1. Introduction

In the central portion of the Ribeira fold belt (Almeida, Amaral, Cordani, & Kawashita, 1973), southeastern Brazil, the Mesoproterozoic volcanosedimentary Serra do Itaberaba Group was deposited in an ocean basin having normal mid-ocean ridge basalt type basaltic rocks that evolved to a back-arc environment. This succession was affected by two medium-grade regional metamorphic events and a third low-grade retro metamorphic event. This geological map covers an area of approximately 16 km², between 23°16'41.824" and 23°18'47.744" latitudes S, and 46°20'57.056" and 46°23'18.933" longitudes W, as a scale of 1:5000. It encompasses the metamorphic products of tectonically deformed paleohydrothermal systems that developed in a back-arc environment, which are spatially and genetically linked to small metamorphosed andesitic-rhyolitic bodies. These systems were responsible for lixiviating of Ca and alkali in deeper parts, carbonatization in shallower parts, and a first large chloritic alteration zone (CZ1) that was crosscut by small chloritic (CZ2), silification, and advanced argillic alteration zones. The metamorphic products of CZ1 are cummingtonite/anthophyllite rocks, whereas those related to CZ2 are Mg- rich chloritites. The metamorphic products of silification and advanced argillic alteration zones are rocks composed of quartz ± specularite and of corundum, margarite, sericite, tourmaline, rutile, and Ca-plagioclase, respectively. Those associated with Ca and alkali depletions are garnet-hornblende amphibolites, whereas those related to carbonatization zones are composed of diopside, hornblende, tremolite/actinolite, carbonate, clinozoisite/epidote, plagioclase, and quartz. Cummingtonite/anthophyllite rocks and Mg-rich chloritites are similar to those associated with metamorphosed Kuroko-type volcanogenic massive sulfide deposits, whereas rocks composed of corundum, margarite, sericite, tourmaline, rutile, and Ca-plagioclase are genetically associated with oceanic high-sulfidation magmatic-hydrothermal gold mineralization.

Neoproterozoic, which record clockwise P-T-t paths with T and P corresponding to 490–650°C, 4–7 kbar and 500–580°C, 4–4.7 kbar, respectively. These events were followed by retrometamorphism in the greenschist facies (Juliani et al., 2000; Julián, Pérez-Aguilar, & Martin, 1997). The Serra do Itaberaba Group comprises, from the bottom towards the top, the Morro da Pedra Preta, Jardim Fortaleza, Nhanduçu, and Pirucaia formations (Juliani et al., in press) (Figure 2).

In the upper part of the Morro da Pedra Preta Formation, during the back-arc evolution, the emplacement of small shallow andesitic-rhyolitic bodies was responsible for the activity of paleohydrothermal systems that affected rocks before metamorphic events (Figure 3). Large chloritic alteration zones (CZ1) developed surrounding feeder zones, which are crosscut by small chloritic (CZ2), silification, and advanced argillic alteration zones (Pérez-Aguilar, 1996, 2001; Pérez-Aguilar, Julián, & Martin, 2000; Pérez-Aguilar, Julián, & Monteiro, 2007; Pérez-Aguilar, Julián, Monteiro, Falllick, & Bettencourt, 2005; Pérez-Aguilar et al.,
Lixiviation of Ca and alkali (Mm6GHA) occurred in deeper parts, which was associated with Ca enrichments in shallower parts (Mm12CAR). Metamorphosed Algoma-type banded-iron formations (BIFs), sulfide-rich metapelites, and gold mineralization are also genetically and spatially related with hydrothermal activity (Beljavskis, Garda, & Juliani, 1993; Beljavskis, Juliani, Garda, Xavier, & Bettencourt, 1999; Garda, Beljavskis, Juliani, & Boyce, 2002; Pérez-Aguilar et al., 2011). Tectonic deformations resulted in disruption and dislocation of the original hydrothermal altered rocks. The ZC1 and ZC2 were parallelized to the structures generated by tectonic deformation, but mainly to those related to the second deformation phase (S2). However, its roots are discordant and cut bedding (S0) inferring that the geometry of these zones broadly corresponds to inverted cone shapes that flare upward (Figure 3).

The metamorphic products of variable hydrothermally altered basic, intermediate, and acid igneous and volcaniclastic rocks related to CZ1, including...
weakly, transitional, moderately, and strongly hydrothermally altered rocks (Mm7CZ1, Mm8CZ1, Mm9CZ1, Mm10CZ1; see Figure 3), encompass rocks with the typical presence of Mg-amphibole(s), which are referred to as cummingtonite/anthophyllite rocks (Figures 4(a) and 5).

Despite the different original compositions of altered rocks, the metamorphic products of weakly altered rocks can be identified by the presence of small amounts of cordierite and/or cummingtonite or gedrite. Transitional rocks typically have two or more coexistent amphiboles (hornblende, hornblende/actinolite, actinolite, cummingtonite, or gedrite) and small amounts of cordierite and garnet may be present. Moderately altered rocks show total replacement of hornblende by anthophyllite and/or cummingtonite. Rocks may be garnet-free or garnet-bearing and cordierite, chlorite, and plagioclase may be present. Strongly altered rocks typically have radiate clusters of coarse-grained Mg-amphibole(s) (cummingtonite, anthophyllite, or gedrite) and Mg-cordierite poikiloblasts, and in addition variable amounts of almandine poikiloblasts may be present (Pérez-Aguilar, 1996, 2001; Pérez-Aguilar et al., 2007) (Figure 4(a)). A complete alteration profile can be seen in Figure 5. The metamorphic products of CZ2 include moderately and strongly altered tuffs (Mm11CZ2) that are referred to as Mg-rich chloritites. Moderately altered tuffs comprise rocks mainly composed of Al-rich hornblende and Mg-chlorite, which may have garnet. Strongly altered tuffs are mainly composed of Mg-chlorite, garnet, and cummingtonite (Figure 4(b)).

Rocks from CZ1 and CZ2 are similar to those described as associated with metamorphosed volcanic massive sulfide deposits (e.g. Chinner & Fox, 1974; Dobbe, 1994; Elliot-Meadows & Appleyard, 1991; James, Grieve, & Pauk, 1978; Pan & Fleet, 1995; Riverin & Hodgson, 1980; Roberts, Oliver, Fairclough, Holiti, & Lahtinen, 2003; Vallance, 1967).

The metamorphic products of silicification and advanced argillaceous alteration zones (Mm13SIL) are rocks composed of quartz ± specularite and of variable amounts of corundum, margarite, sericite, tourmaline, rutile, and Ca-plagioclase, respectively (Pérez-Aguilar et al., 2011) (Figure 4(c)). Those related to carbonatization zones are rocks composed of variable amounts of diopside, hornblende, tremolite/actinolite, epidote/clinozoisite, carbonate, plagioclase, and quartz (Mm12CAR) (Figure 4(d)). Silicification and advanced argillic alteration zones are genetically associated with oceanic high-sulfidation magmatic-hydrothermal gold mineralization (Juliani, Schorscher, & Pérez-Aguilar, 1994; Pérez-Aguilar et al., 2011), the latter do not appear at the scale of the map.

In the Morro da Pedra Preta Formation there are also units mainly composed of metabasites (Mm1), basic to intermediate metatuffs and metabreccias (Mm2), metatuffites (Mm3), metamorphosed intermediate to acid igneous rocks (Mm4), and calc-silicate rocks (Mm5) (Figure 3). Units mainly composed of muscovite-biotite schists (Mj1), graphite schists (Mj2), and rhythmic schists with alternating quartz-rich and muscovite- and/or biotite-rich layers (Mj3) were distinguished within the Jardim Fortaleza Formation (Figure 3). In the
Nhanguçu formation iron-manganiferous schists (Mn1) and muscovite-chlorite schists with andalusite porphyroblasts (Mn2) (Figure 3) were separated.

The São Roque Group is represented by the Estrada dos Romeiros Formation (Ne1) (Juliani et al., in press) that is mainly composed of rhythmic schists with alternating quartz-rich and sericite/chlorite-rich layers. Neoproterozoic to Lower Paleozoic granitic rocks are present (Nv1), as well as Quaternary alluvial sediments (Q).

Related to rocks from the Serra do Itaberaba Group, plotted on the map are attitudes of bedding (S0), of the first and second deformation phases (S1 and S2) that developed under prograde metamorphism, and the third deformation phase (S3) that developed under retrograde metamorphism.

In the area massive sulfide deposits have not yet been found, although soil geochemical anomalies of copper and zinc have been identified (Juliani, 1993). The aim of this work is to present a detailed geological setting where the principal bodies of metamorphosed hydrothermally altered rocks outcrop within the Serra do Itaberaba Group, in order to better

Figure 4. Metamorphosed samples of: (a) a strongly altered rock from CZ1 of original intermediate composition, which is mainly composed of cummingtonite, anthophyllite, cordierite, and garnet; (b) a strongly altered tuff from CZ2 of original basic composition that is mainly composed of Mg-chlorite, cummingtonite, and garnet; (c) an advanced argillic alteration zone predominantly composed of corundum, margarite, and sericite with small amounts of Ca-plagioclase, tourmaline, and rutile; (d) a carbonatized tuff, dark-green areas correspond to preserved parts of a basic metavolcaniclastic rock, which was substituted by a rock mainly composed of carbonate, tremolite/actinolite, epidote/clinozoisite, plagioclase, and quartz; a, b, and d from Pérez-Aguilar et al. (2007).

Figure 5. Outcrop of intermediate-composition metavolcanicalastic rocks encompassing variable hydrothermally altered lithotypes related to CZ1: (1) weakly altered rocks, (2) transitional altered rocks with hornblende predominating over cummingtonite, (3) transitional altered rocks with cummingtonite predominating over hornblende, (4GF) garnet-free and (4GB) garnet-bearing moderately altered rocks, and (5) strongly altered rocks. Dark lines represent boundaries between different altered lithotypes (Pérez-Aguilar et al., 2005).
understand the geological setting, as well as stratigraphic and contact relations with other lithotypes.

2. Materials and methods

Within the area comprised by 23°16′41.824″ and 23°18′47.744″ latitudes S, and 46°20′57.056″ and 46°23′18.933″ longitudes W, covering an area of approximately 16 km², fieldwork was carried out in order to produce a 1:5000 scale geological map. All roads, drainages, and several trails were covered. A higher density of outcrops were described where the main bodies of hydrothermally altered rocks outcrop, including adjacent areas, in order to better establish the geometry of bodies, as well as stratigraphic and contact relations. A total of 696 outcrops were described and information on 55 outcrops collected by Juliani (1993) was also used.

Field data were transferred to a 1:5000 topographic map from the study area, which was built up expanding the Serra do Itaberaba, Pedra Branca, Vasconcelândia, and Itaberaba topographic maps available as a scale of 1:10000 (sheets 85/109, 85/110, 86/109 from the Instituto Geográfico e Cartográfico, IGC, and sheet 4423 from the Empresa Paulista de Planejamento Metropolitano,EMPLASA, both from São Paulo State). A total of 320 rock samples were collected during fieldwork from which 140 petrographic thin sections were made and described, in order to better understand the hydrothermal alteration processes and contact relations.

3. Conclusions

Long-lived premetamorphic paleohydrothermal systems were characterized in the Mesoproterozoic volcanosedimentary Serra do Itaberaba Group that outcrops in southeastern Brazil. Systems developed during emplacement of andesitic-rhyolitic bodies in an evolving back-arc environment and encompass the tectonic deformed metamorphic products of Ca and alkali depleted basic rocks (garnet-hornblende amphibolites) and of chloritic (cummingtonite/anthophyllite rocks and Mg-rich chloritites), silicification (rocks composed of quartz ± specularite), advanced argillic (rocks composed of corundum, margarite, sericite, tourmaline, plagioclase, and rutile), and carbonatization (rocks composed of hornblende, diopside, tremolite/actinolite, clinozoisite/epidote, carbonate, plagioclase, and quartz) zones.

Despite those related to advanced argillic alteration zones, the metamorphic products of the other hydrothermal alteration zones could be represented in a geological map of metamorphic rocks deriving from paleohydrothermal systems at a scale of 1:5000.

The identification of the metamorphic products of paleohydrothermal systems, similar to those associated with Kuroko-type base metal and gold mineralization (e.g. Ishihara, Kanehira, Sasaki, Sato, & Shimazaki, 1974; Shikazono, 2003), expands the potential for base metal and gold deposits within the Serra do Itaberaba Group and the metamorphosed volcanosedimentary successions from the Ribeira fold belt. In this context, activity of black smokers was responsible for the presence of metalliferous sediments within the back-arc environment (e.g. Fouquet et al., 1991).

During fieldwork the identification of cummingtonite/anthophyllite rocks, Mg-rich chloritites, and rocks composed of corundum, margarite, sericite, tourmaline, plagioclase, and rutile can be used as exploration guides in these successions, in order to support prospecting work.

Software

The geological 1:5000 map was first drawn on paper, after which it was scanned and georeferenced in order to produce the geological map and coupled profile using Esri ArcGIS 10.2. The digital elevation model (DEM) was built using the digital surface model from EMPLASA (2010) with a spatial resolution of ca. 1 m.

Acknowledgements

The authors are grateful to Antônio Luiz Teixeira and José Antonio Ferrari for support in handling ArcGIS, to Ricardo Oliveira Santos for helping with ArcGIS related work, and to reviewers Giovanni Musumeci, Heike Apps, and Gustavo Côrrea de Abreu, who significantly improved the map and manuscript.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors thank the São Paulo Research Foundation (FAPESP) [grant number 93/4350-0], [grant number 98/15170-7] and to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for research [grant number 400490-94-3] and for Master and Ph.D. scholarships granted to Annabel Pérez-Aguilar.

ORCID

Annabel Pérez-Aguilar ⓐ http://orcid.org/0000-0003-2476-5502
Caetano Juliani ⓐ http://orcid.org/0000-0002-0128-993X

References

Almeida, F. F. M., Amaral, G., Cordani, U. G., & Kawashita, K. (1973). The Precambrian evolution of the South American cratonic margin south of Amazon river. In A. E. M. Nairn, & F. G. Stehli (Eds.), The ocean basin and margins (Vol. 1, pp. 411–446). New York, NY: Plenum.

Almeida, F. F. M., Hasui, Y., Ponçano, W. L., Dantas, A. S. L., Carneiro, C. D. R., Melo, M. S., & Bistričić, C. A. (1981).
A. PÉREZ-AGUILAR AND C. JULIANI

Mapa geológico do Estado de São Paulo, escala 1:500.000 – Nota Explanativa, v.1. São Paulo: Instituto de Pesquisas Tecnológicas.

Beljavskis, P., Garda, G. M., & Juliani, C. (1993). Características das mineralizações auríferas no Grupo Serra do Itaberaba, Guarulhos, SP. Revista do Instituto Geológico, 14, 21–29. doi:10.5935/0100-929X.19930002

Beljavskis, P., Juliani, C., Garda, G. M., Xavier, R. P., & Bettencourt, J. S. (1999). Overview of the gold mineralization in the meta volcanic-sedimentary sequence of the Serra do Itaberaba Group, São Paulo, Brazil. In C. J. Standley, A. H. Rankin, R. J. Bodnar, N. J. Naden, B. W. D. Yardley, A. J. Cridle, … R. A. Iscer (Eds.), *Mineral deposits: Processes to processing 1* (pp. 151–153). Rotterdam: Balkema.

Chinner, G. A., & Fox, J. S. (1974). The origin of cordierite-anthophyllite rocks in the land’s end aureole. *Geological Magazine*, 111(5), 397–408. doi:10.1017/S0016756800039959

Dobbe, R. T. M. (1994). Geochemistry of cordierite-anthophyllite rocks, Tunaberg, Bergslagen, Sweden. *Economic Geology*, 89, 919–930. doi:10.2113/gsecongeo.89.4.919

Elliott-Meadows, S. R., & Appleyard, E. C. (1991). The alteration geochemistry and petrology of the Lar Cu-Zn deposit, Lynn Lake area, Manitoba, Canada. *Economic Geology*, 86, 486–505. doi:10.2113/gsecongeo.86.3.486

EMPLASA. (2010). *Modelo Digital de Superfície. Produtos de levantamento aero fotogramétrico de 2010–2011*. [Unpublished Report].

Gardia, G. M., Beljavskis, P., Juliani, C., & Boyce, A. J. (2002). Sulfur stable isotope signatures of the Morro da Pedra Preta Formation, Serra do Itaberaba Group, São Paulo State, Brazil. *Geochimica Brasiliensis*, 16, 79–97.

Hacksparser, P. C., Dantas, E. L., Spoladore, A., Fetter, A. H., & Oliveira, M. A. F. (2000). Evidence for neoproterozoic backarc basin development in the central Ribeira Belt, southeastern Brazil: New geochronological and geochemical constraints from the Sào Roque-Açungui groups. *Revista Brasileira de Geociências*, 30(1), 110–114.

Hacksparer, P. C., Juliani, C., Fetter, A., & Dantas, E. L. (2001). Evolution of the central Ribeira Belt, Brazil: Implications for the assembly of west Gondwana. *Gondwana Research*, 4(4), 626–627. doi:10.1016/S1342-937X(05)70430-5

Ishihara, S., Kanehira, K., Sasaki, A., Sato, T., & Shimazaki, Y. (1974). *Geology of the Kuroko deposits*. The society of mining geologists of Japan, Mining Geology Special Issue 6, 435 p.

James, R. S., Grieve, R. A. F., & Pauk, L. (1978). The petrology of cordierite-anthophyllite gneisses and associated mafic and pelitic gneisses at Manitouwadge, Ontario. *American Journal of Science*, 278, 41–63. doi:10.2475/ajs.278.1.41

Juliani, C. (1993). *Geologia, petrogênese e aspectos metalogênicos dos grupos Serra do Itaberaba e São Roque na região das serras do Itaberaba e da Pedra Branca, NE da cidade de São Paulo, SP* (Unpublished PhD Thesis).

Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.

Juliani, C., & Beljavski, P. (1995). Revisão da litoestratigrafia da faixa São Roque/Serra do Itaberaba (SP). *Revista do Instituto Geológico*, 16, 33–58. doi:10.5935/0100-929X.19950003

Juliani, C., Fernandes, C. M. D., Pérez-Aguilar, A., Monteiro, L. V. S., Salazar, A., Londono, A. B., … Rosensaat, M. (in press) *Geologia da Folha Leste de Aitibaia (SF-23-Y-D-I) – Escala 1:100.000*. Programa Geologia do Brasil – Levantamentos Geológicos Básicos IGC-USP/CPRM/MME-SGTM.

Juliani, C., Hacksparser, P. C., Dantas, E. L., & Fetter, A. H. (2000). The mesoproterozoic volcano-sedimentary Serra do Itaberaba Group of the Central Ribeira Belt, São Paulo, Brazil: Implications for the age of overlying São Roque Group. *Revista Brasileira de Geociências*, 30(1), 82–86.

Juliani, C., Pérez-Aguilar, A., & Martin, M. A. B. (1997). Geotermobarometria e evolução metamórfica P-T-d do Grupo Serra do Itaberaba (SP). *Anais da Academia Brasileira de Ciências*, 69, 441–442.

Juliani, C., Schorsch, H. D., & Pérez-Aguilar, A. (1994). Corundum-marginite schists (‘marundites’) in the Precambrian Serra do Itaberaba Group, São Paulo, Brazil: geological relationships and petrogenesis. *Anais da Academia Brasileira de Ciências*, 66, 498.

Pan, Y., & Fleet, M. E. (1993). Geochemistry and origin of cordierite-orthoamphibole gneiss and associated rocks at an Archean volcanicogenic massive sulphide camp: Manitouwadge, Ontario, Canada. *Precambrian Research*, 74, 73–89. doi:10.1016/0301-9268(95)00010-3

Pérez-Aguilar, A. (1996). *Geologia, petrografia e gênese dos granada-cordierita-cummingtonita/antofilita anfibolíticas e rochas associadas do Grupo Serra do Itaberaba, SP* (Unpublished Master Thesis). Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.

Pérez-Aguilar, A. (2001). *Petrologia e litioquímica de rochas de palaeossistemas hidrotermais oceânicos mesoproterozoicos da sequência metavulcanossedimentar do Grupo Serra do Itaberaba, SP* (Unpublished PhD Thesis). Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.

Pérez-Aguilar, A., Juliani, C., & Martin, M. A. B. (2000). Mesoproterozoic paleohydrothermal system in the Morro da Pedra Preta Formation, Serra do Itaberaba Group, São Paulo State, Brazil. *Revista Brasileira de Geociências*, 30, 413–416.

Pérez-Aguilar, A., Juliani, C., & Monteiro, L. V. S. (2007). Petrografia de zonas de alteração hidrotermal mesoproterozoicas do tipo Kuroko no Grupo Serra do Itaberaba (SP) e seu uso na exploração mineral. *Revista do Instituto Geológico*, 27–28(1/2), 31–52. doi:10.5935/0100-929X.20070003

Pérez-Aguilar, A., Juliani, C., Monteiro, L. V. S., Bettencourt, J. S., Fallick, A. E., Barros, E. J., … Oliveira, A. M. S. (2011). Mineralization high-sulfidation submarina mesoproterozoica no Grupo Serra do Itaberaba, SP: implicações metalogenéticas em cinturões metamórficos. In J. C. Franz, J. C. Marques, & H. Jost (Eds.), *Contribuições à metalogia do Brasil* (pp. 149–174). Porto Alegre: UFRGS.

Pérez-Aguilar, A., Juliani, C., Monteiro, L. V. S., Fallick, A. E., & Bettencourt, J. S. (2005). Stable isotopic constrains on Kuroko-type paleo-hydrothermal systems in the Mesoproterozoic Serra do Itaberaba Group, São Paulo.
Perrotta, M. M., Salvador, E. O., Lopes, R. C., O’Agostino, L. L., Peruffo, N., Gomes, S. O., … Lacerda Filho, J. V. (2005). Geologia e recursos minerais do Estado de São Paulo, escala 1:750.000. Programa Levantamentos Geológicos Básicos do Brasil. São Paulo: CPRM.

Riverin, G., & Hodgson, C. I. (1980). Wall-rock alteration at the Millenbach Cu-Zn Mine, Noranda, Quebec. Economic Geology, 75, 424–444. doi:10.2113/gsecongeo.75.3.424

Roberts, M. D., Oliver, N. H. S., Fairclough, M. C., Höliä, P. S., & Lahtinen, R. (2003). Geochemical and oxygen isotope signature of sea-floor alteration associated with a polydeformed and highly metamorphosed massive sulfide deposit, Ruostesuo, Central Finland. Economic Geology, 98, 535–556.

Sachs, L. L. B., & Morais, S. M. (1999). Programa Levantamentos Geológicos Básicos do Brasil: Integração Geológica da Folha São Paulo. Escala 1:250.000, SF-23-Y-C, Estado de São Paulo. São Paulo: CPRM.

Shikazono, N. (2003). Geochemical and tectonic evolution of back-arc hydrothermal systems – implication for the origin of Kuroko and epithermal vein-type mineralizations and the global geochemical cycle (p. 463). New York, NY: Elsevier.

Vallance, T. G. (1967). Mafic rock alteration and isochemical development of some cordierite-anthophyllite rocks. Journal of Petrology, 8(1), 84–96. doi:10.1093/petrology/8.1.84