Assessment of shear zone-derived quartz from the Etam area, southwest Cameroon as potential high-purity quartz resource: petrography, geochemistry and technological studies

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Abstract

This study focuses on the evaluation of the high-purity quartz (HPQ) potential of a shear zone-hosted hydrothermal and metamorphic quartz deposit in Etam, southwest Cameroon. The shear zone quartz-rich rock is monomineralic and consists of both milky and translucent varieties. The combination of ICP-MS and LA-ICP-MS analytical techniques was used to assess the chemical purity of both quartz varieties. These compositional analyses show that all quartz samples have SiO₂ content of 98.46–99.75 wt% with very low concentrations of all the other elements. Translucent quartz when compared to the milky quartz variety shows low concentration of most of the elements including the following principal impurities: Al (mean 107 µg g⁻¹), Ca (mean 27.85 µg g⁻¹) and Fe (mean 26.05 µg g⁻¹). Bubble generation in the samples after flame fusion over a silica plate was assessed to test the suitability of the quartz in industrial uses. The results obtained from the chemical analyses and bubble formation tests indicate that all the samples investigated do not meet the HPQ requirement. However, the translucent quartz shows characteristics of medium-purity quartz and can produce silica glass for some industrial manufacturing even without further purification. In this study, the fluid inclusions in the samples were examined as this bears information on the economic viability of the deposit and provides clues on the genesis of the quartz vein. Also tiny mineral inclusions within individual quartz grains were identified by SEM-EDS. The results of these studies show that the deposit is probably of metamorphic origin marked by crystal-plastic deformation in quartz grains. The veins were later modified by hydrothermal fluid input. The results also indicate that the majority of impurities are likely hosted by fluid inclusions and thus the quartz can be upgraded to HPQ after purification by suitable methods.

Keywords Hydrothermal · Metamorphic · Cameroon · Shear zone · Silica glass · High-purity quartz (HPQ)

1 Introduction

The high-purity quartz (HPQ) market is presently characterized by a stable growth and annually increases by 3 to 5%. Despite this constant increase in the worldwide demand [1–3], quartz raw material resources with high purity are

rare. An alternative solution to assure the HPQ supply for industries today can be the purification of medium- and low-purity quartz to upgrade the quartz grade. HPQ is an important raw material required for the production of silica glass [4, 5], and it is widely used in the electronics industry and advanced telecommunication and navigation devices.

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Muller et al. [6] determined that for quartz to be classified as HPQ, the total impurity content should be less than $50 \mu\text{g g}^{-1}$. The high content of some impurities such as Al, Ti, Ge and Fe affects drastically the quality of quartz [7–11]. For example, Al content can generate devitrification, resulting in cristobalite white spots, whereas Ti and Fe can contaminate the silicon melt [11] derived from HPQ during industrial applications. Another type of impurity in quartz is fluid inclusions. Despite the fact that fluid inclusions are less difficult to remove in quartz compared to metallic impurities (Ti, Fe, Ge), they can also jeopardize the suitability of quartz as an industrial raw material. Some characteristics of silica glasses made from HPQ also depend on the chemical purity and the amount of fluid inclusions in the raw material. Examples are the transparency in UV and visible ranges, resistance to radiation and mechanical strength [10, 12].

Purification of low-purity quartz using industrial processing is often very costly, laborious and constitutes environmental hazard [1, 11, 13, 14]. Medium-purity quartz with good technological behavior necessitates environment-friendly methods of contaminants removal that drastically reduced the treatment cost and time. Proper processing methods such as calcination pretreatment combined with ultrasound-assisted leaching [15] that increase SiO_2 content concentration up to 99.9% and methods using $\text{HCl-NH}_4\text{Cl}$ and $\text{H}_2\text{SO}_4\text{-NH}_4\text{Cl}$ reagents with removal rate between 88 and 99 wt% for some impurities (Al, K and Fe) have been developed [16] to upgrade quartz purity in order to meet industries' quartz glass requirements. In this regard, industries often prefer the application of purification techniques in medium- to high-purity resources.

In southwestern Cameroon, quartzitic rocks and quartz veins occur along major fault/shear zones and metamorphic rocks. The fault rocks range from breccias to mylonites, and most of them are monomineralic composed essentially of milky to transparent quartz. The potential of finding HPQ in these rocks has not been evaluated despite the widespread occurrence of these lithologies in the area. This is the aspect that constitutes the rationale of this study, and the expected results are of more than local importance considering that the potential of finding HPQ in the area exists.

2 Geological setting

2.1 Regional geological setting

Etam area is located in the southwestern sector of the Tombel Plain and belongs to the central domain of the Central African Fold Belt (CAFB) [17–19] in the southwest

Fig. 1 Location of study area: **a** continental structures of Western Gondwana after Pan-African tectonic evolution (modified after Njome and Dewit [42]). Shear Zones: CCSZ (Central Cameroon Shear Zone); (SF) Sanaga Fault; (TBF) Tchollire-banyo Fault; (Pe) Pernambuco Fault; (Pa) Patos Fault. **b** Geological map of Cameroon (modified after Toteu et al. [18]). The Central Cameroon Shear Zone is defined by a system of NE-trending faults comprising Tchollire-Banyo Fault (TBF), Adamawa Fault (AF), Sanaga Fault (SF), and Kribi-Campo Fault (KCF). NWC, Northwestern Cameroon domain; AYD, Adamawa-Yade Domain; YD, Yaounde Domain. **c** Geologic map of the study area

region of Cameroon. The CAFB is a megastructure, generally E–W oriented, and it is about 5000 km in length and about 300 km in width (Fig. 1a), running through Cameroon across the Atlantic Ocean into northeast of Brazil [20–25]. The central domain of CAFB in Cameroon comprises the Paleoproterozoic granulite [18, 26–28] and the Neoproterozoic metasedimentary rocks [29–31] intruded by syntectonic granitoids [25, 32–39] along thrust and shear zones (Fig. 1b), the most prominent being the Central Cameroon Shear Zone (CCSZ). The CCSZ is one of the most important and largest active strike-slip fault zones in Cameroon. It is part of the transatlantic shear zone system referred to as the Central African Shear zone (CASZ) that extends from the interior of Africa across the Atlantic into South America [40]. It is a set of anastomosing transcurrent faults [41] and shows an important mylonitic band trending $\text{N}70^\circ\text{E}$ to $\text{N}30^\circ\text{E}$.

2.2 Geology of Etam

The Etam area has mainly plutonic rocks (granitic and granodioritic) and metamorphic rocks including gneisses and migmatites. These lithologies are associated with a mylonitic band (Fig. 1c) oriented $\text{N}030$ to $\text{N}045$ [43] termed the Etam shear zone (ESZ) [44], which constitutes a segment of CCSZ. The mylonitization event has been attributed to a Pan-African age [40] and has reworked the gneissic foliation. The basement rocks at Etam are extensively covered in some places by the basaltic lavas from the Cameroon Volcanic Line (CVL). All these lithologic units are crosscut by several randomly oriented fracture sets and quartz veins. The quartz veins are few millimeters to several meters wide.

The studied quartz veins in this work are observed in ESZ. This is a clear white rock with no other rock-forming minerals than quartz similar to the Serra de Santa Helena high-purity quartz rock. [43, 44] suggested magmatic protoliths for the mylonitic rocks in Etam. These previous studies also indicated greenschist to amphibolitic metamorphic conditions between 300 and 450°C in the surrounding country rocks, where epidote, neocrystallized quartz and chlorite minerals assemblage coupled with

the albitization of K-feldspar and the formation of perthite were recorded.

The ESZ surrounding rock or wall rock (granodiorite) shows magmatic constituents (Kfs_1 , Qtz_1 , Pl_1 and Bt_1), recrystallized quartz (Qtz_2) and $Ab + Chl$ as products of Kfs_1 alteration. The mylonites in the ductile zone in addition to primary igneous minerals also have secondary constituents (Qtz_2 , Qtz_3 , Pl_2 , Bt_2 , Ms) developed at the expense of Qtz_1 , Pl_1 and Bt_1 through pervasive alteration and recrystallization. Other minerals include amphibole, muscovite, chlorite as well as iron oxide, pyrite and zircon. According to [44], the pervasive alteration in ESZ released K^+ , Na^+ , Ca^+ , Fe^+ and Al^+ ions that circulated in hydrothermal fluids saturated in Si, precipitated in fractures and enriched the quartz veins.

For this study, two quartz veins were mapped and suitable quartz samples were collected for systematic laboratory analyses as detailed in the following sections.

3 Methods

3.1 Fluid inclusion observation using optical microscopy

For the fluid inclusion observation, a small amount of quartz grains sized 70 to 180 μm was placed on a microscope slide. In order to improve the observation of the grains, a film of kerosene was applied over them. The kerosene has a refractive index similar to that of the silica, which reduces undesired surface observations. A Nikon optical microscope operated at 500 $\times$ magnifications was used to acquire transmitted light photographs for fluid inclusion analysis, using a Nikon digital camera. All photographs were taken at room temperature. Using this methodology, it was possible to obtain insights on the nature of the fluid and mineral inclusions present in the grains. Although more complete analyses were not carried out, regarding homogenization temperature and other key properties of the inclusions, it was possible to obtain reliable data on mineral inclusions in the quartz grains. These data were vital in order to propose insights into the genesis of veins.

3.2 Fusion over silica plate

Samples were powdered using a silica mortar and sieved in nylon sieves at the Analytical Geochemistry Laboratory, UNICAMP, Brazil. Particle size distribution was selected between 80 and 200 mesh, i.e., 75 to 180 μm . The manufactured powders were then placed over a silica plate, and a H_2/O_2 flame was applied over it using

a premix torch. Flame conditions, burner distance to the sample and time of fusion were kept the same during all experiments, about 4 mm and 15 s, respectively, although samples took different times until complete fusion. For bubble analysis, the silica plates were photographed using a mineralogical microscope. Photographs of each fused plate were taken and then processed by computational analysis, in order to measure average bubble size and density on each photograph. This is a common test conducted by several silica glass industries in order to evaluate the powder performance during glass making. Bubbles larger than 10 to 15 μm are highly undesired once they can affect the final glass' properties. This procedure is widely used in the literature [10–13, 45].

3.3 Chemical analysis using inductively coupled plasma mass spectroscopy (ICP-MS) on quartz

Quartz samples of 0.1 g were dissolved using 0.5 mL of distilled HF in special vessels. The samples were then kept over a hot plate at 80 $^{\circ}C$ for 1 h in order to enhance the dissolution process. Afterward, temperature was elevated to 110 $^{\circ}C$ for evaporation. Subsequently, 0.5 mL of HF and 0.1 mL of HNO_3 were added and the system was kept closed for 24 h. After this procedure, the samples were recovered using a nitric acid solution of 1% in mass. All solutions were prepared using ultrapure water (18.2 M Ω cm) obtained by Mili-Q system. All used acids were purified by subboiling. The vessels used were previously cleaned with a 5% nitric acid solution and washed with ultrapure water. All measurements were conducted by the ICP-MS technique using an X series II (Thermo) instrument, equipped with collision cell technology (CCT) at the Analytical Geochemistry Laboratory, Institute of Geosciences, UNICAMP, Brazil [45].

3.4 Chemical analysis using laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS)

Quartz composition was further evaluated using a New Wave Research Excimer Laser Ablation UP193FX and an Agilent 7500i quadrupole mass spectrometer. The laser had a pulse rate of 20 Hz, a speed of 15 $\mu m s^{-1}$, a spot size of 50 μm and energy fluency of 5–7 mJ cm^{-2} on the sample surface. Raster ablation was applied on an area of approximately 150 $\mu m \times 300 \mu m$. The approximate depth of ablation was about 50 μm . The carrier gas for transport of the ablated material to the ICP-MS was He mixed with Ar. External calibration was performed using three silicate glass reference materials produced by the National

Institute of Standards and Technology, USA (NIST SRM 610, 612 and 614). In addition, the NIST SRM 1830 soda-lime float glass (0.1% *m/m* Al₂O₃), the certified reference material BAM No. 1 amorphous SiO₂ glass and the Qz–Tu synthetic pure quartz monocrystal were used. Measurements on commercially available IOTA HPQ material as well as reference material BSC CRM 313/1 (high-purity quartz) were performed for further external calibration; reproducibility and accuracy. Each measurement comprised 15 scans of each isotope, with a measurement time varying from a 0.15 s/scan for K in high resolution to a 0.024 s/scan of, for example, Li in low resolution. A linear regression model, including several measurements of the different reference materials, was used to define the calibration curve for each element. For the calculation of P concentrations, the procedure of [46] was applied. Ten sequential measurements on the Qz–Tu synthetic pure quartz monocrystal standard were used to estimate the limits of detection (LOD—3σ of ten measurements). The analytical error ranges within 10% of the absolute concentration of the element.

3.5 Mineralogical quantitative analysis of quartz samples by SEM–EDS

Each quartz sample was crushed and panned in the laboratory. Grains were observed under a scanning electron microscope (SEM) fitted with an energy-dispersive spectrometer (EDS) following procedures described by [47]. The EDS provided geochemical patterns reminiscent of the chemical composition of each phase identified.

4 Results and interpretation

4.1 Petrography and textural studies

Two quartz bodies are studied in this work: (1) quartzite body, showing blocks with variable dimensions (up to 20 m × 8 m) observed in the Etam Shear Zone (ESZ). The quartzite blocks are brecciated and can be traced along strike for over 2.5 km [44] in NNE–SSW to NE–SW direction. On some large blocks, joints and hydrothermal quartz veinlets (up to 15 cm wide) are observed arranged in sub-parallel arrays (Fig. 2a). The veinlets are characterized by a development of recrystallized serrate to elongated blocky quartz grains, where crystals grow from the wall inward (Fig. 2b). Generally, the blocks are monomineralic constituted by milky quartz clasts showing variable dimensions (< 0.2 mm to 8 cm in size) and having the form of polygonal crystals with sharp edges (Fig. 2c). Some are elongated and faceted, healed by a silicified quartz matrix (i.e., an optically continuous silica mass), composed of fine quartz crystals (10–80 μm) showing in some places red spots

(Fig. 2d) of clustered grains (colored material), probably Fe-stained quartz grains trapped within an aggregate of smaller quartz grains.

Two types of breccias are observed in the Etam samples, both in hand specimen and under the microscope (see Table 1 for samples description): (a) Crackle breccias (75–100% clast > 2 mm, Fig. 2e) display small isolated monomineralic quartzite blocks (1.2 × 0.8 m) and represent ~ 5% of the quartzite in the area. They contain from ~ 85 to ~ 98% angular clasts with sharp edges, variable dimensions (2 mm to 8 cm, Fig. 2c) and a siliceous matrix often less than 3%. (b) Mosaic breccias (65–75% clast > 2 mm, Fig. 2f) which show blocks (up to 20 × 12 m) and are also monomineralic are widely spread in the study area, composed of slightly elongated quartz clasts (0.6 mm to 1.2 cm) and occupy 65–73% of the volume of the rock. Some wider intergranular zones are observed with very fine-grained cataclasite indicating sintered material. In some samples, fine-grained materials of the reformed grains show interlocking grain boundaries in some thin sections. (2) A translucent quartz vein (~ 20 cm wide, Fig. 2g) was mapped in the southwestern sector of the study area surrounded by a biotite gneiss country rock. The regional foliation and the vein are parallel and trend N023°E to N030°E with subvertical dips. The vein is composed of highly homogeneous translucent fine-grained pure quartz (Fig. 2h) and ranges from 1 to 3 μm in size. Fluid and mineral inclusions are observed in both deposits, and a detailed description of their petrographic characteristics is provided in the paragraph on fluid inclusions below.

4.2 Geochemistry of Etam quartz

4.2.1 Rock geochemistry by ICP-MS

The bulk rock chemistry of the Etam quartz samples is displayed in Table 2. The samples are characterized by 98.26–99.75 wt% SiO₂. The concentrations of the other major elements are very low (Al₂O₃ = 0.01 to 0.15 wt%, Fe₂O₃tot = 0.1 to 0.59 wt%, MgO = 0.01 to 0.02 wt%, TiO₂ = 0.002 to 0.006 wt%, Na₂O = 0.01 to 0.02). The concentration of K₂O (0.01 wt%) is constant. Most of the trace elements are below the detection limit. When present, their concentrations are low, e.g., Cr (55–220 ppm), Zr (3–4 ppm) and Ba (3–4 ppm).

Only four light rare-earth elements (LREE) are detected by the ICP-MS analysis. Their concentrations vary slightly: La (0.2 to 0.4 ppm), Ce (0.3 to 0.4 ppm), Pr (0.03 to 0.05 ppm) and Nd (0.1 to 0.2 ppm). The quasi-totality of heavy rare-earth elements (HREE) is below detection limits.

Fig. 2 Photograph and photomicrograph of the Etam quartz. **a** Brecciated quartzite block crosscut by quartz veinlets in subparallel array, **b** recrystallized quartz grain growing from the wall inward in quartz vein **c** milky quartz clast, faceted and elongated, up to 12 cm. **d** photomicrograph of cluster of small quartz grain containing red spot, probably iron oxide, **e** crackle breccia, **f** mosaic breccia, **g** aspect of translucent quartz vein translucent quartz vein on the outcrop (yellow lines), **h** hand specimen of the translucent quartz vein

4.2.2 Concentrations of impurities in the quartz determined by LA-ICP-MS

The analysis of representative quartz samples is given in Table 3. Three samples were selected from the brecciated quartz block (milky quartz) and two samples from the translucent quartz vein. A single spot was analyzed in each sample section. In order to better appreciate the chemical

purity of quartz, the elements' concentrations were converted into $\mu\text{g g}^{-1}$. The data illustrated that: (1) milky quartz (samples ESIG15, ESIG18 and ESIG19) has high to moderately high concentrations of trace elements compared to average concentrations in natural quartz [6, 14]: Al (mean $579.66 \mu\text{g g}^{-1}$), Ca (mean $70.7 \mu\text{g g}^{-1}$), Fe (mean $57.36 \mu\text{g g}^{-1}$), K (mean $116.96 \mu\text{g g}^{-1}$), Ti (mean $5.67 \mu\text{g g}^{-1}$), and low concentration for Zr (mean $0.26 \mu\text{g g}^{-1}$) Ce (mean

Table 1 Representative investigated samples description

Sample no.	Sample description	Inclusion types
ESIG15	Averagely cohesive, crackle breccia, medium-size milky quartz clasts healed by very fine grains of siliceous matrix	Monophase, irregular and regular two-phase inclusion, mineral inclusion
ESIG18	Cohesive, mosaic breccia, milky fine quartz clasts cemented by small quartz crystal (10–80 μm)	Cubic crystal inclusion, irregular two-phase and cluster inclusions, mineral and satellite inclusions
ESIG19	Weakly cohesive, crackle breccias with milky large quartz clasts (up to 8 cm) often brittle + siliceous matrix	Dipyramidal monophasic and hexagonal negative crystal two-phase inclusions, mineral inclusion
ESIG21a	Massive, fine translucent quartz grains	Small inclusions, oriented biphasic negative crystal type, dipyramidal monophasic fluid inclusion, needle-like mineral inclusions

0.21 $\mu\text{g g}^{-1}$) and Ge (mean 0.14 $\mu\text{g g}^{-1}$). (2). The translucent quartz is characterized by low concentrations of trace elements compared to milky quartz: Al (mean 107 $\mu\text{g g}^{-1}$), Ca (mean 27.85 $\mu\text{g g}^{-1}$), Cr (mean 3.54 $\mu\text{g g}^{-1}$), Fe (mean 26.05 $\mu\text{g g}^{-1}$), Ge (mean 0.83 $\mu\text{g g}^{-1}$), K (mean 82.4 $\mu\text{g g}^{-1}$), Li (mean 0.51 $\mu\text{g g}^{-1}$), Mg (mean 5.15 $\mu\text{g g}^{-1}$), Na (mean 34.75 $\mu\text{g g}^{-1}$), Ni (mean 1.84 $\mu\text{g g}^{-1}$), Ti (mean 23.75 $\mu\text{g g}^{-1}$), Zr (mean 1.61 $\mu\text{g g}^{-1}$). In Etam quartz, Al, Ca, Cr, Fe, K, Mg, Na, Ni, Ti and Zr represent about 99% of the total impurities in this quartz. Other elements are below the detection limits. In HPQ, Fe is desirable to be under 10 ppm and Ca below 10 ppm as well. All the trace elements in HPQ put together should be less than 50 ppm [6, 14].

In the translucent quartz, the concentration of trace elements is low compared to the milky quartz. An exception is observed for Ag, Co, Cr, Ni, Zn, Zr and Ti. Aluminum is the most important impurity in this quartz, and it is highly variable (107–811 $\mu\text{g g}^{-1}$) between samples (Table 3). It commonly substitutes Si in quartz structure or is incorporated in quartz by the hydrothermal fluids. Titanium concentration is consistently higher in translucent quartz compared to Ti in milky quartz. The variability of Ti concentrations between milky and translucent quartz is probably related to the difference in deformation temperature or the presences of mineral inclusions [48, 49]. Indeed, microscopic studies of translucent quartz permit to observe several rutile mineral inclusions in translucent quartz, which increase their bulk (whole rock) Ti concentration [50]. Potassium content is highly variable in milky quartz. Sample E-SIG19 shows K concentration below the detection limit, and in sample ESIG15, the K content is 261 in $\mu\text{g g}^{-1}$. The concentration of Na in both quartz varieties is reflected by the presence of several cubic salt crystals (NaCl) within fluid inclusions (daughter crystals) observed under the microscope. The calcium and Mg contents are high in all the samples and variable (Ca/Mg ratio varies between from 2.03 to 16.36). Usually, the concentration of these elements is related to mineral inclusions in the quartz crystals or halite phases in the fluid inclusions [11, 14, 51, 52] reflecting the crystallization of quartz in saline

environments [11, 51, 53]. The concentration of Fe is high in all samples. According to [6], the high concentrations of Fe in quartz are predominantly diffusion-controlled. Therefore, ferromagnesian minerals in contact with quartz can induce high Fe content in this quartz. Microscopic observation permitted to distinguish spots of Fe-rich mineral inclusions in quartz grains attesting the accumulation of Fe in the milieu. Lithium shows low concentration (mean 0.51 $\mu\text{g g}^{-1}$) in the translucent quartz compared to the milky quartz (mean 6.79 $\mu\text{g g}^{-1}$), thus suggesting that Li is probably associated with submicroscopic mineral inclusions in the milky quartz [54]. This suggests therefore the low participation of Li in the process of charge-balancing cation for Al, Fe and P. Therefore, the H^+ from the hydrothermal fluid plays a greater role in the charge compensator for cation in the translucent quartz. SEM/EDS analyses were conducted to better understand the aspects of possible mineral inclusions in the translucent quartz, once the whole rock analysis and the fusion tests indicated that this quartz variety is the most promising. Two points (P_1 and P_2) were selected in sample ESIG21a (Fig. 3a) and three (P_1 , P_2 and P_3) in sample ESIG21b (Fig. 3b). The resulting EDS spectra for samples ESIG 21a [Fig. 3a, ESIG21a (P_1) and (P_2)] and ESIG 21b (Fig. 3b, ESIG21b (P_1), (P_2) and (P_3)) show high peaks for O and Si. The absence of any peaks for other elements that could have been contributed by submicroscopic or nanoparticle mineral inclusions indicated that this quartz variety is free of contaminant mineral inclusions.

4.3 Fluid inclusion petrography

Fluid inclusions observed in the Etam quartz samples generally are monophase or two-phase inclusions (Table 1). In this study, the fluid inclusions for the milky quartz samples are studied and the results presented separately from the data derived from samples of the translucent quartz.

Table 2 Major, trace and rare-earth element analyses of Etam quartzite (ICP-MS)

	Milky quartz								Translucent quartz	
	ESIG 5	ESIG 10	ESIG 14	ESIG 15a	ESIG 15b	ESIG 15c	ESIG 18	ESIG 19	ESIG 21a	ESIG 21b
<i>Major elements (wt%)</i>										
SiO ₂	99.75	98.67	98.99	98.26	98.26	99.21	99.4	99.58	98.46	98.46
Al ₂ O ₃	0.03	0.13	0.02	0.13	0.13	0.11	0.05	0.05	0.05	0.05
Fe ₂ O ₃	0.1	0.39	0.51	0.49	0.49	0.32	0.36	0.21	0.58	0.58
MnO	0.006	0.005	0.006	0.005	0.005	0.005	0.006	0.006	0.006	0.006
MgO	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02
CaO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02
Na ₂ O	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TiO ₂	0.004	0.002	0.006	0.002	0.002	0.002	0.005	0.006	0.006	0.006
P ₂ O ₅	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LOI	0.04	0.25	0.02	0.25	0.25	0.25	0.01	0.07	0.07	0.07
Total	100	99.50	99.622	99.187	99.19	99.947	99.901	99.982	99.25	99.242
<i>Trace elements (ppm)</i>										
Be	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sc	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
V	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Cr	220	55	94	100	100	81	199	216	220	220
Co	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ni	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Cu	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zn	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Ga	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ge	1	<0.5	1	<0.5	<0.5	1	1	1	1	1
As	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Rb	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sr	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Y	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Zr	3	4	4	4	4	3	3	4	3	3
Nb	4.1	5.1	4.7	5.4	5.4	3.9	3.1	3.1	3.1	3.1
Mo	<2	<2	<	10	10	<2	<2	8	<2	<2
Ag	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
In	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sb	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cs	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ba	4	3	3	4	4	4	4	3	4	4
Hf	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ta	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Pb	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Bi	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Th	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
U	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
<i>Rare-earth element (ppm)</i>										
La	0.4	0.2	0.3	0.2	0.2	0.3	0.4	0.4	0.4	0.4

Table 2 (continued)

<i>Rare-earth element (ppm)</i>										
Ce	0.3	0.4	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.4
Pr	0.03	0.05	0.05	0.05	0.05	0.05	0.04	0.03	0.03	0.03
Nd	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1
Sm	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Eu	< 0.005	0.01	0.01	0.01	0.01	< 0.005	0.01	< 0.005	< 0.005	< 0.005
Gd	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Tb	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dy	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Ho	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Er	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Tm	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Yb	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Lu	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002

4.3.1 Milky quartz

In the milky quartz, most of the fused grains contain abundant inclusions with small size (Fig. 4, yellow color) ranging from 2 to 12 μm and randomly distributed (Fig. 5a). They are monophasic or two-phase inclusions showing two distinct phases at room temperature: a solid daughter crystal phase and a fluid phase.

- Monophasic fluid inclusions

The monophasic fluid inclusions are fewer in number compared to the two-phase fluid inclusions. Rarely, they are dipyratidal monophasic inclusions (Fig. 5b, orange arrow). Most are irregular and some have the shape of negative crystals.

- Two-phase and three-phase fluid inclusions

The majority of fluid inclusions in the milky quartz are two-phase fluid inclusions. Usually, they are composed of liquid and gas although some have daughter crystals. The presence of halide crystals indicates that the liquid phase is probably brine while gas phase is CO_2 . Often here, fluid inclusions show spherical gas bubbles (Fig. 5c, black arrows) with a range from 5 to 30% of the total volume of the inclusion. Many two-phase inclusions are irregular (Fig. 5c, black arrows) in shape. Smaller regular inclusions are observed with bubbles, often larger than the liquid volume (Fig. 5c, blue arrow). Some two-phase inclusions showing negative hexagonal crystal-shape (Fig. 5d, black arrow) are observed in this quartz.

Solid phases observed in the fluid inclusions mostly display cubic outlines (Fig. 5d, e, red arrow), which are probably salt crystals (NaCl), as attested by the high amount

of Na present in the ICP-MS data analysis (Table 3). Other fluid inclusions are rarely observed, mostly irregular in shape and larger (12 μm) than the solid phases encountered in some inclusions (Fig. 5e, green arrow). Figure 5f (blue light arrow) shows large inclusions with smaller fluid inclusions (satellite inclusions) surrounding it. Tarantola et al. [55, 56] showed that, due to deviatoric stress, inclusions can be deformed and dismembered, giving a large relic inclusion and a cluster of small neonate (satellite) inclusions around it.

4.3.2 Translucent quartz

The inclusions present in the translucent quartz are different from those of the milky quartz samples. The fluid inclusions are much smaller compared to those of milky quartz (Fig. 4) and oriented. Figure 6a shows this orientation (represented by the black line). Most of these oriented inclusions are of the negative crystal type but much smaller. Monophasic inclusions are common and occur as dipyratidal monophasic inclusions (Fig. 6b, orange arrow). Several needle-shaped mineral inclusions (Fig. 6c, gray arrow) which are suggested to be rutile because of the elevated concentration of Ti in LA-ICP-MS analyses (Table 3) are observed in this quartz sample as well as small acicular inclusions, randomly distributed in the grains.

4.4 Fusion of quartz grains over silica plate: bubble formation and bubble characterization

In this section, the results of the quartz/silica plates tested for bubble formation are presented in the form of photographs at various stages of heating. The images were then processed by computational analysis in order to measure average bubble size and bubble density on each

Table 3 Impurities concentrations in quartz samples (LA-ICP-MS)

		Milky quartz			Translucent quartz	
		ESIG15	ESIG18	ESIG19	ESIG21a	ESIG21b
Ag	$\mu\text{g g}^{-1}$	0.002	0.003	0.004	0.011	0.009
Al	$\mu\text{g g}^{-1}$	354	811	574	107	107
B	$\mu\text{g g}^{-1}$	< LD	< LD	51	< LD	< LD
Ba	$\mu\text{g g}^{-1}$	0.82	1.24	0.86	0.42	0.41
Be	$\mu\text{g g}^{-1}$	0.07	0.10	0.05	0.03	0.03
Ca	$\mu\text{g g}^{-1}$	64.3	47.8	100	27.3	28.4
Ce	$\mu\text{g g}^{-1}$	0.11	0.19	0.33	0.08	0.06
Co	$\mu\text{g g}^{-1}$	0.01	0.02	0.01	0.05	0.05
Cr	$\mu\text{g g}^{-1}$	0.85	1.46	1.49	3.43	3.65
Cs	$\mu\text{g g}^{-1}$	0.020	0.033	0.016	0.003	0.003
Cu	$\mu\text{g g}^{-1}$	0.30	0.23	0.88	0.52	0.62
Dy	$\mu\text{g g}^{-1}$	0.006	0.009	0.009	0.002	0.001
Er	$\mu\text{g g}^{-1}$	0.004	0.004	0.005	0.001	0.001
Eu	$\mu\text{g g}^{-1}$	0.001	0.003	0.003	0.001	0.001
Fe	$\mu\text{g g}^{-1}$	36.4	67.8	67.9	26.5	25.6
Ga	$\mu\text{g g}^{-1}$	0.06	0.15	0.05	0.02	0.02
Gd	$\mu\text{g g}^{-1}$	0.004	0.016	0.010	0.003	0.002
Ge	$\mu\text{g g}^{-1}$	0.15	0.12	0.17	0.83	0.84
Hf	$\mu\text{g g}^{-1}$	0.004	0.009	0.008	0.04	0.04
Ho	$\mu\text{g g}^{-1}$	0.001	0.001	0.002	< LD	< LD
K	$\mu\text{g g}^{-1}$	89.9	261	< LD	81.0	83.8
La	$\mu\text{g g}^{-1}$	0.07	0.36	0.11	0.04	0.04
Li	$\mu\text{g g}^{-1}$	5.24	11.4	3.74	0.51	0.51
Lu	$\mu\text{g g}^{-1}$	0.001	< LD	0.001	< LD	< LD
Mg	$\mu\text{g g}^{-1}$	6.78	23.5	6.11	5.64	4.67
Mn	$\mu\text{g g}^{-1}$	0.28	0.53	0.51	0.43	0.55
Na	$\mu\text{g g}^{-1}$	37.2	32.3	41.0	34.7	34.8
Nb	$\mu\text{g g}^{-1}$	0.04	0.04	0.02	< LD	< LD
Nd	$\mu\text{g g}^{-1}$	0.03	0.16	0.08	0.02	0.02
Ni	$\mu\text{g g}^{-1}$	0.44	0.71	0.73	1.82	1.87
Pb	$\mu\text{g g}^{-1}$	0.18	0.17	1.59	0.19	0.11
Pr	$\mu\text{g g}^{-1}$	0.01	0.05	0.02	0.01	0.01
Rb	$\mu\text{g g}^{-1}$	0.95	3.15	0.40	0.38	0.33
Sb	$\mu\text{g g}^{-1}$	0.002	0.002	0.012	0.003	0.004
Sc	$\mu\text{g g}^{-1}$	< LD	< LD	< LD	< LD	< LD
Sm	$\mu\text{g g}^{-1}$	0.006	0.02	0.02	0.004	0.003
Sn	$\mu\text{g g}^{-1}$	< LD	< LD	< LD	< LD	< LD
Sr	$\mu\text{g g}^{-1}$	1.43	1.50	1.34	0.26	0.26
Ta	$\mu\text{g g}^{-1}$	< LD	< LD	< LD	< LD	0.02
Tb	$\mu\text{g g}^{-1}$	0.001	0.002	0.002	< LD	< LD
Te	$\mu\text{g g}^{-1}$	< LD	< LD	0.001	< LD	< LD
Th	$\mu\text{g g}^{-1}$	0.02	0.04	0.05	< LD	< LD
Ti	$\mu\text{g g}^{-1}$	6.60	7.38	3.05	23.3	24.2
Tl	$\mu\text{g g}^{-1}$	0.006	0.017	0.002	0.002	0.001
Tm	$\mu\text{g g}^{-1}$	0.001	< LD	0.001	< LD	< LD
U	$\mu\text{g g}^{-1}$	0.007	0.010	0.02	0.007	0.008
V	$\mu\text{g g}^{-1}$	0.13	0.20	0.05	0.02	0.02
W	$\mu\text{g g}^{-1}$	< LD	0.002	< LD	< LD	0.002
Y	$\mu\text{g g}^{-1}$	0.05	0.04	0.06	0.11	0.11

Table 3 (continued)

		Milky quartz			Translucent quartz	
		ESIG15	ESIG18	ESIG19	ESIG21a	ESIG21b
Yb	$\mu\text{g g}^{-1}$	0.004	0.003	0.004	< LD	0.001
Zn	$\mu\text{g g}^{-1}$	0.23	0.15	0.25	0.17	0.32
Zr	$\mu\text{g g}^{-1}$	0.18	0.33	0.28	1.61	1.61

photograph. HPQ material forms very few or no bubbles during this test.

Three samples of milky quartz and two samples of translucent quartz were selected for silica fused analysis. The size and the average content of bubbles present vary among the samples: 1) Milky quartz samples (ESIG15, ESI18 and ESIG19) are from the brecciated quartz vein. The rock is brittle, and clasts are cemented by smaller quartz crystals. These small quartz crystals (10 to 80 μm in size) are separated upon grinding. Bubble characterization of all the milky quartz samples displays large quantity of bubble formation in fused grains (the green lines encircle the grains that have been effectively fused, where one or more bubbles are shown inside) and bubble size distribution in the range of 10–240 μm with a mean diameter of 75 μm (Fig. 7a, b, blue arrow). However, the majority (80%) of bubbles are from 50 to 80 μm in diameter while about 90% were smaller than 140 μm . Large clusters of small bubbles (less than 30 μm) were commonly observed in several fused grains of milky quartz (Fig. 7b, c, black arrow), and no bubble-free fused grains were observed in this quartz. 2) In translucent quartz, Fig. 7d permits to observe grains before and after fusion. In the fused state, the exact bubbles that form from each grain are distinctively observed. Translucent quartz samples do not produce many bubbles compared to the milky quartz, and also the size of each bubble is drastically reduced. More than 90% of the bubbles are less than 10 μm (Fig. 7d black arrow). Clean grains that have not produced bubbles upon fusion are also identified (Fig. 7d, green arrows) and represent about 40% of volume.

5 Discussion

5.1 Geochemistry and fluid inclusions

A number of factors likely played a role in the chemistry of trace elements in quartz studied in Etam. These are factors such as metamorphism and hydrothermal fluid action. Trace elements concentrations are chiefly regulated by the crystallization temperature [6, 57], the extent of melt fractionation in igneous and pegmatitic quartz [58–60] and the chemistry and acidity of the fluid from which the

quartz crystallized in diagenetic and hydrothermal quartz [61–63].

Monecke et al. [64], Baron et al. [65] define Li, Al, K, Rb, Sr, and Y concentration in quartz as tools that allow distinguishing quartz from metamorphic processes from quartz of hydrothermal origin. Korneliussen et al. [66], Müller et al. [67] show that, despite variations, the previous elements have generally lower concentration in metamorphic quartz compared to hydrothermal quartz. According to [58], the Ge/Ti, Ge/Be, P/Ge and P/Be ratios of quartz are strongly sensitive to the origin and evolution of the granitic melts. The Ge/Ti ratio therefore is the most suitable for analyzing and understanding petrogenetic processes in granitic igneous rocks. Research work discriminating sources of quartz deposit have been carried out previously worldwide and abundant literature is available [3, 6, 11, 45, 52, 67, 68]. Trace elements in quartz are then generally used as tools for differentiating pegmatite, igneous, hydrothermal and metamorphic quartz. These studies are used for benchmarking procedures and comparing results of this study.

From the ICP-MS or LA-ICP-MS analysis, Etam quartz samples show more or less variation between milky and translucent quartz trace elements concentration. Figure 8 a shows similar trend variation in trace elements concentration for both quartz and suggests the similar processes of formation of Etam quartz. Data available [14, 69, 70] show that Al^{3+} , Ti^{3+} and Ge^{3+} commonly substitute Si^{4+} in quartz structure and the charge defect created by these substitutions is compensated by monovalent ions Li^+ , Na^+ , K^+ and H^+ .

The Al/Li ratio is often used to constrain crystallization conditions of quartz [52, 65, 72]. This ratio varied from 67.55 to 153.47 in milky quartz and is 209.8 in translucent quartz samples. Thus, the Al/Li value in Etam quartz is far from the Al/Li ratio in pegmatitic quartz, often < 10 [45, 52] and also far from hydrothermal quartz studied elsewhere [11, 64]. Monecke et al. [64] distinguished metamorphic quartz from hydrothermal quartz by low content of Li, Al, K, Rb, Sr and Y in recrystallized metamorphic quartz. Lithium, Rb, Sr and Y show low concentrations in Etam quartz, similar to most of the metamorphic quartz described in the literature [64, 73, 74]. Aluminum and K concentrations are high and comparable to some pegmatite quartz studied in the world [52], except for sample E-SIG 19 which shows K

Fig. 3 SEM-EDS images and patterns for translucent quartz: **a** image for sample ESIG21a and EDS patterns at point 1 (P₁) and 2 (P₂), **b** image for sample ESIG21b and EDS patterns at points 1 (P₁), 2 (P₂) and 3 (P₃)

below detection limit. Daughter crystals in fluid inclusions in this quartz are mostly salts, and therefore, Al is probably incorporated in the quartz structure added by hydrothermal fluid circulating during metamorphic events. Indeed, milky quartz in Etam was probably (re)crystallized under

greenschist to amphibolitic metamorphic condition [44] in the shear zone. The relative low concentration of Na and K coupled with the low Al/Li ratio suggests that the charge balances are compensated mainly by H⁺ [75] from hydrothermal fluid in milky and translucent quartz, since either

Fig. 4 Histogram showing proportion of fluid inclusions in milky and translucent quartz in Etam

a metamorphic event or the brittle nature of the rock has enhanced fluid flow in the area.

The Ge/Fe ratio (mean = 0.0027) is very low in milky quartz compared to translucent quartz (mean = 0.031) and to hydrothermal quartz studied in Olhos D'agua (Ge/Fe = 0.15) and Corinto (Ge/Fe = 0.3 [45]). It is also much smaller compared to pegmatitic quartz which presents Ge/Fe ratio ranges from 4.5 to 0.1 [52, 76]. According to [76], this low Ge/Fe ratio suggests the early crystallization stage of quartz probably during metamorphic event and containing high concentration of Fe. Furthermore, the rare-earth elements (REE) distribution pattern of this quartz type shows the characteristics of typical metamorphic quartz samples [64, 74] with an enrichment of LREE (Fig. 8b). The samples contain very low to negligible HREE when compared to standard HPQ values [6, 51], and thus

Fig. 5 Photomicrographs of fluid inclusions in milky quartz samples: **a** large in quantities and small in size fluid inclusions in milky quartz, **b** dipyratidal monophasic inclusions probably apatite (orange arrow), **c** Irregular (black arrow) and regular (blue arrow) two-phase inclusions, **d** negative quartz crystals (black arrow) and cubic inclusion (red arrow), **e** mineral inclusion (red arrow) and melt inclusion (green arrow), **f** fluid inclusion surrounded by small inclusion (satellite inclusions)

Fig. 6 Photomicrographs of fluid inclusions in translucent quartz: **a** Negative biphasic crystal inclusions generally oriented, **b** dipyratidal mono-phasic fluid inclusion (orange arrow) and mineral inclusion (pink arrow), **c** needle mineral inclusion, probably rutile (gray arrows)

Fig. 7 Photomicrographs of the fused quartz powders over silica plates where fused grains can be observed with formed bubbles inside. **a** High quantity and very large bubble formation in fused grains in milky quartz, **b, c** large quantity of bubble and clusters of small bubbles (black arrow) milky quartz, **d** cleaned fused grain with free bubble formation (green arrow) and small bubbles in grains (black arrow) in translucent quartz. The green lines circle the grains that have been effectively fused; the red lines circle the “unfused” grains

their chondrite-normalized REE patterns cannot be shown on spider diagram. The absence of a positive Ce anomaly is suggested to reflect the igneous protolith of this quartz.

This corroborates [43, 44] who suggested that the protolith of the fault rocks is probably igneous rocks in Etam.

Fig. 8 Trace elements and REE variation in Etam quartz: **a** some trace element concentration average in Etam quartz, milky and translucent quartz patterns display similar trends with translucent quartz showing low concentration in all elements, except for Ti, **b** chondrite-normalized rare-earth element (REE) distribution patterns of Etam quartz (normalization according to data of Anders and Grevesse [71])

Fluid inclusions in milky quartz display features related to recrystallization under metamorphic conditions as shown by the higher volume of two-phase fluid inclusion with irregular shapes containing brine and CO_2 [77] and the alignment of the inclusions to define trails. However, the abundance and the variability of fluid inclusions suggest that this quartz benefitted from hydrothermal fluids inputs. Impurities contained in it are similar to some hydrothermal quartz data available [16, 64]. Therefore, it is suggested that quartz in Etam was probably formed during metamorphic processes implying circulation of hydrothermal fluid saturated in silica [73], followed by silica precipitation and formation of hydrothermal veins. Some data available [45] reveal that hydrothermally formed quartz of Pan-African age was submitted to some degree of metamorphism. These conditions are similar to the geological context at Etam environment. Furthermore, the Etam area and Santa Helena (Olhos D'água and Corinto) in Brazil are situated in N070E-oriented thrust zone (Fig. 1a) and were probably subjected to the same metamorphic degree

during Pan-African event. Along shear zones, crystal-plastic deformation is an important process in the purification of quartz. Quartz has the capacity to response to stress along ductile shear zones in a combined brittle–ductile manner. Ductile failure results in quartz ribbons, deformation lamellae and undulose extinction and fracture-controlled slip. These features are observed in the pure quartz grains in the Etam shear zone.

5.2 Trace elements incorporation into quartz

The Al concentration in the Etam quartz samples varies (107 to $811 \mu\text{g g}^{-1}$, Table 3). Rusk et al. [61], Götze et al. [78], Rusk et al. [79] demonstrated that high concentration of Ti and corresponding low concentration of Al are closely related to high temperature in hydrothermal quartz. The concentration of Ti in quartz reflects the temperature of recrystallization during metamorphism [48, 49, 57, 58, 67, 80]. Titanium concentration in milky quartz is similar to that of hydrothermal quartz described in the literature. The microscope studies of the Etam quartz did not show rutile as inclusions in milky quartz. Therefore, the Ti concentration in this quartz samples is presumably incorporated in the structure of the quartz and the hydrothermal fluids seem not to have played a major role in its genesis or the fluid was Ti poor. In the translucent quartz samples, the high content of Ti compared to the milky quartz is possibly related to mineral inclusions as needles that seem to be rutile inclusions were abundantly observed under the microscope study. The absence of Ti–Fe-rich mineral (e.g., ilmenite) in this geological environment suggests that Ti was probably added by Ti-rich hydrothermal fluids from other environment.

The high Al concentration in Etam quartz was probably induced during hydrothermal fluid-assisted metamorphism at elevated temperature [45, 64]. Such phase transformations are widespread in the area [40, 44]. Iron concentration is abnormally high in the translucent quartz compared to that of HPQ [6, 51]. Also [6] stated that quartz crystals in contact with Fe-rich minerals show high concentration of Fe. Thus, the Fe concentrations in quartz are predominantly diffusion-controlled. Indeed, clusters of small quartz grains containing red spots, probably iron oxide, were observed in the fluid and mineral inclusion study. The origin of these spots is not known, but probably hydrothermal fluids circulating in the area were Fe-rich.

The high concentration in quartz of Ca, K, Mg and Na is sometimes due to saline environment. But generally these elements are carried in quartz by fluids inclusions or mineral inclusions [11, 73]. Indeed, the microscope observation shows several NaCl crystal inclusions in Etam quartz that probably carried some of these elements.

Fig. 9 Photomicrographs of the fused quartz powders over silica plates. **a** Translucent quartz from Etam, **b** milky quartz from Olhos D'agua, **c** transparent quartz from Corinto, **d** Iota commercial powder [11]. Small black dots represent bubbles

5.3 Technological aspect

Quartz in this study has mainly two-phase fluid inclusions containing saline water and CO_2 . The behavior of quartz upon fusion has been described by several authors [10–12, 45]. The amount of gas liberated during fusion is related to the size and density of fluid inclusions. At Etam, the translucent quartz yielded better fusion test results compared to the milky quartz variety. The results of the bubble formation test for the Etam translucent quartz (Fig. 9a) are compared here to the milky samples (Fig. 9b) and the transparent quartz (Fig. 9c) from Corinto and Olhos D'agua, respectively (samples from the Serra de Santa Helena formation-Brazil) [45], and to the commercial powder, IOTA powder (Fig. 9d).

The comparison shows that the milky quartz samples from Olhos D'agua formed more bubbles compared to the three other samples. Moreover, samples from Etam translucent quartz, transparent quartz or the IOTA powder have formed small bubbles compared to the milky quartz samples during fusion over silica plate. Between sample of translucent quartz from Etam, transparent quartz from Olhos D'agua or the IOTA powder, the variation in terms of bubble size and bubble volume is negligible. These samples therefore seem similar from the point of view of bubbles formation after fusion over

silica plate. Furthermore, the translucent quartz sample from Etam has few bubbles formed, similar to the transparent quartz from Olhos D'agua, which was concluded to be equivalent to commercial IOTA powder [11].

The inclusions in both quartz varieties are different in size, in quantity and types. This observation suggests that either the two quartz varieties were subjected to different geological events (hydrothermal action or metamorphism) that could modify fluid inclusion features in it or inclusions were initially formed differently due to different processes [45]. Furthermore, high-stress tectonic geological environment can induce fluid inclusion deformation due to fluid loss [56, 81–85]. Milky quartz in Etam developed along a brittle–ductile shear zone [44] and shows large inclusions observed surrounded by small inclusions or satellite inclusions. This can be supported by [86] and [55, 56] who showed that due to deviatoric stress, inclusions can be deformed and dismembered, giving a large relic inclusion and a cluster of small neo-nate (satellite) inclusions around them.

The chemical analysis in Table 3 shows impurities in some Etam quartz samples. The translucent quartz variety has more promising results for industrial applications, compared to the milky quartz. According to [45], impurities in fluid inclusions are less hard to eliminate than the incorporated ones in quartz structure. Therefore, the

most principal elements with high concentrations in the translucent quartz are: Al (means $107 \mu\text{g g}^{-1}$), K (means $82.4 \mu\text{g g}^{-1}$), Fe (means $26.01 \mu\text{g g}^{-1}$). According to [11], removing Al impurities from quartz by using HF or concentrated acid mixtures is costly and constitutes environmental hazards. Therefore, for quartz to be suitable as HPQ raw material, it should meet certain natural requirements, or the processing should be done by methods that are less hazardous and more efficient. Indeed, an efficient fluorine-free leaching system to purify quartz has been developed with an objective to establish a fluoride-free technology for improving quartz quality [16]. According to the authors, the method can consistently purify quartz by removing elements impurities up to 88.2 wt%, 99.0 wt% and 98.1 wt%, for the HCl–NH₄Cl system, and 87.5 wt%, 98.1 wt% and 98.2 wt% for the H₂SO₄–NH₄Cl system, respectively, for Al, K and Fe.

Based on chemical studies coupled with bubble formation characteristics in Etam quartz, the milky quartz can necessitate important and costly purification process to meet HPQ standard. The deposit therefore due to the high SiO₂ content (up to 99.75 wt%) can be used as raw materials for the refractory industry with a production of silica stone, silicon and silicon alloys [51]. Translucent quartz in the other hand shows optimistic results as quartz raw material that can be used in some quartz applications industries without necessarily purification processes. It can produce, for instance, silica glass which is common raw material largely used in optical and telecommunication industries.

5.4 Economic appraisal

According to the definition of HPQ, the milky quartz from Etam does not meet the requirement of a high-purity quartz deposit. The sum of the concentration of unwanted elements in this quartz type is $\geq 500 \mu\text{g g}^{-1}$. The translucent quartz variety is fine-grained, translucent and massive. These aspects are often an indication of good fusion behavior [10]. Regarding only the fusion behavior, this quartz type can be used to produce transparent glass. The problematic feature is the chemical purity. With the exception of Li ($0.5 \mu\text{g g}^{-1}$) and B (below detection limit), all the trace elements which determine the purity of quartz as per HPQ definition are above the required limits (Table 3). The Ti and Fe are especially high. These impurities are probably located in the mineral inclusions which can easily be eliminated if proper processing tests are conducted. Translucent quartz show similar characteristics to some samples from the Santa Helena quartz deposit [45] as shown by the fusion over silica plate and bubble formation. Therefore, further investigations for such quartz type in the Etam area are advised. Several veins as translucent

quartz vein with similar orientation exist in the area. These veins crop mostly in metamorphic basement and are easily accessible. The volume of the milky and translucent quartz resource that defines the distinct Etam ridge above the surrounding peneplain is estimated at $\sim 6 \text{ km}^3$ pointing to an exploitable deposit considering that drilling will only add to the subsurface volume.

6 Conclusion

The investigation of Etam quartz samples in the southwest region (Cameroon) by the combination of ICP-MS, LA-ICP-MS, SEM–EDS resolved trace-element analysis and characterized in detail the type, the abundance of trace elements in quartz and the reconstruction of processes responsible for their formation and the amount of trace-element concentrations. The analyses show that the SiO₂ content is very high (98.46–99.75 wt%) with very low concentration of trace elements. The process of formation of both deposit types is suggested to be similar: The translucent quartz is clearly older than the milky quartz although both probably formed under metamorphic conditions and benefited from a contribution of hydrothermal fluids.

The translucent quartz of Etam shows optimistic results as ore resource after analysis. Principal impurities in it are Al (mean $107 \mu\text{g g}^{-1}$), Ca (mean $27.85 \mu\text{g g}^{-1}$) Fe (mean $26.05 \mu\text{g g}^{-1}$) and Ti (mean $23.75 \mu\text{g g}^{-1}$). According to the HPQ definition, quartz from Etam does not meet the requirement of a high-purity quartz deposit. Chemically and technologically, the translucent quartz is medium-purity quartz with good fusion behavior producing very little number of bubbles; thus, it could be used to produce transparent glass. Moreover, the main impurities in translucent quartz are mostly in fluid and mineral inclusions; thus, the purification using efficient method can purify this quartz and produce quartz crucibles with high-purity qualities widely used in industries.

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Authors' contributions CES, CS and MA were involved in study conception and design. CES, CS and MJLN were involved in acquisition of data. CES, CKS, CS, EF and MFMS contributed to analysis and interpretation. CS drafted the manuscript. CES, CKS, EF and MFMS were involved in critical revision of the manuscript. All authors read and approved the final manuscript.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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