

The occurrence of dumortierite in the Espinhaço Range, Minas Gerais, Brazil, and its mineralogical-crystallographic comparison with other specimen

Adolf Heinrich Horn^{1*}
Yves Fuchs²
Soraya de Carvalho Neves³
Etienne Balan⁴
Jorge Linarès⁵

¹ Chemical (Chemieschule Dr E. Elhardt). Geologist and Paleontologist (Ludwig-Maximilians Universität München). Master in Geology and Paleontology (Ludwig-Maximilians Universität München). Ph.D in Geology and Geochemistry (Ludwig-Maximilians Universität München). Post Doctorate in Geochemistry (Université Jean Monet-França). Professor at UFMG.

² Geologist (Faculté des Sciences Paris). Master in Geology. (Université de Nancy). Ph.D in Geology (Université de Nancy). Professor at University Paris-Est Marne-la-Vallée.

³ Geologist (UFMG). Master in Geology (UFMG). Ph.D in Geology (UFMG). Professor at UFVJM.

⁴ Geologist (École Normale Supérieure de Cachan). Ph.D in Geology (Université Denis Diderot). Professor at Université Pierre et Marie Curie.

⁵ Geologist Université Pierre et Marie Curie). Master in Geology (Université PUCP de Lima – Peru). Ph.D in Geology (Université de Grenoble). Professor at the Université de Versailles St. Quentin en Yvelines.

Abstract Samples of dumortierite from various localities of Brazil (Serra do Espinhaço-Minas Gerais, Macaúbas-Bahia) were analyzed with microprobe and the results were compared with those obtained from samples from Louvincourt dumortierite deposit (Quebec, Canada), Lincoln Hill-Champion Mines dumortierite deposit (Nevada, USA) Jack Creek dumortierite deposits (Montana), Acuélos (Chile) and from Madagascar (locality unknown). Infra-red spectroscopy (FTIR), ERP, Mössbauer effect spectroscopy (MS) were performed on the samples. Fourier transform infrared spectroscopy (FTIR), electron paramagnetic resonance (EPR) and Mössbauer spectroscopy have been used to study dumortierite samples of Brazil and of other origins. FTIR spectroscopy shows the existence of various environments for the OH- groups, which are related to substitutions and/or vacancies in the M1 octahedral site. Mössbauer spectroscopy consistently reveals the presence of divalent iron in 2 different octahedral sites, trivalent iron in one octahedral site and minor IVCT or IMMT iron. EPR also shows that isolated Fe³⁺ is present in various types of sites. The other signals ascribed to paramagnetic Fe³⁺ correspond to tetrahedral or more distorted octahedral sites.

Keywords: dumortierite; Espinhaço Range; Rio Paraúna Super Group; Bahia; infra-red.

1. Introduction

Dumortierite is the second most abundant borosilicate mineral after tourmaline in crustal rocks. It has been reported in pegmatites (HUIJSMANN et al., 1982; GREW et al., 1995; GREW et al., 1998, GREW, 1996), per aluminous granites (VISONA; FUCHS, 1997), contact metamorphic rocks (GONZALÈS; RIVANO, 1979) quartzite and per aluminous rocks that have undergone hydrothermal alteration (BEUKES et al., 1987; WILLNER; SCHREYER, 1991; VISSER et al., 1997). Dumortierite has also been found in hydrothermal systems in association with andalousite and pyrophyllite (KAYUPOVA; TILEPOV, 1979; FOIT et al., 1989; PAULET, 1992; PAULET et al., 1991; TANER; MARTIN, 1993; FUCHS; MAURY, 1995; CHOO; KIM, 2002).

The color of many pink and blue rocks and minerals (such as blue or pink quartz can be related to their dumortierite content (GOREVA et al., 2001; CHI et al., 2002). Synthesis of dumortierite was achieved by Werding and Schreyer (1983a, 1983b) who describes later (WERDING; SCHREYER, 1986a, 1986b, 1988, 1990) the exact physical and chemical conditions.

1.1. Regional geology

The dumortierite occurs in units of the Paraúna and Espinhaço Super groups (ALMEIDA; HASUI, 1984; ALMEIDA-ABREU, 1989; CASSEDANNE, 1990) never far from tectonic contacts, and frequently associated to hydrothermal phenomena affecting the metamorphosed sediments. Dumortierite presents either a dark blue (Fazenda Formação 2) or a reddish to pale blue color (Macaúbas; Fazenda Formação 1).

* hahorn@gmail.com

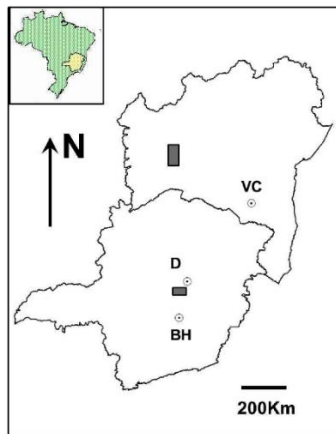


Figure 1 – Localization map of Vaca Morta (a) and Fazenda Bandeirinha (b) working áreas on the map of Minas Gerais State. The cities of Belo Horizonte (BH), Vitória da Conquista (VC) and Diamantina (D) are indicated. Source: IBGE (2014).

The two main localities of dumortierite occurrences are Vaca Morta, near Macaúbas in the South Western part of the Bahia state and Fazenda Bandeirinha south of Diamantina, northeastern of the state Minas Gerais (FIG. 1).

1.2. Localities

1.2.1 Vaca Morta

The dumortierite occurs together with colored to colorless lazulite and with other phosphates like crandallite, scorzalite in the quartzites of Espinhaço Super group (FIG. 2; Lower Middle Proterozoic b).

A subdivision of the Espinhaço units into Boquira and Tiros formation was proposed by Kaul (1970) and more precisely defined by Schobbenhaus (1972).

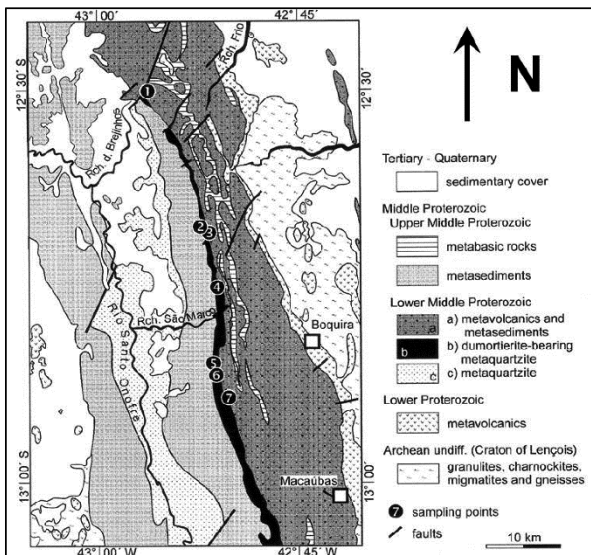


Figure 2 – The detailed map of the Vaca Morta area is from Lopez and Souza (1985). The numbers are identifications of sampling points at different quarries.

Source: modified after Morteani; Ackermann, 2005; Schobbenhaus, 1972a, 1972b.

The dumortierites occurrences are located within 1700-2200Ma old quartzites, that are extremely folded and

fractured and contains hydrothermal Pb-Zn deposits (Boquira Formation), (CASSEDANNE, 1966; CASSEDANNE; MELLO, 1966; FLEISCHER, 1971; VISSER et al., 1997 and HORN et al., 1998A).

The dumortierite rich quartzites are found on the eastern flank of the Serra da Vereda indicated by black unit in the map (CASSEDANNE; FRANCO, 1966) extending over 15km with a thickness of approximately 30m.

This dumortierite deposits are subdivided in three lithological types (FLEISCHER, 1971):

Type 1: A fine quartzite, with little ore, no re-crystallization and visible layering indicated by blue layers from 20 to 50cm thick.

Type 2: A fine highly re-crystallized quartzite with concoidal fractures showing no layering but a homogenous blue color.

Type 3: A quartzitic poorly recrystallized micro-conglomerate with dumortierite and disthene together in blue stains and irregular veins.

1.2.2 Fazenda Bandeirinha

On the map of Diamantina (SE-23-Z-A-III) at 1:100.000, dumortierite occurs with lazulite, some rare sulfide minerals and quartz-veins, cyanite, talc nodules and tourmaline concentrations. The associated rocks are overlain by conglomerates, finer sand lenses, argillitic lenses, sills of Hematite Phyllite and covered by overlain Espinhaço quartzites.

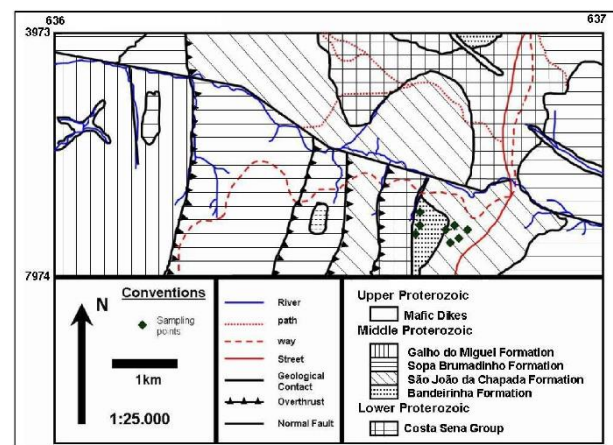


Figure 3 – Location map of the Bandeirinha site indicating geology and sampling points. This map shows also the geological situation and principal accesses to the working area (KNAUER, 1984; ALMEIDA-ABREU, 1989).

Source: Knauer (1984); Almeida-Abreu (1989).

The host rocks of the dumortierite varieties are the quartzites from the upper part of Rio Paraúna Super Group (Barão de Guaicuí Schist) near the tectonic contact with the overlying Espinhaço Super Group. The contact is possibly a strongly tectonically deformed old surface overlaying by intemperized and highly foliated volcano-sedimentary units, so called Hematite Phyllite or a lower conglomeratic to coarse grained sandy units.

The whole sediments were metamorphosed during Brasiliano event to green schist facies level. The subdivision and description were first done by Fogaça et al.,

(1984), Schöll and Fogaça (1979, 1981) and Horn et al., (1996, 1998b).

Within a profile from East to West, the sequences of the mineral and lithological variations are well visible (FIG. 3).

The secondary transportation of dumortierite and lazulite as pebbles, crystals and sand grains is well documented in the papers by Scholl and Fogaça (1979), Fogaça et al., (1984), Hoffmann (1979) and Morteani et al., (1999). The investigated dumortierite specimens were collected in these two distinct areas of Brazil.

2. Sampling

Dumortierite samples were collected at two localities in Minas Gerais and Bahia States which geological environments are relatively well known:

- A. At the Espinhaço Range, south of Diamantina;
- B. In the Vaca Morta Region at the Southeastern part of Bahia state. This area belongs geographically to the occidental Espinhaço Range, and the samples are from Espinhaço Super Group rocks.

The collected samples were compared with dumortierite samples of different worldwide origins.

2.1 Dumortierite from Brazil

2.1.1 Rio Paraúna Super Group (10 samples)

Samples from two defined places were used:

- Near Fazenda Bandeirinha at the tectonic contact with the Espinhaço Super group.
- In the surroundings of Fazenda Formação.

2.1.2 Espinhaço Super Group (5 samples)

- Near Macaúbas in the South-East of Bahia at the locality of Vaca Morta (CASSEDANNE, 1990; HORN et al., 1998; CASSEDANNE; CASSEDANNE, 1975).

2.2 Comparative dumortierite samples from other countries

- One sample from the Louvincourt (Québec, Canada) dumortierite deposit (TANER; MARTIN 1993).
- Five samples from the Lincoln Hill-Champion Mine dumortierite deposit (Nevada, USA): (PAULET et al., 1991; PAULET, 1992).
- A specimen from the Jack Creek dumortierite deposit (Montana, USA) (FOIT et al., 1989; FUCHS; MAURY 1995).
- Two samples from the Aculéis (Chile) dumortierite deposit (GONZALES; RIVANO, 1979).
- A dumortierite specimen from Madagascar (exact origin unknown).

3. Structure of dumortierite

Dumortierite structural formula can be ideally written:

$(Al_{1-x}\square_x)Al_2Al_4Si_3BO_{18-x}(OH)_{3x}$ in which aluminium can be partly substituted mainly by Fe and Ti but also by Mg (Ferraris et al., 2001; CHOPIN et al., 1995). Dumortierite structure was published by Golovastikov (1963) and refined by Moore and Araki (1978) and Alexander et al., (1986). Dumortierite is orthorhombic, space group Pmcn with Z=4 formula units per unit cell.

The structure is characterized by three types of chains of interconnected octahedral, running parallel to [001]. The chains are linked by isolated SiO_4 tetrahedral and planar BO_3 groups (FIG. 4).

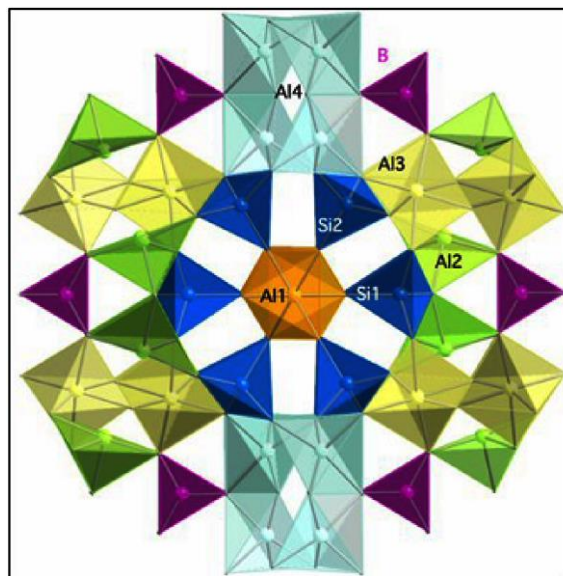


Figure 4 – Structure of dumortierite down to the c axis (Golovastikov, 1963; Moore and Araki, 1978; Alexander et al., 1986). Source: Golovastikov (1963); Moore and Araki (1978); Alexander et al. (1986).

The straight Al(1) chain is formed by face sharing octahedra. This straight Al(1) chain contains void octahedral (vacancy $\square\square$) in the ratio 1:4 (MOORE; ARAKI, 1978). Ordering of vacancies along this Al(1) chain may, thus, induce to dimmers, trimers and more extended one dimensional clusters of occupied face sharing or octahedral.

A second chain is formed by Al(2)Al(3) zigzag structure of edge connected octahedra, doubled by an inversion center.

The third type an Al(4) chain is formed by pairs of face-sharing octahedra which are parallel to [100], in a way that the shortest distance between two Al in this chain occurs perpendicular to [001]. These pairs of face sharing octahedral are connected together by common edges and form kinked “double chain” running so parallel to [001].

4. Methodology

Were executed field investigations at the geological sites and laboratory studies on the samples specimen.

4.1 Field studies

Observations about the mineral currencies, there different properties, the orientation, host rock situation and mineral assemble were done.

4.2 Laboratory investigations

Elemental analyses were performed using the SX 100 electron microprobe of Camparis center (University Pierre et Marie Curie, Paris) at 15kV and 10nA.

For infrared spectroscopy, powdered dumortierite samples (7mg) were pressed with KBr (150 mg) to form a thin disc of 2cm². The spectrums were then recorded in transmission on a Fourier Transform Nicollet 560ESP spectrometer in the frequency range 4000 cm⁻¹-400 cm⁻¹.

For electron paramagnetic resonance (EPR) measurements, calibrated silica tubes (suprasil grade) were filled with dry powdered samples. EPR measurements at 9.42 GHz (X-band) were performed using a Bruker ESP300E spectrometer. The experimental parameters were as follows: 100 kHz frequency modulation and 40 mW microwave power, 5.10⁻⁴ T modulation amplitude. The EPR spectra were recorded in the 0 to 0.9 T magnetic field range. Magnetic field calibration was performed with the DPPH standard ($g = 2.0037 \pm 0.0002$). Frequency calibration was done with a Hewlet Packard frequency meter.

To record Mössbauer spectrum, the powders were stored in a plexiglas crucible having a surface area of 2 cm². The spectrums were recorded on a spectrometer with constant acceleration mode using a ⁵⁷Co source diffused into a rhodium matrix. The hyperfine data were refined with the MOSFIT program (VARRET, 1981), using Lorentzian functions without thickness corrections. The zero velocity corresponds to the centroid shift for an α -Fe foil at room temperature.

5. Results

5.1 Field geological results

5.1.1 Fazenda Bandeirinha

In the investigated area an association between the two Dumortierite types occurs directly at the upper contact of Paraúna Super group near the lower part of the Espinhaço Super group. From eastern contact westwards the reddish blue dumortierite diminishes in quantity whereas after an intensively tectonized quartzite the lazulite concentration grows up in direction of the western contact. The crystals of the reddish blue dumortierite occur as cm-needles on fracture planes, showing a strongly dominant orientation toward a NW direction.

The dumortierite is associated with kyanite nodules, quartz veins and pyrite, arseno- and chalcopyrite, which have suffered an intensive weathering. Lazulite is the dominant mineral versus dumortierite in the lower part of the profile (with a ratio of nearby 99,9 to 0,1) whereas at the higher part the ratio is inverted, dumortierite being the dominant mineral.

5.1.2 Vaca Morta

The dumortierite occurs in the quartz-schist and quartzite without specific orientation. Associated lazulite is very rare. No sulfide is reported.

5.2 Chemical composition of samples

Results of chemical analyses (TAB. 1) show important variations of the Al₂O₃ and SiO₂ content (TAB. 1).

| Nb of analyses | Louvicourt | Lincoln Hill | Jack Creek | Acuélos | Unknown locality | Vaca Morta | Fazenda Formação | Fazenda Formação |
|--------------------------------|------------|--------------|------------|---------|------------------|------------|------------------|------------------|
| | (Québec) | (Nevada) | (Montana) | | Madagascar | Bahia | Minas Gerais | Minas Gerais |
| | Canada | USA | USA | (Chile) | | Brazil | Brazil | Brazil |
| | 28 | 76 | 62 | 26 | 13 | 27 | 12 | 10 |
| SiO ₂ | 29.589 | 30.728 | 26.931 | 29.327 | 31.155 | 30.902 | 31.018 | 30.994 |
| Al ₂ O ₃ | 59.207 | 60.573 | 61.681 | 60.301 | 62.053 | 59.916 | 60.141 | 58.553 |
| TiO ₂ | 1.311 | 0.555 | 1.169 | 0.964 | 0.471 | 1.068 | 0.949 | 0.990 |
| As ₂ O ₅ | 0.066 | 0.282 | 1.343 | 0.679 | BDL | 0.056 | 0.032 | 0.023 |
| Sb ₂ O ₃ | 0.008 | 0.339 | 0.022 | 0.034 | 0.109 | 0.010 | 0.029 | 0.033 |
| FeO | 0.056 | 0.239 | 0.325 | 0.911 | 0.386 | 0.250 | 0.237 | 0.274 |
| ZnO | 0.045 | 0.081 | 0.043 | na | na | 0.026 | na | na |
| MgO | 0.682 | 0.033 | 0.020 | 0.013 | BDL | 0.128 | 0.173 | 0.720 |
| Na ₂ O | 0.016 | 0.009 | 0.010 | 0.026 | 0.012 | 0.004 | 0.004 | 0.004 |
| P ₂ O ₅ | 0.490 | 0.059 | 0.266 | 0.570 | 0.051 | 0.082 | 0.099 | 0.115 |
| B ₂ O ₃ | na | na | na | na | na | na | na | na |
| F | 0.056 | 0.028 | 0.062 | 0.039 | 0.088 | 0.007 | 0.004 | 0.004 |
| Sum | 90.107 | 91.301 | 91.124 | 89.628 | 93.208 | 91.886 | 91.159 | 89.547 |

Table 1 - Microprobe analysis of dumortierite samples (in oxide weight %).

NA = non analysed; BDL = below detection limit; * except for As, Sb = 85, for P and F = 55.

B can not be executed by microprobe.

Análises de microsonda em dumortierita (in % peso).

NA = não analisado; BDL = abaixo do limite de detecção; * com exceção para As, Sb = 85 e F = 55.

B não pode ser determinado com microsonda.

Source: Elaborated by authors.

| | Louvicourt | Lincoln Hill | Jack Creek | Acuêlos | Loc. unknown | Vaca Morta | Fazenda Formação | Fazenda Formação |
|----|------------|--------------|------------|---------|--------------|------------|------------------|------------------|
| | (Québec) | (Nevada) | (Montana) | | Madagascar | Bahia | Minas Gerais | Minas Gerais |
| | Canada | USA | USA | Chile | Madagascar | Brazil | Brazil | Brazil |
| Si | 2.859 | 2.677 | 2.622 | 2.858 | 2.927 | 2,920 | 2,956 | 2,958 |
| Al | 6.744 | 7.153 | 7.075 | 6.914 | 6.858 | 6,854 | 6,755 | 6,760 |
| Ti | 0.095 | 0.020 | 0.085 | 0.070 | 0.028 | 0,033 | 0,077 | 0,068 |
| As | 0.004 | 0.017 | 0.080 | 0.054 | BDL | 0,000 | 0,007 | 0,004 |
| Sb | 0.000 | 0.013 | 0.001 | 0.034 | 0.004 | 0,004 | 0,000 | 0,001 |
| Fe | 0.005 | 0.005 | 0.026 | 0.073 | 0.034 | 0,030 | 0,020 | 0,019 |
| Zn | 0.003 | 0.006 | 0.003 | na | na | 0,000 | 0,002 | 0,002 |
| Mg | 0.098 | 0.005 | 0.003 | 0.002 | BDL | 0,000 | 0,018 | 0,025 |
| Na | 0.003 | 0.001 | 0.002 | 0.005 | 0.002 | 0,002 | 0,001 | 0,001 |
| P | 0.040 | 0.005 | 0.022 | 0.045 | 0.004 | 0,004 | 0,006 | 0,007 |
| F | 0.017 | 0.010 | 0.022 | 0.012 | 0.026 | 0,026 | 0,002 | 0,001 |

Table 2 – Calculated values for the element distribution for structural formula on the basis of the Moore and Araki (1978; idealized formula in apfu). See Table 1 for the explanation of the acronyms. Source: Elaborated by authors.

Idealized structural formulas (TAB. 2) were calculated on the basis of 0.75 OH per formula unit. The number of Si atoms is less than 3 indicating that some substitutions do occur in the tetrahedral Si sites. High P₂O₅ contents (~0.5%) are observed in the Louvicourt and Acuêlos dumortierite. These concentrations are however below the phosphorus contents up to 0.65 wt% observed by Willner & Schreyer (1991) in dumortierite from Busmanland (South Africa,) by Vrana (1979) in dumortierite of Waldheim (Saxony, Germany) (up to 0.90 wt%). The As₂O₅ average content reaches 1.34% in Jack Creek specimens (average) and 0.68% in the Acuêlos ones. Sb₂O₃ content reaches 0.34 wt% in the Lincoln Hill dumortierite but is far below the average value (2.04wt%) of the Ben Lomond dumortierite (Queensland, Australia) (with a maximum up to 4.89 %, Fuchs unpublished data). Relatively high As and Sb content are known in other dumortierite occurrences. As and Sb in dumortierite up to 1.67 and 0.34wt% were also reported by Voloshin et al. (1987) and Grew (1995) found As₂O₅ content from 0.90 up to 1.67 wt%, (0.082 apfu) in dumortierite of a kornerupine bearing pegmatite of Sri Lanka.

These high Sb and As contents lead to the hypothesis that solid solution exist between dumortierite and holtite an orthorhombic mineral (Si_{2.25}Sb_{0.75}) B[Al₆(Al_{0.43}Ta_{0.27}□_{0.30})O₁₅(O,OH)_{2.25}] (VOLOSHIN et al. 1976, HOSKINS et al., 1989) with an As rich member described by A. Pieczka and M. Marszalek (1996) with: (Si_{2.18}Sb_{0.26})B(Al_{6.03}Mg_{0.23}Ti_{0.13}Ta_{0.15}Nb_{0.03}As_{0.02}Fe_{0.02}□_{0.39})(O_{17.44}□_{0.56}) for structural formula.

TiO₂ content varies from 0.47 up to 1.31% far below the 3.05 wt% TiO₂ of the dumortierite in the Namaqua metamorphic quartzite (BEUKES et al., 1987), the 3.80 wt% in dumortierite of the metamorphic rocks from Zambia (VRANA, 1979) and the 4.6% , (0.33 apfu) in the dumortierite of the Rogaland pegmatite (HUIJSMAN et al., 1982).

5.3 Infra-red spectroscopy

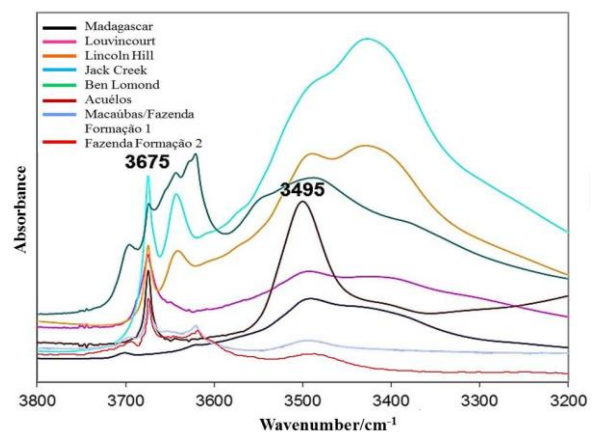


Figure 5 - FTIR spectra of some dumortierite samples in the OH stretching absorption zone. The samples from Macaúbas and Fazenda Formação 1 are similar to the samples from Lincoln Hill and Jack Creek. The samples from Macaúbas and Farm 1 Formation are similar to the samples from Louvicourt, Lincoln Hill and Jack Creek. Source: Elaborated by authors.

The study of the OH stretching bands (3800-3200 cm⁻¹) of dumortierite samples (FIG. 5) brings information on the M1 site occupancy as hydroxyl groups substitute for O(2) and O(7) (i. e. between the M1 octahedron and the [SiO₄] tetrahedron) to charge-balance vacancies in the M1 site. OH groups can also balance the substitutions of Mg²⁺, Fe²⁺ for octahedral Al³⁺ or substitutions of Al³⁺ and/or Fe³⁺ for tetrahedral Si⁴⁺. Dumortierite spectra shows 3 major bands at ~ 3490, ~3620 ~ 3675 cm⁻¹ and a broad band at ~ 3400-3430 cm⁻¹. This last band corresponds to water molecules trapped in the channel type structure of dumortierite. The ~ 3490 cm⁻¹ band is present in all specimens. The ~ 3620 cm⁻¹ and ~ 3675 cm⁻¹ band are present in all samples but very weak in the Madagascar one for the first and totally absent for the second. Other absorption bands are present. Table 3

gives the result of Mössbauer and reflect the complexity of the environment of the hydroxyl groups.

According to Moore and Araki (1978) each Al(1) vacancy requires 3OH- substitutions for O(2) or O(7) oxygen. That means the corresponding OH groups are surrounded by a 7 charges environment (Si^{4+} , Al^{3+} , \square), which would correspond to the absorption band observed at $\sim 3675 \text{ cm}^{-1}$. Similarly, Alexander et al. (1986) showed that the frequency of OH stretching bands could vary as a function of the charge of the cations substituting for Al in the Al(1) site [6]M1. Following this model, substitutions involving R^{2+} elements (Mg, Fe^{2+}) and leading to Si^{4+} Al^{3+} R^{2+} environments (9 charges environments) can be associated to the band observed at 3490 cm^{-1} . Substitutions leading to Si^{4+} R^{2+} R^{2+} environments correspond to 8 charges and can be associated to the band at 3620 cm^{-1} . Other bands may be associated to other substitutions. For example, R^{3+} (Fe^{3+}), or R^{4+} (Ti) can substitute for Al in the [6]M1 site, whereas substitutions of Al^{3+} , Fe^{3+} for Si^{4+} in tetrahedron sites can induce various complicated environments for the OH groups.

5.4 EPR spectroscopy

The X-band EPR spectrum of dumortierite selected samples (FIG. 6) display various signals that can be related to: (i) paramagnetic Fe^{3+} ions, (ii) electron holes trapped on oxygens, (iii) superparamagnetic domains (FIG. 6).

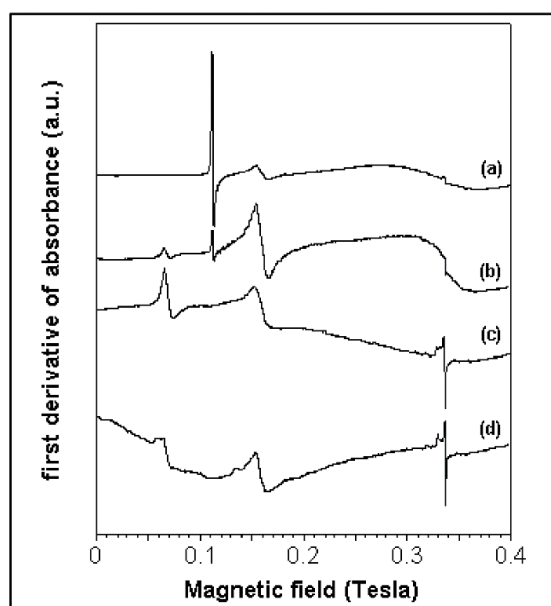


Figure 6 – Room temperature X-band EPR spectra of four selected dumortierite samples: (a) Louvincourt, (b) Lincoln Hill, (c) Acuélos and (d) Jack Creek. The two upper spectra correspond to pink samples whereas the two lower spectrums correspond to blue samples.

Note the broad superparamagnetic signal producing the wavy baseline. The sharp signals are related to paramagnetic species. The spectra of the samples from Brazil (Macaiúbas; Fazenda Formação 1) are similar to the samples a and d.

Source: Elaborated by authors.

Electronic holes are responsible for the thin signal observed at 0.34 T (present in all spectrum but particularly well marked in the Jack Creek (Montana) and Acuélos (Chile) samples. They are related to isolated Fe^{3+} ions in dilute configuration. In contrast, the very broad signal

corresponding to the undulating baseline of the spectrum is related to super-paramagnetic domains, i. e. Fe^{3+} ions concentrated in magnetic domains of nanometric size. The relative Brazil like shown in figure 7 for samples from Jack Creek and Lincoln Hill.

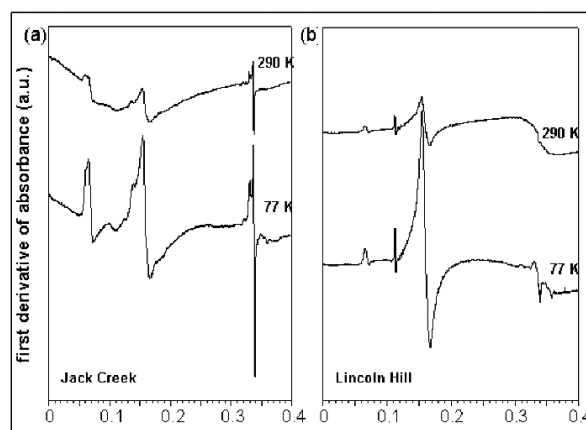


Figure 7 – X-band EPR spectrum of the Jack Creek (left) and Lincoln Hill (right) samples recorded at room (top) and liquid nitrogen temperature (bottom). Note the decrease at low temperature of the relative intensity of the broad signal ascribed to super-paramagnetic phases. Except this variation of relative intensity, the general shape of the spectrum is not strongly affected by the temperature change.

Source: Elaborated by authors.

Other iron species such as large magnetic domains or Fe^{2+} ions cannot be observed by EPR spectroscopy using the above detailed experimental conditions (FIG. 7). The three signals related to isolated Fe^{3+} present some variations of their relative intensity from one spectrum to another. Accordingly, these three signals should correspond to at least three different sites for the incorporation of Fe^{3+} in the dumortierite structure. The strong and sharp signal observed at 0.113 T in the EPR spectrum of pink dumortierite samples (Lincoln Hill, Nevada and Louvincourt, Quebec) is related to a site with a pure axial distortion, i. e. a site symmetry with a n-fold ($n = 3$) rotation axis. It likely indicates the substitution of Fe^{3+} for Al^{3+} in the (M1) octahedron chain located on the 6-fold axis of the dumortierite structure. The axial symmetry of the site further indicates that no substitution occur in the neighboring SiO_4 tetrahedron. In contrast the signals observed at 0.07 and 0.16 T correspond to more distorted sites. In particular, the signal at 0.16T corresponds to a strong rhombic distortion. These signals could be related to Fe_{3+} ions located in tetrahedral sites or in distorted octahedral sites.

5.5 Mössbauer effect spectrometry

Mössbauer spectrometry was used to determine site occupancy and valence state of iron and to obtain $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. Mössbauer spectroscopy of dumortierite is difficult to perform due to their low FeO content (from 0.06 wt % in the Louvincourt dumortierite, the Brazilian samples with around, 0.2 to 0.3% up to 0.91% in the Acuélos dumortierite. Therefore only two samples only could be properly recorded and the spectrum fitted: Acuélos (0.91% FeO) and Jack Creek (0.33% FeO) (FIG. 7). Results are given in TAB. 3. The uncertain results from Brazilian

samples are near to those from Jack Creek, but have to be seen carefully.

Fitting of the Acuélos dumortierite was particularly difficult to achieve because of the importance of sub-crystalline magnetic inclusions (magnetite) that could not be eliminated with physical nor chemical method. However, the Mössbauer results for this sample show two doublets that can be attributed respectively to Fe²⁺ and Fe³⁺ both in octahedral site with dominantly divalent iron in a ratio Fe²⁺/Fetotal ~ 2/3 (TAB. 3).

The Mössbauer spectrum for the Jack Creek dumortierite does not show magnetic signal. A first attempt made to

perform Mössbauer spectroscopy brought misleading results with dominating Fe³⁺. The error came from the process used to isolate dumortierite using HF etching of the sample and probably inducing oxidising phenomena. Further essay based on hand separation of the minerals of the crushed rock under microscope was long but leads to results representing the true oxidation state of Fe in the Jack Creek dumortierite. Fe is mostly divalent (~89%). Fe²⁺ and Fe³⁺ ions appeared to be located in octahedral sites in this sample but there are two different sites for Fe²⁺.

| | K | Speed (mm/s) | | δ | $\Gamma/2$ | Δ | H in K α | % |
|-------------------------|-----|--------------|--------------------|----------|-------------|----------|-----------------|------|
| Acuélos (Chile) | 300 | 10 | magnetic component | 0.374(3) | <u>0.18</u> | -0.22(7) | 513 | 88.7 |
| | | | Fe ²⁺ | 1.10(3) | <u>0.18</u> | 2.588 | - | 7.4 |
| | | | Fe ³⁺ | 0.24(6) | <u>0.18</u> | 0.445 | - | 3.9 |
| Jack Creek Montana, USA | 300 | 4 | Fe ²⁺ | 1.09(1) | <u>0.13</u> | 2.41(2) | - | 66.1 |
| | | | Fe ²⁺ | 1.05(1) | <u>0.13</u> | 1.65(3) | - | 22.6 |
| | | | Fe ³⁺ | 0.25(6) | <u>0.13</u> | 0.71(1) | - | 11.3 |

Table 3 – Mössbauer parameters from the Jack Creek, Acuélos and Macaúbas dumortierite. The results from Macaúbas and Fazenda Formação dumortierite are similar to Acuélos. Source: Elaborated by authors.

6. Conclusions

6.1 Laboratory

Spectroscopic methods enable us to obtain specific information on the site population in dumortierite. The results of infra-red spectroscopy measurements confirm that hydroxyl groups are replacing O(2) and O(7) between a [SiO₄] tetrahedron and an M1 central octahedron when the M1 site is vacant or when a R²⁺ cation substitutes for Al³⁺ in this site. At T<250°C adsorbed water is present in the channel-like structure of dumortierite. Results of EPR, and Mössbauer spectroscopy are remarkably concordant. Fe is present in different types of sites.

1. Fe³⁺ substitutes for Al (1) in the octahedral chain located on the 6 fold axis. In this site EPR signal reveals only pure axial distortion located i. e. a site symmetry with an n-fold (n = 3) rotation axis. The axial symmetry of the site further requires that no substitution occur in the neighboring SiO₄ tetrahedra. The strong signal at 0.113tesla in EPR spectroscopy character phenomenon in Lincoln Hill and particularly in Lovincourt dumortierite (FIG. 5).

2. Unlike the former specimens, paramagnetic Fe³⁺ in the Acuélos and Jack Creek samples is located in more distorted sites which could correspond to tetrahedral sites or distorted octahedral sites.

3. Due to short distances between octahedral centers in the M1 site chains iron-iron pair can be observed.

A thin signal observed at 0.34 T, characterizes electronic holes. It is present in all samples but particularly well marked in the Acuélos and Jack Creek one. It is related to isolated Fe³⁺ ions in dilute configuration. In contrast, a very broad signal corresponding to the undulating baseline of the spectra and related to super-paramagnetic domains, i. e. Fe³⁺ ions

concentrated in magnetic domains of nanometric size is very strong in the Acuélos and Jack Creek samples.

The existence of super-paramagnetic domains can be attributed to iron-iron pairs. This might suggest that these samples do not show only randomly distributed iron atoms (the thin EPR signal at 0.34 T) but that some irons "see" each other.

7. Acknowledgement

We thank CNPq and FAPEMIG for financial and CPMTC and CGE for logistic support.

REFERENCE

- [1] ALEXANDER, V. D.; GRIFFEN, D.T.; MARTIN, T.J. Crystal Chemistry of some Fe- and Ti- poor dumortierites. *Am. Mineral*, v. 71, p. 786-794, 1986.
- [2] ALMEIDA ABREU, P. A. **Geologia das quadrículas Onça e Cuiabá (Gouveia-MG), região mediana-central da Serra do Espinhaço Meridional**. Dissertação de Mestrado em Geologia - Instituto de Geociências, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 1989.
- [3] ALMEIDA, F. F. M.; HASUI, Y. **O Pré-Cambriano do Brasil**. São Paulo: Edgar Blücher, 1984.
- [4] BEUKES, G. J.; SLABBERT, M. J.; DE BRUIYN, H.; BOTHA B. V. J.; SCHOCH. A. E.; VAN DER WESTHUIZEN, W. A. Ti-Dumortierite from the Keimões area, Namaqua mobile belt, South Africa. *N. Jb Mineral*. Abh. n. 157, v. 3, p. 303-318, 1987.

- [5] CASSEDANNE, J. P. Um novo material gemma: Le quartzite a lazulite (Bahia – Brasil). **Revue de Gemmologie**. v. 105, p. 17-18, 1990.
- [6] CASSEDANNE, J. P.; CASSEDANNE, J. O. Note sur la Lazulite de la region de Diamantina (MG). **An. Acad. Bras. Ciênc.** v. 47, p. 283-288, 1975.
- [7] CHI, M.; GOREVA, J.; ROSSMAN, G. R. Fibrous nanoinclusions in massive rose quartz; HRTEM and AEM investigations. **Am. Mineralogist**. v. 87, p. 269-276, 2002.
- [8] CHOO, C.; KIM, Y. Textural and spectroscopic studies on hydrothermal dumortierite from an Al-rich clay deposit, Southeastern Korea. **Mineral. Mag.** v. 4, p. 799-806, 2003.
- [9] CHOPIN, C.; FERRARIS, G.; IVALDI, G.; SHERTL, H. P.; SCHREYER, W.; COMPAGNONI R.; DAVIDSON, C.; DAVIS, M. Magnesiodumortierite, a new mineral from very high pressure rocks (Western Alps) Part II crystal chemistry and petrological significance. **Eur. J. Mineral.** v. 7, p. 525-535, 1995.
- [10] FERRARIS, G.; IVALDI, G.; CHOPIN, C. Magnesiodumortierite, a new mineral from very-high-pressure rocks (Western Alps) Part I: Crystal structure. **Eur. J. Mineral.** v. 7, p. 167-174, 1995.
- [11] FLEISCHER, G. Observações geológicas sobre a dumortierita da Serra das Veredas. **Mineração e Metalurgia**. v. 54, 319, p. 4-21, 1971.
- [12] FOGAÇA, A. C. C.; ALMEIDA-ABREU, A.; SCHORSCHER, H. D. Estratigrafia da sequência supracrustal arqueana da porção mediana-central da Serra do Espinhaço Meridional, Minas Gerais. **Anais, 23º Cong. Bras. Geologia**, Rio de Janeiro. v. 6, p. 2654-2667, 1984.
- [13] FOIT, JR. F. F.; FUCHS Y.; MYERS, P. E. Chemistry of alkali-deficient schorls from two tourmaline-dumortierite deposits. **Am. Mineralogist**. p. 1317-1324, 1989.
- [14] FUCHS, Y.; MAURY, R. Borosilicate alteration associated with U-Zn-Mo and Ag-Au-Zn deposits in Volcanics. **Mineralium Deposita**. v. 30, n. 6, p.449-450, 1995.
- [15] GOLOVASTIKOV, N. J. The crystal structure of dumortierite. **Soviet Phys. Dokly**.10, p. 493-495, 1965.
- [16] GONZALES, M. I.; RIVANO, G. S. Yacimiento de dumortierita en la zona de Aculeo, region Metropolitana. **Actas-Congreso Geologico Chileno 2**, C295-C306, 1979.
- [17] GOREVA, J.; CHI, M.; ROSSMAN, G. R. Fibrous nano inclusions in rose quartz: the origin of rose coloration. **Am. Mineral.** v. 86, p. 466-472. 2001.
- [18] GREW, E. S. Borosilicates (exclusive of tourmaline) and boron in rock-forming minerals in metamorphic environments. **Review in Mineralogy and Geochemistry**. v. 33, p. 387-502, 1996.
- [19] GREW, E. S.; HIROI Y.; MOTOYOSHI Y.; KONDO Y.; JAYATILEKE S. J. M.; MARQUEZ N. Iron-rich kornepupine in sheared pegmatite from the Wann Complex, at Homagama, Sri Lanka. **Eur. J. Mineral.** v. 7, n. 3, p. 623-636, 1995.
- [20] GREW, E. S.; YATES, M. G.; HUIJSMANS, J. P. P.; MC GEE, J. J.; SHEARER, C. K.; WIEDENBECK, M.; ROUSE, R. C. Werdingite, a borosilicate new to granitic pegmatites. **Can. Mineral.** v. 36, p. 399-414, 1998.
- [21] HOFFMANN, C. **Augelite, a rare aluminum phosphate: first find a metamorphic environment**. Stuttgart: E. Schweiz. Verlag, 1979.
- [22] HORN, A. H.; ARANHA, P. R. A.; NEVES, S. C.; VIANA F. L.; ÁDAMO, R. **Novos dados estruturais e mineralógicos sobre a ocorrência de fosfatos e silicatos de Al-Fe na Serra do Espinhaço Meridional, ao Sul de Diamantina, Minas Gerais**. 40. Cong. Bras. Geol. Belo Horizonte. Anais: p. 393, 1998.
- [23] HORN, A. H.; MORTEANI, G.; ACKERMAND, D.; NEVES, S. C. **Die Al-Fe phosphatführenden Muscovitquarzite als Leithorizont für die Grenze zwischen der Rio Paraúna und Espinhaço Supergruppe südlich von Diamantina, Minas Gerais, Brasilien**. Geowiss. Laterinam. Koll., Bayreuth. Anais: p. 65-66, 1998.
- [24] HORN, H. A.; MORTEANI, G.; ACKERMAND, D. **Significância da ocorrência de fosfatos e boratos de alumínio no contato entre os supergrupos Rio Paraúna e Espinhaço na região de Diamantina, Minas Gerais, Brasil**. Geonomos.IV/1, p. 1-10, 1996.
- [25] HOSKINS, B. F.; MUMME, W. G.; PRICE, M. W. Holtite (Si_{2.25}Sb_{0.75})B[Al₆(Al_{0.43}Ta_{0.27}□_{0.30})O₁₅(O,OH)_{2.25}]: crystal structure and crystal chemistry. **Mineral. Mag.** v. 53, p. 457-463, 1989.
- [26] HUIJSMANN J. P. P.; BARTON M.; VAN BERGEN M. J. A pegmatite containing Fe-rich grandidierite, Ti-rich dumortierite and tourmaline from the Precambrian, high grade metamorphic complex of Rogaland, S.W. Norwa. **N. Jb. Miner. Abh.** v. 143, p. 249-261, 1982.
- [27] KAYUPOVA, M. M.; TILEPOV, Z. T. First find of dumortierite concretions. Academy of Science USSR, Doklady, **Earth Science Section**. v. 235, p. 121-123, 1979.
- [28] KNAUER, L. G. A geologia da área do Ribeirão do Inferno, Diamantina, Minas Gerais. **Anais 33º Cong. Bras. Geologia**, 3, Rio de Janeiro, p. 1249-1261, 1984.
- [29] KNAUER, L. G.; SCHRANK, A. A origem dos filitos hematíticos da Serra do Espinhaço Meridional, Minas Gerais. **Revista Geonomos**. v. 1, n. 1, p. 33-38, 1993.

- [30] MOORE, P. B.; ARAKI, T. Dumortierite, $\text{Si}_3\text{B}[\text{Al}_{6.75}\square_{0.25}\text{O}_{17.25}(\text{OH})_{0.75}]$: a detailed structure analysis. **N. Jb. Miner. Abh.** v.132, n. 3, p. 231-241, 1978.
- [31] MORTEANI, G.; ACKERMAND, D. Mineralogy and geochemistry of Al-phosphate and Al-borosilicate-bearing metaquartzites of northern Serra do Espinhaço (State of Bahia, Brazil). **J. Min. Petr.** v. 80, p. 59-81, 2005.
- [32] MORTEANI, G.; ACKERMAND, D.; HORN, A. H. Aluminium phosphates in metamorphic rocks II: Petrography and geochemistry of the aluminophosphate bearing quartzites of the Barão de Guacuí Formation in the Central Serra do Espinhaço Range, Minas Gerais, Brasil. **Europ. J. of Min.** p. 253-274, 1999.
- [33] PAULET, P. H. **Etude des altération hydrothermales à borosilicates de la Humboldt Range, Nevada, USA.** Doctor thesis, Université Pierre et Marie Curie, Paris, 1992.
- [34] PAULET, P. H.; FOIT, JR. F. F.; FUCHS, Y.; MAURY, R.; ROSENBERG, P. E. Zonalité des différents types de borosilicates dans les système hydrothermal à or-argent de la Humboldt Range, Pershing County, Nevada, USA. **C.R. Acad. Sci.** v. 313, n. 10, p. 1155-1162, 1991.
- [35] PIECKA, A.; MARSZALEK, M. Holtite, the first occurrence in Poland. **Mineralogia Polonica.** v. 27, n. 2, p. 3-8, 1996.
- [36] SCHOBENHAUS, C. **Geologia da Serra do Espinhaço entre Porteirinha e Monte Azul, norte de Minas Gerais.** SUDENE, Div. Geol. p 19. Recife (inédito), 1972.
- [37] SCHOBENHAUS, C. Relatório geral sobre a geologia da região setentrional da Serra do Espinhaço – Bahia Central. **Série Geol. regional, SUDENE-Div. Geol., Recife.** v. 19. p. 112, 1972.
- [38] SCHÖLL, W. U.; FOGAÇA, A. C. C. Estratigrafia da Serra do Espinhaço na região de Diamantina. – **Atas 1. Simp. Geol. Minas Gerais, Diamantina.** v. 1, p. 55-73, 1979.
- [39] SCHÖLL, W. U.; FOGAÇA, A. C. C. **Mapeamento geológico das quadrículas Guinda e Gouveia (MG).** Projeto Mapeamento Espinhaço, DNPM/CPRM, Diamantina. p. 51, 1981.
- [40] TANER, M. F.; MARTIN, R. F. Significance of dumortierite in an aluminosilicate rich alteration zone, Louvincourt, Québec. **Can. Mineral.** v. 31, p. 137-146, 1993.
- [41] VARRET, F. M. **In Proc. Inter. Conf. On the Application of the Mössbauer Effect.** Jaipur: Indian National Science Academy, 1981.
- [42] VISONA, D.; FUCHS, Y. Dumortierite a new mineral from Himalayan leucogranites, petrological and geochemical implication. **in 2nd International Symposium on granites and associated mineralizations,** p. 247-248, 1997.
- [43] VISSER, D.; FELIUS, R. O.; MOREE, M. Augelite and cerian crandallite in dumortierite quartzites, Vaca Morta quarry, Vereda range, Macaúbas, Bahia, Brazil. **Mineral. Mag.** v. 61, p. 607-609, 1997.
- [44] VOLOSHIN, A. V.; GORDIENK, V. V.; GELMAN, E. M.; ZORINA, M. L.; ELINA, N. A.; KULCHITSAYA, E. A.; MENSNIKOV, U. P.; POLEJAEVA, L. I.; RIJOVA, R. I.; SOLOV, P. B.; UTOCHINA, G. I. Holtite (first occurrence in the USSR) and its interrelations with other minerals of tantalum in rare metal pegmatite (in Russian). **New Minerals and First Occurrences in USSR.** v.3, n. 106, p. 337-347, 1976.
- [45] VRANA, S. A polymetamorphic assemblage of grandidierite, kornepupine, Ti-rich dumortierite, tourmaline, sillimanite and garnet. **N. J. für Mineral. Monat.** v. 1, p. 22-33, 1979.
- [46] WERDING, G.; SCHREYER, W. Synthetic dumortierites: Their PTX-dependent compositional variations in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-H}_2\text{O}$. **Fortschritte der Mineralogie.** v. 66, p. 168, 1983.
- [47] WERDING, G.; SCHREYER, W. Dumortierite compositional variations as a function of fluid pressure and temperature. **International Symposium of Experimental Mineralogy Geochemistry.** p. 143-144, 1986.
- [48] WERDING, G.; SCHREYER, W. High pressure synthesis of dumortierite. **Terra Cognita.** 3, 165, 1, 1983.
- [49] WERDING, G.; SCHREYER, W. Synthesis, crystal chemistry, and preliminary stability of dumortierite in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-H}_2\text{O}$. **Fortschritte der Mineralogie.** v. 61, p. 219-220, 1983.
- [50] WERDING, G.; SCHREYER, W. Synthetic dumortierite: its PTX-dependent compositional variations in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-H}_2\text{O}$. **Contributions to Mineralogy and Petrology.** v. 105, p. 11-24, 1990.
- [51] WERDING, G.; SCHREYER, W. Synthetic dumortierites: Their PTX-dependent compositional variations in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-H}_2\text{O}$. **Fortschritte der Mineralogy.** p. 168, 1986.
- [52] WILLNER, A.P.; SCHREYER, W. A dumortierite-topaz-white mica fels from the per aluminous metamorphic suite of Bushmanland (South Africa). **N. Jb. Mineral. Mh.** v. 5, p. 223-240, 1991.

A ocorrência de dumortierita na Serra do Espinhaço, Minas Gerais, Brasil, e sua comparação mineralógico-cristalográfica com outras variedades

Adolf Heinrich Horn¹
Yves Fuchs²
Soraya de Carvalho Neves³
Etienne Balan⁴
Jorge Linarès⁵

¹ Químico (Chemieschule Dr E. Elhardt). Geólogo e Paleontólogo (Ludwig-Maximilians Universität München). Mestre em Geologia e Paleontologia (Ludwig-Maximilians Universität München). Doutor em Geologia e Geoquímica (Ludwig-Maximilians Universität München). Pós Doutorado em Geoquímica (Université Jean Monet-França). Professor da UFMG.

² Geólogo (Faculté des Sciences Paris). Mestre em Geologia. (Université de Nancy). Doutor em Geologia (Université de Nancy). Professor da University Paris-Est Marne-la-Vallée.

³ Geóloga (UFMG). Mestre em Geologia (UFMG). Doutora em Geologia (UFMG). Professora da UFVJM.

⁴ Geólogo (École Normale Supérieure de Cachan). Doutor em Geologia (Université Denis Diderot). Professor da Université Pierre et Marie Curie.

⁵ Geólogo (Université Pierre et Marie Curie). Mestre em Geologia (Université PUCP de Lima – Peru). Doutor em Geologia (Université de Grenoble). Professor da Université de Versailles St. Quentin en Yvelines.

Resumo Amostras de dumortierita de várias localidades do Brasil (Serra do Espinhaço-Minas Gerais Macaúbas-Bahia) foram analisadas com microsonda e os resultados comparados com amostras dos depósitos de dumortierita de Louvincourt (Quebec, Canada), Lincoln Hill-Champion Mine (Nevada, USA), do Jack Creek (Montana), do Acúelos (Chile) e do Madagascar (localidade de origem desconhecida). Foram executadas nestas amostras análises com FTIR, ERP, Mössbauer. A espectroscopia FTIR mostra a existência de vários ambientes para o OH- grupos que são relacionadas com a substituição ou a vacância de posições octaédrais M1. Mössbauer espectroscopia indica Fe⁺⁺ em duas diferentes posições octaédrais e Fe⁺⁺⁺ em uma posição octaedral e IVCT e IMMT. ERP mostra também a presença de Fe⁺⁺⁺ em várias posições. Os outros sinais indicam que a Fe⁺⁺⁺ paramagnético a uma posição tetraédrica ou posições octaédrais mais torcidas.

Palavras-chave: dumortierita; Serra do Espinhaço; Supergrupo Rio Paraúna; Bahia; infravermelho.

Informações sobre os autores

Adolf Heinrich Horn (UFMG)

Endereço para correspondência: Avenida Antônio Carlos, 6627 – Pampulha, Belo Horizonte – MG, 31270-901.

E-mail: hahorn@gmail.com

Link para o currículo lattes: <http://lattes.cnpq.br/3318235045962724>

Yves Fuchs (UPEM)

Endereço para correspondência: Université Marne le Vallee, 5 Bd Descartes, 77454, Marne-la-Vallée cedex 02.

E-mail: yves.fuchs@univ-mlv.fr

Link: <http://lge.u-pem.fr/organisation-et-personnel/personnel/fuchs-yves/>

Soraya de Carvalho Neves (UFVJM)

Endereço para correspondência: UFVJM - Campus JK, Rodovia MGT 367, Km 583, nº 5000, Diamantina – MG, 39100-000.

E-mail: soraneves@yahoo.com.br

Link para o currículo lattes: <http://lattes.cnpq.br/3523194409704557>

Etienne Balan (UMPC)

Endereço para correspondência: Université Pierre e Marie Curie, Tour 23-24 4eme etage, case 115, 4 place Jussieu, F-75252, Paris, cedex 05.

E-mail: Etienne.Balan@impmc.jussieu.fr

Link: <http://www.impmc.jussieu.fr/~balan>

Jorge Linares (UVSQ)

Endereço para correspondência: Université de Versailles St. Quentin en Yvelines, 78035, Versailles Cedex, France.

E-mail: jorge.linares@physique.uvsq.fr

Link:

Artigo Recebido em: 09-07-2014

Artigo Aprovado em: 08-10-2014