



Geochemistry and age of mafic rocks from the Votuverava Group, southern Ribeira Belt, Brazil: Evidence for 1490 Ma oceanic back-arc magmatism

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ABSTRACT

This paper presents new SHRIMP U–Pb zircon and ⁴⁰Ar–³⁹Ar hornblende ages as well as elemental and Sr–Nd isotopic data for greenschist to amphibolite facies meta-mafic rocks from the Votuverava Group (Ribeira Belt, Brazil). These mafic rocks appear to be mostly subvolcanic and volcanic rocks and, in part, intrusions coeval with the host sedimentary succession. Magmatic zircons have a U–Pb age of 1488 ± 4 Ma. An ⁴⁰Ar–³⁹Ar hornblende age of 1390 ± 20 Ma suggests cooling after a thermal event. The mafic rocks have chemical compositions of basalt and basaltic andesite (SiO₂ of 45–55 wt.%) of the tholeiitic series. Chemical data indicate the coexistence of rocks with BABB and E-MORB signatures. BABB-like rocks with a Ti/V of 9–20 show depletion in HFSE relative to MORB values and slightly fractionated REE patterns (La_{cn}/Yb_{cn} of 0.8–1.8), while those with a Ti/V of 22–30 have HFSE contents similar to MORB and slightly more fractionated REE patterns (La_{cn}/Yb_{cn} of 1.1–2.8). E-MORB-like rocks display a Ti/V of 27–41 and moderately fractionated REE patterns (La_{cn}/Yb_{cn} of 3.6–5.3). The ε_{Nd}(*t*) values ranged from –3.02 to +3.55. Whole rock Sm–Nd isotopic data yielded a regression with a slope of 1225 ± 68 Ma, which can be interpreted as a mixing line of no age significance that is related to different source components of the metabasic rocks. Elemental and Nd isotopic signatures suggest that the Votuverava metabasites originated from a MORB-type mantle source heterogeneously metasomatized by subduction processes. The data are consistent with magmatic activity in a back-arc basin environment. The 1490 Ma mafic magmatism is associated with a 500-km-long and 60-km-wide Calymmian belt interpreted as an accretionary orogen. Available thermochronological data suggest that this accretionary orogen could have evolved into a collisional orogen in the period 1280–1100 Ma, possibly related to the assembly of Rodinia. During the Brasiliano–Pan African cycle (650–550 Ma), related to amalgamation of West Gondwana, this Calymmian belt represented by the Votuverava Group was dispersed as an exotic terrane along the Ribeira Belt.

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1. Introduction

The Ribeira Belt is a Neoproterozoic (Brasiliano–Pan African) accretionary-to-collisional orogen parallel to the southeastern Brazilian coast whose development was related to the assembly of West Gondwana. Neoproterozoic ages for extensive arc-related granitic plutonism and collisional metamorphism are well documented in the orogen (Janasi et al., 2001; Passarelli et al., 2004;

Prazeres Filho, 2005; Silva et al., 2005; Cury, 2009; Faleiros et al., 2010, 2011a; Salazar et al., 2013). However, the depositional ages of the majority of supracrustal rock successions, as well as of the related magmatism, are still uncertain and are debated due to the scarcity of robust geochronological data. Historically, the metasedimentary rock units of the southern Ribeira Belt have been inferred to be of Neoproterozoic age and are sometimes considered sedimentation associated with a Neoproterozoic suprasubduction zone environment (Soares, 1987; Fiori, 1992; Reis Neto, 1994; Campanha and Sadowski, 1999; Siga et al., 2009). Alternatively, Mesoproterozoic ages have been proposed, with continental rift, passive margin continental platform, back-arc basin, fore-arc basin

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or intra-arc settings (Campanha and Sadowski, 1999; Siga et al., 2009, 2010, 2011a,b; Faleiros et al., 2011b). Recent geochronological data have demonstrated the existence of imbricated Calymmian, Tonian, Cryogenian and Ediacaran metasedimentary rock units (Hackspacher et al., 2000; Campanha et al., 2008; Cury, 2009; Siga et al., 2009, 2011a,b), thereby demonstrating a complex crustal architecture. An important remaining question is which supracrustal units formed in the Mesoproterozoic and Neoproterozoic, and what were their tectonic environments? This has significant implications for the understanding of the tectonic process involved in the assembly of West Gondwana and possibly on the configuration of older Proterozoic supercontinents. The existence of Calymmian-age units raises the possibility of an evolutionary history linked in part with the evolution of the Mesoproterozoic supercontinent Columbia (Rogers and Santosh, 2002; Roberts, 2012, 2013).

The southern Ribeira Belt is divided into the Apiaí and Curitiba terranes, separated by the Lancinha–Cubatão fault zone (Faleiros et al., 2011a). The Votuverava Group is a major metavolcano-sedimentary unit of the Apiaí Terrane (Fig. 1), which is composed of distal turbidites with significant basic magmatism represented by concordant lenses of (metamorphosed) mafic rocks. Previous geochronological studies performed on mafic rocks from restricted portions of the Votuverava Group have provided conflicting results, indicating either Ediacaran (Hackspacher et al., 2000) or Calymmian (Siga et al., 2011a) ages. The tectonic setting of the basic magmatism is also debated. Some authors consider it as reflecting extensional events related to the break-up of continental masses and the development of large peri-oceanic sedimentary basins (Siga et al., 2011a,b), whereas other authors interpret this magmatism as associated with back-arc basin environments (Hackspacher et al., 2000; Faleiros et al., 2011b).

This contribution examines metabasic rocks from the Votuverava Group through geochronological analyses (zircon U–Pb by SHRIMP, hornblende ^{40}Ar – ^{39}Ar), isotopic geochemistry (whole-rock Sm–Nd and Rb–Sr) and major and trace element geochemistry. This study has three objectives: (1) to recognize the tectonic setting of the basic magmatism, (2) to establish the age of the basic magmatic event and thereby constrain when the host sedimentary succession was deposited and (3) to detect any record of tectonic events prior to the Neoproterozoic Brasiliano–Pan African cycle. The results from this work contribute to the elucidation of the tectonic evolution of the southern Ribeira Belt and West Gondwana. Possible links with the evolutionary histories of the Proterozoic supercontinents Columbia and Rodinia are also discussed.

2. Geological setting

The Ribeira Belt is a large crustal domain parallel to the coastline of southeastern Brazil, whose components were amalgamated, deformed and metamorphosed during the Brasiliano/Pan African orogeny (Neoproterozoic to beginning of the Paleozoic) related to the assembly of West Gondwana. It has counterparts in the Kaoko and West Congo Belts in western Africa (de Almeida et al., 1973). The southern Ribeira Belt evolved from a ca. 650–600 Ma accretionary orogen with extensive arc-related granitic magmatism (Janasi et al., 2001; Prazeres Filho, 2005; Silva et al., 2005) to a ca. 600–590 Ma collisional orogen with associated granitic magmatism (Prazeres Filho, 2005; Silva et al., 2005) and associated metamorphism (Faleiros et al., 2010, 2011a). The main cratonic masses involved in this collisional process are the São Francisco-Congo, Paranapanema, Luís Alves and Rio de la Plata cratons (Fig. 1a). The main structures in the Ribeira Belt are controlled by a orogen-parallel continental-scale dextral strike-slip shear system (e.g., Sadowski, 1991; Dürr and Dingeldey, 1996; Campanha,

2002; Egydio-Silva et al., 2002; Campanha and Brito Neves, 2004; Faleiros et al., 2007, 2010, 2011a). As a result, the belt is dominated by tectono-stratigraphic terranes (in the sense of Howell, 1995) of distinct origins, separated by shear zones (Heilbron et al., 2004; Campanha and Faleiros, 2005; Faleiros, 2008; Faleiros et al., 2011a).

The southern Ribeira Belt is divided into the Apiaí and Curitiba composite terranes, separated by the Lancinha–Cubatão fault zone (Fig. 1b). The Curitiba Terrane is composed of migmatitic orthogneisses of the Atuba Complex (Archean to Paleoproterozoic) and metamorphosed passive margin continental platform successions of the Turvo-Cajati and Capiru Formations. The Atuba Complex underwent two main episodes of high-grade metamorphism at 2100–2000 Ma and 650–550 Ma, indicating that it represents a fragment of a Rhyacian–Orosirian mobile belt that was intensely reworked in the Brasiliano collisional orogen (Siga, 1995; Sato et al., 2003, 2009; Faleiros et al., 2011a). The Capiru and Turvo-Cajati Formations underwent high-pressure metamorphism, with maximum conditions of 800–820 °C, 10–12 kbar and clockwise P – T – t (pressure–temperature–time) paths recorded in the Turvo-Cajati Formation (Faleiros et al., 2011a). Monazite U–Th–Pb chemical dating by electron microprobe yields an age of 589 ± 12 Ma for the peak metamorphism (Faleiros et al., 2011a).

Available U–Pb mineral isotopic data (Hackspacher et al., 2000; Weber et al., 2004; Campanha et al., 2008, 2009; Siga et al., 2009, 2011a,b) indicate that the Apiaí Terrane was formed by the amalgamation of supracrustal rock units whose ages ranged from Calymmian (ca. 1500–1400 Ma: Água Clara and Betara Formations and Votuverava Group), to Stenian to Tonian (1200–880 Ma: Lajeado Group), to Tonian (1000–900 Ma: part of the Itaiacoca Group) and to Ediacaran (630–580 Ma: part of the Itaiacoca Group and the Iporanga Formation). The supracrustal rock units of the Apiaí Terrane underwent a Barrovian-type clockwise P – T – t loop metamorphism (Faleiros, 2003, 2008; Faleiros et al., 2010) that, according to K–Ar and Rb–Sr isotopic data, has been inferred to be of Neoproterozoic age (Campanha and Sadowski, 1999). Nevertheless, robust dating of accessory metamorphic minerals has not been performed until now. Paleoproterozoic basement rocks occur in restricted nuclei, such as the Tigre Gneiss, which is composed of heterogeneously sheared syenogranite with a chemical signature of extensional A-Type granites and with zircon U–Pb ages of 1772 ± 10 Ma and 1748 ± 5 Ma (Cury et al., 2002). The Curitiba and Apiaí terranes were intruded by Neoproterozoic granitic plutons (ca. 650–580 Ma) formed in accretionary, collisional and post-collisional episodes (Janasi et al., 2001; Prazeres Filho, 2005; Silva et al., 2005).

2.1. The Votuverava Group

The Votuverava Group was originally defined as a formation in Brazil's Paraná State (Bigarella and Salamuni, 1958) and later extended to São Paulo State (MMA/JICA, 1981, 1982, 1983; Chiodi Filho, 1984; Stein et al., 1986; Campanha et al., 1986; Campanha, 1991; Campanha and Sadowski, 1999). In its current usage, the Votuverava Group (e.g., Faleiros et al., 2010, 2012; Faleiros and Pavan, 2013) includes the Perau, Rubuquara, Nhunguara, Piririca and Ribeirão das Pedras Formations (Piekarz, 1981; Takahashi et al., 1981; Campos Neto, 1983; Perrota, 1996) and other informal or undivided units (Fig. 2). However, it excludes the major carbonate shelf sequences, such as the Lajeado and Antinha groups (Campanha and Sadowski, 1999) and the Ediacaran Iporanga Formation (Leonardos, 1934; Campanha et al., 2008).

The Votuverava Group is composed of metamorphosed fine-grained pelitic successions (slate, phyllite and schist), generally interpreted as distal turbidites. A large number of metabasites and metavolcanic intercalations also occur, together with local and subordinate occurrences of quartzite, calc-silicate rocks, marble and

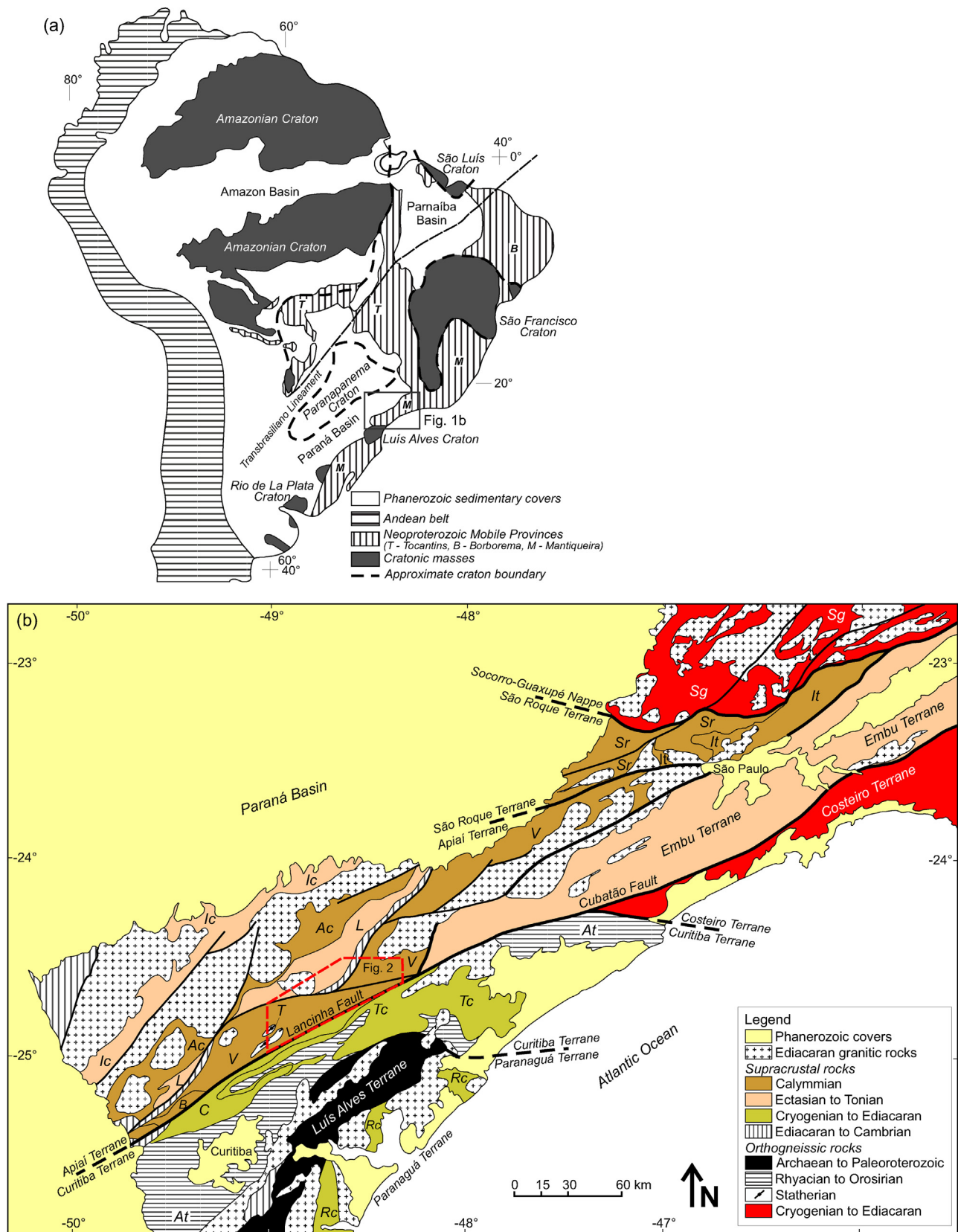


Fig. 1. (a) Simplified geotectonic map of part of South America emphasizing cratonic areas and mobile belts (relative to the Neoproterozoic). (b) Simplified geological map of the southern and central portions of the Ribeira Belt with the location of Fig. 2. Geological units: Itaiaococa Group (Ic), Água Clara Formation (Ac), Lajeado Group (L), Votuverava Group (V), Betara Formation (B), São Roque Group (Sr), Serra do Itaberaba Group (It), Socorro-Guaxupé Nappe (Sg), Tigre Gneiss (T), Capiiru Formation (C), Turvo-Cajati Formation (Tc), Rio das Cobras Formation (Rc), Atuba Complex (At).

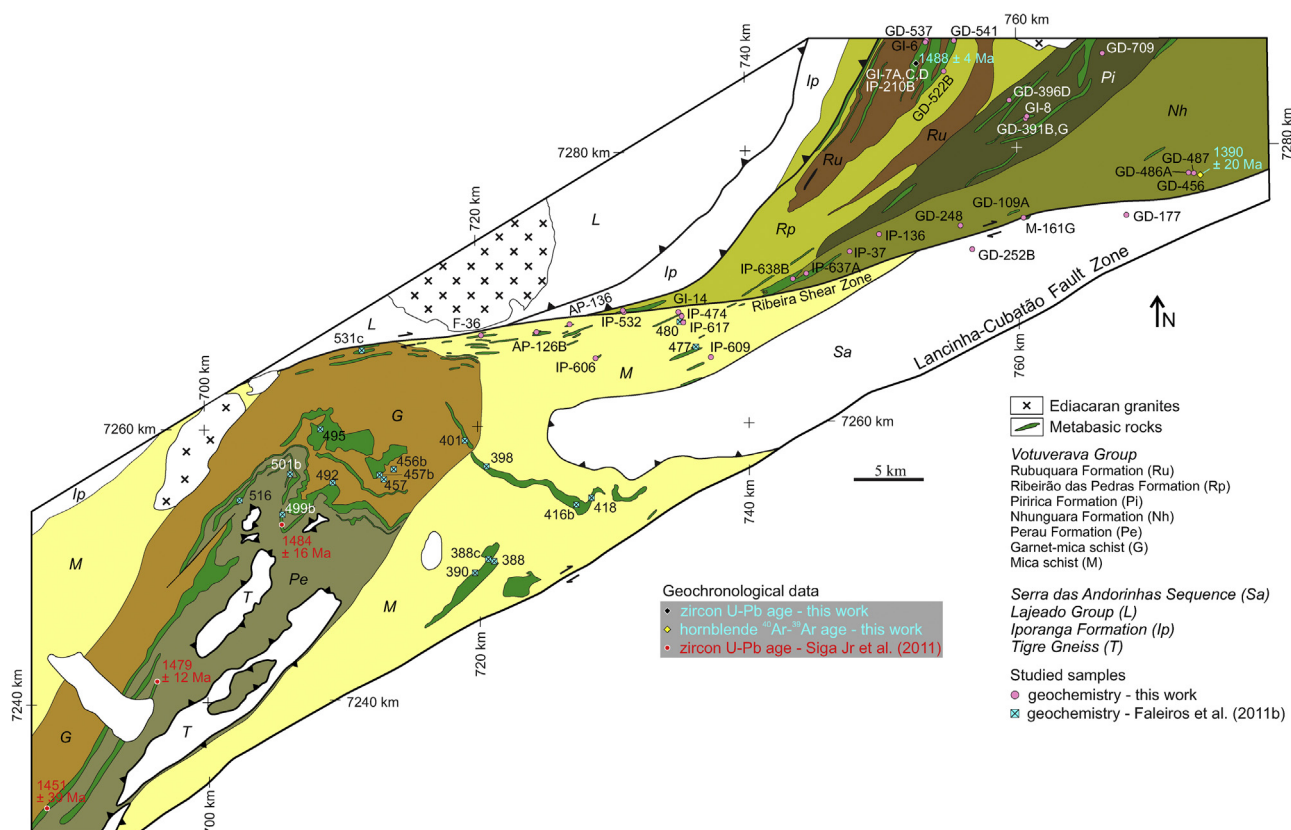


Fig. 2. Simplified geological map emphasizing the Votuverava Group and its formations (modified from Campanha, 1991; Faleiros et al., 2012; Faleiros and Pavan, 2013). Also shown are the locations of the analyzed samples. The map uses the Universal Transverse Mercator (UTM) projection, zone 22 south, with the WGS-84 horizontal datum.

oligomictic metaconglomerate, the last interpreted as channelized dense turbidite flows. Some paleoenvironmental indicators have been found, such as graded bedding in turbidites. There are also thin layers of iron formations, metachert and minor Pb–Zn–Ag–Cu sulfide deposits (Campanha, 1991; Daitx, 1996).

The dominant deformation style of the Votuverava Group is isoclinal folding, with a NE-trending, steep axial planar slaty cleavage or schistosity usually dipping toward the NW. This foliation is locally cut by a near-vertical crenulation cleavage. Kinks and chevrons with vertical NW-striking axial planes and steeply plunging hinges may be sporadically observed cutting the isoclinal structures. There are rare broad and open late antiforms and synforms developed on a bedding-parallel schistosity. A late system of ductile transcurrent shear zones gives rise to the regional configuration of mega shear lenses.

The rocks of the Votuverava Group display a Barrovian-type metamorphic facies series (Miyashiro, 1961, 1973) ranging from lower greenschist (chlorite zone) north of the Ribeira Shear Zone to medium amphibolite facies conditions (kyanite zone) south of this structure (Faleiros, 2003, 2008; Faleiros and Campanha, 2004; Faleiros et al., 2010). Geothermobarometric data obtained from metapelitic and metabasic rocks from the chlorite to the garnet zone yield peak metamorphic conditions of 380–630 °C and 6–8 kbar as well as clockwise P – T – t paths (Faleiros et al., 2010).

Available geochemical analyses of metabasic rocks (Campanha, 1991; Frascá et al., 1997; Faleiros et al., 2011b) indicate chemical signatures of both mid-ocean ridge basalts (MORB) and immature island arc basalts.

An Rb–Sr reference isochron from the Perau Formation yielded a 1212 ± 55 Ma age with an initial ratio of 0.711 (Batolla et al., 1981; Teixeira, 1982). Pb–Pb determinations on galenas from the Perau Formation indicate mantle model ages of approximately 1700 Ma

(Tassinari et al., 1990). Nogueira (1990) obtained Pb–Pb model ages of 1270 Ma and 1303 Ma for galena crystals that occur in Au mineralizations of the Piririca Formation. An Rb–Sr isochron of high-K metavolcanic rocks in the Perau Formation yield an age of 1283 ± 28 Ma (Daitx, 1996). Rb–Sr isochron ages of approximately 700 and 750 Ma with large uncertainties in slates, phyllites and pelitic schists have been interpreted as being due to the metamorphism related to the Brasiliano–Pan African cycle (Campanha, 1991; Daitx, 1996). Zircon U–Pb ages obtained from metabasites of a restricted area south of the present study (Fig. 2) provided Calymmian ages for the Perau Formation: 1484 ± 16 Ma (SHRIMP), 1479 ± 12 Ma and 1451 ± 39 Ma (ID-TIMS) (Siga et al., 2011a).

2.2. Field setting and petrography of the Votuverava meta-mafic rocks

The Votuverava metabasites occur exclusively as concordant lenticular bodies with widths ranging from one meter to one kilometer. In most localities, the superimposed high strain during regional metamorphism has obliterated the relationships of the metabasites with adjacent sedimentary rocks. Furthermore, because of the competent nature of the metabasites relative to the surrounding rocks, they now largely occur as lenticular bodies. Locally, however, in rare low strain zones, it is observed that the rocks preserve igneous textures, essentially of very fine- to fine-grained size, suggesting that the metabasites are of a volcanic to subvolcanic nature, probably coeval with the host sedimentary succession.

Two main types of metabasites occur: fine-grained, with an isotropic or slaty structure and a pale green color, and a medium- to coarse-grained variety with a dark green color and a lens-like structure (often mylonitic). The former occurs

Table 1
Major and trace element geochemical data for meta-mafic rocks from the Votuverava Group. Oxides in wt.%, trace elements in ppm and geographical coordinates in decimal degrees (WGS-84 datum), b.d.l. = below detection limit.

Sample	GD109A	GD177	GD391B	GD391G	GD537	IP210B	IP532	IP609	IP637A	IP638B	AP126B
Chemical group	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B2
Longitude (W)	48.4271	48.3528	48.4263	48.4263	48.4988	48.5079	48.7180	48.6543	48.5854	48.5951	48.7815
Latitude (S)	24.6189	24.6171	24.5535	24.5535	24.5013	24.5170	24.682316	24.712475	24.6570	24.6602	24.6962
SiO ₂	47.55	50.09	46.87	45.36	48.5	49.36	44.83	47.38	47.29	45.61	50.42
Al ₂ O ₃	13.13	14.48	15.94	14.58	13.69	18.56	12.36	12.92	14.45	14.37	14.29
Fe ₂ O ₃	12.6	10.21	8.62	14.82	8.57	6.99	12.70	15.45	9.13	9.16	11.6
MnO	0.196	0.135	0.176	0.243	0.16	0.148	0.24	0.15	0.162	0.151	0.21
MgO	11.42	8.98	9.73	7.92	10.38	8.05	6.04	4.83	10.94	10.98	7.30
CaO	10.45	9.77	15.96	11.52	13.29	10.29	9.61	5.57	15.02	16.67	7.71
Na ₂ O	1.51	2.73	0.75	1.83	0.93	2.37	2.15	3.20	1.04	0.68	2.86
K ₂ O	0.11	0.25	0.18	0.23	0.54	1.36	0.04	b.d.l.	0.03	0.05	0.08
TiO ₂	0.97	0.483	0.37	0.96	0.3	0.33	1.08	1.44	0.44	0.41	1.383
P ₂ O ₅	0.06	0.04	0.03	0.08	0.03	0.05	0.11	0.13	0.03	0.03	0.1
LOI	1.63	2.58	2.29	2.35	2.24	3.12	11.57	7.79	2.44	2.13	3.01
Total	99.63	99.77	100.9	99.9	98.61	100.63	100.71	98.85	100.97	100.24	98.96
Ba	19	37	19	50	99	340	147.0	8.0	14	44	18
Rb	b.d.l.	10.45	14.33	19.20	21.37	59.29	4.43	b.d.l.	b.d.l.	b.d.l.	3.10
Sr	154	143	203	374	78	146	251	62	142	153	364
Zr	45.16	23.07	16.01	49.01	17.44	19.09	65.77	85.27	23.24	21.14	80.59
Cs	b.d.l.	0.38	0.39	0.45	b.d.l.	2.08	2.51	b.d.l.	0.13	0.20	0.29
Ga	15.80	11.74	15.52	18.30	12.04	13.29	14.75	17.68	13.97	13.01	16.13
Ta	0.17	b.d.l.	b.d.l.	0.17	b.d.l.	b.d.l.	0.18	0.20	b.d.l.	b.d.l.	0.47
Hf	1.23	0.68	0.46	1.31	0.48	0.55	1.72	2.34	0.63	0.58	2.16
Nb	3.16	1.26	0.80	2.95	0.69	0.86	3.09	3.55	1.11	1.12	6.54
Y	13.64	8.31	8.38	14.49	8.46	8.82	22.49	31.04	8.82	8.41	23.43
Th	0.17	0.13	0.11	0.21	0.16	0.21	0.29	0.38	0.10	0.09	0.90
U	0.07	b.d.l.	b.d.l.	0.08	b.d.l.	b.d.l.	0.10	0.13	b.d.l.	b.d.l.	0.23
V	277	201	203	288	197	168	340	432	206	200	368
Co	54.63	46.06	40.81	56.69	33.72	28.08	39.43	43.38	36.78	35.16	35.59
Cr	569.37	321.02	276.93	23.90	60.43	287.26	63.00	46.91	633.37	691.11	272.65
Ni	233.01	158.10	153.75	113.16	90.42	92.42	70.15	60.56	207.98	200.08	127.56
La	2.82	1.11	1.68	3.06	1.11	1.38	2.79	3.83	1.70	1.71	9.29
Ce	6.42	3.02	2.74	7.90	2.70	3.20	7.71	10.53	3.42	3.19	18.87
Nd	5.83	2.53	2.69	6.19	1.97	2.33	6.47	8.87	3.13	2.96	13.59
Sm	1.87	0.86	0.90	1.92	0.65	0.77	2.10	3.01	1.05	1.00	3.68
Eu	0.73	0.38	0.49	0.87	0.31	0.36	0.85	1.17	0.51	0.50	1.57
Gd	2.13	1.17	1.27	2.21	1.01	1.12	2.71	3.71	1.41	1.35	3.82
Tb	0.41	0.21	0.23	0.43	0.20	0.22	0.56	0.77	0.25	0.24	0.73
Dy	2.55	1.41	1.44	2.72	1.38	1.51	3.82	5.23	1.61	1.51	4.41
Ho	0.50	0.30	0.28	0.54	0.30	0.32	0.77	1.10	0.32	0.29	0.83
Er	1.47	0.92	0.82	1.60	0.92	0.99	2.42	3.37	0.89	0.87	2.44
Tm	0.21	0.14	0.11	0.23	0.14	0.15	0.36	0.53	0.13	0.12	0.36
Yb	1.33	0.95	0.73	1.56	0.98	1.00	2.31	3.45	0.84	0.77	2.28
Lu	0.20	0.14	0.10	0.21	0.14	0.14	0.36	0.51	0.11	0.11	0.31
Sc	41	41	47	37	51	39	43	43	46	45	48
Cu	128.70	30.19	29.47	38.50	42.20	39.81	144.81	88.61	58.48	87.64	105.30
Zn	51.71	58.30	56.18	107.69	53.89	32.98	83.23	56.01	61.52	37.12	b.d.l.
Ge	1.47	3.35	1.77	2.04	1.50	1.53	1.45	1.61	1.56	1.43	2.02
As	b.d.l.	b.d.l.	b.d.l.	6.62	b.d.l.	6.27	6.46	b.d.l.	11.48	10.94	b.d.l.
Pr	1.09	0.44	0.49	1.16	0.36	0.45	1.20	1.62	0.56	0.57	2.92
Sb	0.51	0.57	3.58	5.73	0.99	1.49	2.81	5.73	b.d.l.	2.94	2.08
Mo	2.72	3.13	2.97	2.66	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Sn	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.39
Sample	F36	GD396D	GD487	GD541	GD522B	IP037B	AP136	GD456	GD486A	IP474	IP606
Chemical group	B2	B2	B2	B2	B2	B2	B3	B3	B3	B3	B3
Longitude (W)	48.8216	48.4383	48.3075	48.4786	48.4863	48.5536	48.7573	48.2988	48.3036	48.6759	48.7382
Latitude (S)	24.6985	24.541065	24.588602	24.5017	24.5220	24.6419	24.6910	24.5901	24.5889	24.6871	24.7133
SiO ₂	53.4	33.82	42.72	49.08	49.31	46.03	49.12	48.41	49.21	49.94	49.46
Al ₂ O ₃	14.1	14.79	11.93	13.76	13.18	14.17	14.37	14.1	14.38	13.67	14.22
Fe ₂ O ₃	13.74	13.03	12.90	12.42	14.95	13.31	11.27	11.03	11.34	14.42	11.53
MnO	0.181	0.29	0.19	0.19	0.173	0.186	0.167	0.157	0.166	0.198	0.158
MgO	5.60	8.87	5.60	6.39	5.86	8.71	6.99	7.08	7.32	6.08	7.28
CaO	7.19	8.25	9.36	11.42	8.83	11.67	11.1	11.89	11.94	9.00	11.93
Na ₂ O	3.27	3.20	2.49	1.76	1.67	1.92	2.18	2.09	2.12	3.02	2.25
K ₂ O	0.05	0.21	0.05	0.17	0.22	0.11	0.05	0.34	0.21	0.27	0.18
TiO ₂	1.412	1.28	1.94	1.23	1.498	1.18	1.45	1.48	1.57	2.299	1.446
P ₂ O ₅	0.2	0.13	0.16	0.1	0.13	0.1	0.17	0.13	0.16	0.2	0.15
LOI	1.31	15.05	11.47	2.15	3.5	3.14	1.76	1.82	1.7	0.58	1.5
Total	100.44	98.90	98.80	98.67	99.32	100.52	98.63	98.55	100.11	99.68	100.11
Ba	35	87	59	59	54	45	17	83	60	103	33
Rb	b.d.l.	9.22	2.79	4.96	36.67	4.00	b.d.l.	8.45	5.52	5.41	3.80

Table 1 (Continued)

Sample	F36	GD396D	GD487	GD541	GD522B	IP037B	AP136	GD456	GD486A	IP474	IP606
Chemical group	B2	B2	B2	B2	B2	B2	B3	B3	B3	B3	B3
Longitude (W)	48.8216	48.4383	48.3075	48.4786	48.4863	48.5536	48.7573	48.2988	48.3036	48.6759	48.7382
Latitude (S)	24.6985	24.541065	24.588602	24.5017	24.5220	24.6419	24.6910	24.5901	24.5889	24.6871	24.7133
Sr	301	289	442	167	141	226	340	393	416	310	506
Zr	142.47	86.91	130.68	64.05	86.25	63.87	106.81	100.03	104.68	167.46	97.57
Cs	0.12	1.32	1.17	0.13	1.30	0.81	b.d.l.	0.20	0.28	0.52	0.25
Ga	20.99	20.33	18.88	16.40	18.78	18.37	17.37	19.05	18.01	21.51	18.15
Ta	0.85	0.35	1.10	0.27	0.33	0.24	0.65	0.71	0.71	1.26	0.66
Hf	3.55	2.26	3.50	1.83	2.34	1.65	2.67	2.77	2.68	4.20	2.50
Nb	9.14	5.44	14.16	5.02	5.20	4.11	9.22	9.46	9.97	14.78	9.19
Y	30.22	20.27	21.69	24.85	26.91	18.04	19.37	19.11	19.78	30.39	19.96
Th	1.72	0.36	1.46	0.58	0.83	0.26	0.93	1.00	1.04	1.82	0.91
U	0.33	0.18	0.42	0.15	0.20	0.08	0.24	0.23	0.27	0.44	0.24
V	382	306	386	346	401	321	320	337	336	409	323
Co	36.28	23.97	37.46	33.45	40.18	42.79	32.24	33.39	34.34	40.11	35.16
Cr	–20.00	223.59	72.92	91.61	80.29	248.73	189.39	248.68	237.29	109.00	120.95
Ni	61.54	114.48	91.77	69.84	73.94	166.35	138.15	141.34	125.84	110.29	123.99
La	6.62	4.10	13.70	6.38	6.89	3.78	9.72	10.12	10.17	19.32	10.67
Ce	13.99	10.91	31.72	15.57	13.47	9.95	21.77	23.31	23.59	35.41	20.68
Nd	11.42	8.59	19.10	9.77	11.83	7.77	14.73	15.28	14.63	26.86	15.12
Sm	3.64	2.60	4.58	2.87	3.47	2.41	3.59	3.86	3.74	6.26	3.74
Eu	1.55	0.83	1.71	1.17	1.44	1.02	1.32	1.45	1.40	2.13	1.43
Gd	4.40	3.05	4.52	3.36	3.92	2.76	3.75	3.77	3.69	6.20	3.80
Tb	0.83	0.60	0.78	0.64	0.77	0.53	0.63	0.66	0.64	1.03	0.64
Dy	5.28	3.83	4.51	4.17	4.96	3.24	3.77	3.96	3.77	5.94	3.78
Ho	1.06	0.75	0.85	0.85	0.99	0.64	0.69	0.74	0.71	1.08	0.71
Er	3.06	2.21	2.36	2.57	3.02	1.86	1.99	2.12	2.04	3.08	2.00
Tm	0.45	0.33	0.33	0.38	0.45	0.27	0.28	0.31	0.29	0.44	0.28
Yb	2.73	2.06	2.03	2.33	2.84	1.65	1.67	1.91	1.80	2.70	1.76
Lu	0.38	0.30	0.30	0.34	0.40	0.24	0.24	0.26	0.26	0.37	0.24
Sc	38	41	32	42	50	42	36	36	36	36	36
Cu	129.02	73.80	91.37	33.97	139.07	94.63	73.23	100.40	109.37	142.44	84.08
Zn	66.68	138.31	97.87	b.d.l.	65.36	81.47	60.63	63.90	38.56	113.27	63.23
Ge	1.59	1.79	1.40	1.35	1.55	1.88	1.50	1.52	1.49	1.94	1.52
As	b.d.l.	33.95	b.d.l.	b.d.l.	b.d.l.	10.95	b.d.l.	b.d.l.	12.34	26.75	b.d.l.
Pr	2.25	1.62	4.17	2.03	2.52	1.47	3.04	3.16	3.11	5.78	3.19
Sb	0.35	4.93	5.04	0.23	0.41	6.76	2.29	2.41	5.08	1.37	1.70
Mo	b.d.l.	b.d.l.	b.d.l.	3.34	b.d.l.	4.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Sn	2.87	b.d.l.	b.d.l.	b.d.l.	1.25	1.23	1.23	b.d.l.	1.04	1.68	1.04

mainly north of the Ribeira Shear Zone and the second south of it. These two rock types correspond to associations of contrasting metamorphic grades. The first association has actinolite + chlorite + epidote $\pm$ plagioclase $\pm$ quartz $\pm$ carbonate (greenschist facies), and the other has hornblende (tschermakite) + plagioclase (andesine) + quartz $\pm$ actinolite $\pm$ epidote (epidote-amphibolite and amphibolite facies). Common accessory minerals include titanite, titanium oxides (Ti-magnetite, ilmenite and rutile) and apatite.

The amphibolite facies metabasites exhibit a nematoblastic texture formed by prismatic amphibole with a preferred orientation. Plagioclase and quartz usually form bands with a granoblastic texture alternated with amphibole-rich bands. One- to two-millimeter porphyroblasts of hornblende, plagioclase and opaque minerals stand out in some samples. The porphyroblasts of amphibole present in the amphibolite facies metabasites generally exhibit textural and chemical zoning related to the progression of metamorphism with actinolitic cores and tschermakitic rims (Faleiros et al., 2010).

Isotropic textures predominate in the greenschist facies metabasites. Locally, subophitic and intergranular igneous textures and remnants of relict igneous clinopyroxene and hornblende are preserved. The igneous hornblende has a dark brown color and is in disequilibrium with the surrounding metamorphic mineral associations. It is petrographically very distinct from the metamorphic hornblende of the amphibolite facies metabasites, which features a dark bluish green color. Mineral chemical analyses performed in dark brown amphibole revealed a composition ranging from edenite to pargasite and ferrous pargasite, corroborating its igneous

nature (Maniesi, 1997). These relict igneous textures and minerals indicate that at least some of the metabasite protoliths crystallized from hydrous magmas.

3. Analytical methods

Major and trace elements, including rare earth elements (REEs), of 22 metabasic samples (Table 1) were determined at Activation Laboratories Ltd. (Actlabs, Canada). Major and minor oxides were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and trace elements by inductively coupled plasma mass spectrometry (ICP-MS). These new data were integrated with available chemical data (Faleiros et al., 2011b; Table 2) obtained using the same methods at Acme Analytical Laboratories Ltd. (Canada), giving a total of 42 analyses. Some of the geochemical diagrams were produced using the GCDKit program (Janousek et al., 2006, 2011).

Zircons were extracted from 100–200-mesh fractions using standard isodynamic and gravimetric techniques at the Geochronology Research Center of the University of São Paulo (CPGeo-USP). The zircons were hand-picked using a binocular microscope and mounted in epoxy together with grains of the FC1 U–Pb calibration standard and then polished to reveal cross sections through the grains. Cathodoluminescence (CL) and scanning electron microscope (SEM) images were used to identify the best domains for U–Pb analysis, avoiding fractures, inclusions or metamict areas that may have experienced Pb loss. Sensitive high-resolution ion microprobe (SHRIMP) U–Pb analyses were performed using a $\sim 25\text{-}\mu\text{m}$ -diameter spot at the Australian

Table 2
Major and trace element geochemical data for meta-mafic rocks from the Votuverava Group (compiled from [Faleiros et al., 2011b](#)). Oxides in wt.%, trace elements in ppm and geographical coordinates in decimal degrees (WGS-84 datum).

Sample	388C	398	416D	418	477	492	499B	514B	388	390
Chemical group	B1	B1	B1	B1	B1	B1	B1	B1	B2	B2
Longitude (W)	48.8159	48.8187	48.7504	48.7418	48.6654	48.9282	48.9640		48.8109	48.8251
Latitude (S)	24.8496	24.7890	24.8109	24.8073	24.7066	24.7968	24.8199		24.8488	24.8573
SiO ₂	51.78	46.51	47.33	44.56	48.10	50.43	49.73	49.74	47.61	43.63
Al ₂ O ₃	13.63	14.37	14.11	15.69	14.01	14.82	14.05	15.37	12.79	12.69
Fe ₂ O ₃	10.02	13.34	11.65	12.91	13.57	8.86	10.17	13.53	15.72	17.72
MnO	0.27	0.21	0.16	0.50	0.20	0.15	0.25	0.42	0.22	0.23
MgO	8.35	7.93	8.04	7.89	7.96	9.60	6.70	7.08	5.99	7.46
CaO	7.90	12.69	11.57	12.84	10.55	10.99	15.64	7.43	9.56	9.11
Na ₂ O	4.05	0.98	1.96	0.88	1.92	2.68	0.33	4.24	3.00	1.69
K ₂ O	0.18	0.17	0.15	0.06	0.09	0.11	0.24	0.12	0.12	0.06
TiO ₂	1.02	1.09	0.96	1.03	1.07	0.58	0.72	1.00	1.74	3.34
P ₂ O ₅	0.09	0.10	0.08	0.09	0.10	0.04	0.05	0.08	0.15	0.32
LOI	2.50	2.40	3.80	3.40	2.40	1.50	1.90	0.80	2.90	3.50
Total	99.79	99.79	99.81	99.85	99.97	99.76	99.78	99.81	99.80	99.75
Ba	195.7	45.3	45.8	37.3	65.3	106.6	25.4	11.5	60.3	16.2
Rb	4.0	2.4	3.8	1.7	1.3	1.0	4.6	0.8	1.5	4.7
Sr	63.1	40.3	231.2	54.1	161.6	164.0	574.7	144.8	219.5	176.5
Zr	52.7	56.3	48.4	51.6	62.7	25.3	25.2	48.1	80.6	186.2
Sc	46.0	50.0	48.0	47.0	47.0	41.0	38.0	46.0	43.0	36.0
Ga	11.4	15.5	16.1	20.3	15.7	11.8	16.8	18.9	19.5	20.9
Ta	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.4	0.8
Hf	1.7	1.9	1.6	1.6	1.9	0.7	0.7	1.4	2.5	5.7
Nb	3.2	3.6	2.9	2.9	4.1	1.5	1.9	3.3	5.7	13.2
Y	22.3	25.4	20.1	22.3	23.6	12.4	14.6	22.4	30.8	44.5
Th	0.2	0.5	0.2	0.2	0.6	0.2	0.4	1.3	0.4	1.6
U	0.1	0.1	0.1	b.d.l.	0.2	b.d.l.	0.1	0.2	0.1	0.3
V	297	346	302	348	344	221	254	358	430	523
Co	43.6	46.9	45.4	49.3	51.0	42.4	31.6	48.7	49.8	63.9
Cr	167.63	143.68	133.42	119.74	61.58	294.21	164.21	17.11	41.05	92.37
Ni	66.6	44.6	51.2	63.7	43.4	27.4	26.4	20.4	39.8	113.9
La	5.4	5.5	3.9	2.6	4.4	1.5	2.5	4.0	6.8	13.7
Ce	9.5	9.7	8.1	8.1	9.5	4.4	6.2	10.7	14.0	34.2
Nd	8.1	8.8	7.0	7.6	7.5	3.4	5.9	7.6	12.6	26.1
Sm	2.57	2.63	2.16	2.13	2.24	1.21	1.66	2.55	3.50	6.53
Eu	0.81	0.91	0.87	0.87	0.86	0.54	0.89	0.85	1.33	2.16
Gd	3.14	3.43	2.94	3.13	3.29	1.67	2.17	3.14	4.52	7.58
Tb	0.63	0.70	0.59	0.62	0.64	0.34	0.43	0.62	0.87	1.41
Dy	3.81	4.35	3.48	3.74	3.81	2.09	2.40	3.52	5.08	7.98
Ho	0.77	0.86	0.71	0.77	0.84	0.43	0.50	0.78	1.01	1.52
Er	2.07	2.51	2.07	2.19	2.30	1.24	1.44	2.34	2.93	4.24
Tm	0.36	0.39	0.32	0.36	0.38	0.21	0.22	0.38	0.48	0.66
Yb	2.01	2.43	1.88	2.01	2.37	1.16	1.38	2.18	2.87	4.01
Lu	0.30	0.37	0.29	0.32	0.38	0.18	0.21	0.33	0.43	0.59
Cu	130.7	165.7	86.1	126.4	150.7	52.2	78.5	186.7	187.7	364.1
Zn	31	23	33	49	46	16	5	47	53	104
As	b.d.l.	b.d.l.	1.70	2.70	4.50	b.d.l.	0.80	b.d.l.	3.70	0.60
Pr	1.67	1.70	1.39	1.35	1.48	0.70	1.08	1.56	2.39	5.11
Mo	0.2	0.4	b.d.l.	0.4	0.2	0.5	0.3	0.3	0.2	0.2
Au	b.d.l.	0.8	b.d.l.	1.4	2.5	b.d.l.	2.0	1.6	1.5	6.3
Pb	0.2	0.1	0.1	0.8	0.3	7.9	18.3	70.2	0.3	0.5
W	0.2	0.2	b.d.l.	0.2	0.2	0.1	5.8	0.6	0.1	0.3
Sample	401	456B	457	457B	495	501B	516	531	480	531C
Chemical group	B2	B2	B2	B2	B2	B2	B2	B2	B3	B3
Longitude (W)	48.8316	48.8860	48.8919	48.8951	48.9382	48.9618	48.9977	48.9023	48.6776	48.908
Latitude (S)	24.7681	24.7879	24.7937	24.7917	24.7625	24.7927	24.8117	24.7058	24.6902	24.708
SiO ₂	47.79	49.62	48.63	47.59	46.85	51.24	49.55	45.82	48.94	49.90
Al ₂ O ₃	14.83	13.21	13.59	13.13	14.92	15.41	13.78	13.15	13.87	14.09
Fe ₂ O ₃	12.72	15.39	15.52	15.83	13.41	10.57	15.95	20.31	14.10	14.21
MnO	0.19	0.21	0.20	0.21	0.20	0.16	0.23	0.26	0.20	0.18
MgO	7.85	6.17	6.19	6.63	7.63	6.57	5.75	5.55	6.37	5.80
CaO	10.91	8.60	9.46	10.61	11.55	10.31	8.47	7.86	8.89	8.71
Na ₂ O	2.77	2.91	2.84	2.55	2.51	3.19	3.09	1.90	3.12	3.15
K ₂ O	0.17	0.13	0.20	0.19	0.21	0.37	0.16	0.21	0.29	0.18
TiO ₂	1.25	2.04	2.07	2.15	1.40	0.97	1.62	3.38	2.64	2.58
P ₂ O ₅	0.12	0.15	0.14	0.16	0.13	0.09	0.09	0.09	0.20	0.19
LOI	1.20	1.40	1.10	0.90	1.00	1.10	1.10	1.30	1.30	0.90
Total	99.80	99.83	99.94	99.95	99.81	99.98	99.84	99.83	99.92	99.89

Table 2 (Continued)

Sample	401	456B	457	457B	495	501B	516	531	480	531C
Chemical group	B2	B2	B2	B2	B2	B2	B2	B2	B3	B3
Longitude (W)	48.8316	48.8860	48.8919	48.8951	48.9382	48.9618	48.9977	48.9023	48.6776	48.908
Latitude (S)	24.7681	24.7879	24.7937	24.7917	24.7625	24.7927	24.8117	24.7058	24.6902	24.708
Ba	36.3	24.4	56.8	55.8	90.4	27.7	37.2	25.1	89.4	19.4
Rb	1.6	2.0	3.5	2.4	2.4	3.6	1.4	3.0	12.2	1.3
Sr	224.1	147.5	187.3	250.2	143.6	162.7	177.7	252.8	329.6	894.9
Zr	71.2	93.0	93.5	95.8	80.3	67.0	87.5	58.1	142.7	134.3
Sc	41.0	41.0	41.0	42.0	41.0	37.0	48.0	55.0	35.0	33.0
Ga	17.7	17.0	18.0	19.1	18.2	17.2	18.4	19.1	20.6	21.5
Ta	0.2	0.4	0.4	0.4	0.2	0.2	0.3	0.2	1.1	0.9
Hf	2.0	2.9	3.2	3.2	2.6	2.2	2.9	1.9	4.3	4.0
Nb	4.5	6.9	7.1	6.7	4.8	4.2	5.4	2.6	16.3	15.3
Y	23.6	29.3	28.2	28.7	24.7	22.9	27.8	29.0	28.2	30.3
Th	0.5	0.8	0.7	0.7	0.4	0.6	1.2	0.4	2.3	1.7
U	0.1	0.1	0.2	0.1	0.1	0.2	0.2	b.d.l.	0.6	0.5
V	309	424	437	429	320	259	377	942	412	383
Co	51.3	51.9	51.6	51.5	51.9	41.2	50.3	59.0	46.9	44.7
Cr	126.58	47.89	47.89	47.89	106.05	13.68	13.68	3.42	51.32	3.42
Ni	25.2	19.7	22.8	15.0	24.3	21.1	12.8	10.2	30.4	20.3
La	6.1	7.3	6.2	7.1	5.1	3.6	4.3	2.9	18.1	14.4
Ce	13.0	20.3	16.6	18.2	13.6	10.5	9.4	5.7	41.4	35.4
Nd	10.9	13.5	14.0	14.9	11.6	8.8	9.2	8.0	26.3	23.9
Sm	3.23	4.03	3.82	4.00	3.28	2.72	3.06	2.54	5.54	5.52
Eu	1.14	1.43	1.42	1.39	1.19	0.79	1.15	1.03	1.81	1.94
Gd	3.71	4.75	4.59	4.78	3.83	3.21	4.09	3.72	5.64	5.89
Tb	0.72	0.90	0.88	0.89	0.76	0.68	0.86	0.77	1.01	1.04
Dy	4.24	5.31	4.98	5.35	4.16	3.92	5.07	4.58	5.45	5.65
Ho	0.83	1.03	1.01	1.01	0.88	0.76	1.01	1.00	0.98	1.06
Er	2.28	2.85	2.89	2.76	2.45	2.25	3.00	2.85	2.67	2.89
Tm	0.35	0.48	0.46	0.48	0.39	0.36	0.48	0.47	0.39	0.45
Yb	2.26	2.60	2.64	2.59	2.29	2.12	2.76	2.84	2.32	2.49
Lu	0.32	0.38	0.40	0.39	0.36	0.33	0.42	0.45	0.33	0.38
Cu	115.8	100.6	203.3	183.3	133.1	217.0	171.8	4.0	199.0	182.9
Zn	20	24	28	27	23	15	30	50	36	27
As	b.d.l.	3.90	b.d.l.	b.d.l.	b.d.l.	b.d.l.	3.80	11.40	10.00	2.00
Pr	2.14	2.62	2.60	2.85	2.17	1.58	1.75	1.37	5.68	5.28
Mo	0.2	0.2	0.1	0.2	0.2	0.3	0.1	0.2	0.4	0.4
Au	0.7	2.7	3.0	4.5	1.2	2.8	4.1	0.7	1.9	3.4
Pb	0.2	0.2	0.1	0.6	0.1	3.5	1.6	1.1	1.8	0.7
W	0.2	0.3	0.3	0.2	0.1	0.9	0.4	0.6	0.8	0.7

National University. Details of the analytical procedure, as well as of the calculation of the analytical errors, are presented in Stern (1998) and Williams (1998). The decay constants and current $^{238}\text{U}/^{235}\text{U}$ of Steiger and Jager (1977) were used to calculate ages. U concentrations were calculated using the SL13 standard ($\text{U} = 238 \text{ ppm}$), and $^{206}\text{Pb}/^{238}\text{U}$ ratios were calibrated using the FC1 standard (concordant, 1099 Ma; Paces and Miller, 1993). The data were presented graphically, and ages were calculated using the Isoplot program (Ludwig, 2003). Data were corrected for common Pb based on measured ^{204}Pb and the Cumming and Richards (1975) model Pb composition for the likely age of the zircons.

^{40}Ar – ^{39}Ar analyses were performed in relict igneous hornblende grains extracted from a greenschist facies metabasic rock sample (GD-456) from the Nhunguara Formation of the Votuverava Group at the University of Queensland Argon Geochronology Earth Sciences Laboratory. Hornblende grains 0.5–2 mm in size were placed in aluminum irradiation disks along with Fish Canyon sanidine standards ($28.02 \pm 0.28 \text{ Ma}$; Renne et al., 1998). Two aliquots were analyzed by laser incremental ^{40}Ar – ^{39}Ar step heating following the procedures detailed in Vasconcelos et al. (2002). The main objective of this study is to evaluate whether the igneous hornblende grains were affected by an Ediacaran metamorphic event or if they record distinct cooling ages related to pre-Ediacaran igneous crystallization or metamorphism.

Whole rock Rb–Sr and Sm–Nd isotopic analyses were performed on 14 samples of metabasic rocks using a VG-354 multi-collector mass-spectrometer at the CPGeo-USP, with analytical procedures described in Torquato and Kawashita (1994) and Sato et al. (1995), respectively. The mass fractionation corrections for the

Sr and Nd isotopic ratios are based on $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. The total procedure blanks were within the range of $0.003 \mu\text{g}$ for Sr, 100–300 pg for Sm and $\sim 50 \text{ pg}$ for Nd. The analytical reproducibility was controlled using the NBS-987 standard for the Rb–Sr method and the La Jolla and BCR-1 standards for the Sm–Nd method.

4. Results

4.1. Whole rock geochemistry

Forty-two whole rock geochemical analyses of metabasic rocks are presented in Tables 1 and 2. The analyzed mafic rocks can be divided in three groups based on the Ti/V versus Nb/Yb ratios (Fig. 3a), which mostly vary within the ranges of 9–21 and 0.7–2.4 (B1), 22–30 and 1.8–3.3 (B2) and 27–41 and 4.9–7.0 (B3), respectively. Petrographically, B1 and B2 are enriched in titanite, plagioclase and quartz and depleted in titanomagnetite and ilmenite in relation to the B3. There is no correlation among the chemical groups, the host rock formations or the variation in the metamorphic grade.

The SiO_2 content varies from 45 to 54 wt.% (anhydrous basis), indicating an essentially basic composition, with all samples exhibiting normative quartz. There is a progressive increase in the Fe_2O_3 , TiO_2 and P_2O_5 and a decrease in the MgO and CaO from B1 to B3 (Tables 1 and 2). The rocks display essentially tholeiitic signatures, as seen in AFM and TAS diagrams (Fig. 3b, c), with only three samples classified as basaltic andesite. There is an incremental

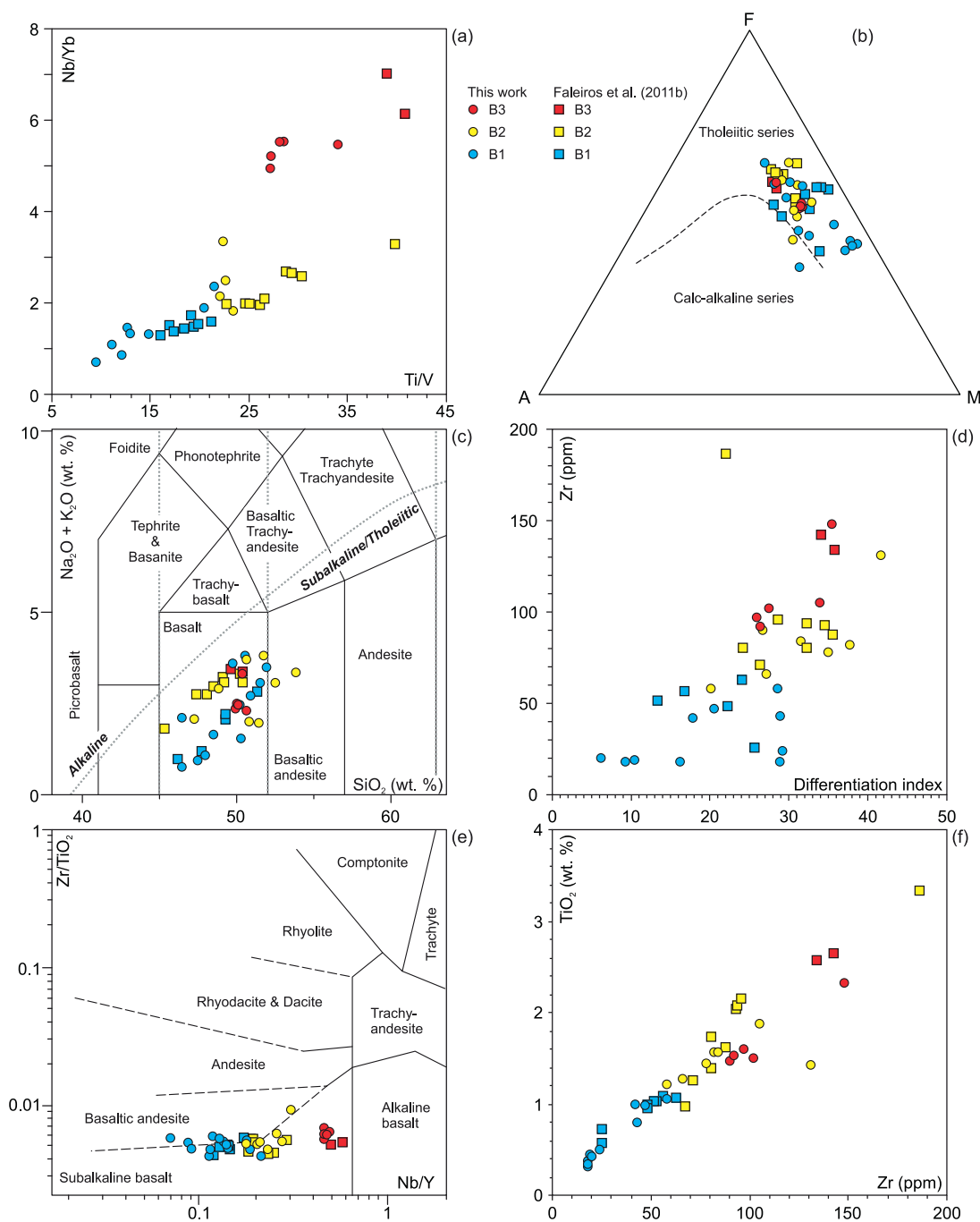


Fig. 3. Classification and petrogenetic diagrams with geochemical data of Votuverava metabasites. (a) Ti/V versus Nb/Yb plot, (b) AFM diagram after Irvine and Baragar (1971), (c) SiO₂ versus total alkalis plot after Le Bas et al. (1986), (d) differentiation index (normative quartz + albite + orthoclase) versus Zr plot, (e) Nb/Y versus Zr/TiO₂ plot after Winchester and Floyd (1977), and (f) Zr versus TiO₂ plot.

increase in the contents of the high field strength elements (HFSE) (e.g., Zr, Y, Hf, Nb, Nd, Ta) from B1 to B3 (Tables 1 and 2; Fig. 3d). Additionally, some B3 rocks display anomalously high HFSE contents (e.g., Y, Nb and Zr; Fig. 3d, Tables 1 and 2). The sub-alkaline basaltic signature of the rocks is highlighted in the Winchester and Floyd (1977) diagram, which uses the Zr/TiO₂ ratio as an index of differentiation and the Nb/Y ratio as a discriminant of alkalinity (Fig. 3e). This shows a progressive increase in the alkalinity from B1 to B3.

The three groups B1–B3 exhibit distinct chondrite-normalized (cn) REE patterns and MORB-normalized (mn) patterns. B1 rocks show an REE concentration of three to 13 times the chondrite

values, slightly fractionated patterns with an (La/Yb)_{cn} ratio from 0.8 to 1.8 and weak negative anomalies of Ce and positive anomalies of Eu (Fig. 4a–d). In the MORB-normalized diagram (Fig. 4e–h), the B1 samples show strong to weak depletion in HFSEs (from Nd to Yb), with an (Nb/Yb)_{mn} ratio from 0.9 to 3.1 (average value of 1.9). A weak to strong Nb–Ta negative anomaly is present in the majority of the samples (Fig. 4e–h), with Nb/Nb* values (= Nb_{mn}/[(Th_{mn} + La_{mn})/2]), normalizing values of the N-MORB of Sun and McDonough, 1989) from 0.2 to 1.1 (average of 0.6). There is a general enrichment in large ion lithophile elements (LILEs), with Rb, Ba and Th contents up to 30, 20 and seven times the MORB values, respectively. Most samples present strong positive

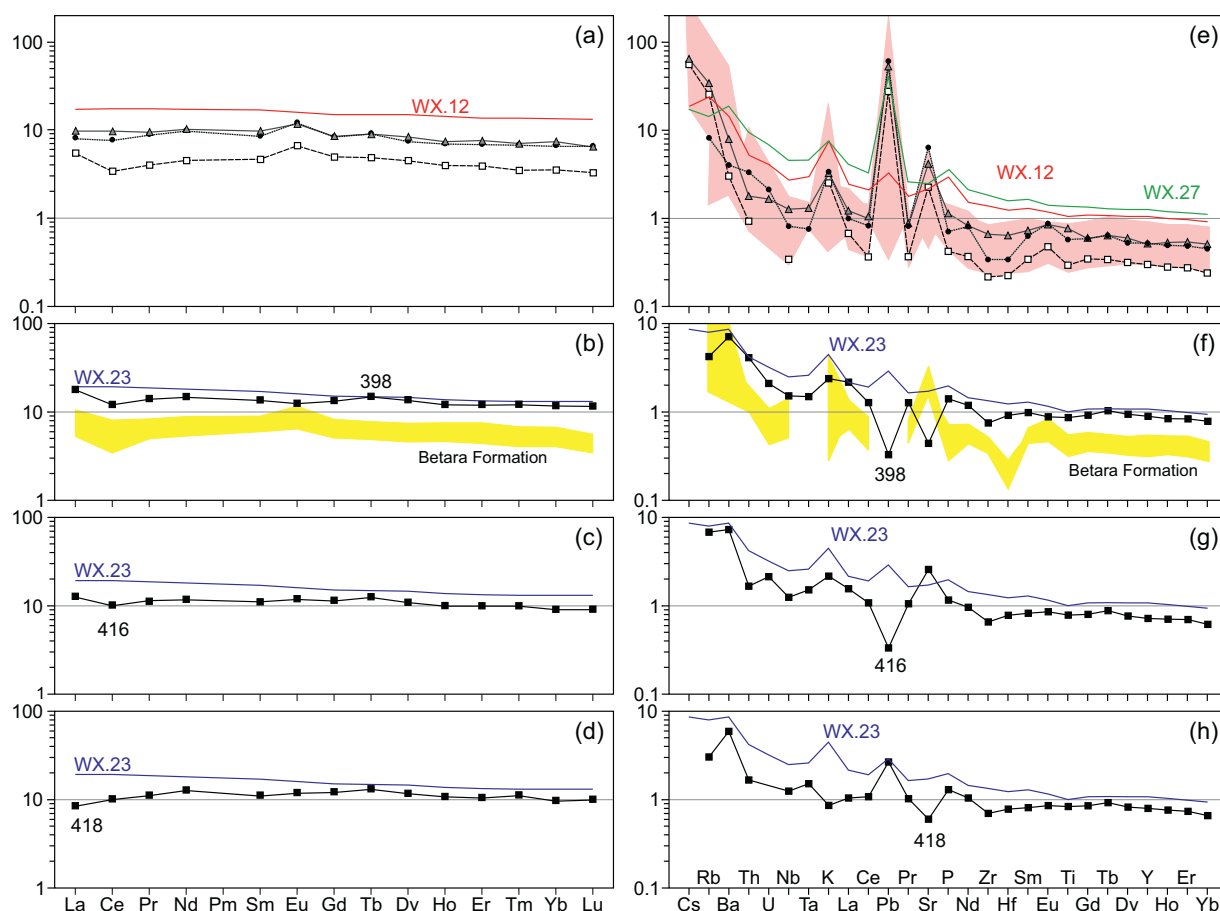


Fig. 4. Rare earth element (a–d) and incompatible element (e–h) spidergrams of the B1 group Votuverava metabasites. The colored field in (e) is the compositional range for all B1 samples. Data for the Betara Formation metabasites after Siga et al. (2011b). Samples WX.12, WX.23 and WX.27 are basalts from the East Scotia Ridge back-arc basin (Leat et al., 2000) for comparison. Normalization values from Sun and McDonough (1989) for MORB and Boynton (1984) for chondrite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

anomalies of K, Pb and Sr (Fig. 4e), but there is no consistency in the behavior of the LILEs, and some samples present weak to strong negative anomalies of K and/or Pb and/or Sr (Fig. 4f–h).

The B2 rocks show an REE concentration from eight to 35 times that of chondrite, slightly fractionated patterns, with an $(La/Yb)_{cn}$ ratio from 1.1 to 2.8 and weak positive anomalies of Nd (Fig. 5a–c). In the MORB-normalized diagrams (Fig. 5d–f), the B2 samples display HFSE contents (from Zr to Yb) approximate to the MORB values with progressive enrichment toward the most incompatible elements, with an $(Nb/Yb)_{mn}$ ratio ranging from 1.8 to 4.4 (average value of 3.2). There is a general enrichment in LILEs, and the Th values reach up to seven times the MORB values. Nevertheless, the behavior of most LILEs, particularly K, Pb and Sr, is inconsistent, displaying strong positive to strong negative anomalies (Fig. 5d–f). A negative Nb–Ta anomaly is present in most samples, particularly those with the lowest Ti/V ratios (e.g., 501, Fig. 5e), and the Nb/Nb* ratio varies from 0.4 to 1.0.

The B3 samples show higher REE concentrations in relation to the other groups, with up to 60 times the chondrite values, moderately fractionated patterns with an $(La/Yb)_{cn}$ ratio from 3.6 to 5.3, and a slightly positive anomaly of Nd (Fig. 6a–c). MORB-normalized patterns are characterized by progressive enrichment in HFSEs toward the most incompatible elements, with $(Nb/Yb)_{mn}$ ratios from 6.5 to 9.2; Y, Ho and Er contents similar to the MORB values; and weak depletion in Yb (Fig. 6d–f). There is a general relative enrichment in LILEs, with all samples displaying a negative K anomaly and most samples exhibiting a positive Sr anomaly

(Fig. 6d–f). The behaviors of Ba and Pb are inconsistent, presenting positive or negative anomalies (Fig. 6d–f). A weak Nb negative anomaly is present in all samples (Nb/Nb* ratios between 0.5 and 0.7).

4.2. U–Pb SHRIMP geochronology

Sample GI-7C is a light green mafic granofels of the Rubuquara Formation that is composed essentially of epidote, actinolite and chlorite. Plagioclase, sericite, titanite, quartz and apatite are the main accessory phases. The rock is fine- to medium-grained, isotropic and presents a preserved subophitic igneous texture with tabular relicts of plagioclase almost completely replaced by cryptocrystalline aggregates of epidote + chlorite ± sericite, along with pseudomorphs of mafic igneous minerals replaced by intergrowths of actinolite and chlorite.

Sample GI-7C yielded 100–200- μ m anhedral to subhedral zircon grains with aspect ratios of 1.5:1 to 5:1 (Fig. 7). In the CL images, some grains appear dark and structureless, whereas others are brighter and have igneous oscillatory compositional zoning (Fig. 5). Fourteen SHRIMP analyses were performed on the centers and edges of the grains. All sites show a moderate to low content of common Pb (Table 3). The analyses have high Th/U ratios, mostly >1.0, which is typical for zircons grown from the late stage of crystallization of basic magma. The U–Pb ages are concordant within analytical errors and indicate a single age population (Fig. 8,

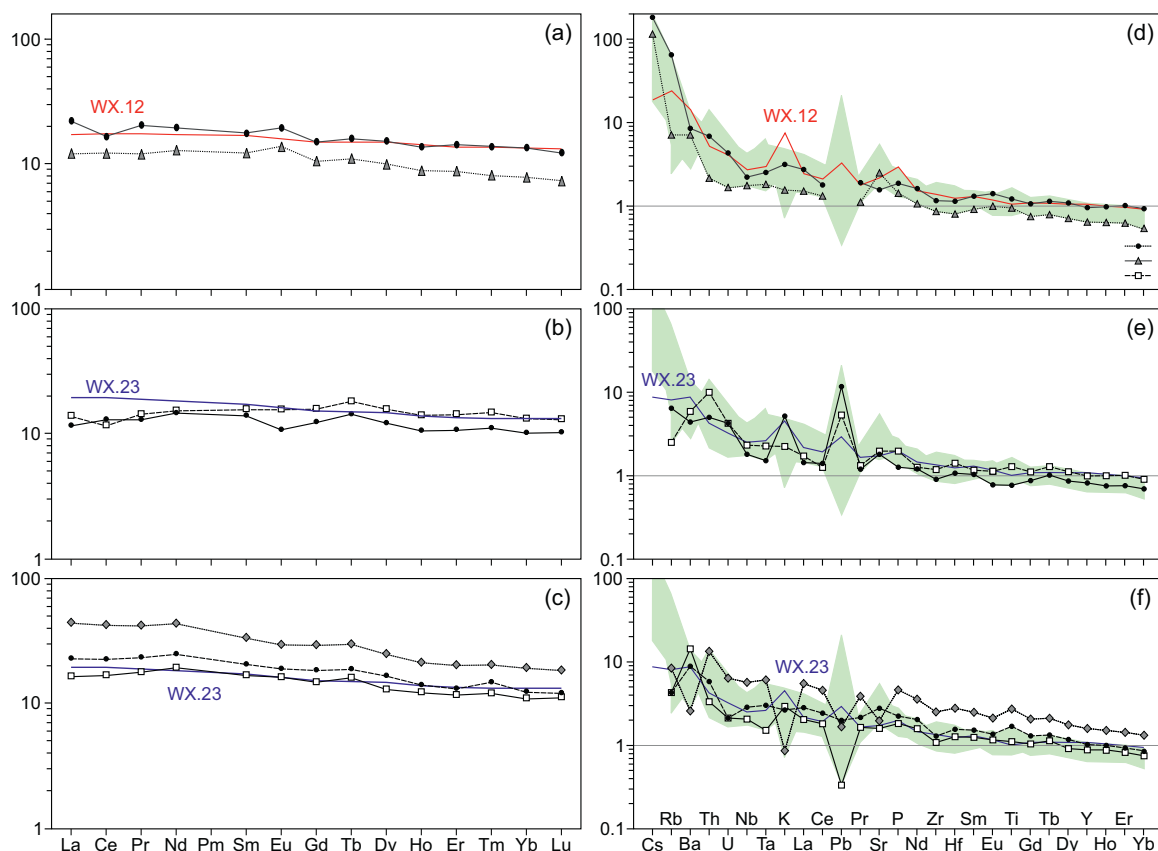


Fig. 5. Rare earth element (a–c) and incompatible element (d–f) spidergrams of the B2 group Votuverava metabasites. The colored field in (d–f) is the compositional range for all B2 samples. Samples WX.12 and WX.23 are basalts from the East Scotia Ridge back-arc basin (Leat et al., 2000) for comparison. Normalization values from Sun and McDonough (1989) for MORB and Boynton (1984) for chondrite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3). All analyses yield a concordia age of 1488 ± 4 Ma, with an MSWD of 0.57 (Fig. 8).

4.3. ^{40}Ar – ^{39}Ar geochronology

Sample GD-456 is a fine-grained green granofels of the Nhunguara Formation and is composed of actinolite (44 vol.%), epidote (44%), brown hornblende (5%) and quartz (3%). Opaque minerals, plagioclase, apatite, titanite and sericite are accessory phases. The rock exhibits a relict igneous texture. Randomly orientated relict tabular plagioclase grains have been largely replaced by cryptocrystalline aggregates of epidote $\pm$ sericite. Domains rich in pseudomorphs of plagioclase alternate with actinolite-rich domains. In the latter, the actinolite is randomly oriented. Quartz preserves its igneous interstitial texture but shows patchy undulose extinction and an absence of recrystallization features, indicating low-temperature ($<300^\circ\text{C}$) deformation (e.g., Stipp et al., 2002; Faleiros et al., 2010). The brown hornblende is euhedral, shows oscillatory compositional zoning and is in disequilibrium with the metamorphic mineral assemblage, being partially replaced by actinolite aggregates. These features suggest that it is of igneous nature. Two grains of brown hornblende of the sample GD-456 were analyzed (Table 4), but only one grain produced a plateau age (1390 ± 20 Ma, Fig. 9), according to the definition of Fleck et al. (1977). This age is inferred as the time of cooling of the rock below 500 – 450°C (the closure temperature of amphibole).

4.4. Sr–Nd whole-rock isotope data

The 14 Rb–Sr and Sm–Nd whole-rock analyses performed in the Votuverava metabasites include three samples of amphibolite lenses interbedded with the mica schists south of the Ribeira Shear Zone and 11 greenschist facies metabasites of the Rubuquara, Nhunguara and Piririca Formations north of the Ribeira Shear Zone (Fig. 2). The analytical results are shown in Table 5.

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated for 1490 Ma vary from 0.69466 to 0.72579 (Table 5; Fig. 10a). The $\varepsilon_{\text{Nd}}(t)$ ranged from +0.10 to +3.55, with the exception of sample F-036, which had a value of -3.02 (Table 5; Fig. 10b). There is an incremental increase in $\varepsilon_{\text{Nd}}(t)$ from B1 to B3 and a negative correlation between $\varepsilon_{\text{Nd}}(t)$ and Sm/Nd (Table 5; Fig. 10b). The Sm–Nd T_{DM} model ages vary between 1640 and 2110 Ma, with an average value of 1760 Ma (Table 5).

5. Discussion

5.1. Element mobility and protolith controls on trace element and isotope geochemistry

There are no Votuverava Group mafic rocks free of metamorphism, and thus, element mobility cannot be quantified. Nonetheless, studies on mafic rocks affected by regional metamorphism indicate that the LILE abundances are strongly susceptible to modification, while the LREE abundances are generally weakly modified, and the HFSE and HREE contents are mostly unmodified (e.g., Becker et al., 1999, 2000; John et al., 2004; Tropper and

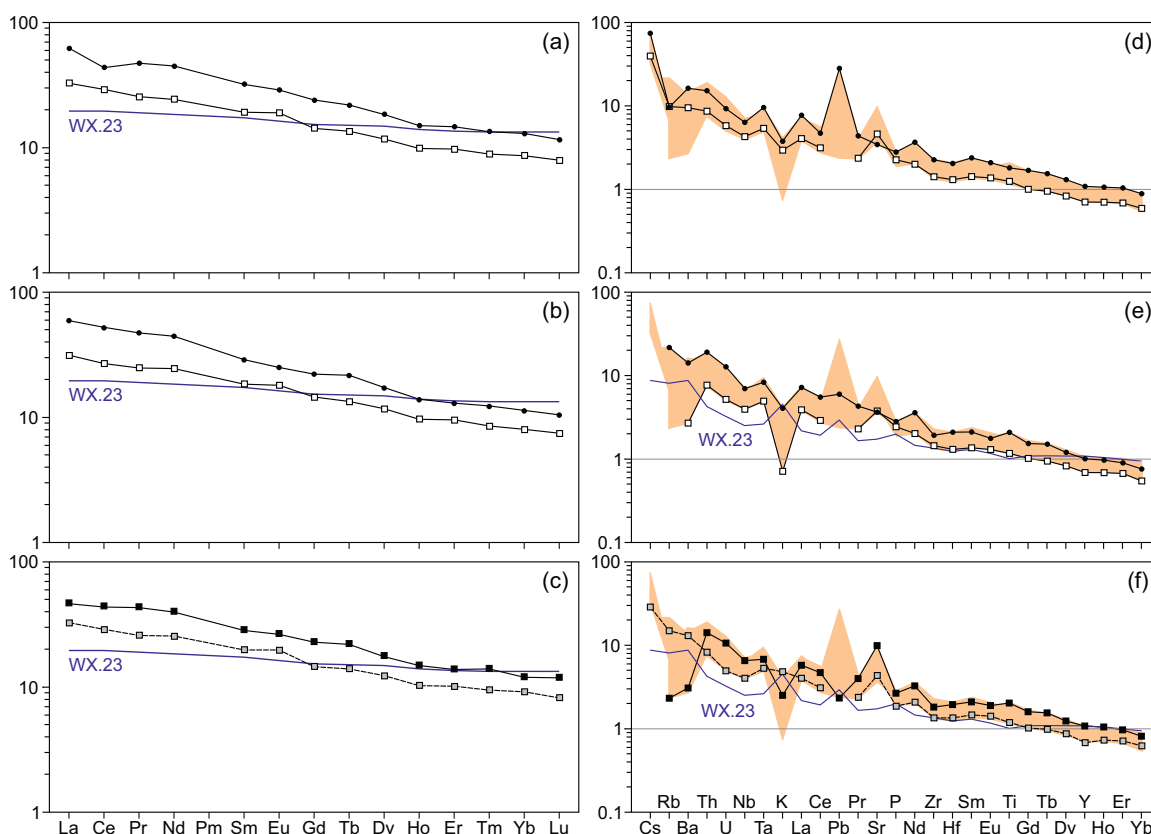


Fig. 6. Rare earth element (a–c) and incompatible element (d–f) spidergrams of the B3 group Votuverava metabasites. The colored field in (d–f) is the compositional range for all B3 samples. Sample WX.23 is a basalt from the East Scotia Ridge back-arc basin (Leat et al., 2000) for comparison. Normalization values from Sun and McDonough (1989) for MORB and Boynton (1984) for chondrite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Manning, 2005; Liu et al., 2007; Tang et al., 2007; Ker et al., 2014). In the MORB-normalized diagrams (Figs. 4–6), Cs, Rb, Sr, Ba, K and Pb show enrichment to depletion, while the Th, REEs and HFSEs display consistent behaviors. This pattern suggests that the LILE abundances were heterogeneously mobilized during metamorphism. Additional evidence for element mobility may be assessed using binary plots of mobile elements versus an immobile element (e.g., La). The plots of La versus Cs, Rb, Sr, Ba, K and Pb present no systematic correlation (Fig. 11a–f), corroborating the major mobility of these elements. Conversely, the plots of La versus Th, U, REE and HFSE show strong positive correlations (Fig. 11g–i), suggesting that protolith abundances of these elements are largely preserved.

The Rb–Sr isotope system provides additional constraints on the element mobility. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are strongly scattered (Table 5), as seen in the plot of initial $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\varepsilon_{\text{Nd}}(t)$ (Fig. 10a), indicating that the Rb–Sr isotopic system was strongly modified by metamorphic processes. The Sm–Nd isotopic system displays a more coherent behavior (Fig. 10a–c), suggesting a major protolith control.

5.2. Tectonic setting of basic magmatism

The Votuverava metabasites present major element abundances within the range of tholeiitic basaltic compositions. However, as discussed above, the chemical data indicate post-magmatic modifications of the LILE abundances, so further interpretation is based on immobile trace elements. The distinction among the B1, B2 and B3 chemical groups of mafic rocks with respect to the Ti/V versus Nb/Yb ratios is evident (Fig. 3a). Depletion in V relative to Ti is a function of the oxygen fugacity of the magma and its source, the degree of partial melting and fractional crystallization

(Shervais, 1982). Modeling of partial melting and fractional crystallization indicates that primary magmas produced by 20–30% of the partial melting under reducing conditions, as in mid-ocean ridges, will result in a Ti/V between 20 and 50, whereas similar melts produced under more oxidizing conditions, as in subduction-related settings, will result in a Ti/V between 10 and 20. Alkaline basalts, such as ocean intraplate basalts, exhibit a Ti/V higher than 50 (Shervais, 1982). Basaltic rock associations with a Ti/V varying from 10 to 50, as is the case for the Votuverava metabasites, are observed in modern and ancient oceanic back-arc basin environments (Shervais, 1982; Leat et al., 2000; Fretzdorff et al., 2002; Farahat, 2010). Shervais (1982) demonstrates that fractional crystallization of silicates does not significantly affect the Ti/V ratios, resulting in differentiation tendencies with near-constant Ti/V ratios. Conversely, the Ti/V ratio can be strongly affected by fractional crystallization of magnetite and/or hornblende, which may be identified by negative correlations between Si (or Zr) and Ti (or V) (Shervais, 1982). Because the analyzed samples show a strong positive correlation between TiO_2 and Zr (Fig. 3f), fractional crystallization of magnetite or hornblende should be disregarded. In this case, therefore, the Ti/V ratio can be considered a good tectonic discriminant.

In addition to the Ti/V ratios, the B1 samples present other characteristics of subduction-related magmas (Pearce, 1982; Pearce and Peate, 1995; Pearce and Stern, 2006; Pearce, 2008): (1) depleted HFSE contents relative to MORB abundances (Figs. 4–6); (2) a negative Nb–Ta anomaly relative to Th and La contents (Figs. 4–6), with Nb/Nb* values primarily between 0.2 and 0.7 (average of 0.6); and (3) enrichment in Th and U relative to MORB values. Furthermore, the relationships between non-conservative/conservative trace element ratios (e.g., Ta/Yb versus Th/Yb, Ce/Nb versus Th/Nb,

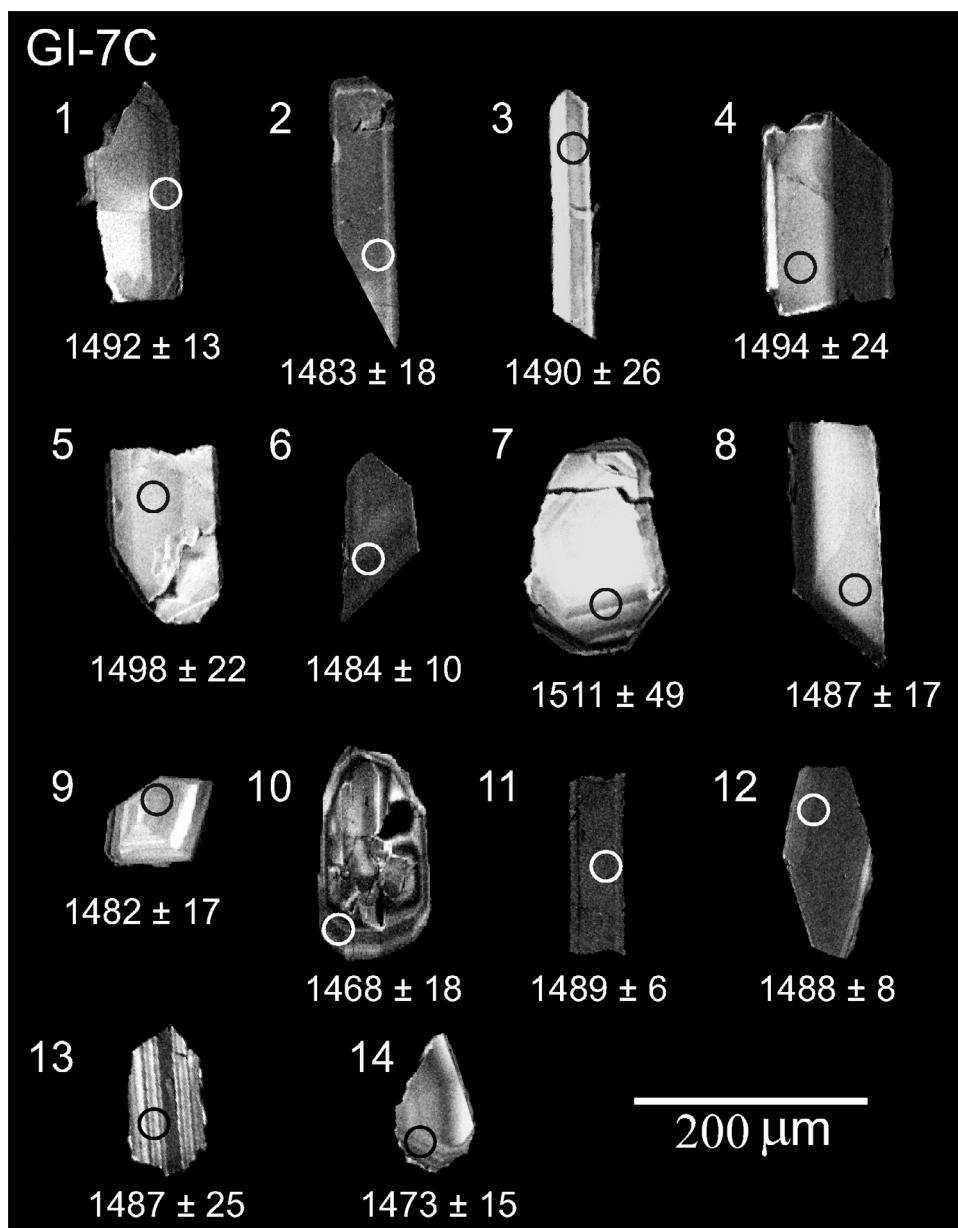


Fig. 7. Cathodoluminescence image of the zircons from the GI-7C sample (Votuverava metabasite).

Th/Yb versus Nb/Yb; Fig. 12) of the Votuverava metabasites are similar to those of subduction-related oceanic basalts, suggesting a variable contribution of the subduction component to the magma source (Pearce, 1982; Pearce and Peate, 1995; Pearce and Stern, 2006; Pearce, 2008). The B1 and B2 trace element behaviors are very similar to the patterns found in modern oceanic back-arc basin basalts (BBABs) (e.g., East Scotia Ridge, Leat et al., 2000; Fretzdorff et al., 2002) (Figs. 4 and 5). Metabasalts with preserved igneous hornblende (e.g., sample GD-456, this work; Maniesi, 1997) also corroborate the existence of subduction-related environments, where slab-related hydrous fluids contribute to the magma (e.g., Barclay and Carmichael, 2004).

The overall chemical patterns of the B2 and B3 groups are similar to transitional and enriched MORB patterns, respectively, possibly with a contribution of a subduction-related component. The existence of metabasic rocks with chemical signatures transitional to MORB and arc-related basalts as well as the large variation in Ti/V ratios (9–41) strongly suggest a back-arc basin environment for the Votuverava Group basic magmatism.

Available elemental and isotopic data (Figs. 4b, f, 10, 12; Siga et al., 2011b) indicate that metabasites from the Betara Formation (~50 km southwest of the study area; Fig. 1) present a B1 group chemical signature. This reinforces the existence of an extensive oceanic back-arc basic magmatism recorded in the southern Ribeira Belt.

5.3. Melt sources

The mostly positive initial ε_{Nd} values and T_{DM} model ages of 1640–2110 Ma suggest a major contribution of juvenile mantle sources with a minor and variable participation of reworked older crustal material. Sm–Nd data presented by Siga et al. (2011a,b) (ε_{Nd} from –3 to +6 and T_{DM} model ages between 1500 and 2100 Ma) for samples of the Perau and Betara Formations are consistent with our data (Fig. 10a, b). The strong negative correlation between Sm/Nd and ε_{Nd} (Fig. 10b) is evidence of a heterogeneous contribution of different melt sources to the Votuverava Group mafic magmatism.

Table 3Analytical SHRIMP results for a metabasic rock from the Votuverava Group (GI-7C sample; longitude: -48.5061° , latitude: -24.5174° , WGS-84 datum), with ratios corrected for the ^{204}Pb .

Spot	Site	U (ppm)	Th/U	Pb* (ppm)	^{204}Pb (ppb)	f206	$^{206}\text{Pb}/^{238}\text{U}$	Error	$^{207}\text{Pb}/^{235}\text{U}$	Error	$^{207}\text{Pb}/^{206}\text{Pb}$	Error	Age (Ma)		$^{207}\text{Pb}/^{206}\text{Pb}$	Error	Conc. (%)
													$^{206}\text{Pb}/^{238}\text{U}$	Error			
1	m, osc/hd, p, fr	533.6	1.03	170	7	0.00098	0.26441	0.00864	3.39721	0.11619	0.09318	0.00064	1512	44	1492	13	101
2	m, hd, p	365.1	2.10	138	4	0.00089	0.25754	0.00837	3.29300	0.11518	0.09274	0.00088	1477	43	1483	18	100
3	m/c, sz, p	197.0	1.22	65	2	0.00088	0.26334	0.00611	3.38119	0.09599	0.09312	0.00127	1507	31	1490	26	101
4	m/c, hd, fr	190.1	1.06	60	0	0.00020	0.26185	0.00538	3.36793	0.08502	0.09328	0.00115	1499	28	1494	24	100
5	c, hb, fr	125.5	0.83	37	0	0.00002	0.25774	0.00664	3.32274	0.09768	0.09350	0.00106	1478	34	1498	22	99
6	c, hd, p/eq	421.6	1.22	135	1	0.00022	0.25817	0.00569	3.30289	0.07688	0.09279	0.00049	1480	29	1484	10	100
7	e, osc, p, fr	150.0	0.75	44	0	0.00018	0.25963	0.00662	3.37101	0.12893	0.09417	0.00240	1488	34	1511	49	98
8	c/m, h, p, fr	190.1	0.65	55	0	0.00011	0.26188	0.00686	3.35709	0.09605	0.09297	0.00081	1499	35	1487	17	101
9	c, h, eq	173.4	0.56	49	0	0.00013	0.25849	0.00720	3.30487	0.10041	0.09273	0.00085	1482	37	1482	17	100
10	e, osc, ov	308.5	1.03	99	4	0.00098	0.26804	0.00677	3.40159	0.09567	0.09204	0.00089	1531	34	1468	18	104
11	c, hd, p	1406.0	1.13	449	0	0.00002	0.26237	0.00784	3.36597	0.10220	0.09305	0.00027	1502	40	1489	6	101
12	c, hd, p	503.7	1.56	172	0	0.00002	0.25570	0.00780	3.27913	0.10248	0.09301	0.00037	1468	40	1488	8	99
13	c, hd, p	214.3	2.01	82	0	0.00002	0.26179	0.00966	3.35546	0.13642	0.09296	0.00121	1499	50	1487	25	101
14	e, osc, fr	344.4	0.95	103	7	0.00151	0.26040	0.00702	3.31344	0.09586	0.09229	0.00071	1492	36	1473	15	101

x,y: grain number followed by analysis number.

Grain habit: p, prism; eq, equant; rd, rounded; fr, fragment.

Site: e, end or edge; m, middle; r, rim/overgrowth; c, core.

Cl image microstructure: osc, oscillatory zoning; h, homogeneous (d, dark or b, bright).

With asterisk: total Pb in ppm.

Without asterisk: isotopic ratios corrected for measured ^{204}Pb . $^{207}\text{Pb}/^{206}\text{Pb}$ data corrected with 900 Ma model Pb of Cumming and Richards (1975).

All errors are 1s.

Table 4 $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende analytical results for the GD-456 sample (longitude: -48.30049° , latitude: -24.589437° , WGS-84 datum), J factors (0.003744 ± 0.000014), system blanks, and $^{40}\text{Ar}/^{36}\text{Ar}$ discrimination (1.0016 ± 0.0034) for the UQ-AGES. The uncertainties are given at the 1σ level.

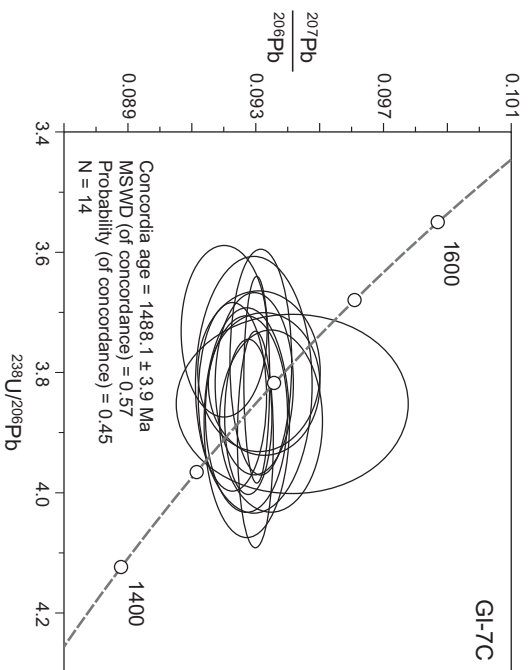
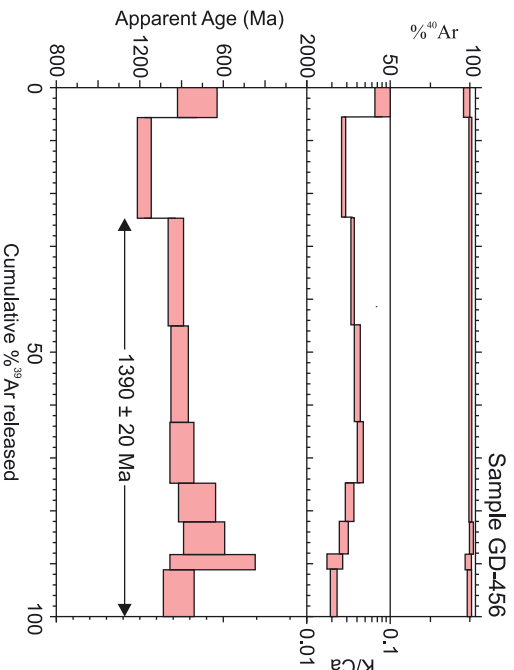
Run ID	$^{36}\text{Ar}/^{39}\text{Ar}$ Error 1σ	$^{37}\text{Ar}/^{39}\text{Ar}$ Error 1σ	$^{38}\text{Ar}/^{39}\text{Ar}$ Error 1σ	$^{40}\text{Ar}/^{39}\text{Ar}$ Error 1σ	$^{40}\text{Ar}^*/^{39}\text{Ar}$ Error 1σ	%Ar 40 * Error 1σ	Age (Ma) Error 1σ	EMV Axial	Ar 39 Moles	Ar 40 Moles
01A	0.0351 ± 0.0094	6.13 ± 0.61	0.0034 ± 0.0024	344 ± 16	335 ± 16	97.12 ± 0.84	1467 ± 49	1.533665	$1.36\text{E}-17$	$4.67\text{E}-15$
01B	0.0077 ± 0.0028	18.74 ± 0.41	0.0034 ± 0.00085	253.2 ± 4.6	255.7 ± 4.8	99.68 ± 0.37	1212 ± 17	1.533665	$4.57\text{E}-17$	$1.16\text{E}-14$
01C	0.0038 ± 0.0027	14.49 ± 0.39	0.0074 ± 0.0011	299.9 ± 5.6	303 ± 5.8	100.01 ± 0.32	1368 ± 18	1.533663	$4.91\text{E}-17$	$1.47\text{E}-14$
01D	0.0042 ± 0.0021	13.08 ± 0.37	0.0076 ± 0.0013	305.6 ± 5.9	308.2 ± 6.1	99.93 ± 0.27	1384 ± 19	1.533670	$4.39\text{E}-17$	$1.34\text{E}-14$
01E	0.0061 ± 0.0032	12.43 ± 0.51	0.0066 ± 0.0015	309.5 ± 8.7	311.4 ± 8.9	99.73 ± 0.35	1394 ± 28	1.533656	$2.77\text{E}-17$	$8.58\text{E}-15$
01F	0.0034 ± 0.005	16.6 ± 1.1	0.0043 ± 0.0022	331 ± 14	335 ± 15	100.09 ± 0.48	1467 ± 44	1.533664	$1.75\text{E}-17$	$5.80\text{E}-15$
01G	0.0026 ± 0.0064	18.8 ± 1.3	0.0089 ± 0.0028	341 ± 16	346 ± 17	100.2 ± 0.6	1499 ± 50	1.533672	$1.47\text{E}-17$	$5.00\text{E}-15$
01H	0.025 ± 0.012	23.6 ± 2.5	0.0039 ± 0.0047	360 ± 34	360 ± 35	98.5 ± 1.1	1540 ± 100	1.533677	$7.03\text{E}-18$	$2.53\text{E}-15$
01I	0.0128 ± 0.0061	26.3 ± 1.1	0.0073 ± 0.0018	303 ± 11	306 ± 12	99.43 ± 0.63	1379 ± 36	1.533679	$2.12\text{E}-17$	$6.42\text{E}-15$
02A	0.136 ± 0.048	19.5 ± 4.6	0.0073 ± 0.0095	1930 ± 410	1910 ± 420	97.99 ± 0.61	3790 ± 350	1.533695	$3.60\text{E}-18$	$6.94\text{E}-15$
02B	0.0163 ± 0.0044	20.84 ± 0.64	0.0052 ± 0.0014	308 ± 7.8	309.4 ± 8.1	98.97 ± 0.49	1388 ± 25	1.533693	$3.09\text{E}-17$	$9.53\text{E}-15$
02C	0.0072 ± 0.002	15.61 ± 0.27	0.0074 ± 0.00073	310.6 ± 4	313.1 ± 4.1	99.7 ± 0.26	1400 ± 13	1.533688	$8.76\text{E}-17$	$2.72\text{E}-14$
02D	0.0062 ± 0.0032	15.56 ± 0.44	0.0043 ± 0.00097	269.2 ± 6.4	271.6 ± 6.6	99.77 ± 0.45	1265 ± 22	1.533688	$3.87\text{E}-17$	$1.04\text{E}-14$
02E	0.0076 ± 0.002	13.54 ± 0.34	0.0054 ± 0.0011	309.3 ± 5.9	311 ± 6.1	99.61 ± 0.28	1393 ± 19	1.533690	$5.16\text{E}-17$	$1.60\text{E}-14$
02F	0.0173 ± 0.0056	13.9 ± 0.66	0.0053 ± 0.0018	279 ± 10	277 ± 11	98.56 ± 0.63	1285 ± 35	1.533683	$2.18\text{E}-17$	$6.08\text{E}-15$
02G	0.009 ± 0.0065	20.07 ± 0.89	0.0069 ± 0.0021	318 ± 12	322 ± 13	99.66 ± 0.63	1427 ± 39	1.533684	$1.91\text{E}-17$	$6.08\text{E}-15$
02H	0.0123 ± 0.0038	22.58 ± 0.8	0.0068 ± 0.0017	352 ± 11	356 ± 11	99.47 ± 0.4	1528 ± 32	1.533686	$2.68\text{E}-17$	$9.44\text{E}-15$
02I	0.048 ± 0.012	29.4 ± 2.1	0.002 ± 0.0033	788 ± 50	792 ± 52	98.48 ± 0.52	2486 ± 88	1.533690	$1.17\text{E}-17$	$9.19\text{E}-15$

 $^{40}\text{Ar}^*$ is the total amount of radiogenic ^{40}Ar obtained by subtracting the atmospheric ^{40}Ar and ^{40}ArK from the total ^{40}Ar measured from the sample.

Table 5

Sm/Nd and Rb/Sr analytical results for metabasic rocks of the Votuverava Group.

Sample	Group	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	Error	$^{143}\text{Nd}/^{144}\text{Nd}$	Error	$\varepsilon_{\text{Nd}}(t)$	T_{DM}^a (Ma)	Rb (ppm)	Sr (ppm)	Rb $^{87}/\text{Sr}^{86}$	Error	Sr $^{87}/\text{Sr}^{86}$	Error	Sr $^{87}/\text{Sr}^{86}(t)$
GD-109A	B1	2.397	7.923	0.1829	0.0006	0.512609	0.000006	2.06	1750	1.00	236.50	0.0122	0.0001	0.70710	0.00008	0.70684
GI-6	B1	0.738	2.090	0.2137	0.0007	0.512809	0.000016	0.10	1891	11.93	93.18	0.3707	0.0029	0.71438	0.00003	0.70645
GI-7C	B1	0.707	2.020	0.2117	0.0007	0.512846	0.000011	1.21	1813	6.83	113.25	0.1746	0.0014	0.71200	0.00008	0.70827
GI-7D	B1	2.112	6.524	0.1958	0.0007	0.512748	0.000009	2.32	1733	0.31	170.66	0.0052	0.0000	0.71048	0.00004	0.71037
IP-638B	B1	0.864	2.516	0.2075	0.0008	0.512857	0.000013	2.22	1740	0.34	143.15	0.0068	0.0001	0.70471	0.00003	0.70456
M-161G	B1	1.342	3.836	0.2115	0.0022	0.512914	0.000010	2.57	1716	11.51	182.15	0.1833	0.0014	0.72971	0.00011	0.72579
GI-8	B1	1.454	3.884	0.2264	0.0008	0.512967	0.000008	0.77	1844	92.6	194.6	1.3800	0.0080	0.72397	0.00001	0.69466
AP-126B	B2	3.317	12.094	0.1658	0.0006	0.512488	0.000008	2.95	1686	1.08	336.50	0.0093	0.0001	0.71466	0.00002	0.71446
F-36	B2	3.294	9.687	0.2056	0.0007	0.51257	0.000011	−3.02	2112	1.47	281.88	0.0151	0.0001	0.71356	0.00002	0.71324
GD-541	B2	2.823	9.237	0.1848	0.0006	0.512658	0.000011	2.65	1708	7.34	146.13	0.1453	0.0011	0.70540	0.00006	0.70229
IP-37B	B2	2.832	9.315	0.1838	0.0006	0.512636	0.000010	2.41	1725	0.77	433.52	0.0052	0.0000	0.70933	0.00001	0.70922
AP-136	B3	3.478	13.409	0.1568	0.0006	0.512431	0.000008	3.55	1643	0.79	306.94	0.0075	0.0001	0.70506	0.00001	0.70490
GD-456	B3	3.380	12.963	0.1577	0.0005	0.512424	0.000010	3.24	1665	6.89	370.39	0.0538	0.0004	0.70551	0.00006	0.70436
GI-14	B3	5.363	21.865	0.1483	0.0005	0.512344	0.000011	3.46	1648	4.98	299.58	0.0481	0.0004	0.70641	0.00002	0.70538

^a Calculated by the two-stage evolution.**Fig. 8.** Tera-Wasserburg $^{206}\text{Pb}/^{238}\text{U}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ diagram with SHRIMP zircon U–Pb data of sample GI-7C (Votuverava metabasite). Errors are depicted at the 1σ level.**Fig. 9.** Incremental-heating spectra for an igneous hornblende grain of sample GD-456, a greenschist facies metabasic rock from the Nhunguara Formation (Votuverava Group).

The relationships between the Nb/Yb and TiO_2/Yb ratios suggest that the B1 and B2 samples were generated by shallow melting (Fig. 12a; Pearce and Peate, 1995; Pearce and Stern, 2006; Pearce, 2008). This compositional pattern is expected and observed in mid-ocean ridge basalts and in subduction-related basalts (e.g., Pearce and Peate, 1995; Pearce and Stern, 2006; Pearce, 2008). Conversely, the B3 samples display Ti contents slightly higher than the mantle array (Fig. 12a), suggesting a deeper melting, which could suggest plume interactions (Pearce, 2008). The Nb/Yb ratios also indicate progressively more fertile mantle sources from B1 to B3 (Fig. 12a, b).

The overall compositional distribution of the Votuveravametabasites is similar to the geochemical patterns found in modern environments of mid-ocean ridges interacting with plumes, such as the Galapagos System, the Iceland–Reykjanes Ridge System and the South American–Antarctica Ridge (Pearce, 2008 and references therein). A very similar pattern is found in basalts from the East Scotia Ridge oceanic back-arc basin (Fig. 12a–d), which interacts with a plume associated with Bouvet Island (Leat et al., 2000; Fretzdorff

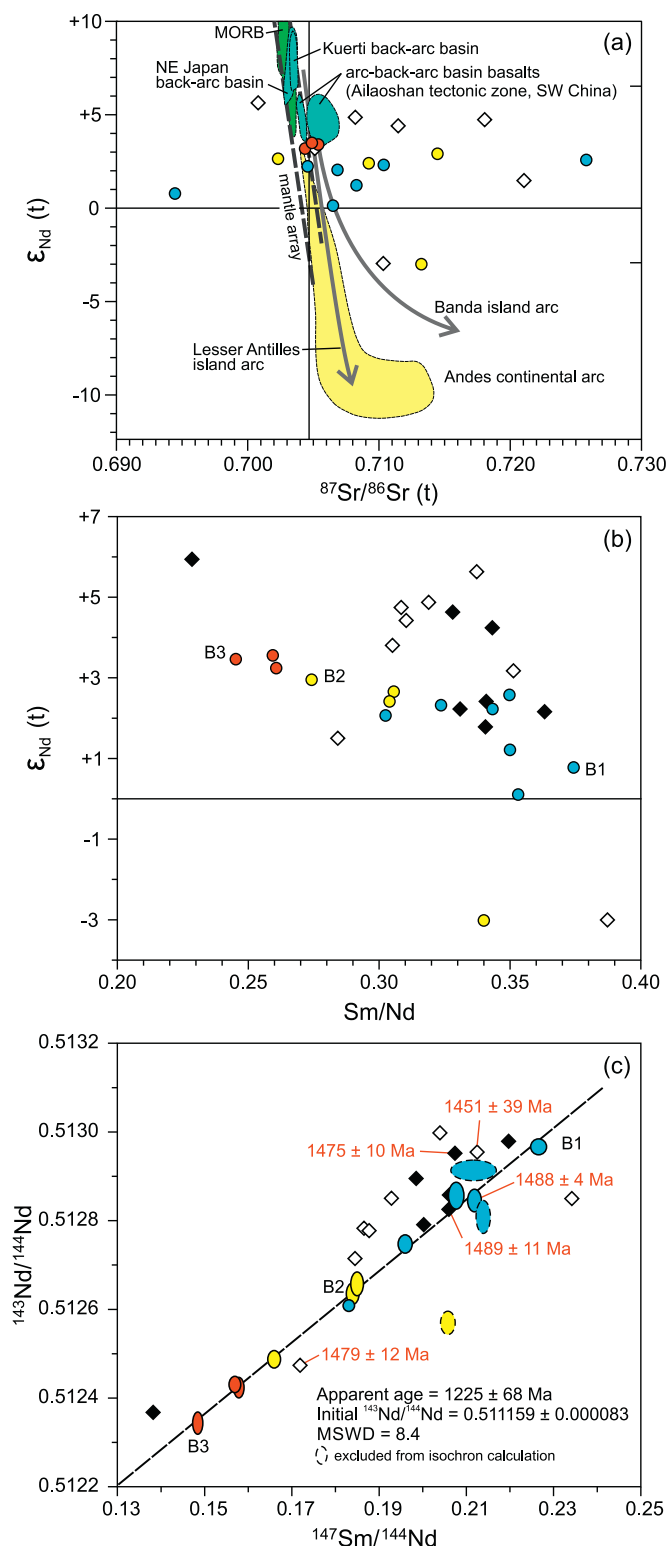


Fig. 10. Plot of initial $^{87}Sr/^{86}Sr(t)$ versus $\epsilon_{Nd}(t)$ ($t = 1480$ Ma). (a) Data fields and trends: MORB and mantle array (Winter, 2010), back-arc basin basalts (Shuto et al., 2006; Jian et al., 2008, 2009a,b; Fan et al., 2010), island arc and continental arc volcanics (McCulloch et al., 1994; Winter, 2010). (b) Plot of Sm/Nd versus $\epsilon_{Nd}(t)$. (c) Sm/Nd isochron diagram of Votuverava metabasites with error ellipses stated at the 2σ level. Also shown are the available zircon U–Pb age data. Circles and ellipses are data from this work. Diamonds are data compiled from Siga et al. (2011a) (white) and Siga et al. (2011b) (black).

et al., 2002). Part of the Votuverava metabasites display Th/Yb ratios higher than the mantle array (Fig. 12b, c), consistent with a variable contribution of the subduction component to the source of the magmatism. The overall geochemical distribution is consistent with a partial association with a subduction component and MORB-type mantle sources and with MORB-type and plume mantle sources. The LILE mobility during metamorphism precludes distinguishing whether the subduction component is dominated by slab-derived fluid or subducted sediment because elements that are abundant in slab-derived fluids (Cs, Ba, Rb, K, Pb, Sr) are more mobile during metamorphism.

5.4. Age of the basic magmatism

Considering the general difficulty in dating mafic rocks by the zircon U–Pb method, the significance of the concordia age of 1488 ± 4 Ma obtained for the GI-7C sample (B1 group) should be discussed. Fourteen U–Pb SHRIMP analyses performed on 14 zircon grains were used in the calculation of the concordia age. Analytically, therefore, the age is of high quality. Conversely, it is necessary to demonstrate whether this age represents the time of the igneous protolith crystallization, inheritance or a metamorphic age.

The third hypothesis should be disregarded because there are no metamorphic zircon overgrowths, and petrographic evidence indicates that the GI-7C sample was affected by lower greenschist facies metamorphism. Several lines of evidence favor the first hypothesis: (1) the analyzed zircon grains are xenomorphic, and there are no rounded (typical of detrital or resorbed xenocrystic) grains (Fig. 7); (2) the dominant textural characteristics of the dated zircon grains, with unzoned or poorly zoned grains (grains 1, 2, 4, 5, 6, 8, 9, 11, 12, Fig. 7) and grains with sector zoning (grains 3 and 13, Fig. 7), are typical of zircon from mafic rocks; (3) there are no prismatic zircon grains with well-defined oscillatory zoning typical of felsic magmas; (4) a single-age population is unexpected for inherited detrital or xenocrystic zircon grains; (5) available zircon U–Pb (SHRIMP and ID-TIMS) data for mafic rocks from the Votuverava Group (Fig. 2; Siga et al., 2011a) and the Betara Formation (Siga et al., 2011b) yielded average ages ranging from 1451 to 1489 Ma, which are, within errors, consistent with the data from sample GI-7C; and (6) there is no detrital zircon population of ca. 1490 Ma in the metasedimentary host rocks, which are largely dominated by zircon ages ≥ 2000 Ma (Basei et al., 2008; Campanha et al., 2009; Faleiros et al., 2012, 2015; Faleiros and Pavan, 2013). Thus, the concordia age of 1488 ± 4 Ma is best interpreted as an igneous protolith crystallization age.

Elemental and isotopic data (Figs. 4b, f, 10, 12; Siga et al., 2011a,b) suggest that all available zircon U–Pb ages come from metabasites with B1 group (BABB-like) chemical signatures. Nonetheless, with the currently available geochronological data, it is not possible to assign different ages to the subunits of the Votuverava Group because B1 rocks occur in all subunits. Thus, we contend that it is most likely that they are related to the same overall ca. 1490 Ma age, as suggested by all available zircon U–Pb data (this work; Siga et al., 2011a,b). Similar zircon U–Pb ages of ca. 1500 Ma were also reported for metabasic rocks from the Água Clara Formation (Fig. 1b) (Weber et al., 2004). Chemical data indicate that the Água Clara Formation metabasites also have BABB-like signatures (Maniesi, 1997), corroborating extensive Calymmian back-arc basin magmatism in the southern Ribeira Belt.

The hornblende ^{40}Ar – ^{39}Ar age of 1390 ± 20 Ma obtained for the GD-456 sample (B3 group) is approximately 100 Ma younger than the zircon U–Pb ages obtained for the Votuverava samples (this work; Siga et al., 2011a,b). This indicates the closure temperature age for ^{40}Ar – ^{39}Ar in hornblende (500–450 °C).

The Sm–Nd results obtained from the Votuverava metabasites plotted in a ^{143}Nd – ^{144}Nd versus ^{147}Sm – ^{144}Nd diagram mostly

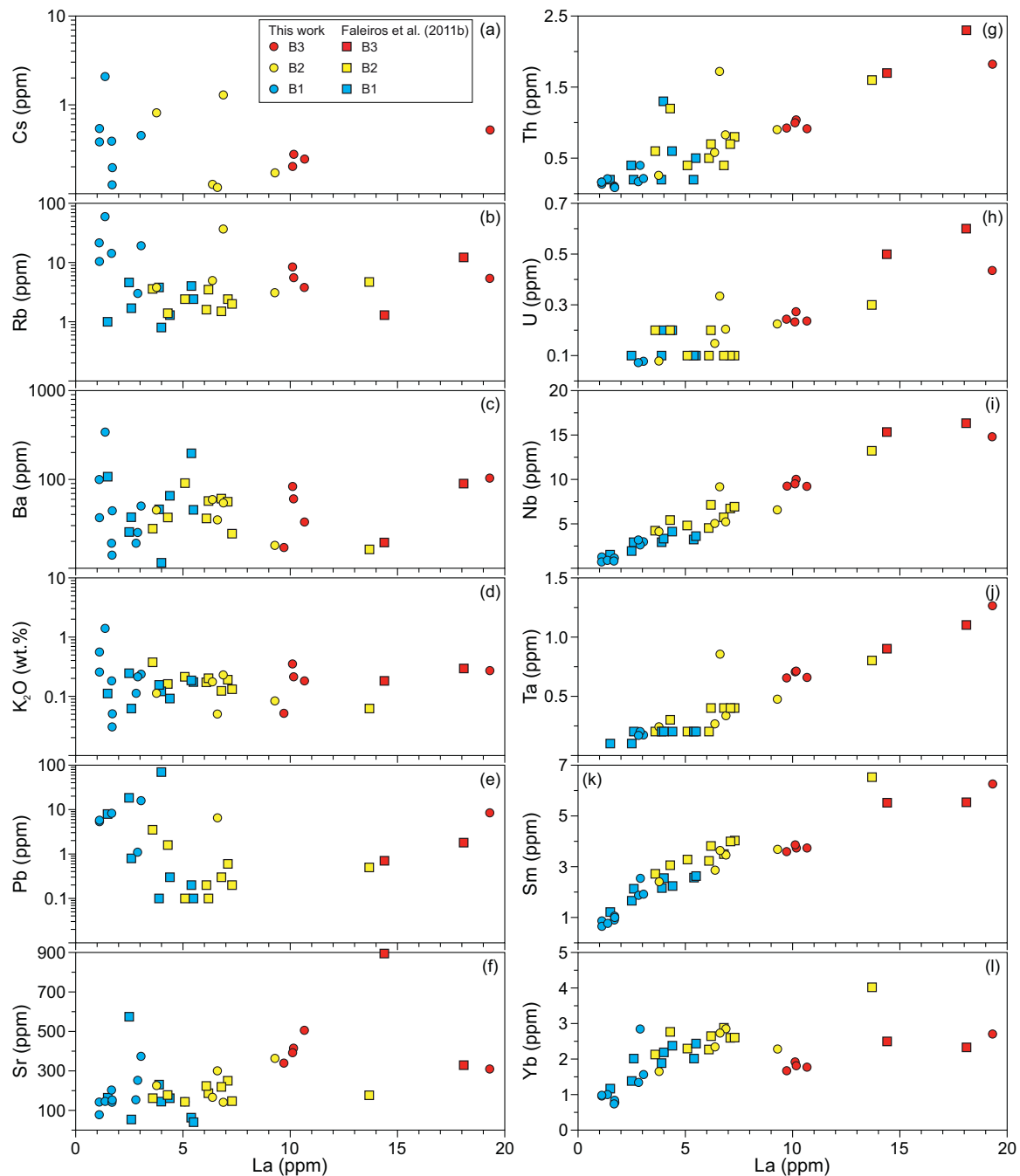


Fig. 11. Plots of La versus LILE (Cs, Rb, Ba, K₂O, Pb, Sr) (a–f) and HFSE (Th, U, Nb, Ta, Sm, Yb) (g–l) contents.

form a linear array with a slope equivalent to $1225 \text{ Ma} \pm 68 \text{ Ma}$ (MSWD=8.4) (Fig. 10c). This apparent age is approximately 270 million years younger than the zircon U–Pb ages and cannot represent the igneous crystallization. As discussed above, the REE abundances were mostly unmodified during metamorphism, and thus, this apparent age cannot reflect a metamorphic event. Geochemical and Nd isotopic data indicate that the Votuverava metabasites show heterogeneous sources, and therefore, it is improbable that all of the samples had the same initial $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios. Thus, the slope in the $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ space might reflect a mixing line of no age significance due to different source components for the basic magmatism, as described by Chauvel et al. (1985) and Friend et al. (2009). In similar cases, depending on the nature of the mixing components, the apparent

age may be too older (Chauvel et al., 1985) or too younger (Friend et al., 2009) than the igneous crystallization age.

5.5. Regional geotectonic implications

Geological mapping and available U–Pb geochronological data (this work; Juliani et al., 2000; Weber et al., 2004; Siga et al., 2011a,b; Faleiros et al., 2012, 2015; Faleiros and Pavan, 2013; Henrique-Pinto et al., 2015) demonstrate the existence of a 500-km-long and 60-km-wide belt composed essentially of ca. 1400–1500 Ma Mesoproterozoic units in the southern and central domains of the Ribeira Belt (Fig. 1b). The age at which this terrane was last a coherent block is still uncertain, primarily due to an intense overprint of Neoproterozoic orogenic metamorphism

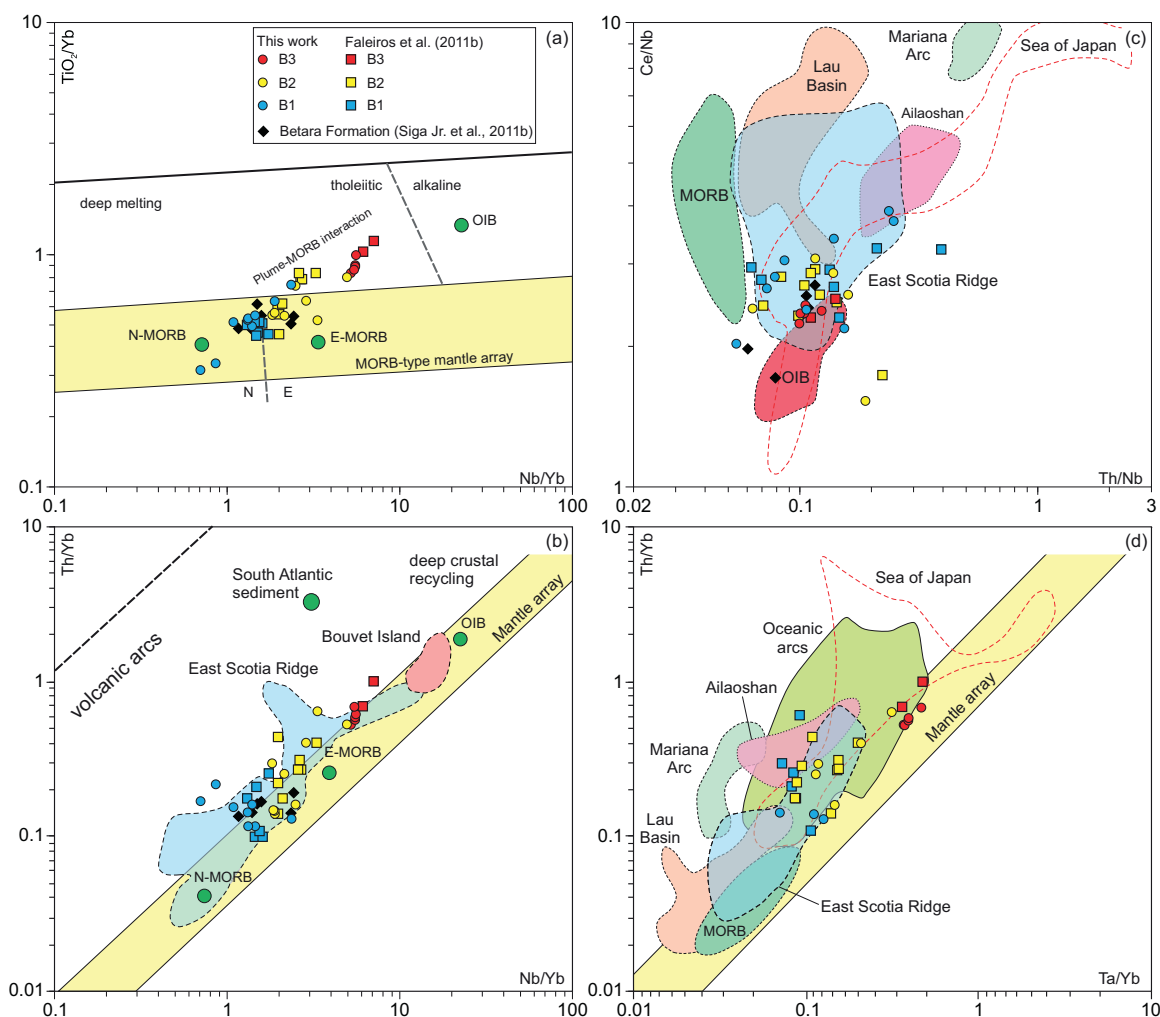


Fig. 12. Petrogenetic and tectonic discriminant diagrams with geochemical data of Votuverava metabasites. (a) Nb/Yb versus TiO_2/Yb plot (after Pearce, 2008), (b) Nb/Yb versus Th/Yb plot (after Pearce, 2008), (c) Th/Nb versus Ce/Nb plot (modified from Sandeman et al., 2006), (d) Ta/Yb versus Th/Yb plot (after Pearce, 1982). Data fields: East Scotia Ridge, Bouvet Island and South Atlantic sediments (Leat et al., 2000; Fretzdorff et al., 2002); Sea of Japan (Poulet et al., 1994); Mariana Arc (Elliott et al., 1997); MORB and OIB (Pearce, 1982); Lau Basin (Pearce et al., 1994); Ailaoshan Tectonic Zone (Fan et al., 2010).

and deformation (Juliani et al., 2000; Faleiros et al., 2010, 2011a). The geological, geochemical and geochronological data presented in this work, in conjunction with available data (Maniesi, 1997; Weber et al., 2004; Siga et al., 2011a,b), suggest the existence of extensive ca. 1490 Ma oceanic back-arc basic magmatism recorded in the southern Ribeira Belt.

In a global perspective, a basic magmatism of ca. 1500–1450 Ma age is reported worldwide in Paleoproterozoic cratonic fragments, as in the São Francisco Craton in Brazil (Silveira et al., 2013) and its African counterpart (Congo Craton) in Angola (Ernst et al., 2012), the Siberia Craton (Ernst et al., 2000, 2008), the Tarim Craton in northwestern China (Wu et al., 2014), the Yangtze Block in southern China (Fan et al., 2013), the Bastar Craton of India (Pisarevsky et al., 2013) and in Baltica (Lubnina et al., 2010). Some of these occurrences were used as evidence for the Columbia configuration of Lubnina et al. (2010) and Silveira et al. (2013), while others inferred this as extensional intracratonic magmatism associated with the breakup of Columbia (e.g., Fan et al., 2013; Wu et al., 2014). Geological, geochronological and Hf isotope data of detrital zircon grains from around the world support the interpretation that the Columbia supercontinent remained a quasi-integral entity throughout the period of 1800–1300 Ma (Roberts, 2012, 2013). Hf data in the detrital zircons indicate largely juvenile signatures during the 1700–1300 Ma period, indicating

a dominance of accretionary orogens related to plate margins (Roberts, 2012, 2013). During the Ediacaran (West Gondwana time), this Mesoproterozoic belt was located between the Paranapanema and Congo Cratons, apparently as an exotic terrane (*sensu* Howell, 1995). The Paranapanema Craton is completely covered by Paleozoic sedimentary rocks from the Paraná Basin (Fig. 1a) and was recognized by data from deep boreholes and geophysical studies (Mantovani and Brito Neves, 2005), precluding detailed studies to reveal its geotectonic relationships.

The existence of the Calymmian belt in the Ribeira Belt raises the possibility of records of orogenic activity older than the Neoproterozoic Brasiliano–Pan African cycle. Available Rb–Sr ages obtained in rocks from the Votuverava Group are 1212 ± 55 Ma (Batolla et al., 1981; Teixeira, 1982) and 1283 ± 28 Ma (Daitx, 1996). Recently, a ^{40}Ar – ^{39}Ar age of 1120 ± 70 Ma was obtained from muscovite grains present in a subhorizontal S_1 slate cleavage of a Votuverava phyllite (Cury et al., 2008). These ages suggest the presence of a Grenvillian-age tectono-metamorphic event in the southern part of the Ribeira Belt. Additionally, a ca. 1100 Ma inheritance has been recognized in zircon grains from Ediacaran granites intrusive in the Embu Terrane (Alves et al., 2013), a unit adjacent to the Votuverava Group (Fig. 1b). Speculatively, the available data could indicate that the ca. 1490 Ma Votuverava Group back-arc system could have been involved in a 1280–1100 Ma collisional

orogeny related with the Rodinia assembly, as reported from elsewhere in the world (Roberts, 2013).

6. Conclusions

- (1) Metabasic rocks in the Votuverava Group are derived in part from volcanism and in part from coeval intrusions and are largely basaltic in composition.
- (2) SHRIMP U–Pb zircon geochronology on a metabasic sample yielded high Th/U magmatic zircons with an age of 1488 ± 4 Ma, which is interpreted as the time of igneous crystallization.
- (3) Sm–Nd results obtained from metabasites plotted in a ^{143}Nd – ^{144}Nd versus ^{147}Sm – ^{144}Nd diagram mostly form a linear array with a slope of 1225 Ma, which is interpreted as a mixing line of no age significance that is related to different source components for the metabasic rocks.
- (4) The trace element and Nd–Sr isotopic chemistry of the metabasic rocks suggests that they were most likely emplaced into a back-arc environment. Essentially positive $\varepsilon_{\text{Nd}}(t)$ values (+0.10 to +3.55) suggest a dominant juvenile mantle source to the basic magmatism.
- (5) The 1490 Ma mafic magmatism is associated with a 500-km-long and 60-km-wide Calymmian belt interpreted as the back-arc component of an accretionary orogen.
- (6) The available thermochronological data suggest that the ca. 1490 Ma Votuverava Group was involved in a 1280–1100 Ma collisional orogeny, possibly related to the Rodinia assembly.

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