Source component mixing controls the variability in Cu and Au endowment along the strike of the Eastern Andean Cordillera in Peru

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Abstract

Mississippian arc magmatic suites of the Au-rich Pataz and Cu-dominated Montañas regions in Peru reveal distinct modes of magmatic-hydrothermal petro- and metallogenesis. The distinction is remarkable due to their broad contemporaneity (336–322 Ma), arc-parallel position, and close distance (< 50 km) to each other. In both arc regions, petrography, geochemistry, and the tectonic setting of magmatic suites suggest a rapid switch from syn-collisional/compressional to post-collisional/extensional (with ‘A₂-type’ signature) emplacement regime. Rocks of the Au-rich Pataz region originate from mixed sources with a contribution from the mantle ($\epsilon_{\text{Hf}} > 0$ and $\delta^{18}\text{O}$ of $\sim 5.3\text{‰}$) and assimilated old crust (variously low ϵ_{Hf} and $\delta^{18}\text{O} > 5.3\text{‰}$). The ultimate source of Au in the mineralised Pataz batholith was oxidised ($f\text{O}_2$ at FMQ buffer; based on zircon trace chemistry) and alkali-, LILE- and HFSE-enriched, most likely represented by the metasomatised mantle. The syn-extensional emplacement of the relatively reduced ($\Delta\text{FMQ} < 0$), but unmineralised, A₂-type suite involved assimilation of reduced crust. Associated, reduced, magmatic-hydrothermal fluids infiltrated the Au-bearing batholith suite and effectively mobilised and transported and concentrated Au. In the Montañas region, rocks are oxidised ($\Delta\text{FMQ} > 0$) and dominantly mantle derived without significant incorporation of crustal material. Samples from the Cu-mineralised suites indicate the additional contribution of a $\delta^{18}\text{O} < 5.3\text{‰}$ source, potentially melted layer-2 gabbro. In addition, the elevated whole-rock La/Yb and Sr/Y ratios are compatible with minor addition of slab-derived material, which may have enhanced Cu endowment in this region. Late-magmatic, oxidised fluids derived from the younger A₂-type suite controlled Cu mobilisation and concentration, while Au behaved largely refractory. In general terms, it is postulated that source mixing in continental arcs is a first-order control of contrasting Cu and Au endowment and that sequential intrusion processes facilitate late-magmatic-hydrothermal mobilisation and concentration of specific metal assemblages.

Keywords Continental arc magmatism · U–Pb geochronology · Whole-rock geochemistry · Hf–O isotopes · Zircon trace elements

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Introduction

The longitudinal continuity (i.e., along strike) and transverse (i.e., across strike) variability of physiographic, magmatic, and metallogenic characteristics in orogens are commonly emphasised. The central Andes are a classic example of an orogeny exhibiting such variability (e.g., Clark et al. 1990; Gutscher et al. 1999). The main transverse discontinuity across the central Andes is the juxtaposition along faults of the Western Cordillera (i.e., the Tertiary–Quaternary Andean margin) and the Eastern Cordillera (i.e., the Paleozoic–Mesozoic proto-Andean margin). Magmatic suites within both the Western and Eastern Cordilleras formed in multiple, broadly subduction-parallel chains, during

Fig. 1 Overview geological maps. **a** Northern part of the Eastern Andean Cordillera with the region around the Pataz–Parcoy–Montañitas districts. Inset shows the longitudinal extent of the Eastern Cordillera from Peru to Argentina, with major orogenic Au (–Sb–W) districts, recent plate tectonic features, as well as tectonic segments defined by Sillitoe (1974). **b** Pataz Au-mining district with localities of samples. **c** Montañitas Cu ± Au occurrence district with localities of samples

distinct time periods. Regional and temporal steepening or shallowing of subducted slabs, subduction erosion, and terrane accretion are generally seen as the main trigger for protracted land- or trenchward arc migration and formation of heterogeneous Andean belts (e.g., Kay et al. 2005). Cyclic switching from lithospheric extension to compression in arcs can be a result of variable dip angle and kinematics of the subducting slab (Collins 2002); extensional basins are related to steep subduction and slab-retreat phases, whereas crustal thickening reflects flat subduction.

The Andes also display a distinct longitudinal variability at the scale of a subducting slab. The main longitudinal discontinuities separate the three Andean volcanic segments (northern, central and southern). Sillitoe (1974) defined a series of tectonic segments along the central Andean orogen (Fig. 1a, inset) and Barazangi and Isacks (1976) attributed this to major slab tear faults and zones of distinct subduction angles within the subducting Nazca plate. Hall and Wood (1985) recognised a complex segmentation of the Northern Andean margin and demonstrated its nature by discontinuities in physiography, volcanism, structure, seismicity, and gravity. In addition to regional and temporal changes in subduction erosion and terrane accretion, much of the along-strike variations are likely attributed to changes in the convergence vectors of the oceanic and continental plates, as well as along-strike variations of subducted slab age, strength, and composition (Gutscher et al. 1999). In addition to the heterogeneity of the subducting slab, the mode of the pre-existing oceanic or continental arc crust plays a major role for arc magmatism. There is a wealth of studies providing evidence for systematic changes in elemental abundances and isotopic composition, as well as geochronology, of magmatism along the strike of arcs. Most noteworthy for the central Eastern Cordillera in Peru are the comprehensive geochronological work of Mišković et al. (2009) and Lu/Hf work of (Mišković and Schaltegger 2009). These studies showed a high magmatic variability along the Eastern Andean Cordillera in terms of Carboniferous ages, chemistry, and isotopic signature.

It has long been recognised that the formation of individual metallogenic belts in an arc system (featuring distinct age ranges and metal associations) is related to arc migration (e.g., Sillitoe and Perelló 2005). Prominent porphyry/epithermal deposits are distributed along the

Western Andean Cordillera, and localised within mostly separated belts of distinct iron, copper–(gold–molybdenum), copper–lead–zinc–silver, and tin–(tungsten–silver) metal associations (Sillitoe 1974). In the Eastern Andean Cordillera, neither a longitudinal nor a transverse variability of metallogenic systems has been recognised: a single major orogenic Au (–Sb–W) belt extends from Columbia south to northern Argentina (Haeberlin et al. 2004; Hagemann 2014). Notwithstanding extensive prior study, the following key questions related to the heterogeneous distribution of metal systems across magmatic arcs remain unsolved and will be tackled in this contribution: (1) how important are the source contributions (mantle wedge, subducting slab, and continental crust) for causing regional longitudinal variations of contemporaneous continental arc magmatism? (2) What is the reason for the variability of metal associations in ore deposits, and how are they genetically linked to magmatism in terms of metal fertility and metal transport? (3) Is there higher metallogenic variability in the Eastern Cordillera along strike than recognised by the few existing regional studies?

The study areas are the Pataz Au-mining area (Schreiber et al. 1990; Haeberlin et al. 2004; Witt et al. 2013) and the recently investigated Sierra Montañitas region, which hosts several Cu ± Au vein zones and a porphyry Cu ± Au prospect (Angerer et al. 2011). The world-class Pataz–Parcoy Au district is one of the northern-most expressions of the orogenic Au (–Sb–W) belt within the central Andes of Peru (Fig. 1a). Published U–Pb ages exist for the Pataz batholith: 338 ± 3 Ma (Witt et al. 2013), 334 ± 6 Ma (Schaltegger et al. 2006), 333 ± 8 Ma (Mišković et al. 2009), and 329 ± 1 Ma (Macfarlane et al. 1999). Sierra Montañitas is situated 10–20 km south-southeast of the Parcoy district and represents the longitudinal extension of the Pataz batholith. The Cu ± Au occurrences in the Sierra Montañitas are unique examples of a porphyry metal system in the Eastern Cordillera (Angerer et al. 2011). We offer a subduction model to explain a distinct heterogeneity of magma sources, and propose that this source variation causes variable metal endowments. Analytical evidence is based on geochronology, oxygen isotopes, hafnium isotopes, and element chemistry of magmatic zircons. Recent advances in zircon-focused petrogenetic studies can elucidate the relationship between magma source for porphyritic rocks (and suites) and local (and regional) metal fertility (Lu et al. 2013, 2016; Dilles et al. 2015; Hou et al. 2015; Gardiner et al. 2017). Zircons are targeted as robust archives recording the magmatic evolution in their Lu–Hf and O isotope systematics (Valley et al. 2005; Hawkesworth and Kemp 2006; Kemp et al. 2006, 2007) and the crystallisation environment in their elemental chemistry (Belousova et al. 2002; Whitehouse 2003).

Igneous suites and metallogeny in the Pataz–Parcoy–Montañitas district

The Eastern Andean Cordillera was the leading continental margin of western Amazonia for at least 900 Ma (Mišković et al. 2009). Intrusive rocks of the Eastern Andean Cordillera are predominantly related to magmatic activity in a continental arc during the Carboniferous to early Permian (340–285 Ma), to extension in the middle Permian to Early Jurassic (275–190 Ma), and then to modern Andean subduction (Mišković et al. 2009). The Pataz–Parcoy goldfields and the Sierra Montañitas are located along the regional Cordillera Blanca Fault, which separates the Eastern Andean Cordillera from the Western Andean Cordillera (Megard 1984). The Pataz–Parcoy goldfields are important contributors to gold production of Peru, having yielded approximately 8 Million ounces Au, since production began in colonial times, mainly from quartz–carbonate–sulphide veins hosted in the Pataz batholith (Macfarlane et al. 1999; Haeberlin et al. 2004; Witt et al. 2014).

Pataz region: rocks and vein-style Au system

The Pataz batholith is situated within a north-northwest striking horst at mid-altitude (3600–4200 m above sea level), limited to the west by volcano-sedimentary units of the Eastern Andean Cordillera and to the east by the Lavasen graben, a repository for the products of Esperanza–Lavasen suite magmatism (Fig. 1b). The batholith mainly consists of medium- to coarse-grained, equigranular, biotite ($\pm$ hornblende) granodiorite, medium-to-coarse-grained hornblende $\pm$ biotite diorites, quartz–diorites, monzo-, and syenogranites (Witt et al. 2014). Witt et al. (2013) distinguished two igneous suites, the “low-SiO₂” (diorite-dominated with massive and cumulate textures) and the “high-SiO₂” suite (granodiorite-dominated with massive and porphyritic textures). The Lavasen Volcanics comprise plagioclase- and K-feldspar–phyric pyroclastic rocks, volcanogenic sedimentary rocks, and re-sedimented pyroclastic rocks, with mostly rhyolite and rhyodacite/dacite chemistry (Witt et al. 2014). The Esperanza subvolcanic complex is located along the western margin of the Lavasen graben. It is a high-level, bimodal complex, comprising mostly latite porphyry and quartz–latite porphyry. Mississippian magmatism began with enriched tholeiitic magmas that formed by melting of metasomatised asthenosphere. These magmas were emplaced as the low-SiO₂ suite diorites (Witt et al. 2014). This stage was followed by volumetrically dominant high-SiO₂ suite granodiorites and granites. Within a few million years, relatively K-rich magmas were emplaced as the ESC and Lavasen volcanic rocks (Witt et al. 2014).

Gold-bearing veins formed along the western margin of the batholith (Schreiber et al. 1990; Haeberlin et al. 2004; Witt et al. 2016). Witt et al. (2016) described three contrasting styles of gold mineralization in the northern Pataz district. Most economic significances are quartz–carbonate–sulphide veins. The sulphide content of these veins is extremely variable, but high-grade shoots contain tens of percent sulphides, predominantly pyrite, arsenopyrite, galena, and sphalerite. The age of the mineralized veins is contentious: although Ar⁴⁰–Ar³⁹ ages of 312–314 Ma have been reported for metasomatic white mica around the veins (Haeberlin et al. 2004). Witt et al. (2016) argued that the white mica is retrograde with respect to mineralization and provides only a minimum age constraint. Hydrothermal alteration and pathfinder element geochemistry in volcanic and volcanoclastic rocks mapped in the Lavasen Graben are consistent with epithermal-style gold systems (Witt et al. 2016). The Esperanza–Lavasen suite magmatism is proposed to have provided fluid and heat for gold in the batholith (Witt et al. 2014).

Montañitas region: rocks and porphyry and vein-style Cu $\pm$ Au system

The Sierra Montañitas (“small mountains”) are a partly subvolcanic, intrusion-dominated region located in a mid-to-high-altitude (3600–4200 m above sea level) section of the Eastern Andean Cordillera, about 50 km south-southeast of the Pataz gold-mining district and directly south-east of the Parcoy district near the town of Buldibuyo. The igneous system of Montañitas consists of two main felsic igneous suites (Fig. 1), the southern granodiorite–granite–dacite–quartz–phyric dacite suite and the northwestern monzogranite–(rhyo-)dacite/rhyolite–(rhyo-)dacite suite. In the Montañitas region, a network of northeast and northwest oriented structures was the controlling structures for the distribution of igneous rocks (Angerer et al. 2011).

Porphyry-style rock alteration with propylitic, phyllic (sericitised), silicified, and sulfidised zones is common in the southern and northwestern dacites, while it is mostly absent in other rocks (Angerer et al. 2011). Some Au-bearing veins are locally exploited by artisanal miners. Two Cu $\pm$ Au-rich mineralisation styles are present in the Sierra Montañitas: (1) major Cu $\pm$ Au- and minor Au–Pb $\pm$ Ag-bearing quartz–chlorite/epidote–pyrite veins in southern monzogranite, granodiorites, and porphyritic dacite, and locally in the northwestern ryodacites. These veins are structurally controlled by northeast to north-northeast and northwest trending fault systems. (2) Porphyry-hosted stockwork/sheeted veins with Cu (and anomalous Au) in the southern porphyritic dacites. These porphyritic intrusions are controlled by northeast trending faults and show local intrusion breccia

textures and potassic alteration, which are the location of most Cu ($\pm$ Au) anomalies.

Sample descriptions

Table 1 provides an overview of the collected samples with their key characteristics. The magmatic suite from the Patáz vein-style Au system is represented in this study by four samples. The medium-grained diorite (*PAT1*) from the low-SiO₂ suite (sensu Witt et al. 2014) shows an equigranular texture with plagioclase, hornblende ($\pm$ clinopyroxene and biotite), and minor quartz (Fig. 2a). The medium-grained granite (*PAT4*) from the high-SiO₂ suite (sensu Witt et al. 2014) shows an equigranular texture with plagioclase, K-feldspar, quartz, and biotite ($\pm$ hornblende) (Fig. 2b). The two samples from the Esperanza–Lavasen suite have previously been described and dated by zircon U–Pb isotopes (Witt et al. 2013, 2014). The quartz–latite from the Esperanza subvolcanic complex (*WWGA5*) is a porphyritic rock showing albite, K-feldspar, and (partially resorbed) quartz–phenocrysts (Fig. 2c). Flow banding and spherulitic textures are well developed in the rocks (Witt et al. 2014). Coarse-grained plagioclase–pyroxene clots, Fe-rich dark green amphibole, and green biotite suggest derivation of the latitic rocks from a subjacent magma chamber (Witt et al. 2014). The rhyolitic sample from the Lavasen volcanic complex (*WWGA6*) is a pumice-rich, re-sedimented breccia with albite, K-feldspar, and minor quartz–phenocrysts (Fig. 2d). Titanite is an accessory phase in all samples except Lavasen rocks.

Samples from the Montañitas Cu $\pm$ Au porphyry- and vein-style system include three rocks from the southern and three from the northwestern suite. The southern suite rocks are nearly equigranular and characterised by a plagioclase–hornblende–quartz assemblage, whereas the northwestern suite is generally porphyritic, richer in K-feldspar and biotite. Titanite is an accessory phase in all samples, and magnetite is only observed in northwestern suite rocks. Sample *mts134* represents the southern granodiorite. Modal compositions include phenocrysts of quartz, plagioclase, subhedral hornblende, and biotite (maximum 5 mm) in a slightly finer holocrystalline quartz–plagioclase–biotite–hornblende matrix (0.1–2 mm grains) (Fig. 3a). The rock characteristically contains hornblende-rich microdiorite xenoliths. Sample *mtc6* comes from the southern monzogranite. It shows a micrographic-to-granophyric quartz–feldspar texture (intergrowth of quartz and orthoclase or plagioclase) (Fig. 3b). Such eutectic textures are typically explained as products of crystallisation during water loss-induced magma undercooling in shallow-crustal position (Winter 2010). The mineralised porphyritic dacite is represented by sample *mts14f2*. It consists of phenocrysts of subhedral-to-anhedral quartz,

saussuritic plagioclases, hornblende, and biotite in a fine-grained equigranular quartz–plagioclase matrix ($\sim$ 0.05 mm grain size) (Fig. 3c). Common resorption of quartz–phenocrysts, i.e., dissolution embayment and round edges, may be explained by pressure decrease during magma ascent or by post-igneous alteration processes. Enclaves of hornfels and porphyritic dacite are common. Sample *mts14f2* shows disseminated chalcopyrite and chalcopyrite and arsenopyrite alteration (up to 4 vol%).

The porphyritic monzogranite (*mtn36*) from the northwestern suite is a medium-grained biotite–granite with mostly bimodal texture (up to 1 cm K-feldspar, plagioclase, quartz, and biotite phenocrysts in a $\sim$ 50 μ m matrix) (Fig. 3d). Phenocrystic-to-fine-grained magnetite is present in the monzogranite. The porphyritic rhyodacite (*mtn23a*) is a bluish-green rock with salmon-coloured K-feldspar and anhedral, rounded quartz, and plagioclase phenocrysts (Fig. 3e). Its fine quartz–plagioclase matrix shows flow textures around phenocrysts and relic perlitic textures. In the absence of evidence for effusive activity, the flow textures are interpreted as intrusive origin indicating highly viscous state of subvolcanic liquid. The strongly sericitised quartz–orthoclase–phyric rhyodacite (*mtc92*) is an example of the hydrothermally altered and mineralised northwestern suite. Flow textures, K-feldspar, and biotite phenocrysts suggest lithological similarity to less altered rhyolites (Fig. 3f).

Analytical methods

Whole-rock geochemistry

Representative amounts of 100–1000 g of samples were sent to ACME labs, Canada for whole-rock geochemistry. Samples were coarsely crushed in a steel jaw crusher and then milled to a powder ($<$ 100 μ m) in a hard steel mill (leading to contamination with minor Fe and Cr), with quartz washes in between to minimise cross contamination. About 30 g of the homogenised powder was analysed by XRF and ICP-MS. For the XRF, a Li borate fusion was used, and for the ICP-MS, a Li borate fusion was followed by nitric acid digestion. Loss on ignition (LOI) at 1000 °C was determined gravimetrically, total sulphur, and carbon by LECO® combustion analyses, and ferrous iron by volume titration following acid digestion. REE abundances are normalised to the chondrite values of McDonough and Sun (1995). The Ce and Eu anomalies are calculated as $Ce_n/(La_n \times Pr_n)^{0.5}$ and $Eu_n/(Sm_n \times Gd_n)^{0.5}$, respectively.

Zircon U–Pb geochronology

Heavy minerals were separated from crushed and milled rock samples using heavy liquid (TBE, tetra-bromo-ethane)

Table 1 Samples of the present study with key characteristics and statistics of zircon analyses (U–Pb ages, O and Hf isotopes, and REE and trace metals)

Sample (rock)	Outcrop location	Longitude (PSAD56)	Latitude (PSAD56)	Regional metal affinity	Igneous suite	Lithology	Alteration	Whole-rock Pb	Zircon U–Pb	Zircon Hf isotope		Zircon O isotope		Zircon REE and trace metal concentrations and derived parameters
										eHf (t) avg	εHf stdev	d18O avg	δ ¹⁸ O stdev	
								SiO ₂	Crystallisation age [Ma]					
Pat1	Papagayo underground mine			Au	Pataz batholith	Quartz–diorite	Propylitic	56.20	334.0 ± 3.4	– 6.92	0.82	7.07	0.32	0.80
Pat4	Papagayo underground mine			Au	Pataz batholith	Monzo-granite	Fresh	76.00	336.3 ± 1.3	– 1.98	0.96	5.62	0.46	0.55
WWGA5	213688.0	9149576.0		Au	Esperanca subvolcanic complex	Porphyritic quartz–latite	Fresh	76.10	333.7 ± 2.4 ^a	– 4.01	0.46	7.35	0.34	0.66
WWGA6	212560.0	9152153.0		Au	Lavasen volcanics	Pumice-rich breccia	Fresh	77.20	334.3 ± 1.8 ^a	0.73	0.95	5.78	0.09	0.51
mts14f2	254944.3	9096323.5		Cu ± Au	Montañitas, southern suite	Porphyritic dacite	Potassic–pyrite	68.60	336.6 ± 3.3	0.92	0.92	4.77	0.82	0.53
mts134	253157.4	9094515.5		Cu ± Au	Montañitas, southern suite	Granodiorite	Fresh	71.20	332.1 ± 3.8	1.06	0.99	4.84	0.42	0.59
mtc6	248242.9	9098167.0		Cu ± Au	Montañitas, southern suite	Monzo-granite	Fresh	73.30	333.5 ± 3.8	– 0.02	0.65	5.33	0.67	n.d.
mtn36	250281.3	9104446.9		Cu ± Au	Montañitas, northwest-ern suite	Monzo-granite	Fresh	70.10	327.9 ± 2.4	0.69	0.66	4.66	0.24	0.69
mtn23a	248546.2	9105804.0		Cu ± Au	Montañitas, northwest-ern suite	(Flow-textured) porphyritic rhyodacite	Fresh	72.50	327.9 ± 3.5	– 0.15	0.51	5.15	0.20	n.d.
mtc92	250564.2	9094060.0		Cu ± Au	Montañitas, northwest-ern suite	Sericitised quartz–ortho-clasephyric rhyodacite	Phyllic	75.20	322.2 ± 2.8	0.05	0.81	5.44	0.72	0.82

Table 1 (continued)

Sample (rock)	Zircon REE and trace metal concentrations and derived parameters												
	Th/U stdev	Ce/Ce* avg	Ce/Ce* stdev	Eu/Eu* avg	Eu/Eu* stdev	(Yb/Gd) avg	(Yb/Gd) stdev	log fO ₂ avg(S&B)	log fO ₂ stdev (S&B)	log fO ₂ avg (Trail)	log fO ₂ stdev (Trail)	Temp [°C] avg	Temp [°C] stdev
Pat1	0.07	31.70	11.89	0.18	0.02	10.33	1.12	-0.17	1.07	-10.85	0.91	834.49	13.87
Pat4	0.15	44.84	27.03	0.25	0.08	16.00	5.41	-2.44	1.19	-13.50	2.19	747.25	41.73
WWGA5	0.17	51.23	21.80	0.16	0.04	10.64	1.66	-3.15	1.63	-14.52	1.66	726.55	38.89
WWGA6	0.08	27.50	22.09	0.19	0.04	10.10	1.94	-2.35	1.51	-18.68	2.84	699.61	18.69
mts14f2	0.09	80.49	37.57	0.21	0.08	20.24	3.10	1.49	1.25	-11.16	2.00	758.28	26.76
mts134	0.21	100.08	51.58	0.16	0.02	19.82	4.40	-2.70	3.65	-12.41	1.76	697.17	27.01
mtc6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
mtn36	0.07	216.26	81.62	0.30	0.09	18.07	3.62	-1.41	1.70	-8.29	2.21	743.65	12.12
mtn23a	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
mtc92	0.26	323.68	210.51	0.35	0.07	15.71	6.32	-0.89	2.16	-6.58	2.77	774.21	59.32

(S&B) means that fO_2 calculated after Smythe and Brenan (2016); (Trail) means that fO_2 calculated after Trail et al. (2012)^a Witt et al. (2013)

and magnetic separation techniques (hand magnet and Frantz). The final separation involved hand picking the zircon grains. These were mounted on epoxy discs together with fragments of zircon reference materials, polished until nearly 1/3 of each grain was removed, and coated with carbon for imaging (backscattered electron and cathodoluminescence) for their internal morphology using a JEOL6400 scanning electron microscope at the Centre for Microscopy, Characterisation and Analysis of University of Western Australia. The epoxy mounts were then thoroughly cleaned and gold-coated to have a uniform electrical conductivity during the SHRIMP analyses. The zircon standard used for Pb/U calibration was BR266 zircon ($^{206}\text{Pb}/^{238}\text{U}$ age = 559 Ma, 903 ppm U; $^{206}\text{Pb}/^{238}\text{U}$ ratio = 0.09059) and OGC1 ($^{207}\text{Pb}/^{206}\text{Pb}$ age = 3465 Ma) to check the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. The isotopic composition of the minerals was determined using SHRIMP II (De Laeter and Kennedy 1998) at the John de Laeter Centre at Curtin University, Perth, using methods originally published by Compston et al. (1992). Circular areas of 20–30 μm were analysed from morphologically distinct areas chosen within zircon grains, together with replicate analyses of the standard in the same epoxy mount. Corrections for common Pb were made using the measured ^{204}Pb and the Pb isotopic composition of Broken Hill galena. For each spot analysis, the initial 60–90 s were used to raster and remove the gold, minimising the inclusion of common Pb from the gold coating. Each analysis consisted of nine determinations (Zr_2O , ^{204}Pb , background, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , ^{242}ThO , and ^{254}UO) repeated in five–six scans. Results with more than 1% common lead correction were not used in age calculations. Data were reduced using SQUID (Ludwig 2001) and plotted on concordia diagrams using ISOPLLOT/Ex software (Ludwig 1999) and error ellipses on concordia plots are shown at the 95% confidence level (2σ).

Zircon O isotope ratios

The sample mounts that were previously used for SHRIMP U–Pb analyses were repolished to ensure that any oxygen implanted in the zircon surface from the O_2 -primary ion beam used for U–Pb analysis was completely removed. Most dated zircons were analysed for O and Hf isotopes, and if possible, the same spot locations were used for all analyses, where cores and rims from the CL images were suspected, and the grain was dated in more than one site. The mount was then re-imaged using reflected and transmitted light, and, finally, evaporatively coated with 30 nm of high-purity gold. Oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$) were determined using a Cameca IMS 1280 multi-collector ion microprobe at the University of Western Australia (samples A-Lat, B-Lav, mtc006, mtc092, mtn023a, mtn036, and mts134) and the Natural History museum in Stockholm (samples PAT-1, PAT-4, and

Fig. 2 Hand specimens and thin section micrographs of samples from the Pataz region. **a1** Quartz–diorite PAT1, equigranular texture with minor epidote–chlorite alteration; **a2** same sample, holocrystalline igneous assemblage, and minor epidote–chlorite alteration and accessory titanite; **b1** monzogranite PAT2, equigranular texture; **b2** same sample, holocrystalline igneous assemblage; **c1** ESC quartz–latite WWGA5, porphyritic texture; **c2** same sample, albite–phyritic igneous texture; **d1** Lavasen rhyolitic, re-sedimented breccia WWGA6; **d2** same sample, laminated sedimentary texture with sericite–limonite alteration

mts14f2). In both labs, the method for oxygen isotope analyses follows that of Nemchin et al. (2006) and Whitehouse and Nemchin (2009). This involved use of a 20 keV Cs⁺ ion beam (+ 10 kV primary, – 10 kV secondary) with an intensity of c. 2.0 nA in aperture illumination mode and a spot diameter of about 15 µm. A normal-incidence electron gun was used to compensate for sample charging. Ion beams were monitored with two Faraday detectors (channels L'2 and H2') at a mass resolution of ~2500. Data from unknown samples were fractionation-corrected relative to measurements of the Temora 2 reference zircon ($\delta^{18}\text{O}$ (VSMOW) = $8.2 \pm 0.01\text{‰}$, 1 σ ; Black et al. 2004). The BR266 reference zircon ($\delta^{18}\text{O}$ (VSMOW) = $13.26 \pm 0.02\text{‰}$, 1 σ ; Zi et al. 2012) was used as a secondary monitor of instrument performance. Every set of five unknowns was followed by two analyses on Temora 2 and two on BR266 zircons. Measurements were performed in chain analysis mode with automatic field aperture centering using the ¹⁶O signal. Each analysis spot was pre-sputtered for 10 s before automated peak centering in the field and contrast apertures was performed. Analyses consisted of 20 four-second cycles, which gave an average internal precision of <0.25‰ (2 σ). Instrumental mass fractionation was calculated using a correction scheme similar to that described by Kita et al. (2009). The spot-to-spot reproducibility (external precision) was <0.2‰ (2 σ) for the BR 266. Drift corrections (0.002–0.006‰) were applied for each session, and an external error of 0.19–0.20‰ (1 σ) based on analyses of the primary standard was propagated into the overall uncertainty for each analysis reported. Method of uncertainty propagation followed Taylor and Kuyatt (1994). Corrected ¹⁸O/¹⁶O ratios are reported in $\delta^{18}\text{O}$ notation, in per mil variations relative to Vienna standard mean ocean water (VSMOW).

Zircon Hf-isotope ratios

The Hf isotopes, together with Yb and Lu isotopes for interference corrections, were acquired with a Thermo-Scientific Neptune multi-collector ICP-MS coupled to a Cohert GeoLas 193 nm ArF laser-ablation sampling system at James Cook University, Townsville, Australia (c.f., Kemp et al. 2009). Laser ablation was carried out for 60 s at repetition rates of 4 Hz and laser fluence of ~6 J/cm² (resulting in drilling rates of ca. 0.2 µm/s and hole depths of

in average 12 µm). Spot sizes of 31, 42, or 58 µm diameter were employed, depending on the available polished area of the zone of interest in the crystal. Ablation was conducted in a modified, low volume sample cell, with the He carrier gas exiting the cell being combined with Ar prior to transport into the ICP-MS via Teflon-lined Tygon[®] tubing (c.f., Kemp et al. 2009). A small (~0.004 to 0.005 l/min) N₂ flow was introduced into the Ar carrier gas to enhance sensitivity (Iizuka and Hirata 2005; Hawkesworth and Kemp 2006). The correction for the isobaric interference of ¹⁷⁶Lu and ¹⁷⁶Yb on ¹⁷⁶Hf was carried out with Yb isotope values reported by Segal et al. (2003). Analyses of the Mud Tank Carbonatite reference zircon (¹⁷⁶Hf/¹⁷⁷Hf = 0.282507 ± 6 , Woodhead and Hergt 2005; Wu et al. 2006) bracketing about 30 unknown measurements was used to correct the systematic offset of data during the analytical session (resulting external normalisation factor for isotopic ratios was 1.000028). Reference zircons used to monitor data accuracy and analytical precision were Temora 2 (¹⁷⁶Hf/¹⁷⁷Hf = 0.282680 ± 31 ; 2 σ ; Wu et al. 2006), FC1 (0.282184 ± 16 ; Woodhead and Hergt 2005) and BR266 (0.281630 ± 24 ; Woodhead et al. 2004).

Zircon trace elements

Zircon grains without visible cracks or inclusions in transmitted light were chosen for trace-element analyses. This was performed by laser-ablation quadrupole ICP-MS at the AAC, JCU using a GeoLas 193-nm ArF laser coupled with a Varian quadrupole ICP-MS operating in normal sensitivity mode. Spot sizes were 21 or 31 µm. Laser pulse repetition rate was 10 Hz. Zirconium, Si, and Hf were analysed on the selected grains prior to laser-ablation analyses by electron probe microanalyser (EMPA) using a Jeol JXA8200 “Superprobe” with wavelengths dispersive spectrometers at the AAC, JCU. The Hf values obtained by EMPA were used as internal standard for calculation of trace-element content measured by laser ICP-MS. NIST612 standard glass was used for calibration and geostandards zircon 91,500 (Wiedenbeck et al. 2004) was analysed to monitor data quality during the session. The following isotopes were analysed: ²⁹Si, ³¹P, ⁴⁴Ca, ⁴⁹Ti, ⁷⁵As, ⁸⁸Sr, ⁸⁹Y, ⁹³Nb, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁶⁰Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷¹Yb, ¹⁷⁵Lu, ¹⁷⁹Hf, ¹⁸²W, ²⁰⁶Pb, ²⁰⁷Pb, ²³²Th, and ²³⁸U. Dwell times were 10 ms, except for ⁴⁹Ti, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, and ²⁰⁷Pb, for which 20 ms was used. The software SILLS (Guillong et al. 2008) was used to calculate the trace-element content (in ppm) from the raw data. All data except for Ca, Sr, As, and W are above quantification limits, the relative uncertainty ranges from 4 to 25% (1 σ). The measured concentrations of trace elements like Ti, Nb, Ta, and the LREE that are present in the zircon lattice at low abundances are highly sensitive to alteration, generally accompanying radiation damage, and the intersection of tiny inclusions like apatite

Fig. 3 Hand specimens and thin section micrographs of samples from the Montañas region. **a1** southern suite granodiorite mts134, with dioritic xenolith in a equigranular texture; **a2** same sample, showing sericitisation of feldspars; **b1** southern suite monzogranite mtc6, weak alteration along fissures; **b2** same sample, holocrystalline texture with abundant hornblende; **c1** southern suite porphyritic dacite (mts14f2), plagioclase–pyric texture with disseminated arsenopyrite and green epidote–chlorite alteration; **c2** same sample, epidote is associated with sulphides; **d1** northwestern suite monzogranite

mtn36, feldspar–biotite–pyric texture; **d2** same sample, fine quartz–feldspar texture with porphyritic plagioclase, orthoclase, and biotite; **e1** northwestern suite porphyritic/re-sedimented rhyodacite mtn23a, orthoclase–quartz–plagioclase–pyric, fine groundmass; **e2** same sample, sedimentary or brecciated texture with fine groundmass and quartz and orthoclase clasts; **f1** northwestern suite quartz–orthoclase–pyric rhyodacite, fine groundmass and strong sericite alteration; **f2** same sample, fine quartz matrix, dominant sericite alteration of feldspars and muscovite porphyroblasts

Fig. 3 (continued)

by the laser. However, none of these effects are significant in time resolved signals from the zircon analyses of this study.

Results

Whole-rock geochemistry data

Geochemical data are given in Table 2. A generally high magmatic differentiation of the samples is indicated by

$\text{SiO}_2 > 68 \text{ wt\%}$ (except diorite PAT-1 of the low- SiO_2 suite). There is a well-defined correlation between SiO_2 and Rb/Sr (Fig. 4a), which suggests no significant major element modification due to rock alteration, with the exception of the potassic altered and mineralised sample mts14f2. Both the Pataz batholith suites and the Montañas magmatic suites are derived from mostly high-K, peraluminous magmas (Fig. 4b, c). A more alkaline signature is evident in PAT4 monzogranite. The concentrations of Th, Nb, Sr, and LREE are higher in the Montañas suite samples with respect to

the Patáz suite (Table 2). These elements are especially enriched in the Montañas northwestern suite. The Nb/Zr and (La/Yb)_{Cl} ratios discriminate the samples from these different locations (Fig. 4d). Sr/Y ratios at and below unity are shown by the ESC and Lavasen samples, while other samples have ratios up to 8 (Table 2).

Zircon morphology and U–Pb ages

Morphology characteristic of zircons and SHRIMP U–Pb geochronology is summarised in Table 3 and a selection of zircon images is given in Fig. 5. Analytical data are provided in Table 4 (online resource). Concordia diagrams for the eight samples are shown in Fig. 6; for WWGA5 and WWGA6, see Witt et al. (2013). Concordant ages are interpreted as the mean crystallisation age of the rock; errors are at a 95% confidence (2 σ).

The Patáz diorite (*sample PAT1*) has an age of 334 ± 3.4 Ma. Two inherited grains give an age of 351 ± 3.2 Ma. The monzogranite (*PAT4*) has an age of 336.3 ± 1.3 Ma, and reveals an inherited grain with an age of 349.5 ± 4 Ma. The ESC quartz–latite (WWGA5) returns an age of 333.7 ± 2.4 Ma (Witt et al. 2013). Inherited grains are present that have ages up to ca. 1200 Ma. The zircons in the Lavasen re-sedimented pumice-rich breccia (WWGA6) reveal an age of 334.3 ± 1.8 Ma (Witt et al. 2013).

Zircons in the granodiorite of the Montañas southern suite (*mts134*) show an age of 332.1 ± 3.8 Ma. This sample contains inherited zircons with ages ranging from 350 to 488 Ma. The monzogranite (*mtc6*) has an age of 333.5 ± 3.8 Ma. The mineralised porphyritic dacite (*mts14f2*) has a Concordia age of 336.6 ± 3.3 Ma. One inherited grain has an age of 366.8 ± 5 Ma. The porphyritic monzogranite from the northwestern suite (*mtn36*) gives an age of 327.9 ± 2.4 Ma. The northwestern suite porphyritic rhyodacite (*mtn23a*) has an age of 327.9 ± 3.5 Ma. The quartz–orthoclase phyric rhyodacite (*mtc92*) shows an age of 322.2 ± 2.8 Ma. There is a considerable $^{238}\text{U}/^{206}\text{Pb}$ -age range of 15 Ma amongst zircons in this sample. Two analyses from two crystals give a date of 311.7 ± 6.4 Ma, and one inherited grain shows a date of 446 ± 7 Ma.

The emplacement ages of the analysed Patáz low-SiO₂ suite diorite and high-SiO₂ suite granite are similar within uncertainty (ranging from ca. 331 to ca. 338 Ma with a mean age of ca. 334 Ma). These ages are consistent with published U–Pb ages for the batholith of 338 ± 3 Ma (Witt et al. 2013), 334.4 ± 6 Ma (Schaltegger et al. 2006), and 333.2 ± 8 Ma (Mišković et al. 2009), and 329 ± 1 Ma (Macfarlane et al. 1999). Ages of the ESC quartz–latite and the Lavasen volcanic rock (333.7 ± 2.4 and 334.3 ± 1.8 Ma, respectively) are almost identical and within the range of the batholith intrusion age (Witt et al. 2013). Across the Sierra Montañas, the Montañas southern suite represents the older suite (> 330 Ma) and the northwestern suite the younger suite (< 330 Ma).

Zircon O and Hf-isotope data

Zircon O and Hf-isotope data are provided in Tables 5 and 6 (online resource). Data are plotted against each other in a binary diagram, where they collectively form a broad band from $\epsilon\text{Hf}(t) + 2$ and $\delta^{18}\text{O} + 4.7$ to $\epsilon\text{Hf}(t) - 7$ and $\delta^{18}\text{O} + 7.5$ (Fig. 7a). The initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in Patáz samples range from 0.28236 to 0.28268, whereas in Montañas from 0.28246 to 0.28270 (ignoring one outlier). In terms of oxygen isotope ratios, the Patáz samples show $\delta^{18}\text{O}$ from 5.1 to 7.9 (ignoring two outliers), whereas the Montañas samples show $\delta^{18}\text{O}$ from 4.3 to 5.7 (ignoring two outliers). The least-differentiated rock in the sample suite, the Patáz quartz–diorite (PAT1), has distinctively low $\epsilon\text{Hf}(t) = -6.9 \pm 0.8$ (2 σ) and high $\delta^{18}\text{O} = 7.1 \pm 0.3\text{‰}$ in a well-clustered distribution. In contrast, the monzogranite (PAT02) in the batholith has higher $\epsilon\text{Hf}(t) = -2.0 \pm 1.0$ and lower $\delta^{18}\text{O} = 5.6 \pm 0.5\text{‰}$. The ESC quartz–latite has $\epsilon\text{Hf} = -4.0 \pm 0.6$ that ranges between the batholith samples, and high $\delta^{18}\text{O} = 7.3 \pm 0.3\text{‰}$. Zircons from the Lavasen volcanoclastic breccia are mantle-like, with $\delta^{18}\text{O} = 5.8 \pm 0.1\text{‰}$ and mostly positive ϵHf values. Carboniferous magmatic zircons in the two Montañas igneous suites show ϵHf values between -1 and 2 and mantle to sub-mantle $\delta^{18}\text{O}$.

Zircon trace-element chemistry

REE, Th, and U data

The zircons in a selection of eight samples were analysed for a suite of trace elements (data in Table 7, online resource). Rare-earth element patterns are similar for zircons of each rock sample, which is indicative of a general absence of post-magmatic alteration of zircons (cf. Whitehouse 2003). Thorium concentrations in zircons vary from 30 to ~600 ppm, U contents from 106 to ~700 ppm. The Th/U ratios in zircons in the samples range from 0.3 to 1.3 and mean values correlate with whole-rock Th/U ratios (see Table 2 for ratios). A pronounced enrichment of heavy REE in chondrite-normalised diagrams is similar in all samples (Fig. 8). This pattern is expected for magmatic zircons, reflecting the greater preference of zircon for the smaller HREE cations (Hoskin and Schaltegger 2003; Trail et al. 2012). Although the overall similarity of the REE patterns is striking, in detail, rocks of the northwestern Montañas suite are distinguished from others by smaller Eu anomalies (Fig. 8), higher Ce concentration, and larger positive Ce anomalies (Fig. 9a).

Titanium-in-zircon thermometer

Apparent crystallisation temperatures of zircons were calculated using the Ti-in-zircon thermometer (Watson and

Table 2 Whole-rock geochemical data and calculations for the sample suite

Sample	Igneous suite		Pataz batholith		Pataz ESC-Lavasen		Montanitas southern			Montanitas northwestern		
	Pat1	Pat4	WWGA5	WWGA6	mts14f2	mts134	mtc6	mtn36	mtn23a	mtc92		
SiO ₂	56.20	76.00	76.10	77.20	68.60	71.20	73.30	70.10	72.50	75.20		
TiO ₂	0.72	0.06	0.13	0.11	0.49	0.37	0.28	0.55	0.33	0.23		
Al ₂ O ₃	14.92	12.18	13.00	12.45	15.70	14.00	13.58	14.46	13.39	12.48		
Fe ₂ O _{3t}	8.38	1.31	1.84	2.07	3.86	2.94	2.36	2.76	2.11	1.06		
MnO	0.15	0.03	0.04	0.05	0.03	0.06	0.06	0.07	0.07	0.03		
MgO	5.99	0.09	0.04	0.01	0.68	0.85	0.39	0.91	0.58	0.16		
CaO	7.95	0.52	0.68	0.07	0.04	3.14	1.25	2.49	1.84	0.08		
Na ₂ O	1.71	2.72	3.78	3.32	0.27	3.55	4.12	3.94	3.56	3.34		
K ₂ O	1.62	6.35	4.02	4.25	3.98	2.47	3.56	3.71	4.20	4.80		
P ₂ O ₅	0.09	< 0.01	0.05	0.01	0.09	0.07	0.05	0.12	0.07	0.03		
LOI	2.45	0.30	0.30	1.02	5.53	0.65	0.70	0.61	0.91	1.01		
Total	100.26	99.56	100.09	100.72	99.39	99.35	99.69	99.78	99.64	98.49		
CO ₂	0.44	b.d.l.	0.04	0.18	1.14	b.d.l.	0.07	b.d.l.	0.40	0.07		
FeO*	6.43	0.71	n.d.	n.d.	n.d.	1.28	1.35	1.23	1.02	0.30		
Fe ₂ O ₃ * (calc)	1.23	0.52	n.d.	n.d.	n.d.	1.52	0.86	1.39	0.98	0.73		
FeO _t (calc)	7.54	1.18	1.66	1.86	3.47	2.65	2.12	2.48	1.90	0.95		
Ga	16.1	14.0	17.0	17.0	21.9	14.1	17.0	15.6	15.0	14.1		
Nb	9.0	8.0	14.1	15.5	10.4	8.3	12.9	15.4	17.9	18.4		
Rb	70.7	155.0	139.5	106.5	146.9	88.8	121.9	140.4	156.4	154.4		
Sr	169.6	29.2	45.6	16.2	19.8	158.0	108.0	267.0	189.7	43.9		
Th	5.5	22.3	15.0	16.9	11.2	9.3	14.0	18.0	18.4	19.0		
Y	22.7	24.5	45.7	50.7	13.0	21.1	37.6	32.3	30.9	32.7		
Zr	148.0	87.2	166.0	169.0	178.4	144.5	194.8	180.2	139.9	149.6		
La	20.7	17.9	47.2	35.7	23.2	22.6	38.3	53.0	42.7	47.0		
Ce	40.8	42.9	98.1	76.0	41.1	47.2	74.4	106.6	89.3	102.7		
Pr	5.0	5.6	11.8	9.4	3.8	5.1	8.9	11.6	9.6	12.3		
Nd	19.0	22.9	44.6	33.9	11.7	18.7	30.2	43.2	34.9	43.2		
Sm	4.1	6.0	9.2	8.1	2.1	3.5	5.6	6.8	5.8	7.3		
Eu	0.9	0.3	1.3	1.1	0.4	0.7	1.0	1.3	0.9	1.1		
Gd	4.3	5.9	8.8	7.9	1.8	3.2	5.3	5.9	4.9	5.7		
Tb	0.7	0.9	1.4	1.4	0.3	0.5	1.0	0.9	0.8	0.8		
Dy	4.0	4.4	8.1	8.6	2.1	3.3	5.4	5.1	4.6	4.6		
Ho	0.9	0.9	1.6	1.8	0.5	0.7	1.2	1.0	1.0	1.0		
Er	2.5	2.6	5.1	5.5	1.6	2.1	3.8	3.2	3.2	3.0		
Tm	0.4	0.4	0.7	0.8	0.3	0.3	0.5	0.5	0.5	0.4		
Yb	2.7	2.1	4.8	5.5	2.0	2.3	3.7	3.3	3.2	3.2		
Lu	0.4	0.4	0.7	0.8	0.4	0.4	0.6	0.5	0.5	0.5		
Fe ₂ O ₃ */FeO*	0.2	0.7	n.d.	n.d.	n.d.	1.2	0.6	1.1	1.0	2.4		
FeO _t #	0.6	0.9	1.0	1.0	0.8	0.8	0.8	0.7	0.8	0.9		
Rb/Sr	0.42	5.31	3.06	6.57	7.42	0.56	1.13	0.53	0.82	3.52		
Th/Nb	0.61	2.79	1.06	1.09	1.08	1.12	1.09	1.17	1.03	1.03		
Th/U	5.50	3.78	4.48	4.20	4.31	4.23	5.00	4.62	3.41	4.87		
Sr/Y	7.47	1.19	1.00	0.32	1.52	7.49	2.87	8.27	6.14	1.34		
Sr/Zr	1.15	0.33	0.27	0.10	0.11	1.09	0.55	1.48	1.36	0.29		
(La/Yb) _{Cl}	5.00	5.50	4.18	6.35	7.45	6.40	6.65	10.24	8.59	9.54		
(Gd/Yb) _{Cl}	1.04	1.81	0.92	1.18	0.57	0.90	0.93	1.15	0.99	1.17		
(Ce/Ce*) _{Cl}	0.99	1.05	1.02	1.02	1.07	1.07	0.99	1.05	1.08	1.05		
(Eu/Eu*) _{Cl}	0.67	0.14	0.43	0.43	0.59	0.67	0.57	0.61	0.51	0.51		

Fe₂O₃* is recalculated based on Fe₂O_{3t} and FeO*; FeO_t# = FeO_t/(FeO_t + MgO)

Fig. 4 Geochemistry of samples from the Pataz and Montañitas region. **a** SiO₂ versus fractionation index Rb/Sr; **b** SiO₂ versus K₂O discrimination after Peccerillo and Taylor (1976); **c** molar A/NK versus A/NKC diagram after Maniar and Piccoli (1989) showing

the peraluminous character of the granitic rocks; **d** (La/Yb)_{C1} versus Nb/Zr shows the variations of HFSE ratios amongst the Montañitas sub-suites. Index C1 means normalisation with chondrite data from McDonough and Sun (1995)

Harrison 2005; Watson et al. 2006). Titanium content in zircon ranges from 3 to 39 ppm and derived temperature ranges from 650 to 900 °C (Table 1). Within samples, the calculated temperature varies between 50 and 200 °C. All samples show broad covariances of temperature and Th/U, which is compatible with progressive Th and U fractionation during cooling (Fig. 9c). Zircon grains from the four Pataz samples indicate an overall temperature decrease with increasing whole-rock SiO₂ content (Table 1). The Ti-in-zircon temperatures are largely consistent with calc-alkaline granitoids of crustal and mantle origin (Pupin 1980; Belousova et al. 2006). Because there is no systematic difference of crystallisation temperatures between granophyric and porphyritic textured rocks, it can be inferred that the most important controlling factor for Ti-in-zircon temperature is

magma differentiation. The unusually high age range and the negative age–temperature slope in zircons for the Montañitas rhyodacite (mtc92) (Fig. 9d) can either be explained by subsolidus zircon alteration or by an inherited zircon population. Because zircons are devoid of any significant alteration of Ti and U/Pb ratios, zircons may have been inherited from reworked, slightly older rocks, which crystallised at lower temperatures. Potential source may be the northwestern suite granites.

The Ti-in-zircon assumes a crystallisation of zircon in a Ti-saturated system. If zircon crystallises in an undersaturated system, the temperature calculated from Ti-in-zircon might underestimate the ‘true’ crystallisation temperature by 40–60 °C (Watson and Harrison 2005). Because titanite is present in most samples, except in Lavasen volcanic

Table 3 SHRIMP U–Pb geochronology data

Sample	Zircon U–Pb Concordia age [Ma]	MSWD	Age from <i>n</i> zircons/total	Inherited ages [Ma] (<i>n</i>)	Concordant younger age [Ma] (<i>n</i>)	Zircon morphology
Pat1	334.0 ± 3.4	2.4	11/13	351 ± 3.2 (2)	None	Euhedral to subhedral, relatively large sizes of 50–300 µm, little magmatic zoning and core-rim compositional zoning Euhedral to subhedral, 30–200 µm, magmatic
Pat4	336.3 ± 1.3	1.4	12/13	349.5 ± 4 (1)	None	Zoning is well defined, few discordant core-rim patterns
WWGA5	333.7 ± 2.4 ^a	0.2 ^a	11/20 ^a	470 (2) ^a 1000 (1) ^a 1200 (1) ^a	None	Mostly euhedral to subhedral laths, 50 to 300 µm
WWGA6	334.3 ± 1.8 ^a	0.69 ^a	15/16 ^a	None	316.3 ± 2.5 (1) ^a	Stubby shapes and up to 200 µm
mts14f2	336.6 ± 3.3	1.3	12/13	366.8 ± 5	None	Small, stubby, well zoned, subhedral, 30–150 µm
mts134	332.1 ± 3.8	4.3	11/14	487.9 ± 6.8 (1) 384.2 ± 5.0 (1) 350.5 ± 4 (1)	None	Predominantly stubby, 30–150 µm
mtc6	333.5 ± 3.8	4.2	11/12	None	None	Euhedral, stubby to elongated, 50–150 µm Magmatic zoning is evident by CL in almost all crystals
mtn36	327.9 ± 2.4	1.8	12/13	None	None	Euhedral and stubby zircon shapes. Cores with discordant zoning morphology and compositional hiatus are present
mtn23a	327.9 ± 3.5	1.2	11/13	None	None	Dominance of long prismatic over stubby shapes
mtc92	322.2 ± 2.8	3.5	12/15	446 ± 7 (1)	311.7 ± 6.4 (2)	Euhedral, stubby to long prismatic. Abundant grains with core-rim relationships

^a From Witt et al. (2013)

rock, titanium saturation is assumed. Nevertheless, due to the unknown variable TiO₂ activity and the possible pressure-dependence of the solubility of Ti-in-zircon, the precision of zircon crystallisation temperatures is limited to at least ± 50 °C (Salters and Stracke 2004; Watson and Harrison 2005). In addition, heterogeneous Ti concentrations at small scale in some zoned zircon may have some impact on the temperature calculations using this thermometer. In general, post-magmatic Ti diffusion modifying the thermometer cannot be ruled out (cf. Trail et al. 2007). However, it is commonly not a major problem in fresh zircons, and the consistency of Th/U ratios with fresh calc-alkaline rocks (Belousova et al. 2002) does not suggest zircon alteration in the studied samples. In addition, mostly parallel LREE fractionation trends do not point to any zircon alteration (Fig. 8). Time resolved signals from laser ablation showed no downhole Ti complexity that would indicate mobility of Ti due to secondary processes.

Crystallisation oxygen fugacity

Oxygen fugacity (*f*O₂) of magmas during zircon crystallisation may be approximated by the redox and temperature

sensitive Ce⁴⁺/Ce³⁺ ratios in zircons (Ballard et al. 2002). According to the experimental results reported by Trail et al. (2012), the Ce⁴⁺/Ce³⁺ ratio in zircon increases with higher oxygen fugacity and lower crystallisation temperatures; with lower temperatures, the larger Ce³⁺ ions are progressively excluded from the crystal lattice. Two published methods are employed to estimate the nominal oxygen fugacity (*f*O₂) of the melt from which the zircons crystallised. The first method (Trail et al. 2011, 2012) is based on Ce anomaly in zircon and crystallisation temperature (obtained by the Ti-in-zircon thermometer). An underlying assumption to this method is that there was no Ce anomaly in the melt prior to zircon saturation (Trail et al. 2011). The validity of this assumption is supported by the absence of significant Ce anomalies in the whole-rock data of the samples (Table 2; Fig. 8). The second method (Smythe and Brenan 2016) is based on the rocks' distinct Ce zircon/melt fractionation, as earlier described by Ballard et al. (2002). This method incorporates whole-rock REE data as melt proxy.

According to the (Trail et al. 2011) method, sample averages show an extremely wide range of *f*O₂ (given as ΔFMQ) of ~ 16 log units, including 1σ. Samples with lower La/Yb ratios (i.e., Pataz suite and Montañitas southern suite) show

Fig. 5 SEM–cathodoluminescence micrographs and isotope results of six selected zircons with O-isotope SIMS pits and circles indicating spot location of O-isotope SIMS (small dashed), U–Pb geochronology SHRIMP (full), and Hf-isotope laser-ablation analyses (large dashed). Except **a**, **d**, images were taken after SIMS analyses, where earlier SHRIMP dating spots have been polished away, and before Hf-isotope analyses. Images **a**, **d** were taken before SIMS, where earlier SHRIMP dating spots have been polished away

lower fO_2 values of -6.0 to $+6.8$ (Fig. 9e). The method of Smythe and Brenan (2016) leads to a different inferred fO_2 distribution (see bars in Fig. 9e). The ΔFMQ range from -10 to $+5$ with minimal significant variations between the samples: zircons from PAT-4, WWGA5, and WWGA6 show $\Delta FMQ \leq 0$, while those from PAT-1 and Montañitas $\Delta FMQ < 0$ and > 0 . Especially, for the two high La/Yb (i.e., high zircon Ce/Ce*) samples from the Montañitas northern suite, the results from the two methods differ strongly. Here, the $\Delta FMQ > 5$ after Trail et al. (2012) is suspicious considering the absence of hematite in these rocks.

This discrepancy in results obtained using the two methods is well known in the literature (Zhang et al. 2013; Smythe and Brenan 2016). The ΔFMQ after Trail et al. (2012) does not clearly correlate with crystallisation temperature (Fig. 9f), while a positive correlation with Ce/Ce* is evident (Fig. 9g). This indicates that zircon Ce anomaly dominantly controls ΔFMQ , and thus, the accuracy of the fO_2 quantification is significantly based on the representability of Ce anomaly. Smythe and Brenan (2016) suggested that the experiments used in Trail et al. (2012) to calibrate Ce anomaly are subject to disequilibrium effects. In addition, the unknown behaviour of co-crystallised phases on the REE budget in zircon needs to be taken into account (Claiborne et al. 2010; Loader et al. 2017). Ubiquitous accessory titanite preferentially scavenges Th and Ce³⁺ and consequently lowers the REE abundance of the melt. This may cause estimates of Ce⁴⁺/Ce³⁺ (hence calculated fO_2) in zircon to be erroneously high. Loader et al. (2017) showed that melts that are crystallising small amounts of titanite would be in equilibrium with zircons that are progressively depleted in MREE with respect to HREE (normalised Yb/Gd $> \sim 50$) and have increasing Eu/Eu* ($> \sim 0.5$) values. However, the present data set with (Yb/Gd)_{C1} < 30 and Eu/Eu* < 0.5 (Table 1) does not support any significant REE fractionation by titanite. In addition, the reasonably uniform Ce anomalies in zircons of the same sample (Fig. 8) and the absence of a covariance between Ce/Ce* and Th/U (Fig. 9b) do not suggest any major distorting mineralogical controls on the Ce-in-zircon distribution. On the other hand, the accuracy of the method of Smythe and Brenan (2016) heavily relies on whole-rock data that are not affected by alteration or other secondary processes. Moreover, in complex plutonic systems involving mixing and crystal transfer between different magma batches, there is not necessary a

genetic relationship between individual zircon crystals and the solidified rock in which these crystals now reside (e.g., Kemp et al. 2005, 2007). The present analytical data do not allow the validity of two approaches for determining magma fO_2 to be evaluated, but it can be assumed that the lowest and highest Ce anomalies represented by the Patáz Lavasen volcanics and Montañitas northern suite, respectively (Fig. 9a) are associated with relative variations in the magma oxygen state. The highest magmatic fO_2 is shown in zircons of the Montañitas northwestern suite which have youngest crystallisation ages (Fig. 9d), highest La/Yb (Fig. 9e), as well as low $\delta^{18}O$ and high ϵHf values (Fig. 7). Such covariance of multiple parameters suggests that fO_2 reflects properties of the magma source. This inference is an important requirement for the following discussion of source-related igneous signatures and metallogeny.

Discussion

Possible magma sources

Source endmembers as indicated by Hf and O isotopes

The ϵHf and $\delta^{18}O$ signatures of the sample set overall reveal a large spread, however, with distinct signatures for most samples. According to Kemp et al. (2007), the binary ϵHf and $\delta^{18}O$ arrangement allows identification of melt sources and, based on the shape and extent of data scattering, mixing trends of various sources (so-called endmember components). For the present data set, three source endmembers, compatible with an arc setting, and with distinct ranges of isotopic signatures are inferred (Fig. 7b).

Source endmember 1: the *subarc mantle* with $\delta^{18}O$ values of $5.3 \pm 0.6\text{‰}$ (Valley et al. 2005) and positive ϵHf . The recorded ϵHf values are much lower than expected for a strongly depleted (MORB-like) subarc mantle, which is characterised by strongly positive ϵHf values (Vervoort and Blichert-Toft 1999) (Kemp et al. 2005). Such a moderate ϵHf with a mantle-like $\delta^{18}O$ signature can be explained either by a relatively undepleted (thus more fertile) mantle source or by the contamination (re-fertilisation) of a previously depleted arc mantle by older mantle-derived melts or metasomatic fluids. In a sub-arc setting, the most likely source of such contaminations is a component derived from the subducted slab by devolatilisation and/or melting.

Source endmember 2: an equivocal component with low (sub-mantle) $\delta^{18}O$ ($< 4.7\text{‰}$) and slightly negative ϵHf . Four potential low- $\delta^{18}O$ sources exist: (1) layer-2 gabbros from the lower parts of a subducting slab (Gregory and Taylor 1981; Alt et al. 1986; Eiler 2001; Bindeman et al. 2005); (2) high-temperature hydrothermally altered rocks, such as volcanic rocks in long lived calderas, i.e., in Yellowstone

Fig. 6 SHRIMP U–Pb geochronology of zircons from eight samples from the Pataz batholith (a, b) and the Montañitas southern suite (c, d, e) and northwestern suite (f, g, h)

(Blum et al. 2016, and references therein); (3) change of the melt isotope composition during crystallisation (Trail et al. 2009); and (4) late-magmatic degassing (Eiler 2001). Late-magmatic degassing is considered as not being efficient enough to generate the recorded decrease from mantle signature by $\sim 1\%$ (Zhao and Zheng 2003; Muñoz et al. 2012). The crystallisation models of Trail et al. (2009) indeed shows that final measured zircon $\delta^{18}\text{O}$ can be influenced by the zircon saturation temperature, melt–zircon fractionations, and the absolute $\delta^{18}\text{O}$ value of the melt. While these crystallisation-inherent factors may enlarge the scattering of zircon O isotope data, the combination with trace elements and Hf-isotope data suggest overriding controls based on the geochemistry of rocks. With respect to high-temperature hydrothermal alteration, a pre-melting exchange with low- $\delta^{18}\text{O}$ surface waters is required (Blum et al. 2016). As supported by the mantle-like (near-0) ϵHf , a likely source rocks would be young, juvenile mantle-derived (sub-)volcanic rocks, which were subject to intense alteration in, for instance, a late-magmatic epithermal fluid system. However, there is no likely source body in the region. Therefore, without completely dismissing the hypothetical hydrothermally altered crustal source, the most likely remaining scenario for source endmember 2 is melts from young (< 20 Ma to retain a slight negative ϵHf) slab material (i.e., layer-2 gabbro), which contaminated the sub-arc mantle.

Source endmember 3: *supracrustal material*, typically metasedimentary rocks, volcanic rocks, or low-T altered mafic rocks with high $\delta^{18}\text{O}_{\text{VSMOW}}$ values ($> 7.5\%$) and variably negative ϵHf , depending on the respective source age (Kemp et al. 2007). Heavy oxygen values (high $\delta^{18}\text{O}$) in magmatic zircons are interpreted to reflect a contribution from melted continental crust that had previously been in chemical communication with low-temperature surface waters (Valley 2003; Valley et al. 2005). Potential negative ϵHf sources are common in the complex Proto-Andean margin: Mišković and Schaltegger (2009) determined a series of distinctively low- ϵHf crustal domains (on average -3 and below, with values as low as -5 to -10). These sources may have contributed their unradiogenic isotopic signatures to magmas formed during crustal reworking.

Au-endowed Pataz low-SiO₂ and high-SiO₂ suite (PAT1 and PAT4)

The lowest ϵHf and highest $\delta^{18}\text{O}$ signatures of all samples are shown by the quartz–diorite (Fig. 7a). The isotopic source signatures are compatible with dominant old supracrustal rocks or an old, high- $\delta^{18}\text{O}$ mafic rock that

experienced low-temperature alteration or derived from a source that had assimilated supracrustal rocks (endmember 3). Because diorites typically derive from mafic sources, it is unlikely that assimilated felsic or metasedimentary crust controlled the high $\delta^{18}\text{O}$. Hence, melting of old, low-temperature-altered mafic rocks is a likely source composition. The low ϵHf can be explained by the assimilation of an older arc, according to Mišković and Schaltegger (2009) the following: San Ignacio ($\epsilon\text{Hf} = -4.87 \pm 1.40$, corresponding Hf model ages of 1955 ± 27 Ga (T_{DM}) and 2358 ± 166 (T_{DM}^{c}) Ga), Sunsás ($\epsilon\text{Hf} = -3.96 \pm 1.32$, T_{DM} 1770 ± 51 Ga, T_{DM}^{c} 2163 ± 107 Ga), Pampean ($\epsilon\text{Hf} = -5.19 \pm 1.36$, T_{DM} 1311 ± 53 Ga, T_{DM}^{c} 1765 ± 93 Ga), or Famatina arcs ($\epsilon\text{Hf} = -5.46 \pm 2.04$, T_{DM} 1251 ± 78 Ga, T_{DM}^{c} 1739 ± 127 Ga). The assimilation of low- ϵHf crust during an early batholith stage is supported by inherited ages slightly older than the actual intrusion age (ca. 340–350 versus 334 Ma) (Table 3). The low ϵHf in the rock indicates a minor, if any, contribution from mantle-derived melts.

For PAT4, a mixing scenario (Fig. 7b) involves a magma derived from undepleted or enriched ($\epsilon\text{Hf} \pm 0$) subarc mantle (endmember 1) and an old high $\delta^{18}\text{O}$ component (endmember 3). Both endmember sources may be the same as inferred for PAT1; thus, a mixing line connects the putative source endmembers of the two batholith samples. A similar origin of low- and high-SiO₂ suite diorite and granite is supported by similar rock ages, (La/Yb)_{CI}, and $f\text{O}_2$ (Fig. 9). Isotopic differences between both samples could result from variations in the relative contribution of sources, as reflected in contrasting positions on the mixing line (Fig. 7b): granite PAT4 incorporated a dominantly depleted mantle signature and less old mafic crust, whereas diorite PAT1 more old mafic crust and less mantle. The position and curvature of the mixing lines honour the internal scatter of data, but are not based on robust calculation.

The large variation of $\delta^{18}\text{O}$ data (4.68–6.44‰) for PAT4 produces a steep linear trend in the binary Hf–O isotope space, deviating from the mixing line (Fig. 7). The linear alignment of $\delta^{18}\text{O}$ may be caused by minor contribution of a third, high- $\delta^{18}\text{O}$ component. Although the identity of this is unconstrained, the elevated incompatible Th content (Table 2) could be an indication for the assimilation of evolved crust reservoir. In reference to Pb and Nd isotope data, Macfarlane et al. (1999) suggested the formation of the high-SiO₂ batholith by 35–70% assimilation of Marañon Complex basement, with the other source component being a mantle-derived melt.

Pataz ESC-Lavasen suite (WWGA5 and WWGA6)

The porphyritic ESC quartz–latite (WWGA5) shows similar isotope values to the quartz–diorite, i.e., same $\delta^{18}\text{O}$ value of 7.3 permil and slightly higher ϵHf value of -4 . These data

Fig. 7 Binary plot $\delta^{18}\text{O}$ versus ϵ_{Hf} for the magmatic zircons of the Pataz and Sierra Montañitas samples. **a** data points (excluding inherited grains); **b** colour-coded data fields with putative sources end members shown as boxes and mixing lines. The ratios of Hf concentrations in the source endmembers for the mixing lines are shown, see text for “Discussion”

suggest the dominance of a supracrustal, or low-temperature altered, mafic source (see section *source endmembers*). To explain the higher ϵ_{Hf} , the source must be either younger (source 3 m) compared with the diorite source, or some

input from coeval mantle is present. On the other hand, whole-rock La/Yb and Nb/Zr (Fig. 4d) are more similar to PAT4. Considering the overall geochemical similarities to the Pataz batholith samples, it is possible that the ESC

Fig. 8 Zircon rare-earth element plots for: **a** Pataz batholith, **b** Pataz ESC quartz-lattice and Lavasen volcanoclastic breccia, **c** Montañitas southern suite, and **d** Montañitas northwestern suite. Corresponding whole-rock data are shown in white (with same symbols)

either represents a reworking of average batholith material (i.e., the source of PAT1 and PAT4), or its melt was generated by tapping both the low- and high-SiO₂ magma chambers.

Zircons of the Lavasen volcanoclastic rock (WWGA6) have prominent affinities to mantle signatures (endmember 1) with a quite narrow $\delta^{18}\text{O}$ range from 5.6 to 6.0‰ and a larger ϵHf range from -1 to $+3$ (Fig. 7a). This sample has the least supracrustal component, supported by lowest La/Yb in the sample set. The Hf–O isotope signatures of the Lavasen volcanoclastics allow for several interpretations. Interpretation 1: in accordance with the model for the ESC quartz-lattice, the Lavasen volcanoclastic rocks are sourced from mantle-derived magma that assimilated portions of the high-SiO₂ batholith or mingled with the high-SiO₂ magma chamber. Interpretation 2: accounting for the similar geochemistry of the ESC and Lavasen volcanic rocks, both samples are two distinct members in a mix of mantle melts and supracrustal or high-temperature altered mafic rocks (as depicted in Fig. 7b). Interpretation 3: accounting for the high probability of a crustal source to produce such a large volume of high SiO₂ rocks, a short time between extraction

of this crust from the mantle and its re-melting is proposed. Such process would retain a ϵHf close to 0. The range of permissible models for the Lavasen volcanic rocks based on isotopic data suggests that emplacement processes or sources contribution were complex.

Cu ± Au-endowed Montañitas southern and northwestern suites

The Montañitas samples show a strong isotopic affinity to a less depleted or re-fertilised mantle (endmember 1) (Fig. 7b). Because there is no clear isotopic signature of supracrustal components in the Montañitas rocks, these highly fractionated magmas most likely differentiated from partial melts of the metasomatised (re-fertilised) mantle. The enrichment of incompatible LILE elements (K, Sr, Th, LREE) and Nb (Table 2) with high La/Yb (Fig. 10a, b), as well as high $f\text{O}_2$, suggested by elevated zircon Ce/Ce* (Fig. 10c, d), are compatible with oxidised and metasomatised mantle. A widely accepted process for sub-arc mantle metasomatism is slab dehydration (Vidal et al. 1989). Richards and Kerrich (2007) established that normal asthenosphere-derived tholeiitic to

Fig. 10 Hf and $\delta^{18}\text{O}$ data in comparison with geochemical parameter: whole-rock $(\text{La/Yb})_{C1}$ versus **a** ϵHf and **c** $\delta^{18}\text{O}$; and zircon Ce/Ce^* versus **b** ϵHf and **d** $\delta^{18}\text{O}$

calc-alkaline arc magmas acquired high La/Yb during upper plate crustal interaction and crystal fractionation. However, the particularly low zircon $\delta^{18}\text{O}$ and mantle-like zircon ϵHf in the Montañitas samples does not support the involvement of upper crustal material.

The partial $\epsilon\text{Hf} < 0$ and sub-mantle $\delta^{18}\text{O}$ signature of zircons from the Montañitas suites (Fig. 7) may imply the contribution of a $\epsilon\text{Hf} < 0$ and sub-mantle $\delta^{18}\text{O}$ source (endmember 2), which is compatible with slab-derived layer-2 gabbro mixed into the sub-arc mantle. Whole-rock geochemical evidence for slab melting in high-pressure zones, i.e., subduction channels, resulting in characteristic sodium-rich melt (“adakite”: Defant and Drummond 1990; Martin 1999; Castillo 2006; Sun et al. 2012) and garnet- or hornblende-rich restite are largely absent in the arc magma samples. However, considering a complex

magma evolution with the predominant source contributor being metasomatised mantle, any whole-rock geochemical signature for high-pressure melting may be obliterated in the highly differentiated partial melts. Hence, an inferred slab contribution to the subarc mantle source of the Montañitas suites, remains as a possible scenario.

In contrast to layer-2 gabbro, upper mafic crust is enriched in ^{18}O (Gregory and Taylor 1981; Alt et al. 1986; Eiler 2001; Bindeman et al. 2005), and obviously, melting of the upper mafic crust must have taken place before scavenging of the lower crust. In absence of rocks with elevated $\delta^{18}\text{O}$ in the Montañitas suites, it can only be speculated that a hypothetical western-most portion of the arc in the Montañitas system recorded such melting of the upper ophiolite plus sediments.

Fig. 11 Discrimination diagrams for syn-collisional versus post-collisional or within-plate ('A-types') magmas: **a** whole-rock SiO_2 versus $\text{FeO}_t/(\text{FeO}_t+\text{MgO})$ diagram with the boundary between ferroan and magnesian magmas (after Frost et al. 2001; Dall'Agnol and de Oliveira 2007); **b** whole-rock $\text{Al}_2\text{O}_3/(\text{K}_2\text{O}+\text{Na}_2\text{O})$ versus $\text{FeO}_t/(\text{FeO}_t+\text{MgO})$ diagram (after Frost et al. 2001; Dall'Agnol and de Oliveira 2007); **c** whole-rock Y versus Nb discrimination diagram for plate tectonic settings of granites (Pearce et al. 1984); **d** whole-rock

Y/Nb versus Yb/Ta diagram after Eby (1992) with fields for island arc basalts and ocean island basalts (IAB, OIB) and for A₁ granitic rocks from rift, plume, and hotspot environment and A₂ granitic rocks from post-collisional, postorogenic, and anorogenic environments (Eby 1992); **e** zircon Th/U versus Nb/Hf (after Hawkesworth and Kemp 2006), with fields for A-type and syn-collisional magmas (latter based on I-type magmas from the Lachlan Fold Belt) from Hawkesworth and Kemp (2006)

Tectonomagmatic evolution along the proto-Andean margin from Pataz to Montañitas

Magmatism in syn- to post-collisional regimes

Geochemical signatures of the high-K calc-alkaline magmatic suites can be associated with tectonic settings of emplacement. Samples PAT4, WWGA5, WWGA6, mtc92, and mts14f2 are ferroan and alkali-rich, granitic magmas (after Frost et al. 2001; Dall'Agnol and de Oliveira 2007) that are typical encountered in within-plate settings (Fig. 11a, b). Other samples are syn-collisional, magnesian granitic rocks. The Y versus Nb discrimination diagram (Pearce et al. 1984) supports within-plate settings for the ESC and Lavasen samples (Fig. 11c), while the Montañitas northwestern suite occupies a transitional position from syn-collisional to extensional. The incompatible element ratios Y/Nb and Yb/Ta (Eby 1992) discriminates island arc from ocean island basalt (Fig. 11d). A_2 -type granites (Eby 1992) have island arc basalt affinity, and an A_2 -type signature is shown by all samples. A_2 -type granites represent magmas that derived from continental crust or underplated crust that has been through a cycle of continent–continent collision magmatism (Eby 1992).

Zircons that crystallised in 'A-type' granites may have markedly different trace-element compositions from those formed from subduction-related or syn-orogenic magmas (Hawkesworth and Kemp 2006). The zircon Nb/Hf ratio (Fig. 11e) reveals that ESC and Lavasen volcanic and northwestern Montañitas zircons show dominantly post-collisional (A-type) signature. Lastly, low Sr/Y ratios at and below unity in ESC and Lavasen samples (Table 2) could also be taken as an indication for thin crust at the time of melt fractionation (Whalen et al. 1987). While this series of geochemical proxies are not unambiguous, it can be argued that samples from the Pataz batholith and the Montañitas southern suites rather show a syn-collisional arc signature, while the magmas of the ESC and Lavasen suite as well as the Montañitas northwestern suites have a post-collisional (A_2 -type) affinity and formed most likely in post-collisional extensional setting. Regional mapping established emplacement of the ESC-Lavasén suite in an intra-mountainous rift (Witt et al. 2013, 2014).

Zircon isotopic signatures partly support the geochemical discrimination into tectonic settings. For the Pataz batholith samples, variable amounts of subarc mantle and reworked (mafic) crust have been invoked as melt sources (Fig. 7b). Reworking of older crust is facilitated by crustal compression and such scenario is compatible with a magmatic setting in a thick continental arc of the proto-Andean collisional margin (Mišković and Schaltegger 2009; Mišković et al. 2009; Witt et al. 2014). The elemental and isotope

chemistry of PAT4 suggests a transitional setting from collision to extension (Figs. 7, 11). The (sub-)mantle $\delta^{18}\text{O}$ and ϵ_{Hf} of ± 0 of the Montañitas rock suites support a mantle source without significant supracrustal reworking. An explanation for subduction-related, high-K, mantle-derived melts would be that these melts form from partial melting of a phlogopite–clinopyroxene-rich mantle, which itself is a product of metasomatism of a garnet–orthopyroxene assemblage (Elkins-Tanton and Grove 2003). A 'hot zone' scenario for deep-crustal fractional crystallisation of hydrous mantle melts (Annen et al. 2005) may have produced in an additional process the felsic melts that ascent to the upper crust during extension. Subtle increase of the whole-rock Nb and Y values and the zircon Nb/Hf ratio (Fig. 11c, e) suggests a transition from more collision (southern suite) to more extension (northwestern suite).

Figure 12 synthesises the contrasting evolution with magma sources for the two regions. The Pataz batholith was emplaced in mid-crustal levels during arc compression (stage 1), following mantle melt extraction and ponding in the lower lithosphere (c.f., Witt et al. 2014). Subsequently, a switch from compression to extension (stage 2), triggered the ascent of the ECS-Lavasén magmas suite. Despite broadly similar geochronological data (Table 3), their overprinting relationships (Witt et al. 2014) support this chronological sequence. In the Montañitas region, emplacement of the suites (stage 1) was triggered by extension, whereas prior ponding in a lower lithosphere 'hot zone' (Annen et al. 2005) is probable. Intrusion of the southern suite is followed by the intrusion and extrusion of the LILE-HFSE-enriched northwestern suite. This chemical shift is likely a result of a change of melt extraction from different mantle domains: the northwestern suite of rocks is sourced from a stronger metasomatised mantle than the southern suite. In principal terms, a rapid transition within a few million years from west to east at Pataz and from southeast to northwest at Montañitas is inferred.

Contrasting magmatic suites along-strike

The ϵ_{Hf} of all felsic samples are within the range determined by Mišković and Schaltegger (2009) for the majority of batholiths along the Eastern Cordillera (Fig. 7a). At a regional scale, the variability of Carboniferous intrusion ages (ca. 300 and 350 Ma) reveals no clear systematics along the strike of orogeny, at least not at a scale of 10 s of km (Mišković and Schaltegger 2009). In the model of Mišković and Schaltegger (2009), who considered a homogenous crustal source, the main continental arc build up led to igneous suites with mean initial ϵ_{Hf} values of -2.4 meaning a minimum ancient crustal contribution of $\sim 50\%$. In contrast, granitoids intruding during regional extension show initial Hf systematics shifting towards positive values (ϵ_{Hf}

Fig. 12 Synthesis models for the emplacement stages at the Pataz and Montañitas arc segments. Geochemical characteristics are summarised in boxes. At Pataz, syn-collisional emplacement of the low-SiO₂ and high-SiO₂ batholith suites took place following mantle metasomatism, melt extraction, and ponding in the lower lithosphere. Stage 2 sees the syn-extensional formation of A₂-Type ESC-Lavasén suite, which is predominantly sourced in the upwelling depleted mantle. Supracrustal components are variably assimilated during ponding stages. At Montañitas, the southern and northwestern suites are both

results of partial melting of strongly metasomatised mantle with variable contribution from the flat subducting slab. Mantle metasomatism, melt extraction and ponding took place during arc contraction, while intrusion and extrusion during extension (stage 1). In the Pataz batholith, Au (with no Cu) becomes mobilised and concentrated in veins by hot, reduced fluids from the ESC-Lavasén suite. Cu (with minor Au) in Montañitas suites become mobilised and concentrated by oxidised fluids derived from the southern or northwestern suites

up to +8.0), indicating systematically larger inputs of juvenile magma. In the Patáz suites, such a shift from initially low- ϵHf in the low-SiO₂ suite to higher- ϵHf in the Lavasen volcanoclastic rocks is recorded, with intermediate positions taken by high-SiO₂ suite and ESC samples. In the Montañitas suites, such a shift is not recorded, as no significant crust was incorporated.

Periodic stress relaxation in the upper crust, leading to localised extension or transtension, are common features in arcs and during such periods deeply sourced magmas are able to intrude along dilatational structures cutting the lithosphere (Hildreth 1981; Hamilton 1988). The change in arc kinematics can be triggered by trench advance or rollback (Dewey 1980) and variation of slab inclination angle (Kay et al. 2005). Across the Patáz and Montañitas regions the magmatic suites were controlled by similar NNW and NE trending fault systems (Fig. 1b, c). These structures were active throughout the entire magmatic cycle, with probable reactivation during extension.

The reasons for the observed parallel-strike variation between contemporaneous Patáz and Montañitas magmatic systems are several: (1) a structural discontinuity along the subducting slab, (2) variations in slab material contributing to the magmas, or (3) variations in the continental arc crust (i.e., age of the basement). All three may contribute to the observed transversal variability. Structural

discontinuity along the slab can be caused by arc-transverse kinks or tears, which may generate differing slab kinematics and associated variations in slab angles (Gutscher et al. 1999; Rosenbaum et al. 2008). Arc-transverse fault zones are common in front and within the Andean margin and provide a structural discontinuity allowing for modifications of the local stress field to achieve regionally distinct strain zones. Local extensional regimes caused magmatism in shallow-crustal level showing within-plate chemistry, whereas compressional regimes in neighbouring domains produced collision-style chemistry and strong crustal contamination. A scenario involving arc-lateral variations of subducting slab material would involve subducted ocean plateaus, oceanic ridges, or continental microplates (c.f. Gutscher et al. 1999). A heterogeneous subducted crust may severely complicate magmatism due to inherently variable source material, slab angles with changing melt regions and slab melting (Gutscher et al. 2000). Partial melting of the slab is more probable in a low angle setting due to a favourable P-T window inducing melting (Gutscher et al. 2000; Oyarzun et al. 2001). It also causes variable deformation and thickening of the arc crust along strike, leading to different amounts of crustal reworking along the arc. In a scenario involving assimilation of a (arc-parallel) heterogeneous continental crust,

Fig. 13 **a** The binary Hf–O plot with same data as in Fig. 7, showing additionally fields of published data from porphyry Cu systems of Yunnan, Western Yangtze Craton, China (Lu et al. 2013), the El Teniente porphyry Cu–Mo deposit, Chile (Muñoz et al. 2012), the OK Tedi porphyry Cu–Au deposit, Papua New Guinea (Van Dongen et al. 2010), and the Cu–Au (copper) magmatic belt, Myanmar (Gardiner

et al. 2017). **b** The (Ce/Nd)/Y versus 10,000 × (Eu/Eu*)/Y diagram of fields for fertile (i.e., relatively oxidised and hydrous magmas from porphyry Cu–Au–Mo deposits) and unfertile (i.e., relatively reduced and relatively dry S-, A-, and I-type magmas) reference suites Lu et al. (2016)

the assimilated rock types will play a role as well as the depth of assimilation.

Controls of magmatic metal endowment

Metal fertility of the magmatic suites

Variations in source fertility and emplacement processes are assumed to exert first-order controls on metal endowment and Cu/Au ratio across a magmatic belt (Sillitoe 2010). Macfarlane et al. (1999) suggested, based on Pb isotopes, that metals in the Pataz quartz–gold veins were derived from the batholith itself. In recent investigations, some less differentiated magmas of the ESC-Lavasen suite were tentatively interpreted as the source of Au (Witt et al. 2013, 2014).

Zircon chemical and isotopic data provide a way to evaluate and discriminate metal affinity and also metal fertility of magmas (Lu et al. 2013, 2016; Dilles et al. 2015; Hou et al. 2015; Gardiner et al. 2017). The power of zircon data lies in the resistance to the effects of alteration of the whole rock and the insight provided into magma source rocks. The present Hf–O isotope data set from Pataz and Montañitas can be discriminated into Au (Pataz batholith suite) and Cu $\pm$ Au (Montañitas suites) affinity (Fig. 13a). Adding published data from Cu, Cu–Au, Cu–Mo, Au, Au–Pb, and Sn–W magmatic suites (Van Dongen et al. 2010; Muñoz et al. 2012; Lu et al. 2013; Gardiner et al. 2017), it becomes noticeable that magma sources may play a significant role in establishing the metal affinity in arc suite (Fig. 13a). Broadly, Cu ($\pm$ Au, Mo) fertility tends to be associated with (relatively “pure”) mantle-derived magmas, whereas Cu-free (but Au, Pb, Sn, and W) magmas show significant supracrustal source components. One exception is OK Tedi Cu–Au with supracrustal $\delta^{18}\text{O}$ (Van Dongen et al. 2010). Significant overlap between some of the fields most likely result from local petrological complexity, such as source mixing, and limits the use of the Hf–O space as a metal affinity discrimination utility.

Fractionation, oxidation, and hydration states in the source melts are viewed as proxies for metal fertility (Richards et al. 2012, and references therein). Blevin and Chappell (1995) established a relationship between Cu, Au, Mo, W, and Sn affinity and magma oxidation state ($\text{Fe}_2\text{O}_3^*/\text{FeO}^*$) and degree of differentiation (Rb/Sr). Accordingly, the evolved samples in the Pataz and Montañitas regions indicate a geochemical affinity to Cu–Mo metallogeny (0.5–3 $\text{Fe}_2\text{O}_3^*/\text{FeO}^*$ and 0.4–6 Rb/Sr ratios; Table 2). However, discrimination of fertile versus unfertile, and Cu versus Au affinity, is not possible with this whole-rock method. The Eu and Ce budget in melts is significantly connected to fertility proxies and provide an alternative avenue to evaluate affinity and fertility. Because the intimate relationship of zircon and host melt REE budget has been established (Ballard et al. 2002), zircon Eu and Ce anomalies may inform overall metal

fertility (Lu et al. 2016; Gardiner et al. 2017; Loader et al. 2017; Zhang et al. 2017). Various diagrams published by Lu et al. (2016) attempt to discriminate barren from Cu ($\pm$ Au, $\pm$ Mo) fertile granitoids based on zircon Eu and Ce anomalies. In the $(\text{Ce}/\text{Nd})/\text{Y}$ versus $10,000 \times (\text{Eu}/\text{Eu}^*)/\text{Y}$ diagram (Fig. 13b) the Cu-rich Montañitas suites plot inside the field for Cu-fertile reference suites, whereas the Pataz samples show slightly lower Ce/Nd (a proxy for Ce/Ce*) and Eu/Eu* plot between the fields. All samples define a positive correlation in the diagram. This trend is compatible to the gross data set for fertile suites and is interpreted by Lu et al. (2016) to indicate high magmatic water content. High water content leads to early and prolific hornblende fractionation and suppresses early plagioclase crystallisation, both of which induce melts with low HREE and insignificant Eu anomaly (Richards et al. 2012). Such geochemical features and correlations are absent in dry, barren reference suite (Lu et al. 2016).

Au from metasomatised mantle and Cu from the melted slab?

As thoroughly discussed in the literature, metasomatic alteration of the subarc mantle may play an important role in metal fertilisation of magmas (Hronsky et al. 2012, and references therein). Supporting evidence comes from mantle xenoliths: examples from the alkalic Tubaf submarine volcano nearby the giant Ladolam Au deposit are intensely metasomatised by a oxidised ($> \text{FMQ}$), C- and S-rich, high density H_2O -rich fluid (McInnes et al. 2001). In addition, upper mantle peridotites with significant Au enrichment have been described from the North China Craton, and are interpreted as having been re-fertilised within the subduction zone (Zheng et al. 2005). The involvement of metasomatised mantle was proposed for the Pataz batholith formation by Witt et al. (2014). This is based on the observations that even least fractionated samples in the low- SiO_2 Pataz suite are enriched in LILE (Rb, Ba, Cs, Th, U, Pb). Major involvement of metasomatised mantle at Montañitas is supported by distinctly more oxidised magmas than in Pataz (Fig. 10a) and high LILE and HFSE in the northwestern Montañitas suite. Devolatilisation of the subducting, water-rich, upper slab may produce agents for sub-arc mantle metasomatism and oxidation (Vidal et al. 1989).

The relationship between slab inclination and arc magmatism (Gutscher et al. 2000) may be crucial for metasomatism and metal endowment of the melt source (Hronsky et al. 2012). Steep subduction produces large amounts of high-degree melts in the mantle wedge, mainly as a result of strong slab devolatilisation (Hronsky et al. 2012). Such high-degree melts may only be moderately metal-endowed because of their intrinsic low ratio of incompatible (Au, Cu, Mo, H_2O , LILE, HFSE) to compatible metals. On the

contrary, magmas produced in the asthenosphere within a shallow slab setting are likely to be low-degree partial melts rich in incompatible elements, because slab-induced cooling restricts melt production (Kay et al. 2005; Hronsky et al. 2012).

In arc settings, large, high-grade porphyry Cu $\pm$ Au deposits are temporally mostly associated with syn- to post-compressional settings, in which crustal relaxation after crustal thickening allow the formation of vertical structural conduits (Richards et al. 2001). It is envisaged that crustal compression in a shallow subduction setting aids development of large mid- to upper crustal magma chambers (Sillitoe 1988, 2010). At the same time as magma is ponding in the crust, magma fractionates and concentrates a fluid phase, instead of being channelled to the surface as undifferentiated volcanic rocks. Changes in crustal stress regime are considered a particularly favourable time period for the formation of metal-rich porphyry deposits, because the highly fractionated and ideally metal-S–H₂O-rich magmas are then able to reach shallow crust (Tosdal and Richards 2001). Slab melting gives rise to SO₂-fertilisation of the subarc mantle because the slab-derived melts (Defant and Drummond 1990) are rich in H₂O and S.

It has been argued that oceanic crust may also be the primary source of Cu in porphyry systems (Hedenquist and Lowenstern 1994). Zhang et al. (2017) show that partial melting of subducted oceanic crust, under oxygen fugacities $> \Delta\text{FMQ} + 1.5$, is favourable for producing primary magmas with Cu contents sufficiently high (i.e., > 150 ppm) for porphyry mineralization. In contrast, mantle peridotites have low Cu and S contents and thus partial melting of mantle peridotite even under ΔFMQ higher than $+1.5$ cannot form Cu-rich magmas (Lee et al. 2012). This has been used to explain the close relationship between porphyry Cu deposits and oxidised magmas with adakitic affinities (Zhang et al. 2017). The formation of Cu-rich veins in the Montañitas suites (at least in the southern dacite) as a result of the contribution of melted slab is suggested based on high $f\text{O}_2$ [zircon Ce/Ce* > 70 and $\Delta\text{FMQ} + 1.5$ according to Smythe and Brenan (2016)] and sub-mantle $\delta^{18}\text{O}$ and ϵHf values.

Contrasting Au and Cu mobilisation in the magmatic-hydrothermal systems

Various hydrothermal fluids have been discussed for the Patáz Au deposit: hot fluids derived from oxidised, felsic magmas associated with the batholith (Sillitoe 2010), metamorphic country rocks by deformation-controlled (“orogenic”) processes without any specific magmatic connection (Haeberlin et al. 2004), and fluids derived from the ESC-Lavasen A₂-type magmas (Witt et al. 2014). Irrespective of the source, it is crucial to keep Cu and Au as long as possible in the magmatic fluid phase, allowing the metal to be

mobilised and transported by late- to post-magmatic-hydrothermal fluids. A series of studies invoked the incorporation of supracrustal rocks enhancing Au endowment in igneous systems (Giggenbach 1992; Hedenquist and Lowenstern 1994; Murgulov et al. 2008; Kemp and Blevin 2009; Lu et al. 2010, 2013). Mainly, it has been argued that assimilation of (meta-) sedimentary material causes a magma changing to more H₂O + S $\pm$ NaCl rich and more reduced and that these conditions are ideal for hydrothermal Au mobilisation (Zajacz et al. 2010; Kouzmanov and Pokrovski 2012). Zircon from the Lavasen suite do show lowest $f\text{O}_2$ values and low crystallisation temperatures compared with other samples (Fig. 9f), indicating assimilation of some kind of water- and potentially organic S-rich crustal material. Hence, this magma potentially provided the best fluid for hydrothermal Au mobilisation.

In comparison to Au, Cu speciation is less specific: experiments show that Cu is most soluble in oxidised Na/(K) CuCl₂ complexes, but can dissolve also as Na/(K)Cu(HS)₂, H₂SCuHS, and Na/(K)ClCuHS complexes (Zajacz et al. 2011). The relative abundance of these complexes is controlled by the H₂S/total chloride and HCl/alkali chloride ratios. The zircon data suggest that the Montañitas magmas are partly oxidised at or above the FMQ buffer (Fig. 10a), meaning a greater S- and Cu-, but lower Au-carrying capacity (Tomkins et al. 2012, and references therein). In a study of zircon Ce⁴⁺/Ce³⁺ ratios and associated $f\text{O}_2$ values in ore-bearing intrusions from the Central Asian Orogenic Belt, Shen et al. (2015) showed that larger porphyry Cu deposits are associated with more oxidised magmas. Hence, in addition to Cu being sourced in the subducted slab, the elevated $f\text{O}_2$ is a likely control of high-Cu but low-Au abundance in hydrothermal veins in the Montañitas.

A high oxidation state in the main magma source (i.e., the metasomatised mantle) inhibits sulphide precipitation and thus is a prerequisite for keeping Cu and Au in the melt. However, the circulation of a reduced fluid is needed to mobilise Au (Zajacz et al. 2010; Kouzmanov and Pokrovski 2012) via fault zones and fractures in the Patáz hydrothermal system. This contradiction can be solved with a two-stage model, involving an initial magmatic precipitation of Au (and Cu) in the batholith followed by a hydrothermal remobilisation of Au during fluid flow generated by the intrusion of the slightly younger, more reduced Lavasen volcanic rocks. On the other hand, Cu ($\pm$ Au) rich mineralisation in the oxidised Montañitas suites suggests hydrothermal mobilisation of metals from less differentiated rocks. Mobilising fluids likely derived from highly fractionated and H₂O- and LILE-enriched rocks of the younger northwestern suite. Hence, a two-stage model is considered also for the Montañitas metallogeny.

Conclusions

Magmatic rock suites of the Pataz and Montañitas regions that have broadly coeval Mississippian ages and are located just some 10 s of kilometres apart parallel to the arc; reveal heterogeneous crustal sources and economic metal endowment. Three distinct source end members are modelled based on whole-rock geochemistry, zircon chemistry, and zircon Hf–O isotopes: (1) depleted and re-fertilised mantle with $\epsilon\text{Hf} > 0$ and mantle-like $\delta^{18}\text{O}$ values, (2) layer-2 gabbro (or high T altered volcanic rock) from the subducting slab with moderately low ϵHf and “sub-mantle” $\delta^{18}\text{O}$ signatures, and (3) various old and slightly reduced supracrustal rocks with variously low ϵHf and heavy $\delta^{18}\text{O}$ signatures. The relative contributions from these sources is mainly a function of the degree of partial melting of the metasomatised mantle, the slab angle and associated degree of lower slab melting, and crustal thickness facilitating ponding, fractionation and assimilation of supracrustal material.

Source mixing is a first-order control of Cu and Au fertility of arc magmas: the subarc metasomatised mantle is oxidised and enriched in alkalis, LILE, HFSE, Cl^- , H_2O , and Au. This source component is variably inherited in rocks of all suites. The melted lower slab adds Cu to the system only in the Cu-endowed Montañitas magmatic suites. Melting of the slab likely occurs within a flat subduction setting, which is triggered by a compressional crustal setting and/or by the subduction of a thick oceanic crust (plateau, ridge). A switch from compression to extension allows the fractionated melts to ascend to (sub-) volcanic level. The various styles of Au and Cu mineralisation at Pataz and Montañitas formed within late-magmatic-hydrothermal systems induced by emplacement of highly fractionated subvolcanic felsic rocks with A_2 -type affinity. A slightly reduced supracrustal component characteristic of Pataz rocks is key to effective Au mobilisation. At Montañitas Au failed to be mobilised efficiently at the regional scale due to lack of supracrustal assimilation and associated reduction of melt $f\text{O}_2$.

This study suggests that the Proto-Andean arc in Peru (Eastern Cordillera) has a complex igneous architecture, and associated metal endowment, of coeval magmatic belts. The juxtaposition of early oxidised and $\text{Au} \pm \text{Cu}$ fertile, magmas and late, highly fractionated and H_2O -rich magmas was critical to the formation of mineralised porphyry- and vein-style ore formation. The existence of more Cu-endowed regions in preserved shallow-crustal porphyry systems, such as at Montañitas, is proposed. The combination of zircon geochronology, trace element, and Hf–O isotope data provide viable proxies of magma evolution, from source mixing to emplacement. Exploration for fertile districts may benefit from the herein utilised methods of “zirconology”.

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