fO_2 and CO_2-N_2 fluid inclusions: remnants of fluid and geodynamic evolution of Ribeira Fold Belt, SE Brazil

fO_2 e inclusões fluidas de CO_2-N_2: vestígios da evolução dos fluidos e geodinâmica da Faixa Ribeira, SE do Brasil

Bento dos Santos, T. M. [1];Munhá, J. M. U. [1];Tassinari, C. C. G. [2];Noronha, F. M. [3]; Guedes, A.[3]; Fonseca, P. E. [4]; Neto, C. D. [2]; Dória, A. [3]

[1] Centro/Departamento de Geologia, Universidade de Lisboa, Ed. C6, 2º, Campo Grande, 1749-016 Lisboa, Portugal
[2] Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562 – Butantã, CEP: 05508-080, SP, Brazil
[3] Centro de Geologia, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
[4] LATTEX, Universidade de Lisboa, Ed. C6, 2º, Campo Grande, 1749-016 Lisboa, Portugal

Abstract

The São Fidelis - Santo António de Pádua (SFSAP) Ribeira Belt sector comprises migmatitic gneisses (kinzigites and khondalites) and charnockites, as well as their deformed counterparts (blastomilonites) that resulted from late shearing and exhumation at the end of the Panafricano – Braziliano Orogeny.

Fluid inclusion (FI) microthermometry, Raman spectroscopy, X-ray diffraction, mineral chemistry and fO_2 modelling, provided the following data: **1)** log fO_2 ranges from -17.799 to -11.538 bar for the temperature range of 896º C to 656 ºC, and indicates fO_2 at QFM +1 for high-T charnockites and fO_2 at QFM –1 for blastomilonites and migmatites, implying that metamorphic rocks underwent reduction (fO_2 decrease) during cooling; **2)** 6 main types of fluid inclusions were observed, from oldest to youngest: a) N_2 (94 to 95 mol%) – CH_4 (5 to 6 mol%) FI; b) CO_2 and CO_2-N_2 (0 to 11 mol%) high to medium density (1.01 – 0.59 g/cm^3) FI; c) CO_2 and CO_2-N_2 (0 to 36 mol%) low density (0.19 to 0.29 g/cm^3) FI; d) CO_2 (94 to 95 mol%) – N_2 (3 mol%) – CH_4 (2 to 3 mol%) – H_2O; e) late low salinity H_2O-CO_2 (Flw from 0.3 to 0.7) high to medium density (0.56 – 0.99 g/cm^3) FI; and f) late low-salinity H_2O FI.

Data integration allows the characterization of fluid and geodynamic evolution of this lower crustal segment in the later stages of the Braziliano cycle. The Ribeira Belt metamorphic fluids evolved from dominated N_2-CH_4 fluids to CO_2-N_2 fluids during oxidizing granulitic metamorphism where CO_2 increased due to water removal by ascending granitic melts; this was followed by late fO_2 decrease induced by cooling - decompression water influx, turning carbonic fluids into CO_2-H_2O mixtures, and progressively into low-salinity H_2O fluids. These features are interpreted as due to rapid pressure drop during the late retrograde/exhumation path of Ribeira Belt. Results show that at about 400-450º C rocks were exhumed to shallow depths, producing generalized low-density CO_2 inclusions, followed by surface water admixture. Khondalites were generated by decreasing fO_2 and subsequent deposition of graphite during cooling and reduced fluid circulation.

Keywords: Ribeira Belt, Fluid inclusion, Oxygen fugacity, Charnockite, P-T-Fluid evolution

Resumo

O sector São Fidelis – Santo António de Pádua (SFSAP) da Faixa Ribeira, é constituído por gnaisses migmatíticos (kinzigitos e khondalitos) e charnockitos, bem como por blastomilonitos que se desenvolveram como resultado da deformação cisalhante e exumação ocorrida no final da orogenia Brasiliana.

Microtermometria de inclusões fluidas (IF), espectroscopia Raman, difracção de raios-X, química mineral e modelação de fO_2 forneceram os seguintes elementos: **1)** variação de log fO_2 de -17.799 a -11.538 bar para o intervalo de temperaturas entre 656 e 896º C, e indicações de que os charnockitos de alta temperatura apresentam fO_2 a QFM +1, enquanto os blastomilonitos e migmatitos apresentam QFM -1, implicando que as rochas estudadas experimentaram um decréscimo de fO_2 durante o arrefecimento; **2)** 6 tipos principais de IF foram observadas: a) IF de N_2 (94 a 95 mol%) – CH_4 (5 a 6 mol%); b) IF de CO_2 e CO_2-N_2 (0 a 11 mol%) de densidade media a elevada (1.01 – 0.59 g/cm^3); c) IF de CO_2 e CO_2-N_2 (0 a 36 mol%) de baixa densidade (0.19 a 0.29 g/cm^3); d) IF de CO_2 (94 a 95 mol%) – N_2 (3 mol%) – CH_4 (2 a 3 mol%) – H_2O; e) IF tardias de H_2O-CO_2 (Flw de 0.3 a 0.7) de baixa salinidade e densidade média a elevada (0.56 – 0.99 g/cm^3); e f) IF aquosas tardias de baixa salinidade.

A integração destes dados permitiu caracterizar a evolução geodinâmica e dos fluidos presentes neste segmento crustal nas fases finais do Ciclo Brasiliano. Os fluidos metamórficos da Faixa Ribeira terão evoluído de composições dominadas por N_2-CH_4 para CO_2-N_2 durante o metamorfismo granulítico oxidante através da concentração de CO_2 por remoção de água para granitos ascendentes. Posteriormente, terá ocorrido decréscimo de fO_2 provocado pelo influxo de água durante o processo de arrefecimento e descompressão, tornando os fluidos carbónicos em aquo-carbónicos e progressivamente em aquosos de baixa salinidade. Esta evolução dos fluidos é interpretada como devida a uma rápida queda de pressão durante as últimas fases de retrogradação/exumação da Faixa Ribeira. Os dados sugerem que aos 400-450º C, as rochas foram exumadas até profundidades superficiais, gerando abundantes IF carbónicas de baixa densidade, seguidas de entrada de água e sua mistura. Os khondalitos formaram-se por decréscimo de fO_2 e subsequente deposição de grafite durante o arrefecimento e reduzida circulação de fluidos.

Palavras-chave: Faixa Ribeira, Inclusões fluidas, Fugacidade do oxigénio, Charnockito, Evolução P-T-Fluido

Introduction

Although fluid inclusion studies have long been a concern among metamorphic geologists to unravel the mysteries of the lower crust (Touret, 1971), work has yet to be done in order to understand the dynamics of fluid evolution in the Braziliano Cycle. Thus, this work addresses T, P, fO_2, age, origin and evolution of fluids in the Ribeira Belt in order to constrain the retrograding P-T-Fluid path of this granulitic belt.

Geologic setting and field observations

The studied São Fidelis – Santo António de Pádua (SFSAP) sector is located in the central-north Ribeira Belt, SE Brazil. The Ribeira Belt is a NE-SW to NNE-SSW trending Neoproterozoic belt formed in the Braziliano Orogeny by the collision of the São Francisco and West Congo cratons, from which resulted Western Gondwana (Cordani, 1971). Ribeira Belt is a complex orogenic belt composed of several geological units, separated by deep dextral shears. The SFSAP sector is located SE to one of these mega-shears, the Além Paraíba – Santo António de Pádua shear (APPS) that vigorously deformed the area rocks imposing a NE-SW trending transpressive shear deformation associated with high-grade granulite facies metamorphism, producing generalized migmatization. Outcrops in the area comprise: (1) migmatitic paragneisses (metatexites), commonly interlayered with amphibolites and marbles; (2) diatexites; (3) massive and incipient-type charnockites; and (4) blastomilonites that resulted from late retrogression of the major rock types. Also present in the area are khondalites (graphitic gneisses) that resulted from incipient charnockitization of metatexites in areas of contact with charnockites.

Oxygen Fugacity calculations

Oxygen fugacity was determined for 6 charnockites, 1 migmatite, 3 blastomilonites and 1 amphibolite, using the QUILF algorithm (Andersen & Lindsley, 1988). MH temperature determinations ranged from 370 to 771º C, indicating post-metamorphic Ti-magnetite oxidation in accordance with observation of exsolution of ilmenite from magnetite. Thus, Ti-magnetite compositions were reconstructed at the appropriate P-T range (Bento dos Santos et al., 2006) in order to estimate the metamorphic fO_2 conditions. MH, OHQ and AHQ (Harlov, 1992) oxygen fugacity estimates range from $10^{-11.538}$ to $10^{-17.799}$ bar for the calculated temperature range of 896º C to 656. Figure 1 shows that high-T charnockites (and amphibolites) have fO_2 values above the QFM buffer (QFM +1), whereas migmatites and blastomilonites provide fO_2 at QFM -1. Thus, the inferred fO_2 evolution suggests that metamorphic fluids experienced relative reduction during cooling. This is consistent with field and petrographic observations indicative of late graphite deposition in khondalites.

Fluid Modelling

Fluid modelling in the C-O-H system was performed in order to determine fluid compositional variations (H_2O, CO_2, CO, CH_4 and H_2) at a given T, P and fO_2. Results show that CO_2-rich fluid inclusions should be stable during charnockite formation (at the estimated P, T, fO_2 conditions), whereas aqueous fluids (with minor CH_4 and CO_2) were dominant in migmatites (and blastomilonites).

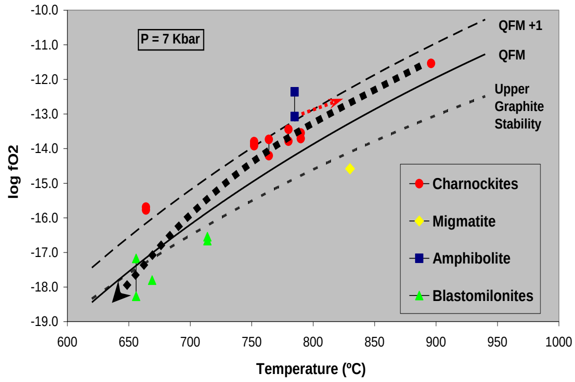

Fig. 1 – fO_2 of the studied samples at respective metamorphic peak temperatures (Bento dos Santos et al., 2006).

Fluid Inclusion (FI) and Raman Studies

Fluid inclusions were analysed in 4 charnockites, 1 diatexite, 2 migmatites, 2 khondalites and 2 blastomilonites (amounting to several hundred measurements in quartz and garnet crystals). Inclusions are typically < 10 µm in size and are referred as primary, secondary or late, according to their relative textural relations following Roeder (1984) classification. On this basis 6 fluid inclusion groups were defined, and their evolving characteristics are summarized in Table 1. G3a is the most common FI type; G4 FI group is characteristic of khondalites (that lack G2 and G3 FI).

Graphite analysis

Raman Spectroscopy and X-ray diffraction analyses of khondalite graphites indicate late deposition within a temperature range of 333º C to 449º C (Beyssac et al, 2002).

Table 1: Summary of fluid inclusion microthermometry and Raman Spectroscopy results.

Group	Composition	Phases	Occurrence	Flw	Tm CO_2	Tm Ice	Th CO_2	TH	CO_2	N_2	CH_4	d (g/cm^3)	Salinity (Wt% Eq. NaCl)
1	N_2-CH_4	Mono	P	-	-	-	-	-	-	94 - 95	5 - 6	-	-
2a	CO_2; CO_2-N_2	Mono	P	-	-58.1 : -59.6	-	-16.3 : 6.2 (L)	-	92 - 100	0 - 8	-	0.86 - 1.01	-
2b	CO_2; CO_2-N_2	Mono	P or S	-	-58.5 : -63.2	-	6.4 : 10.9 (L)	-	89 - 100	0 - 11	-	0.79 - 0.86	-
2c	CO_2; CO_2-N_2	Mono e Bi	P or S	-	-58.4 : -62.2	-	13.4 : 30.1 (L)	-	94 - 100	0 - 6	-	0.59 - 0.81	-
3a	CO_2; CO_2-N_2	Bi	P or S	-	-57.2 : -59.5	-	17.3 : 31.0 (C)	-	64 - 100	0 - 36	-	0.19 - 0.29	-
3b	N_2-CO_2; N_2	Mono	P or S	-	-	-	-	-	0 - 30	70 - 100	-	-	-
4	CO_2-N_2-CH_4-H_2O	Bi	P or S	0 - 0.1	-60.0 : -62.8	-	8.7 : 19.0 (L)	-	94 - 95	3	2 - 3	0.73 - 0.82	-
5	CO_2-H_2O	Bi	S - Late	0.3 - 0.7	-58.8 : -59.7	-3.7 : -5.4	9.5 : 13.1 (L)	232 : 404 (L)	100	-	-	0.56 - 0.99	6.1 - 10.5
6a	H_2O	Bi	Late	0.6 - 0.95	-	-0.1 : -4.5	-	86 : 367 (L)	-	-	-	0.57 - 0.93	0 - 7.2
6b	H_2O	Bi	Late	0.9 - 0.95	-	-4.0 : -9.3	-	98 : 174 (L)	-	-	-	0.97 - 0.99	6.5 - 13.2

P-T-Fluid evolution

FI microthermometry indicates that the SFSAP sector rocks evolved in equilibrium with $N_2 \pm CH_4$ and CO_2-N_2 rich fluids at high metamorphic temperatures. During the retrograding path fluids became progressively enriched in water, generating CO_2-H_2O fluids and late low-salinity H_2O fluids. Representative FI were used for isochore calculations presented in Fig. 2. Observation of the P-T-Fluid evolution shows that all FI are late, (relative to the peak of metamorphism), being trapped during cooling and decompression (exhumation) of their host metamorphic rocks.

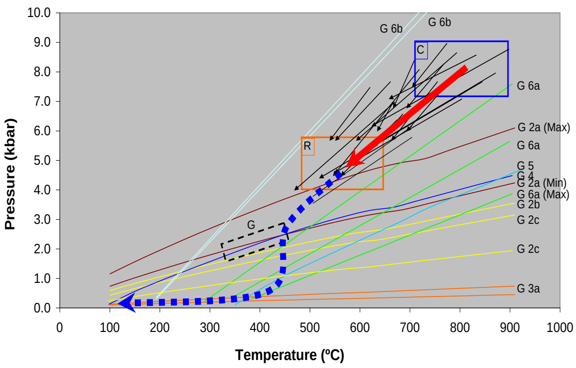

Fig. 2: P-T-Fluid evolution (C and R: core and rim temperature estimates (Bento dos Santos et al., 2006); G: Graphite temperature estimates for this study).

Discussion

CO_2 is the most oxidized fluid in the C-O-H system and its influx into lower crust from deep-seated sources has been advocated to explain charnockite development (Newton et al., 1980), which consistent with the oxidized conditions estimated for SFSAP charnockites. However, Touret (1971) and Cesare et al. (2005) argued that Fe^{3+} reduction during biotite dehydration-melting could cause graphite oxidation, producing CO_2 and globally rising fO_2 (if water is leaving the system). Thus, early CO_2 predominance in SFSAP fluids is interpreted as a result of relative concentration of the least mobile fluids, whereas water is preferentially removed by ascending melts. This process would also induce relative oxidation, as estimated for the studied charnockites.

The late P-T-Fluid path involved cooling and decompression until about 450º C, followed by a significant pressure drop (probably associated with orogenic collapse). Indeed, graphite deposition in khondalites is a relatively late process that took place after significant cooling down to 450º C - 330 ºC. Accordingly, graphite deposition should be coeval with late tectonic imbrication (orogenic collapse) and the consequent cooling and decompression, enhancing permeability and admixture of reducing H_2O-rich fluids into the system. This stage is related to the formation of (early) low-density CO_2 fluid inclusions (G3a in Fig. 2) and (late) low-salinity H_2O fluids, as the rock pile progressively approached the surface, interacting with shallow aquitards/aquifers.

Conclusions

Fluid evolution reflects compositional readjustments related to rapid decompression and cooling during the late stages of the Ribeira Belt exhumation path. Results indicate that high-T (> 550 ºC) fluids were dominated by CO_2 – N_2 components. At 450º C rocks were already exhumed to 3–10km depths, producing generalized low-density CO_2 (+ H_2O) inclusions, followed by interaction with shallower aquifer waters. fO_2 decreased substantially during cooling and mixture of CO_2 and H_2O, causing late graphite deposition.

Incipient charnockitic development by "CO_2 influx" is possible for some khondalites, but this process does not explain the massive charnockite formation in Ribeira Belt. We suggest that CO_2-rich, high-T metamorphic fluids should have resulted mainly from CO_2 concentration after water removal to ascending granitic melts, as originally proposed by Fyfe (1973).

Acknowledgements

FAPESP, POCA-PETROLOG (CEGUL, UI: 263; POCTI/FEDER) and GEODYN (POCTI – ISFL – 5 – 32) and a PhD scholarship from FCT (SFRH/BD/17014/2004) co-financed by FEDER provided support for field and analytical work. Teresa Palácios, Álvaro Pinto, Nuno Leal and Línia Martins are gratefully acknowledged for long-term logistic and moral support. Critical comments by the reviewer contributed to clarify the ideas expressed in this paper and we gratefully acknowledge.

References

Andersen, D., Lindsley, D. H., 1988. Internally consistent solution models for Fe-Mg-Mn-Ti oxides: Fe-Ti oxides. *Am. Min*., 73, 714-726.

Bento dos Santos, T., Munhá, J., Tassinari, C., Dias Neto, C., Fonseca, P., 2006. Petrologia, Geoquímica e Geocronologia de Granulitos no sector São Fidélis – Santo António de Pádua, RJ, SE Brasil. *Ext. Abst. VII Cong. Nac. Geol.*, 1, 241-244.

Beyssac, O., Goffé, B., Chopin, C., Rouzaud, J. N., 2002. Raman spectra of carbonaceous material in metasediments: a new geothermometer. *Jour. Met. Geol.*, 20, 859-871.

Cesare, B., Meli, S., Nodari, L., Russo, U., 2005. Fe^{3+} Reduction during biotite melting in graphitic metapelites: another origin of CO_2 in granulites. *Contrib. Min. Pet*., 149, 129-140.

Cordani, U. G., 1971. Síntese da geocronologia Pré-Cambriana da região costeira atlântica meridional da América do Sul. *Ext. Abst. 25th Cong. Bras. Geol.*, 179-180.

Fyfe, W. S., 1973. The granulite facies, partial melting, and the Archaean crust. *Phil. Trans. Royal Soc. London*, A273, 457-461.

Harlov, D. E., 1992. Comparative oxygen barometry in granulites, Bamble Sector, SE Norway. *Jour. Geol.*, 100, 447-464.

Newton, R. C., Smith, J. V., Windley, B. F., 1980. Carbonic metamorphism, granulites and crustal growth. *Nature*, 288, 45-50.

Roeder, E., 1984. *Fluid Inclusions*. Mineralogical Society of America, Reviews in Mineralogy, 12, 644.

Touret, J., 1971. Le facies granulite en Norvège méridionale. II. Les inclusions fluides. *Lithos*, 4, 423-436.