

MULTISTAGE KUROKO-TYPE PALEO-HYDROTHERMAL EVOLUTION AND ASSOCIATED HIGHLY POSITIVE OXYGEN ISOTOPE ANOMALIES IN VOLCANIC ROCKS OF THE MESOPROTEROZOIC SERRA DO ITABERABA GROUP, SÃO PAULO, BRAZIL

ANNABEL PÉREZ-AGUILAR¹, CAETANO JULIANI², LENA V.S. MONTEIRO³, ANTHONY E. FALICK⁴ & JORGE S. BETTENCOURT²

¹ Instituto Geológico-SMA, Av Miguel Stéfano, 3900, CEP 04301-903, São Paulo, SP, Brazil, annabelp@igeologico.sp.gov.br; ² Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, CEP 05508-080, São Paulo, SP, Brazil; ³ Instituto de Geociências, Universidade Estadual de Campinas, Rua João Pandiá Calógeras, 51, CEP 13083-970, Campinas, SP, Brazil; ⁴ Scottish Universities Environmental Research Centre, Scotland, UK

INTRODUCTION

A multistage hydrothermal history could be characterized within the Mesoproterozoic metamorphosed volcano-sedimentary Serra do Itaberaba Group (SIG), which is part of the Ribeira Fold Belt (Almeida et al., 1973; Juliani & Beljavskis, 1995; Juliani et al., 2000). This volcano-sedimentary sequence is partially covered by the Neoproterozoic siliciclastic São Roque Group (Juliani et al., 1986; Hackspacher, 1999), being the whole sequence of supracrustal rocks crosscut by several Neoproterozoic to Phanerozoic granitic plutons, and affected by several NE-SW trending shear zones (Almeida et al., 1981). The SIG was affected by two progressive medium- to low-grade regional metamorphic events, which occurred during the Mesoproterozoic and the Neoproterozoic.

The paleo-hydrothermal systems were developed in a mid-ocean ridge environment and in a following back-arc basin stage associated with the emplacement of relative small andesitic to rhyodacitic intrusions (Pérez-Aguilar et al., 2000; Pérez-Aguilar, 2001). Genetically associated to paleo-hydrothermal systems, are found the metamorphic products of a large chloritic alteration zone (CZ1) and restrict chloritic (CZ2), argillic, and advanced argillic alteration zones, which crosscut CZ1. These hydrothermal alteration zones are similar to those present in Kuroko-type deposits (Franklin, 1993; Ohmoto, 1996). Also present are metamorphosed carbonatization, potassification, and silicification alteration zones, Algoma type BIFs, tourmalinites, gold-bearing graphite/sulfide pelites, and Cu and Zn soil anomalies (Juliani, 1993; Juliani et al., 1992; Pérez Aguilar, 2001; Pérez-Aguilar et al., in press).

RESULTS

For the igneous metabasites (+5.9 to +16.9‰), basic metavolcaniclastic rocks (+8.3 to 10.1‰), intermediate meta-igneous (+14.1 to 17.6‰) and meta-volcaniclastic (+15.3 to 17.8‰) rocks from the CZ1, the oxygen isotope data reflect well-defined trends of increasing $\delta^{18}\text{O}$ values with progressive intensity of the hydrothermal alteration processes. Samples from CZ2 yield whole-rock $\delta^{18}\text{O}$ values of +9.0 and +10.6‰, and δD value of -88‰. Plagioclase margarite corundum schist (marundite) from argillic alteration zone shows $\delta^{18}\text{O}$ value of +9.7‰ and δD of -55‰ (Pérez-Aguilar et al., in press).

The $\delta^{18}\text{O}$ values for the fluid in equilibrium with quartz from strongly altered rocks of the CZ1 (+5.8 to +14.4‰) were calculated for a range of temperatures between 200 to 300 °C, consistent with those of chloritic alteration zones. The calculated oxygen and hydrogen fluid composition in equilibrium with muscovite ($\delta^{18}\text{O} = +3.2$ to 8.5‰; $\delta\text{D} = -32$ ‰) and margarite ($\delta^{18}\text{O} = +5.4$ to 8.5‰; $\delta\text{D} = -20$ to -32‰) from rocks associated to marundites were calculated for a temperature interval compatible with those of pre-metamorphic argillic and advanced argillic alteration (~200 to 300 °C).

MULTISTAGE HYDROTHERMAL EVOLUTION

Integrated geological, petrological, and oxygen and hydrogen stable isotopes help to constrain four different hydrothermal alteration events (Pérez-Aguilar et al., in press). The first hydrothermal alteration event was associated to a nonsteady, essentially fracture-controlled, ocean crust cooling that established a widespread exchange of seafloor rocks with marine water at low temperatures and high water/rock ratios. This process resulted in a heterogeneous ^{18}O whole-rock enrichment (up to +15.5‰) and minor chemical changes. A second hydrothermal alteration event occurred in a deeper crustal level, during which seawater underwent isotopic exchange with previous heterogeneously ^{18}O enriched rocks, at high temperatures and low water/rock ratios, becoming fluids extremely enriched in heavy oxygen. The third and fourth stages were genetically linked to the emplacement of shallow andesitic to rhyodacitic intrusions in the back-arc basin environment. The estimated oxygen isotope composition of the fluid in equilibrium with quartz from CZ1 rocks, which were formed at the third alteration event, reflects ^{18}O -enriched fluid, which is mostly likely interpreted as ^{18}O -evolved seawater inherited from previous second stage. This third stage is characterized as a steady convective system associated with the discharge of hot ^{18}O enriched evolved seawater, which underwent isotopic exchange with relative cold

rocks at different water/rock ratios. High water/rock ratios favored strong rock alteration and extremely high heavy oxygen rock anomalies. The fourth stage was associated with higher temperature fluids if compared with those of previous alteration stages, mainly composed by evolved seawater with a subordinate magmatic component.

Related metamorphic products from the CZ1 are characterized by the presence of rocks with different amounts of anthophyllite and/or cummingtonite (cummingtonite-anthophyllite rocks), which are similar to those described in metamorphosed volcanogenic massive sulfide deposits (James et al., 1978; Riverin and Hodgson, 1980; Elliot-Meadows and Appleyard, 1991). Relative high $\delta^{18}\text{O}$ whole-rock values have also been observed in wall-rocks associated to massive sulfide deposits of Aljustrel in the Carboniferous Iberia Pyrite Belt (Spain), the Silurian Blue Hill (Maine, USA), and Kidd Creek and Mobrun in the Archean Abitibi greenstone belt (Canada) (Barriga and Kerrich, 1984; Beaty et al., 1988; Munhá et al., 1986; Hoy, 1993). These values have been interpreted as evidence of high ^{18}O ore-forming fluids and/or due to a first low temperature near seafloor alteration stage (Barriga and Kerrich, 1984; Beaty et al., 1988; Munhá et al., 1986; Hoy, 1993).

CONCLUDING REMARKS

Geological, petrological and stable isotope data strongly support a multistage paleo-hydrothermal evolution in the Mesoproterozoic SIG. The systematic stable isotope variations, represented by well-defined trends of increasing $\delta^{18}\text{O}$ values with progressive alteration intensity, are evidence that, in the SIG, hydrothermal isotope signatures were preserved, despite the overprinting of two medium- to low-grade metamorphic events that affected these rocks. The extremely high $\delta^{18}\text{O}$ anomalies from the CZ1 rocks and related hydrothermal fluids were achieved due to a long-lived hydrothermal system. The identification of several pre-metamorphic hydrothermally altered zones and superimposed hydrothermal events in this group, similar to those observed in Kuroko-type base metal mineralizations, so as different hydrothermal events associated with gold mineralization (Beljavskis et al., 1999), expands the mineral potential for the occurrence of base metal deposits in the Serra do Itaberaba Group and in the volcano-sedimentary sequences of the Ribeira Fold Belt.

Acknowledgments

FAPESP research grants: 93/4350-0 and 98/15170-7); CNPq research grant: 400490-94-3

References

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

Almeida, F.F.M. de, Hasui, Y., Ponçano, W.L., Dantas, A.S.L., Carneiro, C.D.R., Melo, M.S. de, Bistrichi, C.A., 1981. Mapa geológico do Estado de São Paulo, escala 1:500.000 – Nota Explicativa. São Paulo, 1. Instituto de Pesquisas Tecnológicas Monografia 6.

Barriga, F.J.A.S., Kerrich, R., 1984. Extreme ^{18}O -enriched volcanics and ^{18}O -evolved marine water, Aljustrel, Iberian pyrite belt: transition from high to low Rayleigh number convective regimes. *Geochimica et Cosmochimica Acta* 48, 1021–1031.

Beaty, D.W., Taylor, Jr., H.P., Coad, P.R., 1988. An Oxygen isotope study of the Kidd Creek, Ontario, volcanogenic massive sulfide deposit: evidence for high ^{18}O ore fluid. *Economic Geology* 83 1–17.

Beljavskis, P., Juliani, C., Garda, G.M., Xavier, R.P.; Bettencourt, J.S., 1999. Overview of the gold mineralization in the metavolcanic-sedimentary sequence of the Serra do Itaberaba Group, São Paulo, Brazil. In: Standley, C.J. et al. (1999) *Mineral Deposits: Processes to Processing* 1. Balkema, 151–153.

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.

Franklin, J.M., 1993. Volcanic-associated massive sulphide deposits. In: Kirkham, R.V., Sinclair, W.D., Thorpe, R.I., Duke, J.M., (Eds.). *Mineral deposit modeling*. Geological Association of Canada Special Paper 40, 315–334.

Garda, 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.

Hackspacher, P., Dantas, E.L., Godoy, A.M., Oliveira, M.A.F. de, Fetter, A., Van Schmus, W.R., 1999. Considerations about the evolution of the Ribeira Belt in the São Paulo State – Brazil, from U/Pb geochronology in metavolcanic rocks of the São Roque Group. South American Symposium on Isotope Geology, 2, Vila Carlos Paz, Argentina, Anais, pp. 192–195.

Hoy, L.D., 1993. Regional evolution of the hydrothermal fluids in the Noranda district, Quebec: evidence from $\delta^{18}\text{O}$ values from volcanogenic massive sulfide deposits. *Economic Geology* 88, 1526–1541.

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.

Juliani, C., 1993. Geologia, petrogênese e aspectos metalogenéticos dos grupos Serra do Itaberaba e São Roque na região das serras do Itaberaba e da Pedra Branca, NE da cidade de São Paulo. Unpublished PhD Thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.

Juliani, C., Beljavskis, P., Schorscher, H.D., 1986. Petrogênese do vulcanismo e aspectos metalogenéticos associados: Grupo Serra de Itaberaba na região do São Roque – SP. 34th Congresso Brasileiro de Geologia, Goiânia, Anais 2, pp. 730–743.

Juliani, C., Schorscher, H.D., Pérez-Aguilar, A., Beljavskis, P., 1992. Cordierita–granada–cummingtonita anfibolitos no Grupo Serra do Itaberaba (SP): evidência de alterações hidrotermais–metassomáticas pré-metamórficas. 2nd Jornadas Científicas, Boletim do Instituto de Geociências da Universidade de São Paulo Special Publication 12, 59–61.

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

Juliani, C. and Beljavskis, P., 1995. Revisão da litoestratigrafia da faixa São Roque/Serra do Itaberaba (SP). *Revista do Instituto Geológico* 16, 33–58.

Juliani, C., Hackspacher, 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, 82–86.

Munhá, J., Barriga, F.J.A.S., Kerrich, R., 1986. High 18O ore-forming fluids in volcanic-hosted base metal massive sulfide deposits: geologic, $18\text{O}/16\text{O}$, and D/H evidence from the Iberian Pyrite belt; Crandon, Wisconsin; Blue Hill, Maine. *Economic Geology* 81, 530–552.

Ohmoto, H., 1996. Formation of volcanogenic massive sulfide deposits: the Kuroko perspective. *Ore Reviews*, 10, 135–177.

Pérez-Aguilar, A., 2001. Petrologia e litoquímica de rochas de paleossistemas hidrotermais oceânicos mesoproterozóicos da seqüência 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 paleo-hydrothermal 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., Fallick, A.E., Bettencourt, J.S. In press. Stable isotopic constraints on Kuroko-type paleo-hydrothermal systems in the Mesoproterozoic Serra do Itaberaba Group, São Paulo State, Brazil. *Journal of South American Earth Sciences*.

Pérez-Aguilar, A., Juliani, C., Monteiro, L.V.S., Bettencourt, J.S., 2002. Isótopos estáveis de rochas de paleossistemas hidrotermais oceânicos mesoproterozóicos do Grupo Serra do Itaberaba, SP. 2nd Simpósio Sobre Vulcanismo e Ambientes Associados, Belém, Boletim de Resumos, pp. 44.

Riverin, G., Hodgson, C.J., 1980. Wall-rock alteration at the Millenbach Cu–Zn Mine, Noranda, Quebec. *Economic Geology* 75, 424–444.