambres, Chuquicamata, El Salvador, Mantos Blancos) for quartz-hosted melt inclusions unaffected by such fluid overprint, but could find such material only in late- and post-ore dykes and stocks. The only melt inclusions large enough for microanalytical work were detected in latitic post-ore dykes from El Salvador.

Analytical techniques

The quartz phenocrysts were polished until individual melt inclusions were exposed at the sample surface. Major elements and some trace elements were measured by a combination of electron and proton microprobe analysis. Routine electron microprobe analysis was performed with a Cameca SX 100 in Clausthal (20 kV, 20 nA; alkalis by defocused beam and 15 kV, 10 nA). Proton-induced X-ray emission analysis (PIXE) was performed in Heidelberg (2.5 MeV, calibration by a number of NIST and natural glass reference materials),

as described by Traxel *et al.* (1995) and Wallianos *et al.* (1999).

We used the Cameca ims 6f SIMS in Potsdam to conduct *in situ* analyses of the boron contained within individual melt inclusions. The analyses used a nominal -12.5 kV , filtered $^{16}\text{O}^-$, and a 30 nA primary beam, which was focused to a $\sim 30 \mu\text{m}$ diameter spot on the sample's surface. Secondary ions ejected from the sample during the sputtering process were accelerated through a $+10 \text{ kV}$ extraction field. We operated the mass spectrometer with 25 V energy band-pass and at a mass resolution of $M/\Delta M \approx 1600$, which is sufficient to eliminate all significant isobaric molecular interferences. Data collection consisted of either 40 or 80 cycles of the mass sequence: 5.75 background (0.1 s), ^{10}B (20 s), ^{11}B (10 s), ^{30}Si (2 s), ^{41}K (2 s) and 41.25 background (0.1 s). Because of excessively

high count rates it was necessary to apply a 40 V energy offset to both the Si and K peaks. A single analysis required between 31 and 61 min of data acquisition. Instrument calibration employed the NIST SRM610 synthetic glass, which contains $356 \mu\text{g g}^{-1} \text{ B}$ (Pearce *et al.*, 1997) and which has a boron isotopic composition of $\delta^{11}\text{B} = -1.05\text{‰}$ (Kasemann *et al.*, 2001).

The external reproducibility of the $\delta^{11}\text{B}$ data, based on repeat measurements of the glass reference material, was $\sim \pm 3\text{‰}$. There is an instrumental mass fractionation for boron isotope analysis of natural basaltic to rhyolitic glasses. Rosner *et al.* (2008) identified an average 3.4‰ difference between the NIST glasses (SRM 610 and 612) and melt inclusions. The same study also gives a revised boron isotopic composition of -0.66‰ for SRM 610. Therefore, we corrected

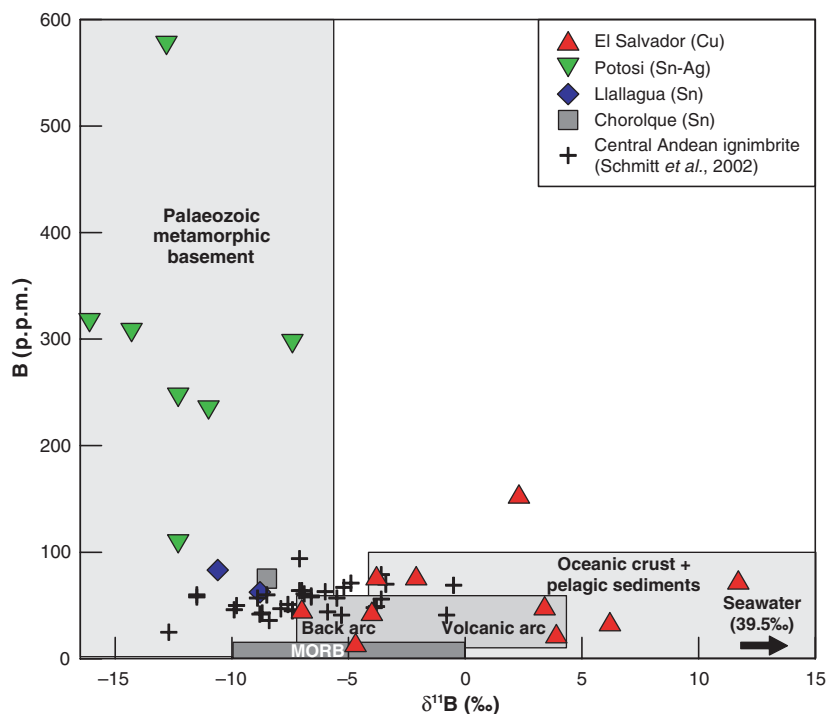


Fig. 3 Boron concentration vs. isotopic boron composition of melt inclusions of the El Salvador copper porphyry and the tin porphyries of Cerro Rico de Potosi, Llallagua and Chorolque with bulk-rock reference data from Kasemann *et al.* (2000) for the Palaeozoic Andean basement, Rosner *et al.* (2003) for the Central Andean volcanic arc and back arc, and Spivack and Edmond (1987), Ishikawa and Nakamura (1993) and Smith *et al.* (1995) for oceanic crust, pelagic sediments and seawater, respectively. The melt inclusion data for 10 to 1 Ma ignimbrite samples from the Altiplano-Puna region of NW Argentina from Schmitt *et al.* (2002) are corrected for 3 permil instrumental isotope fractionation (vide Rosner *et al.*, 2008). These samples are from a back-arc position and overlap with the basement composition.

our original analytical data, acquired before the study of Rosner *et al.* (2008), by a constant factor of -3% (Table 1).

Results

Our boron concentration and reconnaissance isotope data are given in Table 1 and are plotted along with some reference data in Fig. 3. The boron isotope data of the melt inclusions from El Salvador in Chile have a wide range from -7 to $+12\%$ $\delta^{11}\text{B}$, which overlaps the reference fields for oceanic crust and pelagic sediments, and for Andean volcanic-arc rocks. This wide range is displayed not only by different quartz samples, but also by different melt inclusions within the same quartz crystal (sample E10 a and b). The boron isotope data from the Bolivian tin porphyries range from -16 to -7% $\delta^{11}\text{B}$, and overlap with the reference field for the Palaeozoic metamorphic basement of the Central Andes (Kasemann *et al.*, 2000), and the global estimate for average continental crust of -13 to -8% (Chaussidon and Albarède, 1992).

Discussion

The positive B isotope data of the El Salvador melt inclusions up to 12% require a source enriched in ^{11}B relative to mantle or MORB, which have boron isotope values between -10 and 0% (Spivack and Edmond, 1987; Ishikawa and Nakamura, 1993; Chaussidon and Marty, 1995; Ryan *et al.*, 1995). We interpret the positive B isotope data as reflecting a 'seawater' signature, likely related to devolatilization of seawater-altered subducted rocks. Altered oceanic crust is known to have a wide compositional range both in terms of boron abundance and boron isotopic composition, i.e. $\delta^{11}\text{B}$ values of -4 to $+25\%$ (Smith *et al.*, 1995). Bulk-rock boron isotope data from the Recent Central Andean volcanic front have a much smaller variation range of $+2$ to $+4\%$ ($n = 8$), and their boron budget also appears to be controlled by slab-derived fluids (Rosner *et al.*, 2003), while boron isotope data on melt inclusions in ignimbrites from the ~ 10 Ma to Recent Altiplano-Puna Volcanic complex in NW Argentina reflect a dominantly crustal boron source with

a minor contribution from the subduction environment (Schmitt *et al.*, 2002). The variable up to very heavy boron isotope signature of the El Salvador system is unusual for arc volcanism, and may indicate the involvement of a serpentinized mantle wedge enriched in heavy boron from forearc fluids. At erosive margins, ^{11}B -rich forearc serpentinite slivers could be dragged down to the root zone of arc magmatism and then release heavy boron on serpentine breakdown (Benton *et al.*, 2001; Tonarini *et al.*, 2007).

We cannot exclude that boron was lost from the El Salvador system during magmatic fractionation and possible fluid-melt separation. However, such processes, including dehydration reactions during subduction, would produce a shift towards more

negative delta B values in the melt fraction because of the preference of heavy B for hydrous fluids (Hervig *et al.*, 2002). The pre-degassing melt of the El Salvador system would therefore have an even more positive boron isotope composition than measured in the melt inclusions.

Boron loss during fluid-melt separation may also have affected the elemental boron abundances. However, the low B abundance in the melt inclusions from El Salvador, where tourmalinization is not observed, and the high B abundance in the melt inclusions of the Bolivian tin porphyries, where pervasive tourmalinization is typical, strongly support for the assumption that the initial magmatic boron abundance at El Salvador was significantly lower than in the Bolivian

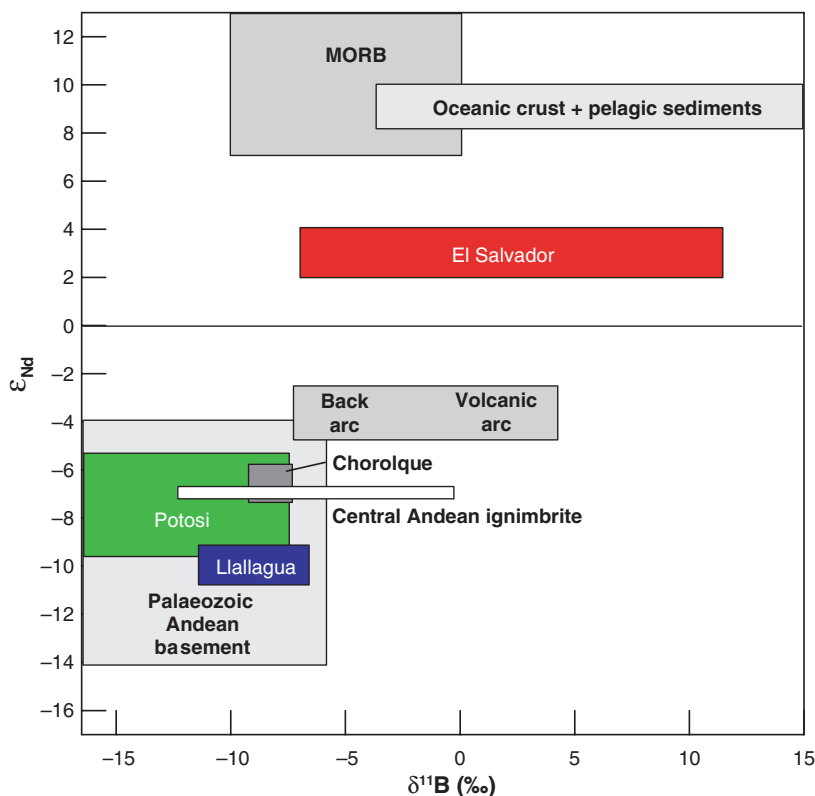


Fig. 4 Boron and neodymium isotope ranges for the El Salvador copper porphyry system (bulk rock ϵ_{Nd} -data from Maksaev, 1990) and the Cerro Rico de Potosi, Llalagua and Chorolque tin porphyry systems (bulk rock ϵ_{Nd} -data from Lehmann *et al.*, 2000). Reference bulk-rock data (grey boxes) for MORB: $\delta^{11}\text{B}$ from Chaussidon and Marty (1995), ϵ_{Nd} from Saunders *et al.* (1988); oceanic crust and pelagic sediments: Spivack and Edmond (1987), Ishikawa and Nakamura (1993) and Smith *et al.* (1995); Central Andean volcanic arc and back arc: Rosner *et al.* (2003). Central Andean ignimbrites $\delta^{11}\text{B}$ (melt inclusion) from Schmitt *et al.* (2002); ϵ_{Nd} (bulk rock) from Schmitt *et al.* (2001); Palaeozoic Andean basement: $\delta^{11}\text{B}$ (tourmaline and metamorphic rocks) from Kasemann *et al.* (2000), ϵ_{Nd} (bulk rock) from Lucassen *et al.* (2001).

tin porphyries. Post-entrapment alteration probably did not affect the boron signature of the melt inclusions, as can be deduced from systematic correlation trends between boron and a number of trace elements in melt inclusions and bulk rock samples from the Bolivian tin belt (Lehmann *et al.*, 2000).

Figure 4 compares the neodymium and boron isotope compositions of the studied porphyry systems with selected reference data. The ϵ_{Nd} range of +2 to +4 for El Salvador is typical of Cenozoic copper porphyry systems in Chile (Maksaev, 1990), and is commonly explained as a mantle signature. No combination of crustal- and mantle-derived boron can explain the positive $\delta^{11}\text{B}$ range in the El Salvador melt inclusions, implying that an input of heavy B from the subducted, seawater-altered oceanic plate must be involved. Contrastingly, the negative $\delta^{11}\text{B}$ data from the Bolivian tin porphyries coincide with the boron isotope composition of the Central Andean basement. The same similarity is observed in the neodymium isotope composition of tin porphyries and regional continental crust (Lehmann *et al.*, 2000). The boron isotope composition of these porphyries could be influenced by ^{11}B -depleted fluids from the deep slab, which may result from boron isotope fractionation during progressive dehydration (Rosner *et al.*, 2003). However, given the high abundance of boron in the melt inclusions from the tin porphyry systems and the fluid-mobile behaviour of boron during dehydration, i.e. early boron loss from the subduction environment, this deep slab contribution must be small.

Figure 5 compares bulk-rock and melt-inclusion boron data from the copper and tin porphyry systems with titanium (relatively compatible and fluid-immobile), which is a proxy for magmatic evolution in felsic systems. The bulk-rock boron abundances are controlled by hydrothermal overprint (large variations in boron contents at relatively constant Ti levels). The high bulk-rock B abundances in the Bolivian porphyry systems reflect their pervasive tourmaline alteration, also seen in boron abundances of several thousand p.p.m. B in fluid inclusions (Müller *et al.*, 2001).

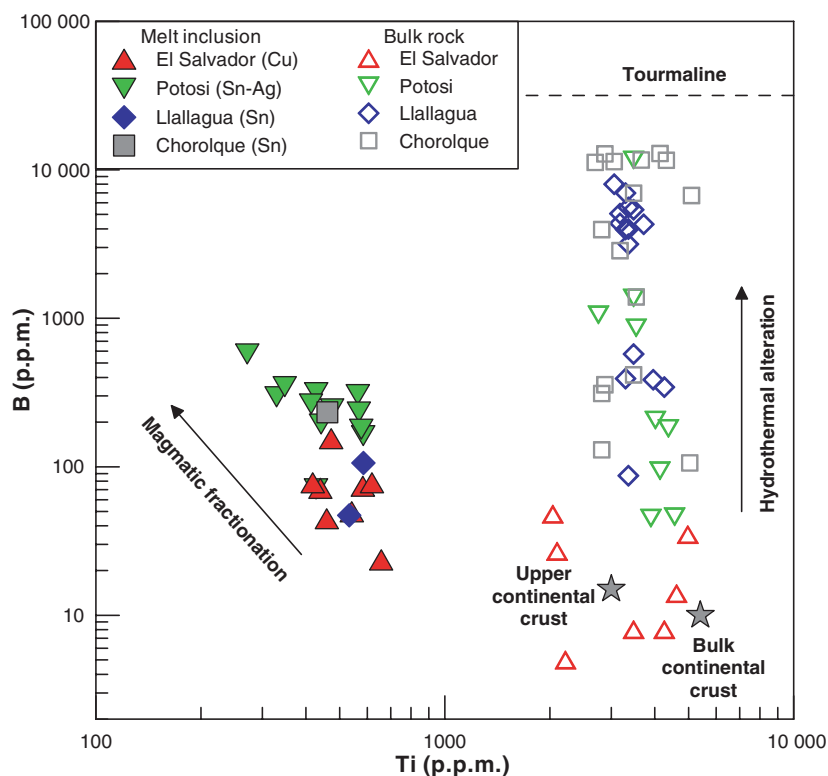


Fig. 5 Variation plot for boron and titanium abundances in quartz-hosted melt inclusions (filled symbols) and bulk rock (open symbols) from the El Salvador copper porphyry and the Cerro Rico de Potosi, Llallagua and Chorolque tin porphyry systems. Reference points for upper and bulk continental crust are from Taylor and McLennan (1995).

The 'seawater' signature in the boron isotope composition of the melt inclusions from El Salvador is probably also expressed by the highly oxidized character of the magmatic-hydrothermal system, where abundant anhydrite \pm magnetite formed during early potassic alteration, typical of copper porphyries (Gustafson and Hunt, 1975). Magmatic anhydrite is reported from other copper porphyry systems (Barth and Dorais, 2000; Audétat *et al.*, 2004). A high oxidation state is required in the early evolution of copper porphyry systems in order to allow efficient transfer of chalcophile elements from the hydrated mantle wedge into arc magmas (Mungall, 2002). The influence of a seawater-derived slab fluid is not visible in the Bolivian tin systems, which appear to be dominated by intracrustal partial melts. The boron enrichment in the melt inclusions likely reflects pelitic source rocks of the igneous system. Average pelitic rocks have about 100 p.p.m. B, compared

with bulk continental crust with about 10 p.p.m. B (Taylor and McLennan, 1995). A pelitic (and carbonaceous) source could also explain the more reduced nature of the magmatic-hydrothermal tin porphyry systems as recorded both by the lack of magmatic magnetite (Lehmann *et al.*, 1990) and occurrence of early hydrothermal pyrrhotite (Kelly and Turneaure, 1970). A reduced magmatic and hydrothermal system seems to be required for both efficient tin enrichment during magmatic fractionation and high tin solubility in aqueous fluid systems (Lehmann, 1990). The significant distinction in boron isotope composition between the copper and tin porphyries reflects these fundamentally different metallogenic settings.

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