STABLE ISOTOPE STUDY ON METAMORPHOSED HIGH-SULFIDATION ALTERATION ZONES (MARGARITE-CORUNDUM SCHISTS) FROM THE SERRA DO ITABERABA GROUP

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Abstract

Paleo-hydrothermal systems developed in the Mesoproterozoic metamorphosed volcanosedimentary Serra do Itaberaba Group, within the central segment of the Ribeira fold belt, during the installation of a back- are associated to the emplacement o relative small and shallow intermediate intrusions. These systems were responsible for the formation of chloritic and argillic alteration zones similar to those associated to Kuroko-type base metal deposits. In addition, advanced argillic alteration zones (high-sulfidation) were recognized in the Serra do Itaberaba Group. These alteration zones developed due to the interaction of basic and intermediate rocks with acid and sulfate-rich fluids. Afterwards, some of these rocks were reworked in closed saline sea basins. The final products were Al-enriched clays due to intensely cation lixiviation. The metamorphic products of these Al-enriched clays are rocks mainly composed of corundum + margarite + rutile \pm muscovite (marundites). Preliminary δ^{18} O whole-rock data obtained for marundites vary from 6.9 to 10.1‰, associated to relative high enrichments of rocks in W, Co and Th. These isotopic signatures suggest the participation of magmatic fluids derived from intermediate to acid intrusions in the genesis of argillic and advanced argillic alteration zones.

Keywords: Serra do Itaberaba Group; oceanic environment high-sulfidation; margarite-corundum schists

1 Introduction

The Serra do Itaberaba Group corresponds to a Mesoproterozoic metamorphosed volcano-sedimentary sequence, which is partially covered by siliciclastic Neoproterozoic São Roque Group (Juliani & Beljavskis, 1995; Juliani *et al.*, 2000a; 2000b; Hackspacher *et al.*, 1999). These groups are localized northeast São Paulo city, within the central segment of the Ribeira fold belt (Almeida *et al.*, 1973), which were intruded by several Neoproterozoic to Phanerozoic granitic rocks, and crosscut by wrench NE-SW thrust shear zones (Almeida *et al.*, 1981). The Serra do Itaberaba Group was subdivided in the Morro da Pedra, Nanguçu, and Pirucaia formations (Juliani, 1993; Juliani & Beljavskis, 1995). Paleo-hydrothermal systems developed in the upper part of the basal volcano-sedimentary Pedra Preta formation associated to relative small and shallow andesitic to rhyodacitic intrusions emplaced during the installation of a back-arc basin (Juliani, 1993; Juliani *et al.*, 1992; Pérez-Aguilar, 1996; 2001; Pérez-Aguilar *et al.*, 2005). Paleo-hydrothermal systems were responsible for the genesis of restrict chlorite (CZ2), argillic and advanced argillic alteration zones that crosscut a first large chloritic alteration zone (CZ1) (Pérez-Aguilar *et al.*, 2005; Fig. 1), being alteration zones similar to those associated to Kuroko-type base metal deposits (Sangster, D.F., 1972; Franklin, J.M., 1993; Ohmoto, H., 1996). The Serra do Itaberaba Group was affected by two medium-grade regional metamorphic events followed by greenschist facies retrometamorphism (Juliani *et al.*, 1997).

2 Mararite-corundum schists

The genesis of margarite-corundum schists is interpreted as due to overprinting geological processes (Juliani *et al.*, 1994). A first event was responsible for the presence of argillic and advanced argillic alteration zones that developed in fluid channel-ways due to the interaction of acid sulfate-rich fluids (high-sulfidation) with basic and intermediate volcanic and igneous rocks. Afterwards these clays were reworked in these channel-ways or in saline closed sea basins. These processes were responsible for the lixiviation of most cations, including Si, leading to a very Al-rich residue. In the sequence rocks were overprinted by two medium-grade metamorphic-deformational events. The metamorphic products of Al-rich clays correspond to rocks essentially composed of corundum + margarite + rutile (Juliani, 1993; Juliani *et al.*, 1994).

Al-rich rocks from the Serra do Itaberaba Group are present as few to hundred meters intercalations within metabasic, metavolcanoclastic, and metapelites. Two occurrences from these rocks, known since several years ago, outcrop nearby Mairiporã (Guaravirituba occurrence) and Santa Isabel (Pedra Branca occurrence) cities (Lefevre, 1958; Barbour, 1987, Coutinho *et al.*, 1982; Juliani *et al.*, 1986). These rocks are essentially composed of margarite, corundum and rutile. being mineralogical and chemically similar to those metamorphic rocks first described by Hall (1920), present in the Barberton greenstone belt, and which were referred to as marundites. Because of similarities, Al-rich rocks from the Serra do Itaberaba group are also referred to as marundites. Afterwards two new marundite occurrences have been discovered, one in the Ribeirão Itaberaba (Itaberaba occurrence) also near Santa Isabel city and the other in the area nearby Guarulhos city (Guarulhos occurrence). Marundites from the Itaberaba occurrence shows an unusual mineralogical composition being rocks composed of margarite, corundum, tourmaline, anorthite, and rutile, which were interpreted as produced after

hydrothermal alteration of igneous rocks (Juliani, 1997). Muscovite schist and margarite schist, both typically without quartz, are commonly associated with marundites. These rocks could be products of changing K⁺, Al³⁺ and Ca²⁺ activities in the hydrothermal fluids (Martin & Juliani, 1994; Juliani, 1997).

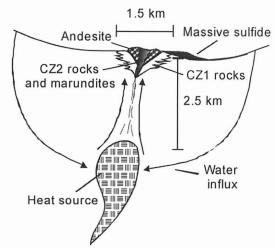


Figure 1 - Schematic reconstruction of the Serra do Itaberaba paleo-hydrothermal systems (Pérez-Aguilar et al., 2005).

3 Results

Marundites from the Pedra Branca occurrence show $\delta^{18}O$ values varying from 6.9 to 7.7‰, whereas associated margarite-chlorite schist (16.6‰) and muscovite schist (9.8‰) display higher $\delta^{18}O$ values. Muscovite from the latter has $\delta^{18}O$ and $\delta D = +9.9$ and -80%, respectively. Guaravirituba marundites shows $\delta^{18}O$ values varying from 7.5 to 9.2‰, having been obtained for associated muscovite-chlorite schist a $\delta^{18}O$ of 9.1‰ and for associated muscovite schist a $\delta^{18}O$ value of 9.2‰. Margarite from margarite schist associated with this occurrence has $\delta^{18}O$ and $\delta D = 9.9$ and -100%, respectively.

Marundites from the Itaberaba occurrence show $\delta^{18}O$ values varying from 8.5 to 9.7‰. Hydrogen isotopic composition from these marunditos is –55‰. The oxygen isotope value of a related metamorphosed chloritized intermediate rock from the first large chloritic zone (CZ1), spatially related with the Iataberaba marundite occurrence, is 17.2‰. One analyzed sample from the Guarulhos has $\delta^{18}O$ value of 10.1‰.

4 Discussion and concluding remarks

Oxygen stable isotope data obtained for marundites from the Serra do Itaberaba Group vary from 6.9 to 10.1%. These isotopic signatures in addition to relative high enrichments of marundites in W, Co and Th (Juliani, 1997), suggest the participation of magmatic fluids derived from intermediate to acid intrusions for the genesis of argillic and advanced argillic alteration as pointed out by Pérez-Aguilar *et al.* (2005). Thus, the Serra do Itaberaba marundites could represent the metamorphic product of low-temperature argillic and advanced argillic hydrothermal alteration generated by acid and sulfate-rich fluids circulating near the ocean floor and associated with intermediate to acid intrusions.

The Pedra Branca ($\delta^{18}O = 6.9$ to 7.7%), Guaravirituba ($\delta^{18}O = 7.5$ to 9.2%), Itaberaba ($\delta^{18}O = 8.5$ to 9.7%), and the Guarulhos ($\delta^{18}O = 10.1$ %) occurrences show an increasing trend of $\delta^{18}O$ values. This is probable due to gradual increasing participation of magmatic water in fluids, due to the proximity of igneous rocks.

The margarite-chlorite schist associated to marundites from the Pedra Branca occurrence corresponds to a strongly transformed intermediate igneous rock, which was first affected by the first chloritic alteration event related to CZ1. overprinted by hydrothermal processes associated to argillic alteration. The δ^{18} O value of 16.6% suggests that the second hydrothermal event did not substantially modify high oxygen isotope signature related to CZ1 alteration, being δ^{18} O value similar to that obtained for related chloritized metamorphosed intermediate rock form the CZ1 (17.2‰). As discussed by Pérez-Aguilar *et al.* (2005), these high δ^{18} O values were acquired due to interaction of rock with highly evolved hot seawater. The δ^{18} O value of 9.1‰ obtained for the muscovite-chlorite schist is interpreted as inherit from second chloritic alteration event related to CZ2 and acquired during argillic alteration event, having both events similar δ^{18} O signatures (Pérez-Aguilar *et al.*, 2005). The δ^{18} O values obtained for associated muscovite schists from the Pedra Branca and Guaravirituba occurrences (9.8‰ and 9.2‰, respectively) could reflect the argillic alteration event.

Hydrothermal stable isotope signatures from marundites were preserved besides the overprinting of two medium-grade metamorphic evens. The characterization of high-sulfidation alteration in ocean environment where are also present chloritic alteration zones similar to those associated to Kuroko-type base metal deposits so as gold mineralizations (Juliani, 1993; Beljavskis *et al.*, 1999; Garda *et al.*, 2002), shows the importance of these lithotypes for the metallogenetic modeling of paleo-hydrothermal systems of the Serra do Itaberaba Group.

Acknowledgments

The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo (grant 95/2337-2) and Conselho Nacional de Desenvolimento Científico e Tecnológico for research grant 800549/93-7.

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 & Stehli F.G. (eds.) *The ocean basin and margins*. New York, Plenum 1, pp. 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.
- Barbour Jr. E. 1987. Prospecção de ouro na área Morumbi-Mairiporã SP. São Paulo, IPT/PRÓ-MINÉRIO, 50p. (IPT, Relatório 25.437).
- 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. (ed.) *Mineral Deposits: Processes to Processing*, 1. Balkema, pp. 151-153.
- Coutinho J.M.V., Rodrigues E. de P., Suemitsu A., Juliani C., Beljavskis P., Perosa, P de T.Y. 1982. Geologia e petrologia da sequência vulcano-sedimentar do Grupo São Roque na Serra de Itaberaba SP. *In:* SBG, Congresso Brasileiro de Geologia, 32, Anais, v.2, p. 624-640.
- 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, pp. 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. *In:* South American Symposium on Isotope Geology, 2, Anais, pp. 192–195.
- Hall A.L. 1920. Corundum in the Northern and Eastern Transvaal. Geological Survey of South Africa Memoir 15.
- 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. PhD Thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.
- Juliani C. 1997. Estudo petrogenético das ocorrências de marunditos (margarita-coríndon xistos) do Grupo Serra do Itaberaba, nas regiões de Mairiporã e Santa Isabel (SP). Relatório Final, Fapesp, Processo 95/2337-2.
- 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. *In:* SBG, Congresso Brasileiro de Geologia, 34, 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. *Boletim do Insituto de Geociências da Universidade de São Paulo*, 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. & 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. 2000a. 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 Geociência*, **30**: 82–86.
- Juliani, C., Hackspacher, P.C., Dantas, E.L., 2000b. Serra do Itaberaba Group: a Mesoproterozoic volcano-sedimentary unit at São Paulo State, Brazil. *In*: USGS, International Geological Congress, 31 [CD-ROM]
- 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.

- Lefevre V. 1958. Resumo do relatório das atividades do Instituto Geográfico e Geológico de São Paulo, durante o ano de 1954. *Boletim do Instituto Geográfico e Geológico*, 13(único): 19-37, 1955/1958.
- Martin M.A.B. & Juliani, C. 1994. Geologia, petrografia e gênese dos marunditos (margarita-coríndon xistos). *In:* SBG, Congresso Brasileiro de Geologia, 38, Boletim de Resumos Expandidos, v.3, p. 77-78.
- Ohmoto H., 1996. Formation of volcanogenic massive sulfide deposits: the Kuroko perspective. *Ore Geology Reviews*, 10:35–177.
- Pérez-Aguilar A., 1996. Geologia, petrografia e gênese dos granada-cordierita-cummingtonita/antofilita anfibolitos e rochas associadas do Grupo Serra do Itaberaba, SP. Master Thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.
- Pérez-Aguilar A., 2001. Petrologia e litoquímica de rochas de paleossistemas hidrotermais oceânicos mesoproterozóicos da sequência metavulcanossedimentar do Grupo Serra do Itaberaba, SP. PhD Thesis, Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.
- Pérez-Aguilar A., Juliani C., Monteiro L.V.S., Fallick A.E., Bettencourt J.S., 2005. Stable isotopic constrains on Kurokotype paleo-hydrothermal systems in the Mesoproterozoic Serra do Itaberaba Group, São Paulo State, Brazil. *Journal of South American Earth Sciences*, **18**:305–321.
- Sangster D.F. 1972. Precambrian volcanogenic massive sulphide deposits in Canada: a review. Geological Survey of Canada, Paper 72.

