Emerald dating through \(^{40}\text{Ar}/^{39}\text{Ar}\) step-heating and laser spot analysis of syngenetic phlogopite

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Abstract

Emerald, occurring in K-metasomatic rocks developed at the contact of the Carnaíba leucogranite with serpentinite (Bahia State, Brazil), has been dated using an original \(^{40}\text{Ar}/^{39}\text{Ar}\) procedure. It combines step heating and spot fusion experiments on two types of phlogopite crystals: (1) bulk samples and individual grains extracted from the enclosing K-metasomatic host rocks; and (2) syngenetic solid inclusions precipitated along growing zones of the emerald host crystals. The second procedure uses in situ laser probe experiments on rock sections. In spite of the huge amounts of excess \(^{40}\text{Ar}\) detected in adjacent emerald, we could measure reliable ages of \(1951 \pm 8\) Ma and \(1934 \pm 8\) Ma for the Trecho Velho and Braulia occurrences, respectively. Spot fusion data had higher discrepancy than the step heating data, but minute crystals of phlogopite included in emeralds bearing excess argon do not reveal excess argon. A muscovite belonging to the same granite hydrothermal complex gave a plateau age of \(1976 \pm 8\) Ma, which may correspond to a higher closure temperature of the K–Ar system during the cooling of the whole pluton and associated hydrothermal halo.

These accurate measurements lead to the following conclusions: (1) direct emerald dating is possible; (2) in spite of a polyphase history during the Transamazonian orogenesis (2 Ga), combined step heating and spot fusion experiments give a better precision for granite-related emerald mineralization than the scattered ages obtained by Rb–Sr and K–Ar methods; (3) the late-Transamazonian tectonothermal retrograde event which probably caused the dispersion of previous Rb–Sr and K–Ar data is not revealed by our procedure; (4) the emerald mineralization and K-metamorphism appear to be linked with the thermal history of the leucogranite; (5) in addition to its use in polyphase crustal domains, accurate \(^{40}\text{Ar}/^{39}\text{Ar}\) dating is of major interest in the field of metallogenic models, even, for instance, for mineralizations characterized by disturbed isotopic systems, which record effects as excess argon.

1. Introduction

Emerald is a green–blue variety of beryl (\(\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}\)), which results from the substitution of chromium for aluminium in the crystal structure. Beryl is the most common mineralogical expression of beryllium, which is considered to be an incompatible element, concentrated during the final stages of granitie and pegmatitic evolutions. Chromium, in contrast, is a typical compatible element, mantle derived, and concenti-
trated in ultramafic bodies. Exceptional geological conditions are needed, therefore, to bring together these two elements within the emerald crystal structure, which explains the scarcity of this valuable gem. Geological environments propitious to such juxtaposition are suture zones, granite/greenstone terrains and metamorphosed shales [1]. The Brazilian deposits from Bahia state [2] are good examples of such a process: emeralds are found in K-metasomatized rocks associated with leucogranites and pegmatites intruding serpentinite bodies. The metasomatic rocks are believed to represent the channels of fluid-rock interaction between pegmatitic veins and serpentinites [3,4]. Emerald mineralization therefore appears to be a good witness of granitic emplacement in Archean-Early Proterozoic cratons during continental collisions. However, the polyphase tectonothermal history of such crustal domains caused the frequent resetting of isotopic systems [5,6]. Direct and precise dating of emerald might contribute to a better understanding of the interaction between highly differentiated granite and basement rock during continental accretion.

Natural emerald can contain measurable quantities of Rb. Therefore, the Rb–Sr method was first used for direct emerald dating of the Brazilian deposits (Socoto-Bahia State, Brazil), [7]. These first Rb–Sr determinations, although yielding age ranges compatible with the Transamazonian orogeny (2 Ga), show high discrepancies between model ages of contemporaneous K-metasomatite phlogopite (1814 Ma) and emerald (1180 Ma).

Direct K–Ar dating of beryl and its emerald variety appears difficult due to large amounts of excess argon, which occupies, along with other volatiles (H₂O), inert gases (He) and alkali ions (Li, Na, K, Rb and Cs), the hexagonal channels defined by the six-membered silica tetrahedron ring. Values of 82–99% excess argon relative to radiogenic argon have been reported [8,9]. Therefore, the only promising way for precise emerald dating remains, at the moment, the indirect dating of host rocks or K-bearing mineral inclusions which reflect their paragenesis and are very often present in natural emeralds [10,11].

In situ laser probe $^{40}$Ar/$^{39}$Ar experiments on minute syngenetic solid inclusions in emerald, combined with $^{40}$Ar/$^{39}$Ar step heating on bulk samples and single grains from the host rock, can be carried out on the $^{40}$Ar/$^{39}$Ar device of the University of Nice, France [12,13]. This method was attempted on the Carnaiba deposit from Brazil (Bahia state), which produces emeralds with minute phlogopite grains precipitated along the growing zones of the gems. Phlogopite also represents the main gangue mineral of the host rock, thus allowing comparative $^{40}$Ar/$^{39}$Ar dating. This approach requires that the dated minerals are: (1) really co-genetic (this will be discussed in detail in this paper); and (2) completely free from excess argon. Due to the close spatial association of the high excess argon-bearing emeralds and the dated phlogopite hydrous inclusions, we anticipated that some excess argon should also affect the latter. Our results invalidate this statement.

2. Regional geology

The Carnaiba granite and its related emerald deposits belong to the Transamazônia (2 Ga) leucogranites plutons of the Jacobina-Contendas Mirante belt [14–16], which form an elongated structure over 500 km long in the eastern part of the Archaean and lower Proterozoic São Francisco craton (Bahia State, Brazil). The Carnaiba granite is a small, circular (4 km in diameter), homogeneous and fine grained, two-mica leucogranite [17] emplaced within a dome structure of the Jacobina lower Proterozoic formations, which overthrusts the Archaean basement from east to west (Fig. 1). The Jacobina series are composed of thick metaquartzite units, metaconglomerates, mica schists, banded iron formations and intercalated, thin meta-ultrabasic slices (100–300 m thick) bearing stratabound chromitite deposits, which have been retrogressed into serpentinites (Fig. 1). The serpentinite layers are cross-cut by the intrusive granitic pluton or occur as enclaves in the top of the roof-pendant.

The genesis of the Carnaiba-type emerald deposit appears to be well constrained [4,18,19].
Emerald is found in the contact metamorphic rocks of the granite aureole (Fig. 1), within a dense swarm of pegmatites crosscutting the serpentine slices. The development of emeralds results from a metasomatic process. This is due to the infiltration of hydrothermal fluids throughout both the pegmatites and serpentinites which lead to chemical exchanges, such as, for example: (1) the desilification and albitization of pegmatites; (2) the biotitization of serpentinites, which resulted in the development of monomineralic mica zones, the so-called K-metasomatites or phlogopitites; and (3) the deposition of emerald and accessory molybdenite and scheelite, within the K-metasomatites or less frequently the albitized pegmatites. During the metasomatic exchanges, the chromium, substituted within the lattice of beryl and giving it its valuable colour, was extracted from the serpentinites. The emerald occurrences were then cross-cut by quartz-molybdenite-muscovite-yellow beryl veins generated during a late hydrothermal phase in the general emerald depositional event.

Later, a barren tectonothermal overprinting, characterized by folding, boudinage, crenulation and a weak chloritization of biotite, affected the granite and the emerald-bearing K-metasomatites. This retroomorphic event is attributed to the ultimate tectonic pulses of the Transamazonian orogenesis, since this part of the Sào Francisco craton is free of tectonochemical events of Brasiliano age (0.6-0.5 Ga) [14,15].

The polyphase geological history of the Carnaiba area probably explains the wide dispersion of radiometric data obtained on granites and related K-metasomatites. An Rb-Sr isochron age at $1883 \pm 87$ Ma [16] has been proposed for the Carnaiba granite, whereas the associated K-metasomatites yield an age of $1869 \pm 28$ Ma [3]. Muscovites and biotites from the Carnaiba granite yield K-Ar isochron ages of $1980 \pm 30$ Ma and $1890 \pm 32$ Ma, respectively [20], whereas the K-metasomatites gave an age of $1935 \pm 20$ Ma [20]. Such a wide range of ages, determined on muscovite and biotite from the granite and associated contact-metamorphosed surrounding rocks, appear to be probably due to the late Transamazonian tectonochemical overprint, which partly disturbed the original Rb-Sr and K-Ar radiogenic systems, and thus gives scattered ages.

![Fig. 1. Geological sketch map of the Carnaiba granite and emerald mining district.](image-url)
Fig. 2. Location and \(^{40}\)Ar/\(^{39}\)Ar ages of the laser spot-fusion analysis on the slab samples from Braúlia (BaF12-1-1) and Trecho Velho (TVFl 6).
It therefore appears necessary to constrain the age of the metasomatic halo and the emerald mineralization accompanying the Carnaiba granite intrusion more precisely. This would allow further valuable comparisons with other leucogranites emplaced within the Jacobina-Contendas Mirante belt [16,20–22], and better knowledge of the Transamazonian orogenesis. Such a goal is made possible by the use of the $^{40}\text{Ar}/^{39}\text{Ar}$ method which needs fewer samples for analysis than the Rb–Sr or K–Ar techniques, and individual biotite grains or a few grains of ultra-pure unchloritized biotite can be used. The shape of the resulting $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating spectrum can also be used to validate plateau ages.

3. Sample description

The present study has been carried out using samples of emeralds, K-metasomatites and molybdenite- and muscovite-bearing quartz veins selected in the Trecho Velho and Braúlia prospecting pits (Fig. 1). Two different emerald-bearing ores were studied; Sample TVFI 6 (Trecho Velho) consists of emerald and its K-metasomatite host rock included in metasomatized serpentinites. The K-metasomatite is coarse grained and composed of phlogopite (2 cm long), apatite and minor quartz. Sample Ba FL2-II-1 (Braúlia) belongs to an albiteitized pegmatite vein showing irregular phlogopite pockets and/or veinlets 1-10 cm in length. In both cases, emerald contains syngenetic phlogopite inclusions (Fig. 2).

The muscovite Ba 102 belongs to a molybdenite–yellow beryl–quartz vein which cross-cuts the emerald-bearing K-metasomatites in the Braúlia deposit.

Phlogopite and muscovite crystals analyzed by the induction and laser step-heating techniques were carefully separated by hand picking. Electron microprobe data and the analytical proce-

### Table 1

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<th>TVF16</th>
<th>TVF16</th>
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Microprobe analyses (Muscovite and phlogopite) were performed at the University of Nancy 1, Service Commun d’Analyses, Analytical conditions: accelerating voltage, 15 kV, sample current 6–8 nA, silicate crystals as standards, and ZAF correction procedure. Chemical analysis of emerald is from CRFG, wet chemical analysis using 500 mg of sample.

* Phlogopite outside emerald.
* Phlogopite inside emerald.
### Table 2

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<th>Atmospheric Contamination (%)</th>
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<th>(^{40}\text{Ar}^{*}/^{39}\text{Ar}_{\text{K}})</th>
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<th>Error (±1σ)</th>
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**Integrated age = 1934.9 ± 1.3**

### Single grain laser analysis Sample BaF12-II-1 Analysis M303

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**Integrated age = 1921.1 ± 1.8**
**Table 2 (continued)**

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Integrated age = 1850.4 ± 2.7

**Bulk sample induction furnace analysis Sample Ba102a Analysis M267**

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<th>(^{39})Ar * / (^{39})Ar K</th>
<th>Apparent age (Ma)</th>
<th>Error (± 1σ)</th>
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Integrated age = 1975.0 ± 1.4

- The muscovite Ba102 contains 3.4% FeO and 3.4% MgO, placing it in the phlogite series. Phlogopite presents two distinct compositions: the crystals included within the TVFI 6 emerald or in the K-metasomatite enclosing rock display identical
compositions, having 18% annite (Fe + Mn/Fe + Mn + Mg ratio; Table 1), whereas the Ba FL2-II-1 K-metasomatite shows a higher annite content (36%, Table 1). This annite content difference reflects the host rock composition: the Braúlia K-metasomatite was developed from a pegmatite, whereas the Trecho Velho K-metasomatite derives from a serpentinite which originally had a lower Fe/Mg ratio [3], which buffers the metasomatic process forming biotites with a higher Mg content.

ICPAE spectrometry and chemical analysis of an emerald crystal from Trecho Velho (CATV) were investigated (Fig. 2). The laser-probe device and procedure of the University of Nice (France) are described elsewhere [12,13]. The samples were irradiated in the Osiris reactor (Saclay, France) with a total integrated flux of $10^{19}$ n/cm² and rotated during irradiation. The flux monitor was the hornblende MMhb-1 [23]. Analytical data are presented in Figs. 2 and 3 and Tables 2 and 3; age calculations are made using isotope correction procedures, recommended decay constants [25] and are given with 1σ standard error estimates. The error on the irradiation factor, $J$, is not included in the calculation of individual age errors in the step heating experiments. For the plateau age calculation, we included the error due to the flux, which is ±0.4% on each level of irradiation where the standard was analyzed. Owing to a higher contribution of this error bar relative to the other factors, we obtained a constant error bar of 8 Ma on the

<table>
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<th>Spot No.</th>
<th>Atmospheric contamination (x 10⁻⁹ cc STP)</th>
<th>³⁹Ar/³⁹ArK</th>
<th>Age (Ma)</th>
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plateau ages for all samples. Because of the flux gradient along the vertical axis of the irradiation can, and the large dimension of the rock slab, we estimate the error bars on laser spot ages at ± 0.8%. This explains the errors of ± 15–16 Ma on most of the laser spot ages (for which the error due to the flux gradient is dominant) and the same minimum error bars on the calculated means.

5. $^{36}\text{Ar}/^{39}\text{Ar}$ dating results

Step heating experiments: Bulk sample induction furnace analyses were performed on muscovite Ba 102 and K-metasomatite phlogopite BaFl2-II-1 samples. Single grains of K-metasomatite phlogopite BaFl2-II-1 and TVFl 6 were also analyzed through the laser step-heating procedure. The isotopic ratio and apparent ages are reported in Tables 2 and 3 and the corresponding age spectra in Fig. 3. All samples display remarkable flat age spectra, yielding plateau ages at 1976 ± 8 Ma for muscovite Ba 102 (bulk sample), 1951 ± 8 Ma for phlogopite TVFL 6 (single grain), 1942 ± 8 Ma (bulk sample) and 1926 ± 8 Ma (single grain) for phlogopite Ba Fl2-II-1 (Fig. 3). These plateau ages were calculated with more than 90% of the total $^{39}\text{Ar}$ released (except for bulk sample BaFl2-II-1: 81%) and are, in this

![Fig. 3. (a) $^{36}\text{Ar}/^{39}\text{Ar}$ spectra of the Braflia phlogopite. (b) Comparison of $^{36}\text{Ar}/^{39}\text{Ar}$ spectra of the Braflia (BaFl2-II-1) muscovite (Ba 102) and phlogopite (BaFl2-II-1) and the Trecho Velho (TVFl 6) phlogopite.](image-url)
way, within 0.5% of the integrated calculated ages (Table 2).

**Spot fusion experiments**: Spot fusion experiments were performed on phlogopite crystals from K-metasomatite enclosing rock, on phlogopite inclusions within the emerald crystals and on emerald. The age results and the location of the spots are presented in Fig. 2 and isotopic data in Table 3. For the Braúlia sample BaF12-II-1 (Fig. 2), a good concordance appears (spot 10 excepted) between the analyses performed on phlogopite inclusions and those on the K-metasomatite: the mean age for the largest inclusion (1 mm long; spots 7 and 8) is 1948 ± 16 Ma. One spot (no. 12) on a small inclusion (0.1 mm long) yields 1956 ± 16 Ma. The most precise age on a smaller solid inclusion (0.2 mm long; spot 10) gives a younger age of 1911 ± 15 Ma. The bulk sample age spectrum shows a regular increase in ages at low temperatures (Fig. 3), which appears more clearly than for single grains. This may be related to the higher degree of alteration in the bulk sample.

6. Discussion of ages

6.1 Phlogopite ages

For the phlogopite BaF12-II-1, a concordance within the error bars is found (Fig. 3) between the plateau ages displayed by the bulk sample and single grain (1942 ± 8 Ma and 1926 ± 8 Ma, respectively) of the metasomatite, the laser spot fusion ages obtained on the metasomatites (weighted mean age: 1956 ± 16 Ma; spots 2–6, 13 and 14), and the inclusion in the emerald (weighted mean age: 1949 ± 16 Ma; spots 7, 8 and 12), one small inclusion age excepted (spot 10: 1911 ± 15 Ma). No excess argon could be detected even on small phlogopite inclusions. The bulk sample age spectrum shows a regular increase in ages at low temperatures (Fig. 3), which appears more clearly than for single grains. This may be related to the higher degree of alteration in the bulk sample.

The step-heating experiments performed on one single grain of sample TVFI 6 displayed a plateau age of 1951 ± 8 Ma, which is not concordant with the previous results at the 1σ confidence level (Table 2). The laser spot ages on both the metasomatites and the phlogopite inclusions are more scattered (from 1923 ± 15 to 2517 ± 20 Ma). These variations seem to be correlated with variable 37ArCa/39ArK ratios (from 0.0 to 0.14) and atmospheric contamination. If we reject the two results (spots 2 and 6) affected by the highest atmospheric contaminations (37% and 4296, respectively), we observe a positive correlation between the ages obtained and the measured 37ArCa/39ArK ratios (Table 3). This may indicate that the higher ages are the results of a contamination of the phlogopite by emerald (the 37ArCa/39ArK ratio measured on pure emerald is 1.45; spot 11 of BaF12-II-1). This interpretation is supported by the fact that the laser beam was parallel to the cleavage planes of micas in the TVFI 6 slab and perpendicular in the case of BaF12-II-1. During the laser heating procedure of the spot fusion experiment, we could observe, in some cases, a large opening of the cleavage planes of the phlogopites, allowing a deeper penetration of the laser beam, which could warm up the host emerald or hidden inclusions. It should be noticed that Ca-bearing inclusions; that is, apatite and plagioclase, are common in the K-metasomatite paragenesis of the Carnaíba deposit [18], which may play the same contaminant role as emerald if they contain excess argon.
The ages obtained for both samples by step heating were more precise and clustered than the spot fusion analyses. This was due to: (1) a better knowledge of the flux gradient; and (2) a higher purity of the mineral phases analyzed in the separate minerals than in the slab plate. We therefore propose ages of 1934 ± 8 Ma (weighted mean of the two step heating experiments) and 1951 ± 8 Ma for the phlogopites BaFl2-II-1 and TVFl 6, respectively.

6.2 Muscovite age

The muscovite Ba 102 yields a plateau age of 1976 ± 8 Ma (Fig. 3), which is clearly older (even at the 2σ confidence level) than the plateau age obtained on the phlogopite BaFl2-II-1. In spite of a small difference in age (2%), this result is in apparent contradiction with field relationships; muscovite belongs to the quartz-molybdenite veins crosscutting the emerald-bearing K-metasomatites. This aspect is discussed in the following section.

7. Thermochronology of the Carnaiba pluton and related hydrothermal processes

The 40Ar/39Ar ages obtained on phlogopites from the two sites of Trecho Velho (1951 ± 8 Ma) and Braúlia (1934 ± 8 Ma) are concordant using a 2σ confidence level (± 16 Ma), whereas the muscovite Ba 102 displayed a plateau age at 1976 ± 8 Ma, which is clearly older than the ages obtained on the Braúlia phlogopites. Clear geological and geochemical evidence shows that granite emplacement, the formation of emerald contained in K-metasomatites, and later hydrothermal quartz-molybdenite vein development are nearly contemporaneous. This is shown by the fact that: (1) the quartz-molybdenite vein system presents the same bulk geochemical spectrum (Mo–W–Be) as the granite–metasomatite complex; (2) fluid inclusion study of emerald-bearing metasomatites yield homogenization temperatures of about 400°C, identical to the temperatures measured for the quartz–molybdenite veins [Giuliani, pers. commun., 1992].

Fig. 4. Total variation range of 40Ar/39Ar ages from the Braúlia and Trecho Velho emerald deposits considering "plateau" and "spot" ages.
If we consider as reliable the ages of 1976 ± 8, 1951 ± 8 (plateau ages) and 1934 ± 8 Ma (the means of the two plateau ages at 1942 and 1926 Ma) for the muscovite Ba 102, the phlogopite TVFI 6 and Ba F12-II-1, respectively (Fig. 4), we may tentatively explain the age differences as representing the successive closure of the K–Ar system of the minerals, rather than crystallisation order, during cooling of the whole granite–hydrothermal system, in spite of the low difference of the three ages (the maximum difference is 2%). The closure temperature possibly decreases from muscovite Ba 102, to phlogopite TVFI 6 (annite content 15%), then to phlogopite BaF12-II-1 (annite content 36%). The inverse correlation between the closure temperature of biotites and the annite content (related to the Fe/Mg ratio) has been proposed from hydrothermal experiments [26].

8. Conclusions

The dating of minerals bearing excess argon is possible using 40Ar/39Ar laser spot and step heating analyses of syngenetic phlogopite occurring as inclusions within emerald crystals and their K-metasomatic gangue. Minute phlogopite crystals included in beryls bearing excess argon do not show any excess argon. For two emerald deposits located at the contact of the Carnaiba leucogranite, Bahia State, Brazil, the results show phlogopite ages of 1951 ± 8 and 1934 ± 8 Ma, which are concordant at the 2σ confidence level.

The higher discrepancy of spot fusion data compared with step heating data may result from: (1) the deeper penetration of the laser beam when it is parallel to the cleavage plane of the micas, which may release argon from hidden extra mineral phases; and (2) flux gradients during irradiation, which is not easily monitored on relatively large (> 5 mm) polished slab samples.

The entire results, for both syngenetic phlogopites of emerald deposits and muscovite belonging to a quartz–molybdenite vein crosscutting the emeralds, are concordant with the fast cooling of the whole granite–hydrothermal system.

This work helps to establish the formation age of the Carnaiba granite-related emerald deposits as being within the Transamazonian (2 Ga) orogenesis.

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References

Emerald dating through $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating and laser spot analysis of syngenetic phlogopite

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