Wollastonite–scapolite–clinopyroxene marble of the Anápolis-Itauçu Complex, Goiás: more evidence of ultrahigh-temperature metamorphism

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Abstract Impure marble in a quarry near Goianira in the Anápolis-Itauçu Complex, central Brazil, contains blocks of contrasting calc-silicate rocks with different bulk compositions, producing a range of mineral assemblages during granulite facies metamorphism. The subject of this paper is the common host impure marble from the quarry outcrop, which is composed of calcite, clinopyroxene, quartz, ternary feldspar, titanite, wollastonite and scapolite. Wollastonite and scapolite only occur together in layers of appropriate bulk composition, and the coexistence of these minerals is diagnostic of ultrahigh-temperature (UHT) metamorphism ($T > 900^\circ\text{C}$). In thin section, although rare, wollastonite and scapolite are observed in mutual contact. More commonly, wollastonite exhibits a corona of calcite+quartz, but where wollastonite is close to scapolite, these minerals are separated by a corona of grossular with plagioclase+calcite+quartz. The coexistence of wollastonite+scapolite in contact is inferred to record the metamorphic peak and the coronae are interpreted as an early post-peak retrograde feature. Another indication of UHT metamorphism is the presence of ternary feldspar, in which exsolved andesine occurs in an orthoclase host. Titanite yields a TIMS U-Pb age of 632 ± 6 Ma, which we interpret as a post-peak cooling age during regional UHT metamorphism. Zircon from intrusive rocks nearby the marble yields a SIMS U-Pb age of 626 ± 2 Ma. Since these two ages overlap within uncertainty, we cannot rule out the possibility that contact metamorphism was the heat source for UHT metamorphism.

Keywords: Anápolis-Itauçu Complex, Brasília Fold Belt, calc-silicate rock, ultrahigh temperature metamorphism, wollastonite+scapolite.

Resumo *Wollastonita-escapolita-clinopiroxênio mármore do Complexo Anápolis-Itauçu, Goiás: evidência adicional de metamorfismo de temperatura ultra-alta.* Em pedra próxima a Goianira, Goiás, ocorrem mármore impuro e rochas calcissilicáticas com grande variedade de associações metamórficas. O objetivo principal do presente trabalho é o mármore impuro da pedra, composto por calcita, clinopiroxênio, escapolita, wollastonita, titanita, feldspato ternário, quartzo e ilmenita. Wollastonita e escapolita ocorrem em porções de composição adequada e a ocorrência dos dois minerais em contato é diagnóstica de condições de metamorfismo de temperatura ultra-alta ($T > 900^\circ\text{C}$). Em lâmina petrográfica, raramente a coexistência de wollastonita e escapolita é observada. Normalmente wollastonita apresenta coroa de calcita+quartzo e quando está próxima à escapolita, são separadas por coroa complexa de grossulária com quartzo, plagioclásio e calcita. A coexistência de wollastonita e escapolita ocorreu durante o auge do metamorfismo e as coroas de reação foram originadas durante o resfriamento após o pico metamórfico. Outra evidência de metamorfismo de temperatura ultra-alta é a presença de feldspato ternário, em que exsoluções de andesina ocorrem em ortoclásio. Idade ID-TIMS U-Pb em titanita é de 632 ± 6 Ma, interpretada como idade de resfriamento após o pico do metamorfismo de temperatura ultra-alta. Idade de grãos de zircão de intrusivas máficas das proximidades de Goianira é 626 ± 2 Ma. Como existe sobreposição dessas idades, considerando as incertezas, não é possível descartar que o metamorfismo de temperatura ultra-alta tenha como fonte o calor do magma intrusivo.

Palavras-chave: Complexo Anápolis-Itauçu, Faixa Brasília, metamorfismo de temperatura ultra-alta, rocha calcissilicática, wollastonita+escapolita.

INTRODUCTION Ultrahigh temperature (UHT) refers to crustal metamorphism where temperatures exceed 900°C (Harley 1998). Such extreme granulites were previously described in Brazil in rocks from the Itabuna-Salvador-Curaçá Belt in Bahia (Stormer Jr.

1973, Leite 2002), and the Niquelândia Complex (Ferreira Filho *et al.* 1998), Barro Alto Complex (Moraes & Fuck 2000) and Anápolis-Itauçu Complex (Moraes *et al.* 2002, Baldwin *et al.* 2005) in Goiás. In Brazil, UHT granulites occur as isolated outcrops within ‘common’

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granulites, in similar fashion to those described from Antarctica (Harley & Hensen 1990) and India (Brown & Raith 1996). Most commonly, UHT granulites are recognized by the diagnostic mineral assemblages that occur in pelites, which are sapphirine+quartz, aluminous orthopyroxene+sillimanite+quartz, hercynite-rich spinel+quartz, and osumilite+garnet (Harley 1998). However, calc-silicate rocks also may contain diagnostic UHT mineral assemblages, e.g. where wollastonite and scapolite occur together as a stable mineral assemblage. In Brazil, wollastonite+scapolite were previously described in marbles from Caconde, Minas Gerais (Oliveira & Alves 1976). Here we describe the first occurrence from the Anápolis-Itaçu Complex of wollastonite in stable coexistence with scapolite in impure marble.

THE ANÁPOLIS-ITAÇU COMPLEX The Brasília Fold Belt borders the western margin of the São Francisco craton. The two tectonic divisions of the belt are as follows (Fuck *et al.* 1994): an eastern, external zone comprising sedimentary and metasedimentary cratonic cover sequences that are progressively more deformed and metamorphosed to the west; and, a western, inner zone that is composed of the Araxá Group, the Anápolis-Itaçu Complex, the Goiás Massif, and the Goiás Magmatic Arc. The Araxá Group comprises turbidite-type sediments, volcanic rocks, ophiolitic mélange and granite intrusions, with metamorphism ranging from greenschist to amphibolite facies conditions, whereas the Anápolis-Itaçu Complex comprises granulites, volcano-sedimentary sequences and intrusive granites. The Goiás Magmatic Arc consists of Neoproterozoic juvenile arc rocks, comprising volcano-sedimentary rocks, and tonalite and granodiorite gneisses; arc magmatism extended between 900 and 800 Ma, and pre-collisional calc-alkaline magmatism lasted until *ca.* 640 Ma (Pimentel *et al.* 2000). The Goiás Massif comprises Archean granite-greenstone terrains, Paleoproterozoic orthogneiss, and folded Proterozoic cover rocks (Pimentel *et al.* 2000, 2004).

The Anápolis-Itaçu Complex (AIC) occupies a NNW-oriented area (260 km x 70 km) and is bounded on both sides by mylonite zones separating the complex from the Araxá Group on the east, and from the Goiás Magmatic Arc on the west. The AIC comprises an orthogneiss unit derived from tonalite, granodiorite, and mafic-ultramafic layered bodies; a paragneiss unit, including aluminous granulite, garnet-sillimanite gneiss, calc-silicate rocks, marble, and quartzite; other rocks include volcano-sedimentary sequences and a large number of elongate, NW-SE-oriented granite intrusions (Lacerda Filho *et al.* 1991). Recent geochronological data from the AIC indicate that magmatism and metamorphism occurred *ca.* 650–620 Ma, related to final ocean closure between the São Francisco, Paranapanema and Amazonian cratons (Piuzana *et al.* 2003, Pimentel *et al.* 2004, Laux *et al.* 2004).

UHT granulites in the AIC have been iden-

tified at three localities (Moraes *et al.* 2002). North of Goiânia (ML-67), an impure quartzite preserves aluminous orthopyroxene+sillimanite+quartz and sapphirine+quartz assemblages; reaction microstructures and high Al_2O_3 in orthopyroxene (12.9 wt. %) allowed the inference of a composite *P-T* path, with discrete decompression followed by a near-isobaric cooling stage from $T > 1,000^\circ C$ at > 9 kbar to $< 900^\circ C$ (Moraes *et al.* 2002, Baldwin *et al.* 2005). Near Damolândia (PT-62) and in the Monjolo stream (ANA-287), sapphirine occurs in both quartz-rich and quartz-poor rocks. In both rocks a succession of complex reaction microstructures of symplectites and coronae allows inference of a composite *P-T* path, involving a decompression segment to < 8 kbar at $> 1,000^\circ C$, followed by a near-isobaric cooling to $< 600^\circ C$ at < 6 kbar (Moraes *et al.* 2002). UHT granulites were known only locally within Anápolis-Itaçu Complex (Moraes *et al.* 2002), but recently several new occurrences of spinel+quartz, which also may be diagnostic of UHT metamorphism, were discovered between Itaçu and Petrolina de Goiás (Moraes *et al.* 2006), and now the main subject of this paper is another new occurrence. The calc-silicate rocks described here are located 3 km from Goianira (Fig. 1); they are well exposed in a quarry and form a lens within 'common' granulites. The contact relationship between the calc-silicate lens and surrounding granulites is poorly constrained. It is also not known if the Goianira-Trindade mafic-layered intrusion (Nilson 1984), that is intrusive in the country granulites, is in contact with the calc-silicate rocks or not. Our future work is going to concentrate on mapping the calc-silicate lens and host granulites.

WOLLASTONITE-SCAPOLITE CALC-SILICATE ROCKS FROM ANÁPOLIS-ITAÇU COMPLEX

The main rock is a white, medium-grained, foliated impure marble, which includes lenses and nodules of calc-silicate rock with different bulk compositions, with sharp contacts. All rocks have calcite, clinopyroxene, ternary feldspar (orthoclase with plagioclase exsolution, Fig. 2a), titanite, quartz, and wollastonite or scapolite; plagioclase is rare and may occur as anti-perthite or in coronae, as described below. Most rocks have a granoblastic fabric with silicates surrounded by calcite. Wollastonite may have a thin corona of calcite+quartz (Fig. 2b). Although rare, wollastonite and scapolite are observed in direct contact in some thin sections (Fig. 2c), but more commonly they are separated by a complex granular intergrowth of grossular-rich garnet+quartz+plagioclase±calcite (Fig. 2d, e). Some scapolite grains are replaced by plagioclase+calcite. Titanite forms sub-idioblastic grains (Fig. 2c), rarely presents ilmenite at its rims and occurs widespread, and in contact with all other phases. These microstructures indicate that the rocks may have crossed one or more of the following reactions during cooling and/or decompression and cooling, according to the different equilibration volumes (abbreviations after Kretz 1983):

Figure 1 - (a) Map of Brazil with location of main tectonic units and study area. (b) Sketch geological map of the southern portion of the Brasília Fold Belt with distribution of the Anápolis-Itauçu Complex and the surrounding units (after Laceda Filho et al. 1991 and Pimentel et al. 2000). Box marks the area shown in more detail in (c). (c) Geological map of the Anápolis-Itauçu Complex in the neighbourhood of Goiânia and Goianira, with the locality discussed in this study.

MINERAL CHEMISTRY Chemical compositions of minerals were obtained using an Electron Probe Microanalyzer (JEOL JXA-8900 SuperProbe) in the Center for Microanalysis and Microscopy at the University of Maryland. For precise spot chemical analysis of mineral composition, operating conditions were 15 kV, 20 nA, with a 5-10 μ beam size. Natural materials were used as standards for all elements.

Calcite is the pure Ca end-member. Scapolite has Eq An (equivalent anorthite content) between 0.62 and 0.83, with most grains with 0.66; Cl and SO₃ concentrations are very low, <0.01% and <0.02%, respectively, which is typical of high-Ca scapolite. Garnet is

Ca rich, with a composition dominated by grossular (grs₉₈and₂). Feldspar occurs as ternary phase, with orthoclase (or₉₅ab₁₅) as the host grain and exsolved plagioclase (an₃₇); the reintegrated composition is or₇₄ab₁₉an₇. Clinopyroxene has X_{Mg} around 0.70 and is zoned, with decrease of Al and increase of Fe from core to rim. Representative chemical compositions of all phases are given in table 1.

P-T CONDITIONS Clinopyroxene is the only Fe-Mg phase present in the rock, as garnet is almost pure grossular and all other phases are Ca-rich. Consequently, conventional thermobarometers cannot be used to calculate *P-T* conditions. Therefore, *P-T* conditions must be constrained from phase equilibria in the CASHC model system. We used the *T* vs. *X*_{CO₂} projection drawn for 10 kbar by Moecher & Essene (1990). The presence of wollastonite with abundant calcite and wollastonite+scapolite is sufficient to infer *T* >900-950°C. The fluid present during metamorphism had

Figure 2 - Backscattered electron images and photomicrograph. (a) Ternary feldspar, with andesine (An₃₇) exsolutions within orthoclase host. Scale bar is 0.7 mm long. (b) Wollastonite with a thin film of quartz and calcite. Scale bar is 0.7 mm long. (c) Wollastonite and scapolite in direct contact; titanite, ternary feldspar and calcite are also observed in the field of view. Plane polarized light; scale bar is 1.0 mm long. (d) Complex corona separating wollastonite from scapolite. Corona is composed of grossular+plagioclase with minor quartz and calcite. Scale bar is 0.7 mm long. (e) Composite corona composed of successive layers of quartz, calcite and grossular+plagioclase, separating wollastonite, in the center, from scapolite. Scale bar is 0.3 mm long.

Table 1 - Representative chemical composition of main minerals determined by electron probe microanalyzer.

Mineral	Cpx	Cpx	Wol	Grt	Pl	Or	Sep
	core	rim					
SiO ₂	51.65	51.93	50.87	40.13	59.16	64.66	45.62
TiO ₂	0.14	0.06	0.03	0.01	-	-	-
Al ₂ O ₃	3.26	1.86	0.00	22.71	26.24	19.23	31.08
Fe ₂ O ₃			0.47	0.76	0.04	0.00	-
FeO	9.40	9.78	0.02	0.01	0.00	0.00	-
MnO	0.14	0.16	0.11	0.06	-	-	-
MgO	11.47	11.74	0.07	0.08	-	-	-
CaO	24.14	24.67	48.27	37.71	7.07	0.03	20.01
Na ₂ O	0.13	0.06	0.00	0.00	7.40	1.03	1.61
K ₂ O	0.01	0.01	0.01	0.00	0.19	14.57	0.00
Totals	100.33	100.25	99.84	101.50	100.10	99.54	98.32
oxygens	6	6	6	12	8	8	-
Si	1.933	1.950	1.979	2.974	2.635	2.979	6.832
Ti	0.004	0.002	0.001	0.000	-	-	-
Al	0.144	0.082	0.000	1.984	1.378	1.044	5.488
Fe ³⁺	0.000	0.019	0.014	0.042	0.001	0.000	-
Fe ²⁺	0.294	0.288	0.001	0.000	0.000	0.000	-
Mn	0.004	0.005	0.004	0.004	-	-	-
Mg	0.640	0.657	0.004	0.009	-	-	-
Ca	0.968	0.992	2.012	2.998	0.337	0.002	3.212
Na	0.009	0.004	0.000	0.000	0.639	0.092	0.468
K	0.001	0.000	0.000	0.000	0.011	0.857	0.000
Sum	3.99	4.000	4.014	8.012	5.001	4.974	16
X _{Mg}	0.69	0.70					-
An					34.5		82.93

low X_{CO_2} , but it was not pure H₂O due to the lack of epidote-group minerals or any other hydrous phase in the rock. In domains where wollastonite occurs, it is surrounded by a thin corona of quartz+calcite, indicating that reaction 1 was crossed during cooling and/or decompression and cooling. In the domains with wollastonite+scapolite, a corona of grossular-rich garnet+quartz+anorthite in the presence of calcite was most likely formed by crossing reactions 2 and 3, and as quartz started to be available, anorthite may have been formed by reactions 4 or 5. These reactions form two possible paths. Crossing reactions 2 and 4 implies decreasing X_{CO_2} with almost no cooling, and crossing reactions 2, 3, and 5 implies cooling with a small decrease in X_{CO_2} . We prefer the second interpretation, because it implies a similar P - T path to those inferred for other portions of the Anápolis-Itaçu Complex (Moraes et al. 2002, Baldwin et al. 2005). A value of X_{CO_2} between 0.1 and 0.3 is inferred to be consistent with these reaction microstructures (Fig. 3).

The $T > 900$ - 950°C inferred from the

Figure 3 - X_{CO_2} vs. T diagram modified from Moecher & Essene (1990). Wollastonite+scapolite in contact are only stable above $\sim 900^\circ\text{C}$ under low X_{CO_2} conditions.

mineral assemblages (mainly the coexistence of wollastonite+scapolite) might be overestimated, as the diagram was calculated for the CASHC system, and

the scapolite composition is at the lower extreme of the meionite composition range, which will expand the scapolite stability field to lower T . However, this shift is not large, and the presence of ternary feldspar also suggests high T , around 1,000°C.

GEOCHRONOLOGY Concentrates of titanite grains were separated for U-Pb dating. After crushing, titanite grains were separated using a conventional gravimetric (DENSITEST®) technique and hand picking. For conventional TIMS U-Pb analysis, all fractions were dissolved in a concentrated solution of HF and HNO₃ using microcapsules in Parr-type bombs. Solution was laid in a hot plate (*ca.* 125–140°C) for three days. A mixed ²⁰⁵Pb–²³⁵U spike was used. Chemical extraction followed a standard anion exchange technique with Teflon microcolumns, following a modified routine set by Krogh (1973). U was collected with HBr following the procedure by Parrish *et al.* (1992). Pb and U were loaded onto a single Re filament with H₃PO₄ silica gel. Isotopic analysis was carried out at the Geochronology Laboratory of Universidade de Brasília, using a Finnigan MAT 262 multicollector mass spectrometer. Laboratorial blank is better than 15 pg. Ages were calculated with PBDAT (Ludwig 1993) and ISOPLOT-Ex (Ludwig 2001). Results are presented in Table 2, and errors of isotopic ratios are given as 2σ.

U-Pb in titanite yielded a date of 632 ± 6 Ma (Fig. 4). As titanite closure temperature for U-Pb system may be as high as 700°C (Frost *et al.* 2000), we in-

Figure 4 - Concordia diagram for ID-TIMS U Pb age for titanite from wollastonite-scapolite-clinopyroxene marble from Goianira.

terpret this age to record post-peak retrograde cooling and not the age of peak conditions during regional UHT metamorphism. However, we infer that peak metamorphic conditions probably were not much earlier than this age.

DISCUSSION The coexistence of stable wollastonite+scapolite and the presence of ternary feldspar confirm another occurrence of an ultrahigh-temperature mineral paragenesis in the Anápolis-Itaçu Complex, albeit in a different bulk composition than in Al-Mg rich rocks. U-Pb dating has shown that some mafic rocks have crystallization ages between 6 to 34 Ma younger than the metamorphic peak in the Anápolis-Itaçu Complex (Laux *et al.* 2004, Hollanda *et al.* 2006). The impure marble described here is close to the Goianira-Trindade mafic-layered intrusion, but up to now, it has not been possible to determine the structural relationship between them. Zircon grains from a leucogabbro yielded a SIMS U-Pb age of 626 ± 2Ma, interpreted to record igneous crystallization (Hollanda *et al.* 2006). This age overlaps within uncertainty the TIMS U-Pb age of 632 ± 6 Ma obtained from titanite from the impure marble. Thus, we cannot rule out the possibility that contact metamorphism by the Goianira-Trindade mafic-layered intrusion was the heat source for UHT metamorphism, at least locally. However, it is more probable that asthenospheric heat was the source for the regional UHT metamorphism within the Anápolis-Itaçu Complex, and the basaltic magmatism more likely was the result of asthenosphere decompression as previously proposed (Moraes *et al.* 2002).

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Table 2 - Titanite U-Pb isotopic data of Goianira marble.

Sample/fraction	2	3	4
Size (mg)	0.142	0.148	0.178
U ppm	69.9	62.9	77.6
Pb ppm	8.1	6.9	19.2
Pb ²⁰⁶ / Pb ²⁰⁴	664.28	927.26	62.66
Pb ²⁰⁷ */ Pb ²³⁵	0.875	0.855	0.811
(pct)	1.25	0.92	0.77
Pb ²⁰⁶ */ U ²³⁸	0.103	0.102	0.099
(pct)	0.94	0.89	0.43
Correl. Coefi. (rho)	0.7575	0.9734	0.6191
Pb ²⁰⁷ */ Pb ²⁰⁶ *	0.061	0.0604	0.0588
(pct)	0.82	0.21	0.61
Pb ²⁰⁶ */ U ²³⁸ Age	635.6	629.7	613.8
Pb ²⁰⁷ */ U ²³⁵ Age	638.4	627.6	602.9
Pb ²⁰⁷ */ Pb ²⁰⁶ * Age	648.1	620.0	562.1
± (Ma)	18	4.6	13
Quant.	5	8	9

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