Anatase crystals of unusual habit in quartz veins from the Diamantina region (Espinhaço Range, Minas Gerais)

http://dx.doi.org/10.1590/0370-44672017710069

Mario Luiz de Sá C. Chaves
Professor
Universidade Federal de Minas Gerais - UFMG
Instituto de Geociências
Belo Horizonte - Minas Gerais - Brasil
mlschaves@gmail.com

Joachim Karfunkel
Professor
Universidade Federal de Minas Gerais - UFMG
Instituto de Geociências
Belo Horizonte - Minas Gerais - Brasil
jkarfunkel@yahoo.com

Vladimir Bermanec
University of Zagreb
Institute of Mineralogy and Petrology
Hortovac bb 10000 - Zagreb - Croatia
vberman@public.carnet.hr

Vladimir Zebec
Croatian Natural History Museum
Demetrova - Zagreb - Croatia
vladimir.zebec@pfos.hr

Ricardo Scholz
Professor
Universidade Federal de Ouro Preto - UFMG
Escola de Minas
Ouro Preto - Minas Gerais – Brasil
r_scholz_br@yahoo.com

Luiz Alberto D. Menezes Filho
(In Memoriam)

Abstract

The Espinhaço Range, in the Diamantina region (central part of the State of Minas Gerais), is known worldwide as a famous source of associated occurrence of quartz, rutile and/or anatase crystals. The latter is also a classic accompanying mineral of diamonds in the alluvial placers. Primary anatase is related to hydrothermal quartz veins cutting geological units of the Espinhaço Range. In the last decade, outstanding large sized anatase crystals (up to 4 cm) in such veins have been reported from two areas, showing unusual habits and partial intergrowth with rutile. They are colorless, ocher brown, or golden yellowish, often double terminated, and iron rich. Due to their strong adamantine luster and pseudo-octahedral habit, some resemble diamonds. Two different morphological types have been studied: a simple crystal habit solely with {011} faces, and double terminated complex anatase crystals with one or more of the following forms: {011}, {012}, {013}, {017} and {112}. The geological environments as well as general mineralogical characteristics are also described.

Keywords: anatase, quartz veins, Diamantina region, Espinhaço Range.

1. Introduction

Diamond alluvial deposits have been discovered in the vicinities of Tijuco village, nowadays Diamantina town (central part of the State of Minas Gerais – Figure 1a), officially, in 1729, and for more than 140 years, the region was the most important source worldwide, before the discovery of diamonds in South Africa in the late 1860's. In diamondiferous gravel-concentrates, several heavy minerals have been designated since the old times as "satellites", or accompanying minerals, due to their permanent occurrence in these deposits. They should not be mistaken for indicator minerals (e.g. Cr-pyrope, diopside and Mg-ilmenite), a term used in the diamond prospecting literature.

Anatase is one of the most important accompanying minerals, which has been described in detail from the placers and quartz veins since the 19th century (e.g. Gorceix, 1880; Derby, 1900; Hussak, 1917; Guimarães, 1934; Cassedanne & Cassedanne, 1974). In the mid- 1990s unusual, odd, funny-looking anatase came to the Diamantina mineral market; they were mined in the Datas de Cima farm (Datas County). In 2002 another anatase deposit was discovered near the Caxambu farm (Gouveia County). Anatase up to 4 cm long (on "c" axis) was recovered in these occurrences, but the overall size varies around 1 cm.

Several articles involve the geological, mineralogical and geochronological aspects of the quartz veins in the Espinhaço Range, a mountain chain that crosses the states of Minas Gerais and Bahia (e.g., Foord *et al.*, 1994; Chaves *et al.*, 2003, 2006, 2010, 2017; Chaves, 2007; Chaves & Menezes Filho, 2017), due to their geotectonic and economic importance. The present report describes the anatase crystals and the geologic framework of these two new occurrences, as well as the crystallographic explanation for the forms of the crystals, and their chemical compositions. The article also aims to describe the temporal relationship between anatase and rutile in the region.

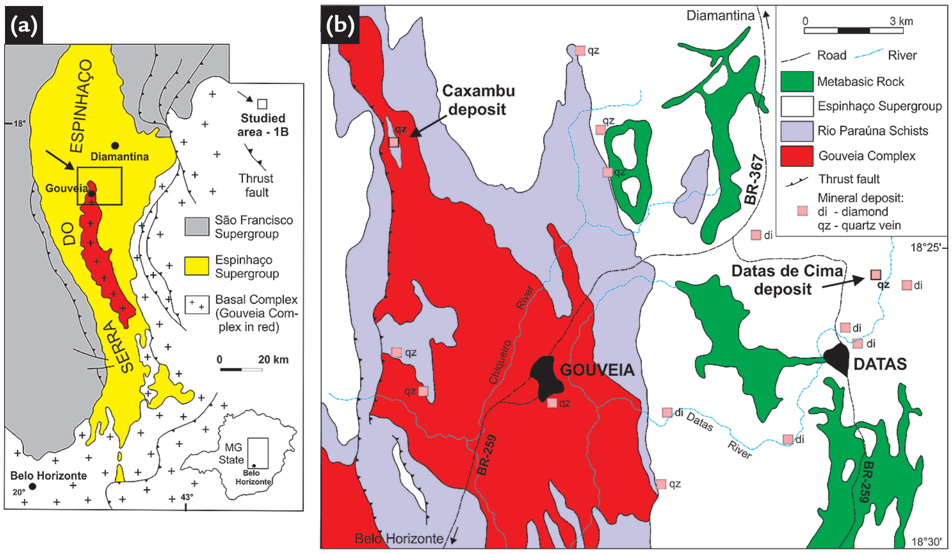

Figure 1
(a). General geologic map of the southern Espinhaço Range, with the arrow showing the focused area south of the Diamantina town in Minas Gerais State (MG).
(b). Geologic map of the Datas-Gouveia region with the locations of the two studied Datas de Cima and Caxambu anatase deposits (modified from Fogaça, 1996).

2. Geological setting

The main stratigraphic unit that sustains the Espinhaço Range is the Espinhaço Supergroup, a Paleo to Mesoproterozoic metasedimentary sequence, probably deposited between 1.75 to 1.20 Ga (Dossin *et al.*, 1990; Chemale Jr. *et al.*, 2012). It is formed mainly by quartzite, interbedded with layers of phyllite and diamond-bearing metaconglomerate. In the south of Diamantina, comprising the nearby counties of Datas and Gouveia (where the anatase deposits subject of this article were found), there is a structural "window" that exposes archean granitic rocks of the Gouveia Complex, and marginal schists of the Rio Paraúna Volcano-Sedimentary Sequence (Archean?). The anatase deposit of Caxambu farm is associated with these rocks, whilst the Datas deposit is related to quartzites belonging to the basal sequence of the Espinhaço Supergroup (Figure 1b).

A myriad of quartz veins cuts mostly the lithologies of the Espinhaço and Rio Paraúna sequences and was formed by hydrothermal activity originated by metamorphic processes that occurred during the final stages of the Brasiliano Cycle, ca. 490 Ma (Chaves *et al.*, 2010, 2017). The Espinhaço fold belt lies east of the most important geotectonic mega-unit of central-eastern Brazil, the São Francisco Craton (Almeida, 1977). The veins vary from a few millimeters up to several meters wide; they are normally associated with more intense deformation zones, such as geologic contacts, thrust faults and axis of folds (Chaves *et al.*, 2003; Chaves, 2007).

3. Mineral deposits

In the Datas deposit (Figures 1b and 2) the quartz vein shows an average thickness of 80 cm, with a N15°E direction and 65°SE dip, concordant with the metamorphic foliation of the fine-grained quartzite, belonging to the Sopa-Brumadinho Formation (Espinhaço Supergroup). It has some pockets that contain quartz crystals

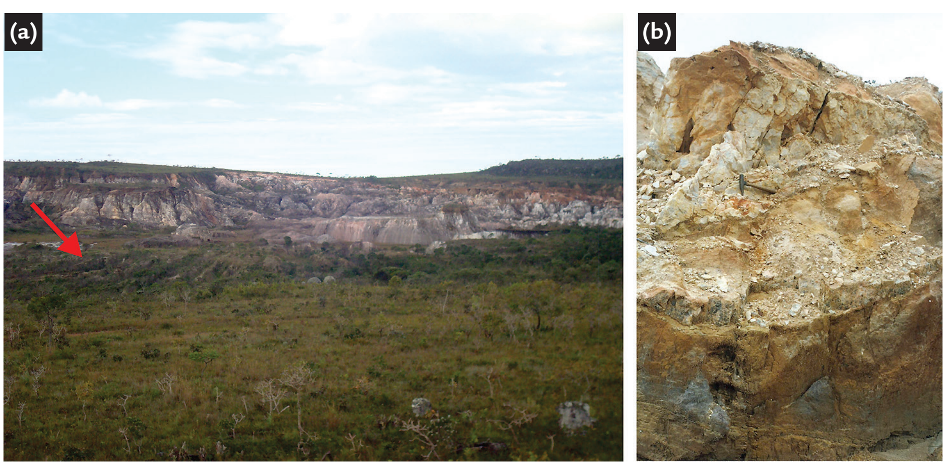

Figure 2
(a). Panoramic view of the diamond exploration area north of Datas town showing the old Datas de Cima diamond mine (red arrow points toward the location of the anatase deposit). (b). View of the mined quartz vein.

(mostly milky), which have been mined by diggers in 1995-1996, and 2008. Anatase was then kept by the explorers, more as a collection mineral. The generally low quality of the quartz crystals forced the diggers to abandon this area, and to return to their original activities – the diamond exploration. These relict anatases came to the Diamantina mineral market only some years ago. They showed a light tan to dark brown, shiny appearance with the crystal size along the "c"-axis triple or more the length along the "a"-axis, having bipyramidal shape with needle-like apexes, almost like a top-toy.

The Caxambu deposit (Figures 1b and 3) was mainly mined between 2002 and 2004; the anatase crystals were found inside a white clay matrix originated by the weathering of a fine-grained schist (Rio Paraúna Supergroup) containing quartz veins that also produced low commercial grade hyaline and smoky quartz. This deposit showed an irregular shape, with the host rock foliation varying between N5-10°E/45-50°SE. Two small pits were opened, at a distance of 20 m between each other; the veins are about 0.3-0.6 m wide and their length is near 5 m long. On both pits the excavation continued to a depth of 3 m, without any sign of reduction of the vein width. The specimens show a complex parallel growth of bipyramid crystals, with a light tan to caramel color, measuring up to 3 cm, partially to totally coated by tiny acicular copper-colored rutile crystals.

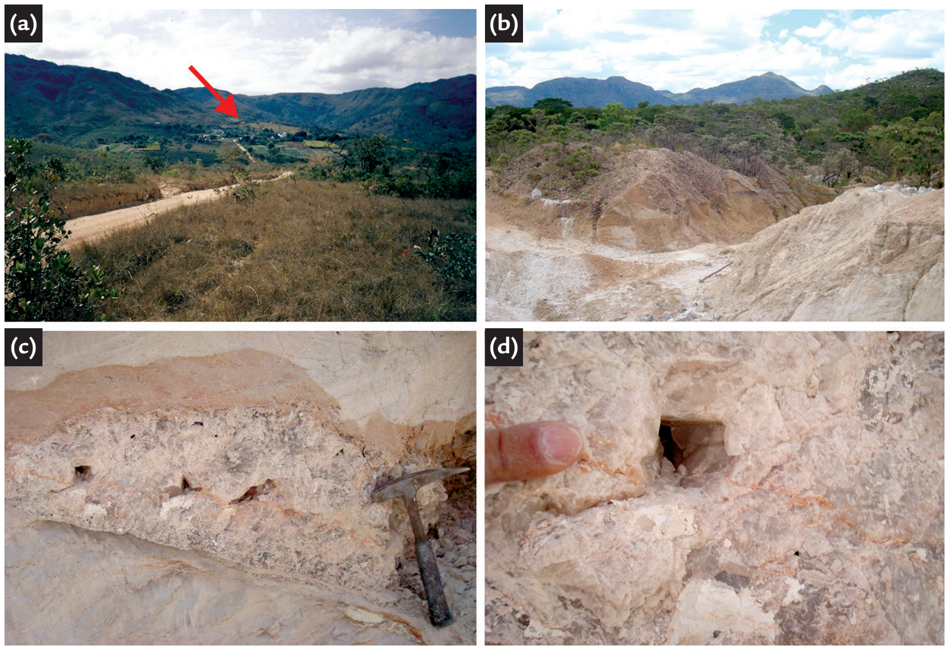

Figure 3
(a). Panoramic view of the Caxambu farm area (Gouveia County), showing a flattened area where Basal Complex rocks outcrop, surrounded by quartzite hills of the Espinhaço Supergroup (red arrow marks the location of the anatase deposit).
(b). Detail of one of the shafts cutting argillaceous schists in which the deposit is located.
(c). Irregular quartz vein about 20 cm wide with negative prints of the anatase crystals.
(d). Detail of one of these 1.5 cm cavity.

4. Morphology of the crystals

The anatase crystals commonly found in the diamond-bearing placer deposits from the Diamantina region (known as "sericoria" by local diggers) have been subject of detailed studies by several authors for over one hundred years (e.g., Derby, 1900; Hussak, 1917; Guimarães, 1934; Cassedanne & Cassedanne, 1974). The most common habit is pseudo-octahedral and the crystals are seldom rounded, pointing towards a very short alluvial transport (Figure 4a). The color varies widely from deep blue to colorless, yellow to gold, white to silver, and brown to copper red. The size is usually small, and the largest crystals rarely exceed 1 cm; anatase occurs inside and outside the quartz crystals only in the hydrothermal quartz veins (Figure 4b).

Many crystal faces for these alluvial crystals have been determined and described by old studies (listed by Hussak, 1917): {001}, {111}, {112}, {101}, {113}, {115}, {117}, {201}, {301}, {107}, {1.1.14}, {5.1.19}, {5.0.19}, {5.5.12}, and {5.5.11}. All authors have already mentioned pyramidal specimens with typical summit apexes. Hussak (1917) also report the common "paramorphosis" (an old term for a type of pseudomorphism) of anatase to rutile in the region. However, on the two studied deposits the morphological characteristics of anatase crystals were similar, although quite different from the previously described, and will be detailed separately.

Figure 4
(a). Parcel of "common" form of gray-bluish anatase crystals found in diamond-bearing alluvial placers from the Jequitinhonha River (Diamantina).
(b). Detail of a quartz specimen also with a "common" form of brown-yellowish anatase crystal on quartz from other local in the Datas region.

4.1. Datas de Cima farm, Datas

Unusual anatase crystals were found in 1995 at Datas de Cima farm, most of them measuring less than 1 cm along the "c" axis, although some reach 2-3 cm long (Figure 5a). They are translucent to near opaque, show a light tan to dark brown color and shiny appearance. Several crystals present a general pseudo-octahedral center and a growth of an elongated pyramidal faces on both sides (Figure 5b). The ratio between the "c" and "a" axis can reach three or more; some specimens showed an overgrowth of rutile needles over the anatase.

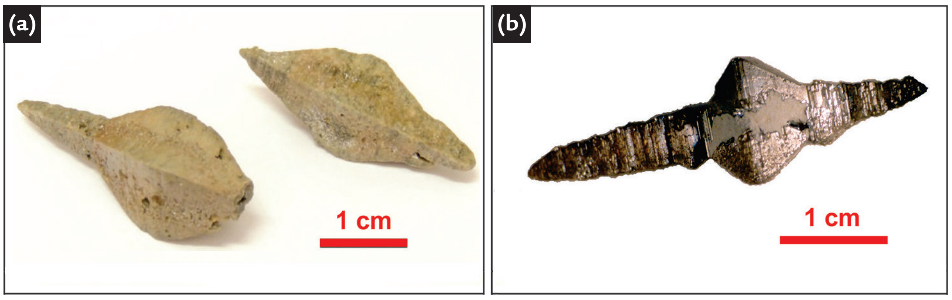

Figure 5
(a). Typical anatase crystals showing double bipyramidal forms from the Datas de Cima deposit.
(b). A more elongated crystal from this deposit, showing different forms in its central part.

Part of the crystals has a simple combination of forms {011}, {012}, {013} and {017}. Many crystals grew parallel in direction of c-axis. The central part of the crystal is larger and every further form is smaller; forms {013} and {017} are measured just on the ends of the formation (illustrated by the Figures 5b and 6a-b). The other crystal aggregates also consist of one larger central part and many smaller parallel growths on both sides – top and bottom. However, all smaller crystal growths are of equal size. These parts show combinations of two forms {011} and {012}. Besides such crystals, there are also usually more parallel crystal growths on the corners of the larger central part of the crystal in the formation with the combination of the forms {001}, {012}, {013} and {017} (Figure 6b).

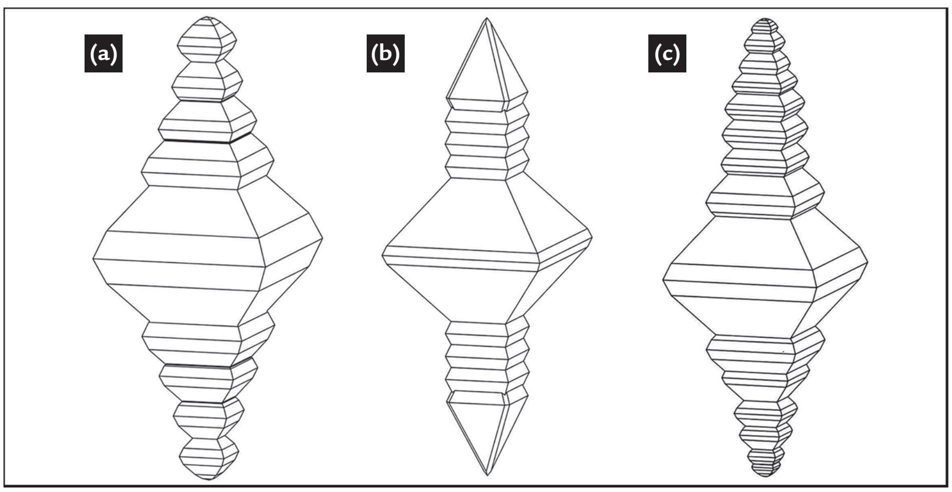

Figure 6
Idealized drawing of slightly different anatase crystallographic models of the second type from Datas de Cima deposit (case (a) represents the crystal from Figure 5b).

Some other anatase crystals consist of one larger central part of the crystal with measured forms {011} and {012}, similar to the first described, but all smaller crystal growths are of equal size and the last crystal growths in the series have additional small faces of form {112} (Figure 6c). However, there are also anatase crystals in parallel growth which are similar to the other described, but the faces of form {011} are somewhat bigger and of equal surface as faces of form {012} (Figure 7a-b). Other unusual forms, even more complex, also occur in this deposit, sometimes coated by rutile needles.

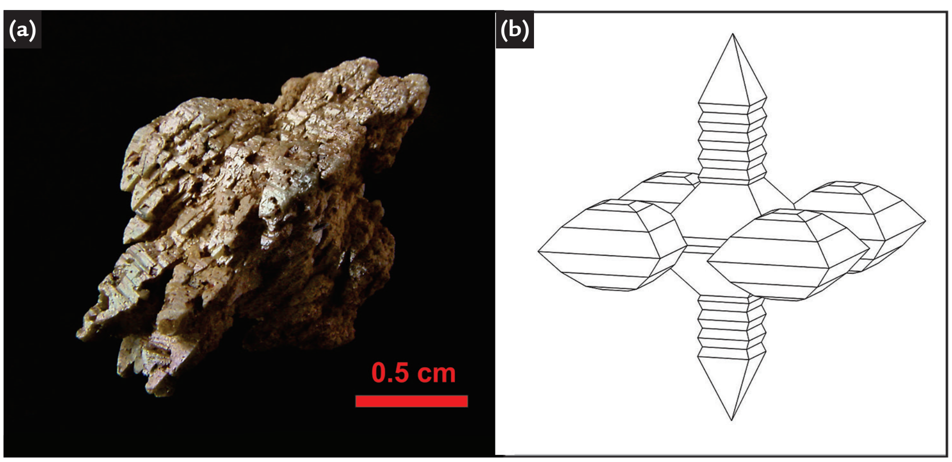

Figure 7
(a) Anatase crystal with parallel growths.
(b) A possible idealized drawing for these aggregates.

4.2. Caxambu farm, Gouveia

In the Gouveia deposit at least three major pockets were found; the most important was the first one in 2002. It contained over 1,000 anatase crystals measuring from 1 to 3.5 cm with "c"/"a" ratio varying from one to four (Figure 8a), and a parallel growth of smaller parts over the main pyramidal faces. Several of these specimens showed a complex parallel growth of bipyramidal crystals, with a light tan to caramel color, often partially to totally coated by tiny acicular copper-colored rutile crystals.

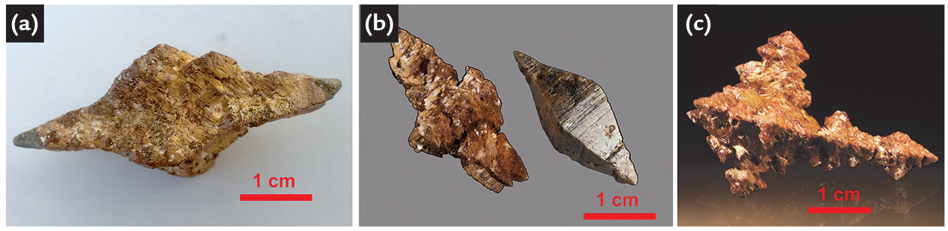

Figure 8
(a). Anatase crystal partially coated by rutile from Caxambu farm.
(b). Anatase crystal coated by two stacks of rutile needles (left) and with a "near-commom" form, without rutile coat (right).
(c). Anatase crystal completely coated by rutile.

After the anatase was formed the copper-colored rutile needles probably started to crystallize, growing epitaxially parallel to one of the edges of the pyramidal faces. On some specimens the growth of rutile is only incipient, and it can only be seen with a magnifier. However the majority of these specimens have a coating over 1 mm, followed by the growth of two other stacks of rutile needles, at 60°; these two additional stacks grew at disordered angles from the anatase crystal faces (Figure 8b, left). The second pocket, also found in 2002, contained several hundreds of anatase crystals, without rutile, showing a "c"/"a" ratio of two (Figure 8b, right).

On many specimens the anatase is totally coated by rutile. However, when crystals are broken, a pure anatase core can be seen, suggesting that pseudomorphism of rutile after anatase didn't occur. A partial dissolution of the anatase occurred simultaneously with the deposition of the rutile, because the outer layers of rutile needles occur at parallel levels to the remaining visible anatase crystal faces.

The last mined pocket (found in 2004) also contained several hundreds of crystals with the same forms, but with rutile needles (also copper-colored and growing epitaxially over the anatase) forming "patches" on the anatase surface. The intensity of the cover is varied; some crystals were half coated by rutile with other half of pure anatase (Figure 9a), whilst others were all coated by rutile except on the two apexes, where pure anatase still remains (Figure 9b). Complex forms of anatase aggregates randomly coated by rutile is common (Figure 9c-d).

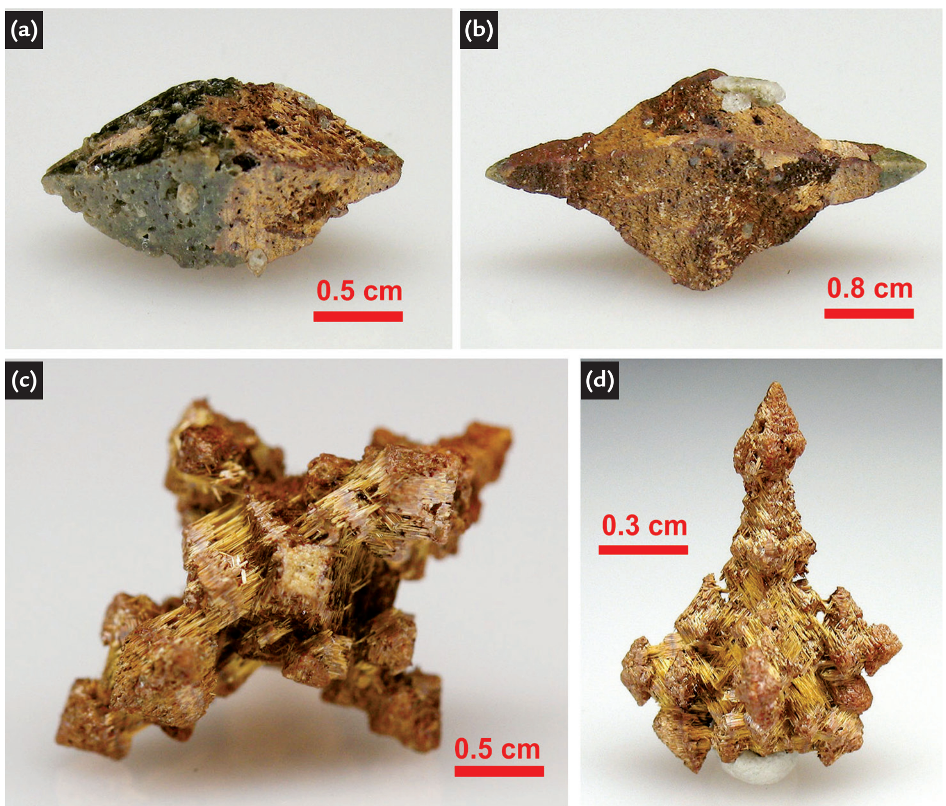

Figure 9
(a). Anatase crystal half coated by rutile.
(b). Anatase crystal coated by rutile except on the two apexes, where pure anatase still remains; some tiny quartz crystals also occur (c/d). Complex forms of anatase crystals intensely coated by rutile.

5. Mineral chemistry

According to Deer *et al.* (1962), very few chemical analyses were available for the mineral, but the main elements liable to be found in minor amounts include Fe and/or Sn. Chemical composition of anatase from Diamantina region was analyzed in the Physics Department of the Federal University of Minas Gerais, with JEOL-JXA8900R electron microprobe (Table 1). An accelerating potential of 15 kV, a specimen current of 20 nA and a beam diameter about 20 μm were used, with the following standards: rutile – to TiO_2 and magnetite – to FeO. Anatase and rutile were previously determined on the basis of X-ray diffraction on powdered samples.

Data from the Caxambu deposit (Gouveia) compared with the gray-bluish anatase from the Jequitinhonha River placer (Diamantina) showed significant variation of the iron content (Table 1). The FeO content of Caxambu samples is around 1.00% with a maximum value of 1.21%, while in samples of Jequitinhonha River, this content is about 10 times lower, around 0.10%, indicating different P/T conditions of growth and/or different host rocks. For comparisons, it can be clearly seen that the samples from the Cipó River are similar to those from the Jequitinhonha River, while the Capão do Lana (Ouro Preto) and unknown location (Diamantina) resembles the samples studied in this work.

No.	TiO_2	FeO	Al_2O_3	V_2O_5	SnO_2	PF	Total
G-1	99.68	0.67	Nd	Nd	Nd	Nd	100.35
G-2	98.86	1.17	Nd	Nd	Nd	Nd	100.03
G-3	98.49	0.93	Nd	Nd	Nd	Nd	99.42
G-4	98.45	1.21	Nd	Nd	Nd	Nd	99.66
J-1	99.66	0.08	Nd	Nd	Nd	Nd	99.74
J-2	99.93	0.11	Nd	Nd	Nd	Nd	100.04
J-3	99.78	0.13	Nd	Nd	Nd	Nd	99.91
J-4	99.81	0.14	Nd	Nd	Nd	Nd	99.95
RC-a	98.98	0.15	0.15	0.00	0.00	0.77	100.15
RC-b	98.86	0.00	0.00	0.86	0.00	0.53	100.25
CL	98.60	1.40	0.00	0.00	0.00	0.00	100.00
D-un	98.36	1.11	0.00	0.00	0.20	0.00	99.67

Table 1
Electron microprobe analyses in representative samples of yellow-golden crystals of anatase from Caxambu deposit, Gouveia (G-1 to G-4), and gray-bluish crystals from Jequitinhonha River, Diamantina (J-1 to J-4) (means of five spots; all iron content as Fe^{2+}; Nd, not determined). Literature comparisons: RC-a and RC-b, Rio Cipó, Diamantina region; CL, Capão do Lana topaz mine, Ouro Preto; D-un, unknown locality in Diamantina region (Deer *et al.,* 1962).

There are also many cavities and other solid inclusions within anatase crystals. According to Bermanec *et al*. (2004), besides rutile, two types of mica (Ti-rich and Ti-poor varieties), zircon, monazite-(Ce), and Mg-Fe carbonate (just slightly richer in Mg-component) were recognized using scanning electron microscope coupled with EDS. Prismatic, long, almost black thin crystals, probably tourmaline (schorl), occur associated with anatase only from Caxambu samples.

Unit cell dimensions of anatase were also determined (Datas anatase) to be a=3.773(2), c=9.475 and V=134.9(2), that can suggest that there are no important substitutions within crystal structure (Bermanec *et al*., 2004).

6. Concluding remarks

The Datas-Gouveia region is especially rich in the TiO_2 polymorphs rutile and anatase (very rarely brookite). According to Hussak (1917), the "paramorphosis" of anatase to rutile is completely absent in other diamond-producing areas (Bahia State; Triângulo Mineiro, western part of Minas Gerais State; Tibagi River in Paraná State; as well as in Goiás and Mato Grosso states), where anatase and rutile also occur associated with alluvial diamond. The actual knowledge confirms Hussak's observation. This indicates special and particular growth and crystallization conditions of the quartz veins from the Espinhaço Range.

There are two completely different crystal habits of anatase in the Diamantina region. The first is simple clear pseudo-octahedral, identified commonly in Jequitinhonha River gravel samples, however rarely in the Datas de Cima and Caxambu deposits. The second are complex bipyramidal crystals in parallel growth that resemble small swords. Thaggregate latter crystal habit is quite uncommon and has not yet been described in relevant literature.

The high anatase-rutile association of the crystals in the pockets from the Gouveia deposit suggests that the physical chemical conditions were at the stability limit of both minerals, with predominance of anatase. After anatase has been crystallized, it started to be epitaxially coated by rutile needles, with slightly different orientation on the anatase crystal faces; this coating could be partial to complete.

Probably, during the beginning of crystallization the conditions of pressure and temperature were lying in the anatase P/T stability field close to the rutile field as demonstrated by Dachille *et al*. (1968) for specimens from other regions. According to these authors, the growth of rutile occurs due to temperature increase. After the end of the full anatase growth, the crystals were partially to completely coated by rutile.

The origin of a possible titanium chemical anomaly in quartz veins from the Datas-Gouveia area of the Espinhaço Range deserves further studies involving the metavolcanic rocks that occur in the region.

Acknowledgements

The first author thanks the CNPq for granting the research productivity scholarship.

References

ALMEIDA, F. F. M. O cráton do São Francisco. ***Revista Brasileira de Geociências***, v. 7, p. 349-364, 1977.

BERMANEC, V. et alii. Unusual anatase crystal from the Diamantina region (Minas Gerais, Brazil). In: INTERNATIONAL GEOLOGIC CONGRESS, 32, 2004, Florence. Abstracts... Florence: IMA, 2004. Part 1, p. 218.

CASSEDANNE, J. P., CASSEDANNE, J. O. Les anatases de Diamantina (Minas Gerais): minéralogie et importance paléogéographique. ***Anais da Academia Brasileira de Ciências,*** v. 46, p. 83-97, 1974.

CHAVES, M. L. S. C. O megaveio de quartzo da serra da Catinga (Datas/Gouveia, MG). ***Geociências,*** v. 26, p. 109-117, 2007.

CHAVES, M. L. S. C., MENEZES FILHO, L. A. D. Minerais do grupo da crichtonita em veios de quartzo da serra do Espinhaço (Minas Gerais e Bahia). Geologia USP, ***Série Científica,*** v. 17, p. 1-10, 2017.

CHAVES, M. L. S. C. et alii. Estruturação "em rosário" dos depósitos de quartzo hidrotermal do morro do Juá (Gouveia, MG). ***REM-Revista Escola de Minas,*** v. 56, p. 15-20, 2003.

CHAVES, M. L. S. C. et alii. Monazita associada a veios de quarto hidrotermal na serra do Espinhaço (MG). In: CONGR. BRAS. GEOL., 43, 2006, Aracaju. ***Anais...*** Aracaju: SBG, 2006. p. 62.

CHAVES, M. L. S. C. et alii. Monazita em veios de quartzo da serra do Espinhaço Meridional (MG): mineralogia, geocronologia e implicações geológicas. ***Revista Brasileira de Geociências,*** v. 40, p. 506-515, 2010.

CHAVES, M. L. S. C. et alii. Idades U-Pb em xenotímio-(Y) de um veio de quartzo com almeidaíta e parisita-(La), novos minerais encontrados na serra do Espinhaço (Novo Horizonte, Bahia). ***Geociências,*** v. 36, 2017 (submitted).

CHEMALE Jr., F. et alii. Unravelling a Proterozoic basin history through detrital zircon geochronology: the case of the Espinhaço Supergroup, Minas Gerais, Brazil. ***Gondwana Research,*** v. 22, p. 200-206, 2012.

DACHILLE, F. et alii. Pressure-temperature studies of anatase, bookite, rutile and TiO_2-II. ***American Mineralogist,*** v. 53, p. 1929-1839, 1968.

DEER, W. A. et alii. Rock-forming minerals, London: Longman, 1962, (v. 5 - Non-silicates). 371 p.

DERBY, O. A. On the association of argillaceous rocks with quartz veins in the region of Diamantina, Brazil. ***American Journal of Science,*** v. 7, p. 343-348, 1900. (Ser. V).

DOSSIN, I. A. et alii. Compartimentação litoestratigráfica do Supergrupo Espinhaço em Minas Gerais: os grupos Diamantina e Conselheiro Mata. ***Revista Brasileira de Geociências,*** v. 20, p. 178-186, 1990.

FOGAÇA, A. C. C. Mapa Geológico da Folha Diamantina, Minas Gerais. Belo Horizonte: Convênio COMIG/IGC-UFMG, 1996. (1 mapa).

FOORD, E. E. et alii. Plumboan crichtonite from the Fazenda Guariba, Minas Gerais, Brazil. ***Mineral Record,*** v. 25, p. 133-135, 1994.

GORCEIX, H. Sur le gisement du diamant au Brésil. ***Societé Mineralogique de France Bulletin,*** t. III, p. 36-38, 1880.

GUIMARÃES, D. ***À margem de "Os Satellites do Diamante".*** Belo Horizonte: Serviço Geológico do Estado de Minas Gerais, 1934. 58p. (Monografia 2).

HUSSAK, E. ***Os satellites do diamante.*** Rio de Janeiro: Typographia do Jornal do Commercio, 1917, 57 p.

Received: 28 April 2017 - Accepted: 6 September 2017.