P, T, X conditions of crystallization of Imperial Topaz from Ouro Preto (Minas Gerais, Brazil): Fluid inclusions, oxygen isotope thermometry, and phase relations

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Abstract

The intense orange-yellow to cherry-red topaz found in quartz, hematite, dolomite, euclase veins in the area of Ouro Preto (Minas Gerais, Brazil) is known in trade as "Imperial Topaz". Only pink topaz from the Mardan District in Pakistan has similar gemmological properties and paragenesis. Fluid inclusion data, oxygen isotope geothermometry and considerations on the stability of kaolinite, pyrophyllite and carbonates found as inclusions in the Imperial Topaz from Ouro Preto indicate that topaz crystallized at about 360 °C and 3.5 kbar. A high CO_2 activity precluded fluorination of the carbonates and stabilized topaz relative to fluorite. Fluorine and beryllium, needed to form topaz and euclase, as well as CO_2 were presumably provided by metamorphic fluids produced by the Brasiliano tectonothermal event at about 600 Ma.

Keywords: Imperial Topaz, Brazil, microthermometry, oxygen isotope thermometry, metamorphism.

1. Introduction

The occurrence of intense orange-yellow to cherry-red topaz was reported from the Ouro Preto area, Minas Gerais (MG), Brazil as early as 1772 (SILVA and FERREIRA, 1987) and again in 1786 (ROLFF, 1971). In the gem trade, topaz from Ouro Preto is known as "Imperial Topaz" (GÜBELIN et al., 1986).

The colouring elements and mechanisms giving the Imperial Topaz from Ouro Preto its rather unique colour are still debated. According to PETROV et al. (1977) and SAUER et al. (1996), the colour is due to the presence of Cr^{3+}. GANDINI et al. (2000) identified by EPR (Electron Paramagnetic Resonance) the presence of Cr^{3+}, Mn^{3+}, Fe^{3+}, V^{4+} and Ti^{4+} as possible chromophoric elements. According to RAGER et al. (2001), however, the colour of Imperial Topaz is caused only by electron defect centres and not by the content of spe-cific transition metals as assumed by GANDINI et al. (2000) and SAUER et al. (1996).

Many articles have been written on topaz from Ouro Preto (e.g., SPIX and MARTIUS, 1831; ESCHWEGE, 1833; GORCEIX, 1881; DERBY, 1901; JOHNSON, 1962; OLSEN, 1971; ATKINSON, 1908, 1909; BASTOS, 1964, 1976; FLEISCHER, 1972; D'ELBOUX and FERREIRA, 1975, 1978; KELLER, 1983; CASSEDANNE and SAUER, 1987; CASSE-DANNE, 1989; SAUER et al., 1996; BELLO et al., 1994, 1995, 1996; FERREIRA, 1991; GANDINI et al., 1991, 1992a, b, c; GANDINI, 1994; SCHWARZ, 1997). Worldwide, only the pink topaz from Ghundao Hill, Mardan District in Pakistan has gemmological properties similar to those of Imperial Topaz from Ouro Preto (GÜBELIN et al., 1986).

At Ouro Preto Imperial Topaz occurs as mostly euhedral biterminated and undeformed crystals with a diameter of up to 4 cm and a length of 10 cm. Dolomite, hematite, rutile, quartz, kao-

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linite, pyrophyllite, chloritoid and tremolite are found as inclusions (FERREIRA, 1983, 1991; PIRES et al., 1983; GANDINI, 1994).

The formation of the Imperial Topaz has generated controversy. KELLER (1983), FERREIRA (1983) and BELLO et al. (1996) ascribe formation of topaz-bearing veins to fluids that emanated from Upper Cretaceous to Lower Tertiary acid magmatic rocks situated in Precambrian metasediments of the study area. However, in the study area no acid magmatic activity of such age is known. The only Cretaceous magmatism in the area is of basaltic composition and coeval with the volcanism that produced the plateau basalts of the Serra Geral Formation, i.e., the basalts of the Parana Basin (SCHORSCHER, pers. comm., 2001). OLSEN (1972) and PETROV et al. (1977) ascribe the formation of topaz to fluids of metamorphic origin and undefined age. According to PIRES et al. (1983), topaz crystallized during the peak of the

regional metamorphism, before the second deformation. The main regional metamorphism in the study area according to SCHOBBENHAUS et al. (1984), is of Transamazonic age, i.e., about 1900 Ma, but was overprinted by the Brasiliano tectonothermal event at about 600 Ma. No reliable P, T estimates of the topaz-forming event can be found in the literature. Fluid inclusion data presented in BELLO et al. (1994, 1995, 1996) give only approximate formation temperatures and pressures for topaz crystallization due to the lack of an independent temperature estimate.

In the area of Ouro Preto, Imperial Topaz continues to be mined by small to medium enterprises or individual miners (garimpeiros). Rapidly changing ownership often produces a fast change in mining activities and in the name of the mines.

The present paper reports estimates of the P, T conditions, and the composition and origin of the fluids during the topaz-forming event based on
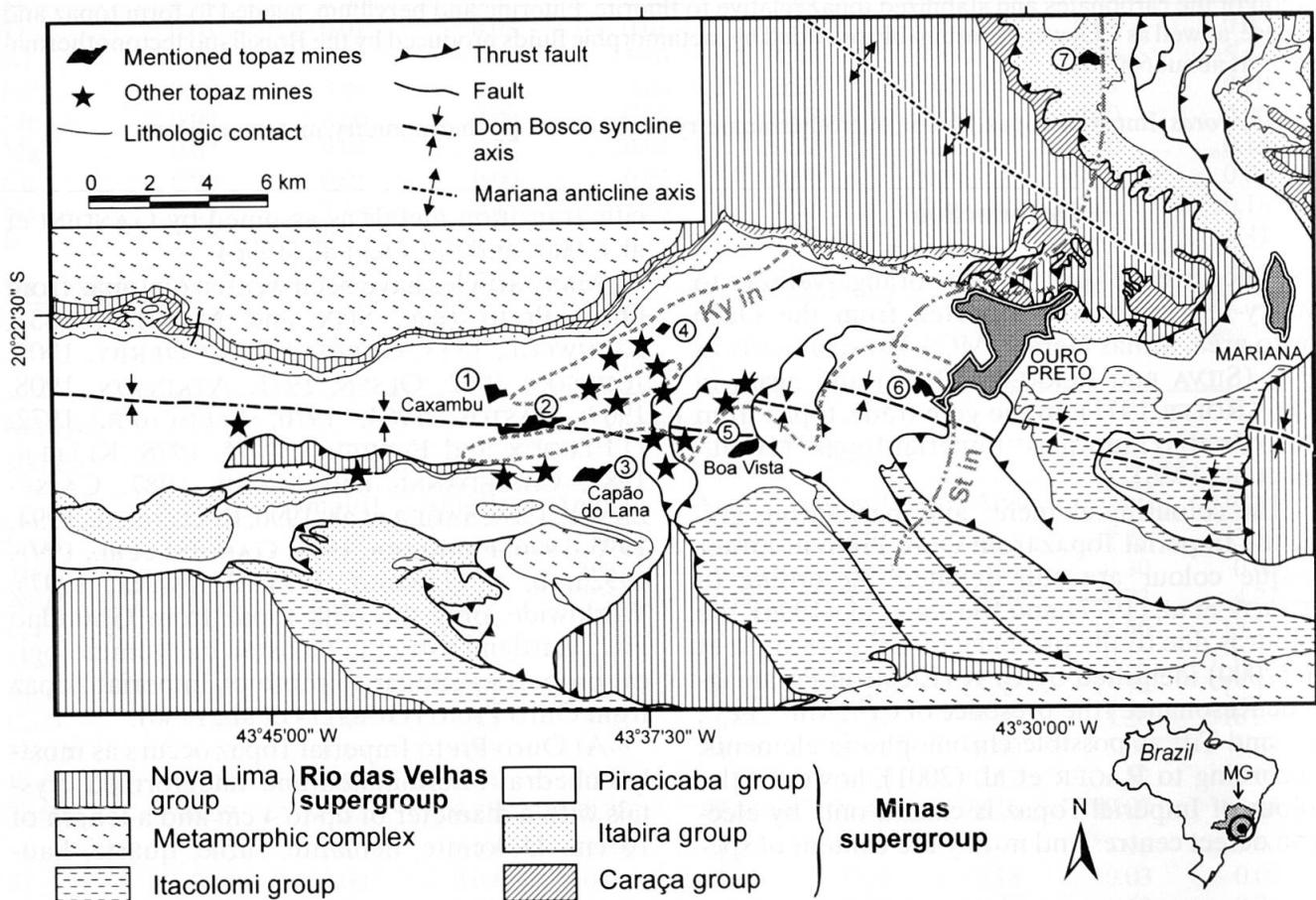
Fig. 1 Geological sketch map of the study area according to GANDINI (1994), modified from DORR II (1958) and NALINI JR. (1993), giving the location of the topaz mines. Kyanite(ky)-in and staurolite(st)-in isogrades are given according to PIRES (1989). Notice that all mines are found near the kyanite-in isograd, and outside the staurolite-in isograd. The mines are predominantly found in the rocks of the Piracicaba Group. Numbers refer to topaz mines mentioned in the text; GPS coordinates are given in brackets. 1 = Caxambu (20°24'36.8'' S, 43°40'1.0'' W), 2 = Dom Bosco (20°25'1.9'' S, 43°40'0.8'' W), 3 = Capão do Lana (20°25'48.3'' S, 43°38'26.2'' W), 4 = Bocaina (20°27'19.4'' S, 43°37'16.1'' W), 5 = Boa Vista (20°25'14.3'' S, 43°35'22.3'' W), 6 = Vermelhão (20°24'11.2'' S, 43°31'59.7'' W), 7 = Antônio Pereira (20°18'15.5'' S, 43°28'32.4'' W). Stars mark other known topaz mines.

existing and new fluid inclusion data, solid inclusions in topaz, oxygen isotope data of quartz and hematite coexisting with topaz, and phase relations in the country rocks.

2. Geology

A geological sketch map of the study area is given in Fig. 1 (GANDINI, 1994). The numbers refer to topaz mines mentioned in both text and figure captions. Stars mark other known topaz mines. The geographic coordinates of the sampled and/or mentioned topaz mines are given in Fig. 1. The major part of the topaz mineralisation is found in rocks of the Piracicaba group which forms the east–west trending Dom Bosco syncline (Fig. 1). The kyanite(ky)-in and staurolite(st)-in isogrades are given according to PIRES (1989). Most mines occur close to the "kyanite-in" isograd and well outside the "staurolite-in" isograd. The only topaz deposit found outside the Dom Bosco syncline is that of Antônio Pereira (No. 7 in Fig. 1), located in rocks of the Itabira group which form the Mariana anticline (FERREIRA, 1991; DORR II, 1958). The Itabira group consists of itabirite, i.e., banded iron formation (BIF), dolomitic itabirite and marble.

The Piracicaba group belongs, together with the Itabira and the Caraça groups, to the Minas supergroup (FERREIRA, 1991). Rocks of the Piracicaba group are metaquartzites, phyllites, metagreywackes (DORR II, 1958, 1969), and carbonate-bearing phyllites as well as dolomitic marbles (FERREIRA, 1991). Topaz-bearing veins are highly discontinuous, strike NW–SE and show a subvertical dip. In addition to topaz, the veins may contain kaolinite, quartz, mica, hematite, and rarely euclase ($BeAlSiO_4(OH)$). The topaz-bearing veins of Ouro Preto are the type locality of euclase (GAINES et al., 1997). In most cases the country rocks of the topaz-bearing veins are strongly altered due to tropical weathering and consist of a brownish clay-like material which is called "*borra de café*" (coffee grounds) by the miners. Due to this very strong alteration, reliable information about the primary country rock is lost. Occasionally, topaz occurs in quartz-hematite veins cutting dolomitic marbles of the Piracicaba group, for example at the Bocaina mine (PIRES et al., 1983, GANDINI, 1994; see Fig. 1). GANDINI (1994) reports inclusions of euhedral dolomite not only in Imperial Topaz from the Bocaina deposit, but also in that from Antônio Pereira, Vermelhão and Capão do Lana deposits (Fig. 2).

The pink topaz from Ghundao Hill (Pakistan), the only topaz similar to the Imperial Topaz of Ouro Preto, also occurs in veins cutting recrystalized limestone (GÜBELIN et al., 1986).

3. Methods

Routine microthermometric examinations have been carried out with a CHAIXMECA MTM-85
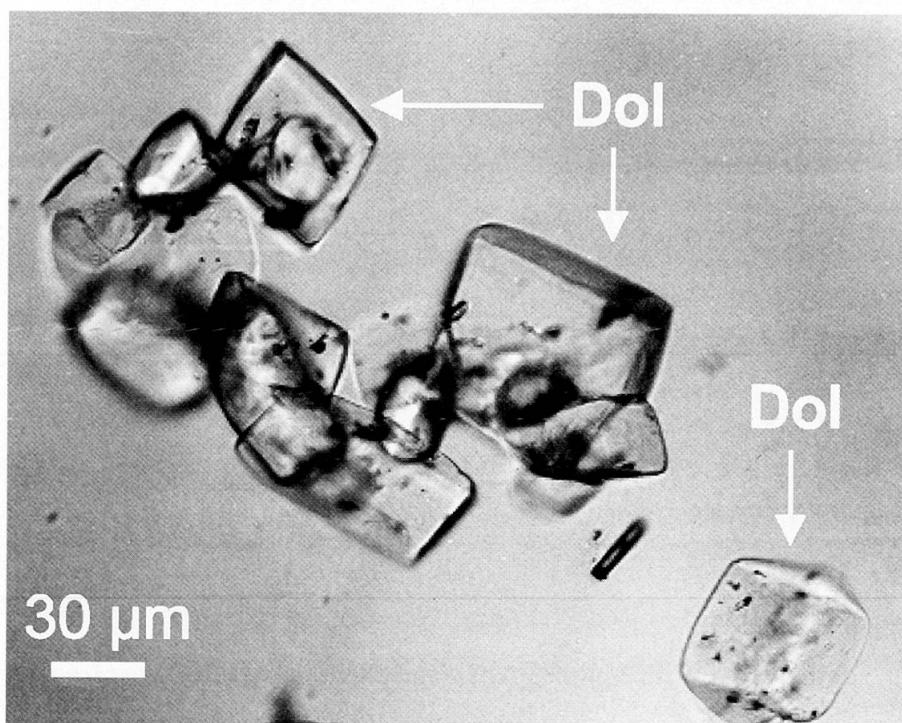

Fig. 2   Euhedral dolomite crystals included in topaz from the Antônio Pereira deposit.

heating-freezing stage (POTY et al., 1976), and Leitz 10× and 50× objectives on double-polished, 0.5-1.0 mm thick plates cut parallel to the *c* axis of the topaz crystals. Microthermometry was carried out in the fluid inclusions laboratory at the Instituto de Geociências, Universidade de São Paulo.

As indicated in the handbook of CHAIXME-CA, fluid inclusions in quartz from Calanda (Switzerland), Merck Signotherm® for low temperature and Merck MSP® products for high temperature ranges were used for the calibration of the CHAIXMECA stage. For isochore calculations, the FLINCOR software (BROWN, 1989) was

used which is based on BOWERS and HELGESON (1983, 1985) equations for the system H_2O–CO_2–NaCl.

For the oxygen isotope analysis, oxygen was extracted from quartz and magnetite at the IM-GRE (**I**nstitute of **M**ineralogy, **G**eochemistry and Crystal Chemistry of **R**are **E**lements, Moscow) by reaction with BrF_5 and converted to CO_2 over hot graphite according to CLAYTON and MAYEDA (1963). The isotope composition was measured on a Finnigan MAT 251 mass spectrometer and is reported as δ values relative to V-SMOW in per mil (‰). Analytical reproducibility was within 0.2%.
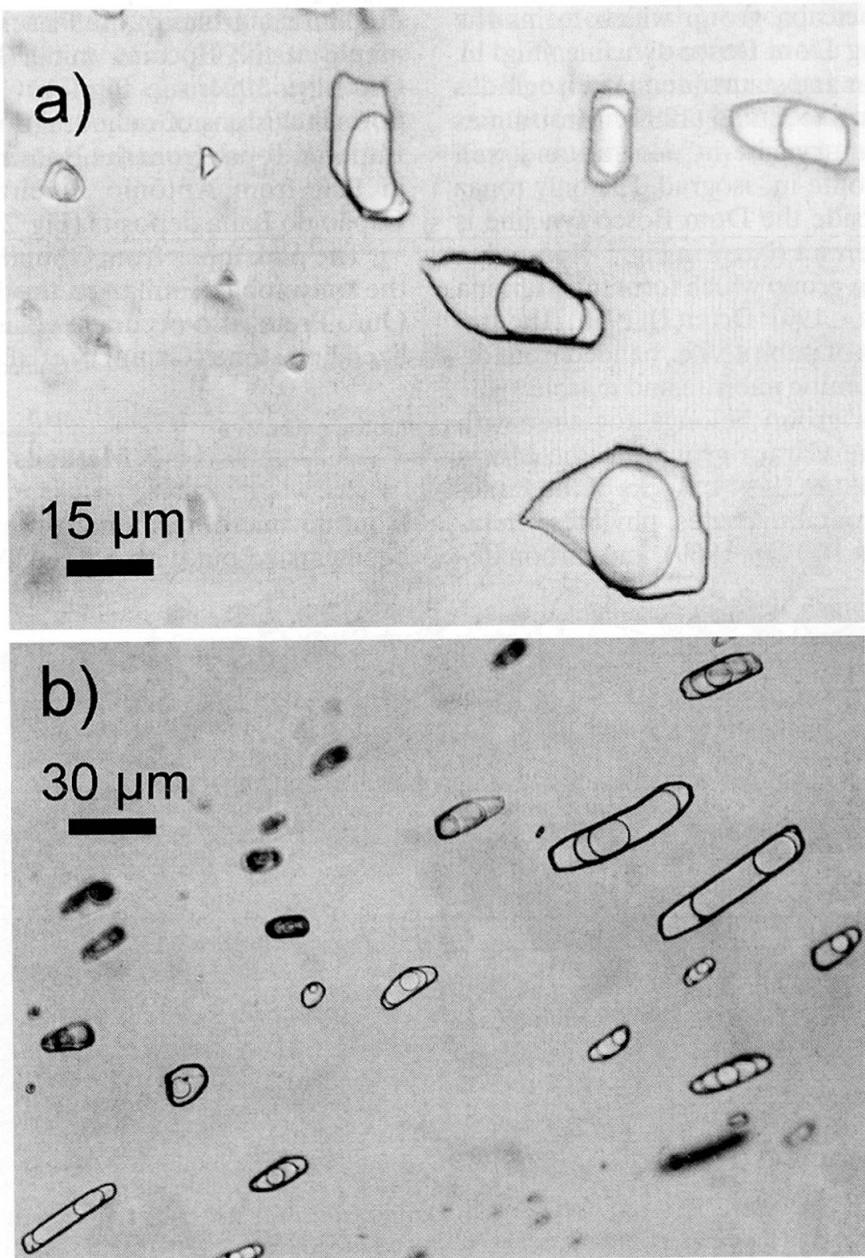
Fig. 3 Microphotograph showing typical 2-phase (a) fluid inclusions in Imperial Topaz from the deposit of Capão do Lana, and 3-phase (b) fluid inclusions in Imperial Topaz from the Dom Bosco deposit. Different gas/liquid ratios in the fluid inclusions suggest trapping below the solvus in the system H_2O/CO_2-NaCl. Due to very low CO_2 contents, no liquid CO_2 phase can be seen at room temperature in the inclusions of Capão do Lana.

4. Results

4.1. OXYGEN ISOTOPE THERMOMETRY

The oxygen isotope composition was determined on quartz and hematite intergrown with topaz from the Capão do Lana deposit. From the intimate intergrowth, an equilibrium among the three mineral phases can be assumed. The oxygen isotope composition of quartz was $\delta^{18}O = +15.6 \pm 0.3$ ‰, that of hematite was $\delta^{18}O = +1.8 \pm 0.04$ ‰. From these data and the equation given by ZHENG and SIMON (1991), an equilibrium isotope temperature of 360 ± 7 °C was calculated.

4.2. FLUID INCLUSIONS

4.2.1. Microscopy

The abundant fluid inclusions (FI) in Imperial Topaz crystals all consist of two or three phases at room temperature (25 °C) but show differences in gas/liquid ratio, morphology, dimension and orientation (Fig. 3a, b). The inclusions can have the shape of negative crystals or an irregular form (for more details see GANDINI et al., 1991).

The size of fluid inclusions varies between 4 µm and 460 µm. For the microthermometry, only inclusions with a diameter between 10 to 50 µm have been considered. Trails of fluid inclusions parallel to the c axis or to the basal pinacoidal cleavage, and also to the prisms {0kl} and {h0l}, and to the dipyramid {111} of the topaz crystals were commonly observed. In the following, only fluid inclusions which show an orientation parallel to the crystallographic elements of the host topaz are considered as primary. Fluid inclusions that are aligned along healed intragranular fractures without any relation to the crystallography of the host crystal have to be considered as pseudosecondary and are not taken into consideration (ROEDDER, 1984). Randomly distributed fluid inclusions have also been observed in the crystal.

4.2.2. Microthermometry

For the present study, microthermometric data have been obtained for 280 primary fluid inclusions from five different topaz crystals from the Boa Vista mine, 600 inclusions found in sixteen samples from Capão do Lana mine, and for 360 fluid inclusions from ten topaz crystals from the Caxambu mine. We also made use of fluid inclusion data from GANDINI et al. (1992b) and BELLO et al. (1995, 1996). The volume ratio CO_2/H_2O was estimated by comparison with charts given by SHEPHERD et al. (1985), and the associated error is approximately 10%. The following observations have been made:

1) All primary fluid inclusions in individual crystals produce similar microthermometric data regardless of their shape, dimension and orientation. According to GANDINI (1994), this is also true for the pseudosecondary fluid inclusions.

2) According to the respective temperature of CO_2 homogenization (Th CO_2 L-V), the CO_2/H_2O volume ratio and the consequent bulk CO_2 density of fluid inclusions, the different topaz crystals of the Boa Vista (BV) deposit can be divided into the types BV1, BV2 and BV3, that of Capão do Lana (CL) into the types CL1, CL2 and CL3, and that of the Caxambu (CX) into the types CX1 and CX2 (Table 1). Within each type of fluid inclusions, only slight variations in CO_2/H_2O ratio and sometimes also in total homogenisation (Th CO_2-H_2O) can be found. Total homogenisation may occur into the H_2O phase, the CO_2 phase, and rarely also near to the critical state. The following observations can be made:

3) Microthermometric data, IR and Raman spectroscopy of fluid inclusions suggest that they belong to the H_2O–NaCl–$CO_2\pm(CH_4$–$N_2)$ system. Melting of solid CO_2 (Tm CO_2) mostly occurs below the triple point temperature of pure CO_2 (–56.6 °C). This suggests the presence of other components such as N_2 and H_2S in the CO_2 phase (HEDENQUIST and HENLEY, 1985).

4) For fluid inclusions in topaz from the Caxambu and Capão do Lana deposits, salinity has been calculated from the melting temperature of the clathrate (Tm clath). In samples of type BV1 and BV2 homogenisation of CO_2 did always occur below the melting temperature of the clathrate (Tm clath). Therefore, salinity had to be determined in these samples by using the diagrams of DIAMOND (1992). For samples of type BV3, salinity had to be determined from the melting of ice (Tm ice) because the low CO_2 contents of the fluid inclusions did not allow formation of clathrate (HEDENQUIST and HENLEY, 1985). In all deposits the salinity increases with increasing H_2O content.

5) The total homogenisation temperature Th CO_2-H_2O for the fluid inclusions of type BV1, BV2, BV3, CX1, CX2, CL1, CL2 and CL3 range from 230 to 320 °C (Table 1). Total homogenisation can take place into CO_2 or H_2O, or rarely close to the critical state; the result obviously depends on the amount of CO_2 (Table 1).

Table 1 Microthermometric data of fluid inclusions in topaz from the Boa Vista, Capão do Lana, and Caxambu deposits. For additional data see also GANDINI et al. (1992b) and BELLO et al. (1995, 1996).

Sample Group	Tm CO_2 [°C]	Th CO_2 L-V [°C]	CO_2 [vol.%]	Tm clath. [°C]	Tm ice [°C]	Th CO_2-H_2O [°C]	dCO_2 [g/cm³]	d [g/cm³]	salinities [wt.% NaCl equiv.]	P [kbar]
Boa Vista (BV) Deposit										
BV1	-57.4/-56.8	-5.2/-3.6 (L)	70/90	5 - 9	-	230/280 (CO_2)	0.95	0.96/0.98	4.2/10.3	1.8/2.9
BV2	-57.8/-57.0	-2.8/-1.2 (L)	50/80	6 - 9	-	240/300 (CO_2)	0.94	0.96/0.99	3.8/8.8	1.8/3.0
BV3	-57.4/-57.0	26.8/28.4 (L)	20	-	-10/-8	300/320 (H_2O)	0.66	1.00	11.6/14.0	2.2/2.6
Capão do Lana (CL) Deposit										
CL1	-58.2/-56.6	8.0/11.2 (L)	35/60	5 - 9	-	290/310 (CO_2,cr)	0.85/0.87	0.93/0.99	2.4/9.1	2.1/2.8
CL2	-57.2/-56.6	10.4/14.4 (L)	30/50	6 - 8	-	290/300 (H_2O,CO_2,cr)	0.93/0.86	0.94/0.98	4.0/7.5	2.4/2.7
CL3	-57.8/-56.6	20.8/23.2 (L)	10/30	4 - 7	-	280/300 (H_2O)	0.74/0.77	0.96/1.04	5.8/10.6	2.0/3.4
Caxambu (CX) Deposit										
CX1	-57.0/-57.6	14.4/16.8 (L)	30/40	2 - 7	-	300/310 (CO_2,H_2O)	0.81/0.82	0.95/1.01	5.8/13.3	2.4/2.7
CX2	-56.6/-58.4	18.4/22.4 (L)	20/30	1 - 7	-	270/310 (H_2O)	0.75/0.79	0.96/1.03	5.8/14.4	1.9/2.6

(L) homogenisation to liquid; (CO_2) homogenisation to carbonic phase; (H_2O) homogenisation to aqueous phase; (cr) homogenisation to critical state; (d) bulk fluid density.

5. Discussion

RAMBOZ et al. (1982), ROEDDER (1984) and BODNAR et al. (1985) showed that a homogeneous CO_2-bearing saline aqueous solution can separate into a salt-rich aqueous fluid and a CO_2-rich fluid. Trapping of the immiscible phases will produce two different types of fluid inclusions with the same homogenisation temperature, but with different homogenisation behavior. CO_2-rich inclusions will homogenise into the CO_2 phase, whereas H_2O+NaCl-rich inclusions homogenise into the aqueous phase. Trapping of two coexisting immiscible fluids is shown as fluid inclusions with different, but constant, H_2O/CO_2 ratios (BODNAR et al., 1985; ROEDDER, 1984). As summarised above, fluid inclusions in Imperial Topaz of the deposits studied show slightly different H_2O/CO_2 ratios and may homogenise into the CO_2 phase, the H_2O phase or at a temperature close to the critical state of the H_2O/CO_2 system.

Using the above-mentioned criteria given by RAMBOZ et al. (1982) and ROEDDER (1984), the coexistence in the studied topaz of fluid inclusions with different H_2O/CO_2 volume ratios and similar homogenisation temperatures, but different homogenisation behavior, indicate trapping of fluid inclusions on the solvus of the H_2O–NaCl–CO_2 system. Occasional trapping near the top of the

solvus did also occur, as shown by fluid inclusions with intermediate H_2O/CO_2 volume proportions and homogenisation near the critical point (Table 1). If immiscibility is assumed, then the lowest Th CO_2–H_2O values measured on coeval inclusions would give an estimate for the trapping temperature, because these inclusions can be considered representative of the end-member fluid composition trapped on the solvus (ROEDDER, 1984).

Fluid inclusions from different types of topaz crystals from different, but also from the same deposit display distinct salinities and CO_2 content (see Table 1). This probably indicates a variation in fluid evolution due to interaction between the mineralising solution and the host rock. For type CL1, CL2 and CL3 topaz crystals, the trapping pressure is estimated in a P,T diagram by combining isochores with Th CO_2–H_2O temperatures (Fig. 4 a, c, e). The given isochores have been calculated with the FLINCOR® program package (BROWN, 1989) that uses the equations of BOWERS and HELGESON (1983, 1985). Frequency diagrams for Th CO_2–H_2O of fluid inclusions in the respective types of topaz crystals are also given (Fig. 4 b, d, f).

Fluid inclusions of all 3 types of topaz show a rather similar CO_2/H_2O ratio so that the isochores define in all cases a rather narrow field. A combination of Th CO_2–H_2O and isochores gives for trapping of fluid inclusions in the topaz of the
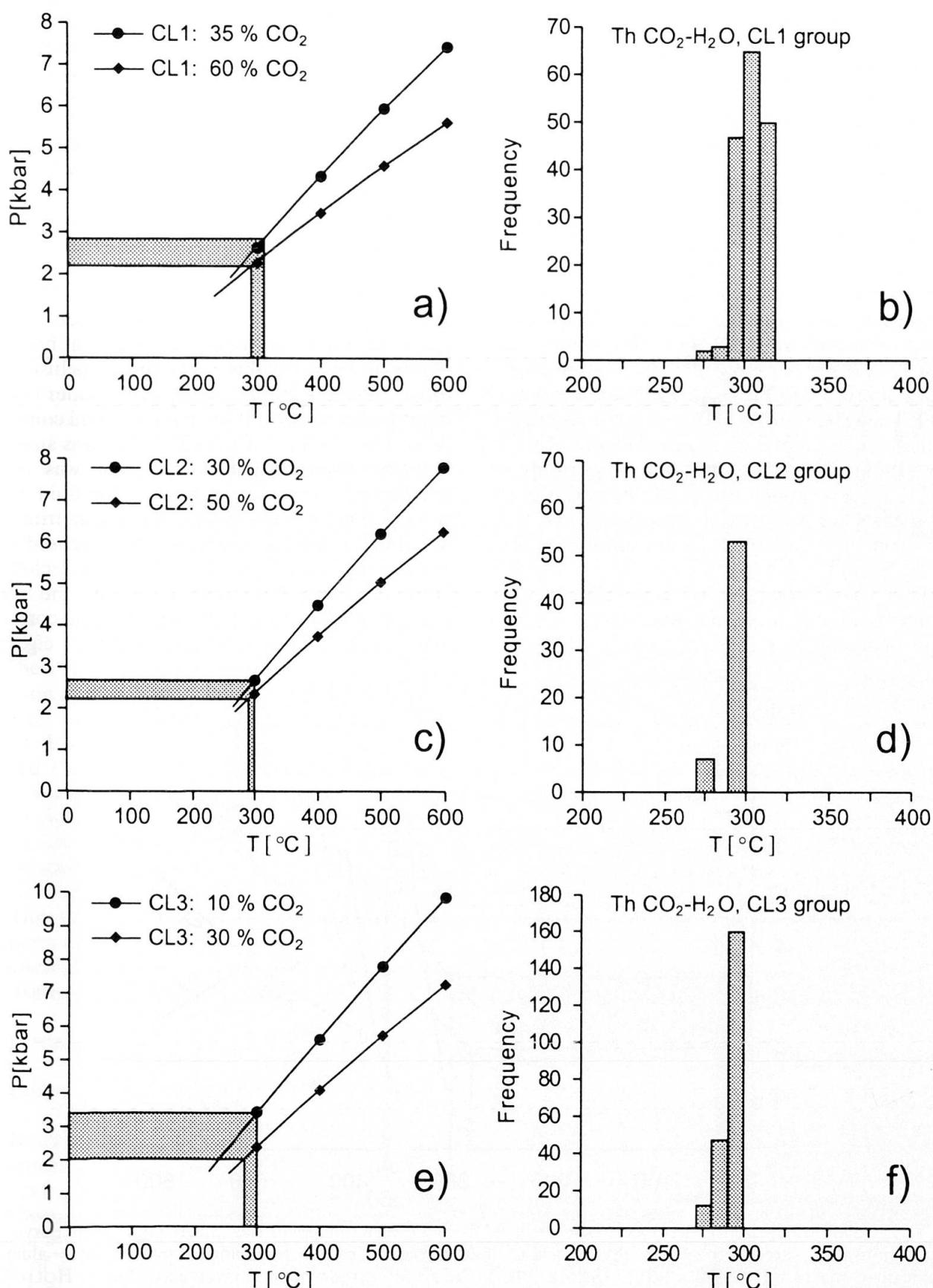
Fig. 4 (a, c, e): Isochores for fluid inclusions of topaz crystals of type CL1, CL2 and CL3, respectively. The isochores have been calculated with the FLINCOR® program package (BROWN, 1989) according to the equations of BOWERS and HELGESON (1983, 1985). The respective Th CO_2–H_2O temperatures are given in frequency diagrams (b, d, f).

Capão do Lana deposit a pressure between 2.0 and 3.4 kbar (Fig. 4). Considering all three deposits studied, the pressure range is 1.8 to 3.4 kbar (Table 1). This rather large range in the P, T estimates can be due to a real variation in P, T conditions during crystallization of different topaz crystals in the same and in different deposits, or can be due to an uncertain determination of trapping temperature.

THOMAS (1982, and pers. comm.) mentions fluid inclusion homogenisation temperatures in Imperial Topaz of 270 ± 11 °C and 272 ± 7 °C (n = 21). Most of the fluid inclusions decrepitate at only a slightly higher temperature of 274 ± 12 °C.

Stability data for the reactions kaolinite + quartz = pyrophyllite + H_2O (THOMPSON and TRACY, 1979) and pyrophyllite = aluminiumsilicate + quartz + H_2O (SPEAR, 1993) are displayed in a P, T diagram for $P_{tot} = P_{H_2O}$ (Fig. 5), where the Al_2SiO_5 triple point is given according to HOLDAWAY (1971). The oxygen isotope temperature of 360 °C, as determined for quartz-hematite pairs, and the isochores of fluid inclusions of topaz type CL3 from the Capão do Lana deposit are also shown. From Fig. 5 it follows that the inferred P, T range of 3.5 to 5 kbar and 360 °C is well within the stability field of pyrophyllite. Kaolinite is stable at lower temperatures in respect to pyrophyllite.

Both minerals are present as solid inclusions in topaz (PIRES et al., 1983; FERREIRA, 1983, 1991). The fact that topaz is found in veins surrounded by a halo of strongly altered rocks leads to the conclusion that the country rocks, at least in the surroundings of the veins, were infiltrated by fluids. Isothermal infiltration metamorphism with changing fluid composition may lead to the same sequence of reactions as changing P or T conditions (SPEAR, 1993). An increase in the CO_2 content of the fluids would decrease the stability fields of pyrophyllite and kaolinite (Fig. 5). However, CO_2 contents between 10 and 30 vol% CO_2 would not take pyrophyllite out of the P, T range defined by the isochores and the oxygen isotope thermometry. Nevertheless, the fact that both kaolinite and pyrophyllite are found as inclusions in topaz indicates that topaz did grow under changing P, T conditions and/or changing fluid compositions. The absence of kyanite inclusions suggests that the stability field of kyanite was never reached. The variation in X_{CO_2} of the fluid inclusions points to a crystallization of topaz from fluids of metamorphic origin, where increased CO_2 contents could have been produced by decarbonation reactions. Water-rich fluids, on the other hand, as well as fluids with high fluorine contents may result from dehydration reactions, e.g., the
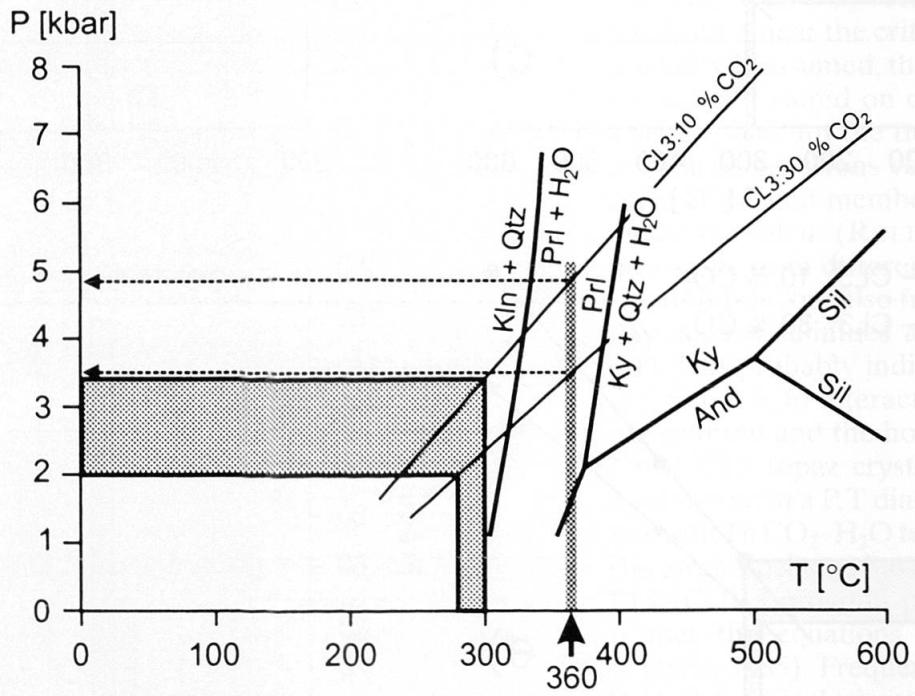

Fig. 5   P, T diagram displaying the isochores as deduced from our own fluid inclusion data, the univariant curves for the reactions kaolinite + quartz = pyrophyllite + H_2O (THOMPSON and TRACY, 1979) and for pyrophyllite = aluminiumsilicate + quartz + H_2O ($P_{H_2O} = P_{tot}$) (SPEAR, 1993). The Al_2SiO_5 triple point is given according to HOLDAWAY (1971). The oxygen isotope temperature of 360 °C was deduced from quartz/hematite pairs. The shaded area shows the inclusion trapping conditions. The dashed arrows give the pressure range defined by the oxygen isotope temperature and the CL3 isochores. Abbreviations: Kln = kaolinite, Qtz = quartz, Prl = pyrophyllite, Ky = kyanite, And = andalusite, Sil = sillimanite.

breakdown of F-rich, OH-bearing phyllosilicates during prograde metamorphism. A metamorphic origin of the fluids is also supported by the absence of peraluminous magmatic rocks as typical sources of F-rich fluids in the study area.

Topaz is a solid solution between the end member fluortopaz (FT), $Al_2SiO_4F_2$, and a hypothetical hydroxyl-topaz (OHT), $Al_2SiO_4(OH)_2$. The F/OH exchange may be described by

$$Al_2SiO_4F_2 + XH_2O = Al_2SiO_4F_{2-X}(OH)_X + XHF \quad (1)$$

The composition of natural topaz ranges from nearly pure FT in rhyolites to a composition relatively rich in OHT, up to $Al_2SiO_4F_{1.4}OH_{0.6}$ (BARTON, 1982). According to BARTON (1982), topaz from Ouro Preto contains about 25 mol% of OHT. For Imperial Topaz, THOMAS (1982) reports an F content of 16.05 ± 0.22 wt% based on X-ray diffraction data according to ROSENBERG (1967) and RIBBE and ROSENBERG (1971) ($\Delta_{021} = 3.909 \pm 0.006$, n = 23), and from $2V = 52.16 \pm 0.91°$ a fluorine content of 16.4 ± 0.2 wt% according to RIBBE and ROSENBERG (1971) and of 15.43 ± 0.24 wt% according to KONNO and AKIZUKI (1982). The high OHT component as determined by the different methods classifies Imperial Topaz from Ouro Preto as product of a low-temperature hydrothermal event, because the OH content of topaz coexisting with other aluminous phases increases with decreasing temperature (BARTON, 1982). Low-temperature formation is also supported by the optically anomalous behavior of most topaz crystals from Ouro Preto (BARTON, 1982). Similarly low F contents are reported from topaz of the Brewer mine, South Carolina (ROSENBERG, 1967), and from alpine veins (SOOM et al., 1988).

The presence of pyrophyllite and kaolinite suggests that the following reactions can be used to schematically describe the low-temperature topaz formation and the compositional buffering:

$$pyrophyllite + HF = topaz + quartz + H_2O \quad (2)$$

$$kaolinite + HF = topaz + quartz + H_2O \quad (3)$$
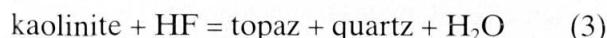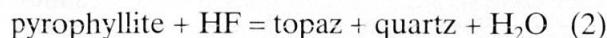
BURT (1975, 1981) and BARTON (1982) drew attention to the fact that the reaction which involves topaz may include Be minerals, because an increasing fluorine activity leads to decomposition of aluminous Be minerals to topaz. The presence of euclase, $BeAlSiO_4(OH)$, in paragenesis with topaz at Ouro Preto suggests formation of topaz and euclase by a reaction like:

$$beryl + HF = topaz + euclase + H_2O \quad (4)$$
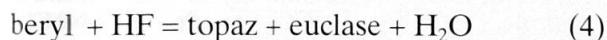
where "beryl" may also represent a Be- (and F-) rich fluid phase of metamorphic origin. Fluorine as well as small amounts of beryllium, required for the formation of topaz and euclase, may have been accommodated by the phyllosilicates in different, mostly sedimentary, protoliths of the Piracicaba group. If fluid circulation is focussed into veins, as is the case in the study area, the breakdown of these minerals in a prograde metamorphism will liberate enough F and Be (and H_2O) to produce a topaz mineralisation, as well as few euclase crystals as described by PIRES (1989). An example of Be liberation from phyllosilicates in a regional metamorphic event and associated crystallization of beryl (emerald) and phenakite is given by GRUNDMANN and MORTEANI (1989). Crystallization of topaz in the prograde stage of metamorphism is likely, judging from the fact that topaz deposits are found also in areas where kyanite is a stable phase in the country rock (Fig. 1), whereas no kyanite but only kaolinite and pyrophyllite are found as inclusions in topaz.

According to BARTON (1982), the presence of topaz is generally bound to rocks with low calcium contents or to rocks where Ca is restricted to fluorite. In this context, the general absence of fluorite in the topaz deposits of the Ouro Preto area is noteworthy. In spite of very strong weathering, which precludes determination of the whole-rock chemical composition, it seems very likely that the host rocks of some quartz–hematite–topaz veins did not contain appreciable amounts of Ca (e.g., as calcite, dolomite, or calcic plagioclase). In Ca-rich rocks, fluorite is typically produced by fluorination reactions that prevent formation of topaz. Such low Ca contents in the host rocks may explain why the topaz mineralisation is found just in one, rather thin, lithological horizon.

The presence of carbonate inclusions in topaz from this mineralisation without any fluorite but with carbonate gangue or in carbonate rocks, as described by FERREIRA (1983) and GANDINI (1994), can be explained by a high CO_2 activity in the metamorphic fluids that shifted equilibrium from fluorite towards topaz. The Al-activity in the fluids was fixed (buffered) by the presence of Al-silicate (such as kaolinite and pyrophyllite). Direct evidence for CO_2-rich fluids is given by the fluid inclusions. CO_2-rich fluids are typically produced by prograde metamorphism of carbonate-bearing metasediments. CO_2-rich fluids are rarely produced by felsic magmas, such as those considered by BURT (1981) and BARTON (1982) and, in the present case, by KELLER (1982), FERREIRA (1982) and BELLO et al. (1996). In this genetic con-

text, and not only for the unusual range of colour, the Imperial Topaz occurrences around Ouro Preto seem to be rather unique.

6. Conclusion

This fluid inclusion study, combined with oxygen isotope geothermometry and considerations on the sequence of tectonothermal events and stability of mineral inclusions in Imperial Topaz point to a crystallization of topaz at a pressure between 3.5 and 5 kbar and temperature of 360 ± 7 °C from CO_2- and F-rich fluids of metamorphic origin during the Brasiliano tectonothermal event at about 600 Ma. The lower pressure estimate of 3.5 kbar corresponds to the upper one determined by fluid inclusion data. The rather high pressure estimated for the crystallization of Imperial Topaz is consistent with the experimental data of BALLER et al. (1990), WUNDER et al. (1993, 1999), and WIRTH and WUNDER (2000), who suggested a high-pressure crystallization of OH-topaz.

The F needed for the formation of topaz, and the Be required for the crystallization of euclase, may have been liberated (together with quartz and hematite) by metamorphic breakdown of F- and Be-bearing phyllosilicates in the metapelitic protolith of the host rocks during the Brasiliano tectonothermal event. Low Ca contents in a specific horizon of the country rocks may explain why the veins are topaz-bearing only in a rather thin horizon of the country rocks. The much rarer occurrence at Ouro Preto of topaz mineralisation in dolomitic marbles without any fluorite may indicate a high Al activity or a high CO_2 activity, or both, in the topaz-bearing fluids preventing the formation through fluorination reactions of fluorite instead of topaz.

References

ATKINSON, A.S. (1908): Report on topaz in Brazil. Minerals Yearbook, U.S. Bureau of Mines, 842 pp.
ATKINSON, A.S. (1909): Mining for gems in Brazil. Engineering and Mining J. 19, 1234–1235.

BALLER, T., FOCKENBERG, T., ROSS, C., RUBIE, D.C., SCHREYER, W., SEIFERT, F. and WUNDER, B. (1990): Hydroxyl-Topas, eine neue Hochdruckphase im System Al_2O_3-SiO_2-H_2O (ASH). Ber. Deutsch. Mineral. Ges., Bh. Eur. J. Mineral. 2, p. 10.
BARTON, M.D. (1982): The thermodynamic properties of topaz solid solutions and some petrologic applications. Am. Mineral. 67, 956–974.
BASTOS, F.M. (1964): The topaz mines of Ouro Preto. Lapidary J. 18, 918–920.
BASTOS, F.M. (1976): Imperial Topaz from Brazil. Lapidary J. 30, 1836–1840.
BELLO, R.M.S., SVISERO, D.P., GANDINI, A.L. and FUZIKAWA, K. (1994): Estudo microtermométrico de inclusões fluidas do topázio imperial da jazida de Boa Vista, Ouro Preto, MG. 38° Congr. Bras. Geol., Balneário Camboriú, SC, 1, 636–637.
BELLO, R.M.S., GANDINI, A.L., FUZIKAWA, K. and SVISERO, D.P. (1995): Estudo microtermométrico de inclusões fluidas do topázio imperial da jazida de Boa Vista, Ouro Preto, MG. Rev. Escola de Minas 49, 2, 111–116.
BELLO, R.M.S., FUZIKAWA, K., GANDINI, A.L., VALARELLI, J.V. and SVISERO, D.P. (1996): Fluid inclusion microthermometry of Imperial Topaz from Capão do Lana deposit, Ouro Preto, Minas Gerais State, Brazil. An. Acad. Bras. Ci. 68, 1, 91–102.
BODNAR, R.J., REYNOLDS, T.J. and KUEHN, C.A. (1985): Fluid-inclusion systematics in epithermal systems. In: BERGER, B.R. and BETHKE, P.M. (eds): Geology and Geochemistry of Epithermal Systems. Society of Economic Geologists, Rev. Econ. Geol. 2, 73–97.
BOWERS, T.S. and HELGESON, H.C. (1983): Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2-NaCl on phase relations in geologic systems: Equation of state for H_2O-CO_2-NaCl fluids at high pressures and temperatures. Geochim. Cosmochim. Acta 47, 1247–1275.
BOWERS, T.S. and HELGESON, H.C. (1985): FORTRAN programs for generating fluid inclusion isochores and fugacity coefficients for the system H_2O-CO_2-NaCl at high pressures and temperatures. Computers Geosci. 11, 203–213.
BROWN, P.E. (1989): FLINCOR: A microcomputer program for the reduction and investigation of fluid inclusion data. Am. Mineral. 74, 1390–1393.
BURT, D.M. (1975): Beryllium mineral stabilities in CaO-BeO-SiO_2-P_2O_5-F_2O_{-1} and the breakdown of beryl. Econ. Geol. 70, 1279–1292.
BURT, D.M. (1981): Acidity-salinity diagrams – application to greisen and porphyry deposits. Econ. Geol. 76, 832–843.
CASSEDANNE, J.P. (1989): Famous mineral localities: The Ouro Preto topaz mines. Mineral. Rec. 20, 221–233.
CASSEDANNE, J.P. and SAUER, D.A. (1987): La topaze impériale. Rev. de Gemmologie 91, 2–9.
CLAYTON, R. and MAYEDA, T.K. (1963): The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotope analysis. Geochim. Cosmochim. Acta 27, 43–52.
D'ELBOUX, C.V. and FERREIRA, C.M. (1975): Topazio na região de Ouro Preto. Boletim do Departamento de Geologia, UFOP, Publicação especial 1, 73–79.
D'ELBOUX, C.V. and FERREIRA C.M. (1978): Topázio na região de Ouro Preto. Soc. Intercambio Cultural e Estudos Geol., Semanas de Estudos 14/15, 14–52.
DERBY, O.A. (1901): On the mode of occurrence of topaz near Ouro Preto, Brazil. Am. J. Sci. 11, 25–34.
DIAMOND, L.W. (1992): Stability of CO_2 clathrate hydrate + CO_2 liquid + CO_2 vapour + KCl-NaCl solu-

tions: experimental determination and application to salinity estimates of fluid inclusions. Geochim. Cosmochim. Acta 56, 273–280.

DORR II, J.V.N. (1958): Symposium on the stratigraphy of the Minas Series in the Quadrilátero Ferrífero, Minas Gerais, Brazil. Boletim da Sociedade Brasileira de Geologia 7, 2, 57–69.

DORR II, J.V.N. (1969): Physiographic, stratigraphic and structural development of the Quadrilátero Ferrífero, Minas Gerais, Brazil. US Geol. Surv. Prof. Pap. 641 A, 109 pp.

VON ESCHWEGE, W.L. (1833): Pluto Brasiliensis. G. Reimer Verlag, Berlin, 622 pp.

FERREIRA, C.M. (1983): Vulcanismo ácido no Quadrilátero Ferrífero e sua relação com algumas ocorrências e/ou depósitos minerais. Anais do 1° Simp. Geol. Minas Gerais, Belo Horizonte, Brazil, 128–133.

FERREIRA, C.M. (1991): Topázio de Ouro Preto, Minas Gerais. In: SCHOBBENHAUS, C., QUEIROZ, E.T. and COELHO C.E.S. (eds): Principais depósitos minerais do Brasil, IV, parte A, 303–308.

FLEISCHER, R. (1972): Origin of topaz deposits near Ouro Preto, Minas Gerais, Brazil, discussion. Econ. Geol. 67, 119–120.

GAINES, R.V., SKINNER, H.C.W., FOORD, E.E., MASON, B. and ROSENZWEIG, A. (1997): Dana's new mineralogy. 8th Ed. John Wiley, New York, 1819 pp.

GANDINI, A.L. (1994): Mineralogia, inclusões fluidas e aspectos genéticos do topázio imperial da região de Ouro Preto, Minas Gerais. Diss. Mestrado, USP, São Paulo, 1–212.

GANDINI, A.L., BELLO, R.M.S., FUZIKAWA, K., SVISERO, D.P. and FERREIRA, C.M. (1991): Caracterização das inclusões fluidas dos topázios imperiais da região de Ouro Preto, MG. Boletim IG-USP, Série científica 22, 61–72.

GANDINI, A.L., BELLO, R.M.S., FUZIKAWA, K., MARCIANO, V.R.P.R.O., PIMENTA, M.A., and SVISERO, D.P. (1992a): Microtermometria, absorção no infravermelho e espectroscopia micro Raman dos componentes químicos das inclusões fluidas dos topázios imperiais de Ouro Preto, MG. 37° Congr. Brasi. Geol., SBG/SP, São Paulo, 2, 111–113.

GANDINI, A.L., BELLO, R.M.S., FUZIKAWA, K., SVISERO, D.P., FERREIRA, C.M. and VALARELLI, J.V. (1992b): Estudos microtermométricos de inclusões fluidas em topázios imperiais da jazida de Caxambu, Ouro Preto - MG. Rev. Escola de Minas 45, 1/2, 191–193.

GANDINI, A.L., MENDES, J.C. and SVISERO, D.P. (1992c): Dados mineralógicos preliminares de topázio imperial da região de Ouro Preto, Minas Gerais. 37° Congr. Bras. Geol., SBG/SP, São Paulo, 2, 110–111.

GANDINI, A.L., RAGER, H., SCHOTT, S., SCHÜRMANN, K., TARAN, M. and ROESER, H. (2000): Investigação da cor alaranjada no topázio imperial da região de Ouro Preto, Minas Gerais (Brasil). 1° Simpósio Brasileiro de Tratamento e Caracterização de Gemas. Resumos p. 55.

GORCEIX, H. (1881): Estudo geológico das jazidas de topázio da província de Minas Gerais. An. Esc. Minas Ouro Preto, Brasil, 1, 15–38.

GRUNDMANN, G. and MORTEANI, G. (1989): Emerald mineralization during regional metamorphism: The Habachtal (Austria) and Leydsdorp (Transvaal, South Africa) deposits. Econ. Geol. 84, 1835–1849.

GÜBELIN, E., GRAZIANI, G. and KAZMI, A.H. (1986): Pink topaz from Pakistan. Gems and Gemology 22, 3, 140–151.

HEDENQUIST, J.W. and HENLEY, R.W. (1985): The importance of CO_2 on freezing point measurements of flu-

id inclusions: Evidence from active geothermal systems and implications for epithermal ore deposition. Econ. Geol. 80, 1379–1406.

HOLDAWAY, M.J. (1971): Stability of andalusite and the aluminium silicate phase diagram. Am. J. Sci. 271, 97–131.

JOHNSON, R.F. (1962): Geology and ore deposits of the Cachoeira do Campo, Dom Bosco and Ouro Preto quadrangles, Minas Gerais, Brazil. US Geol. Surv. Prof. Pap. 341-B, 1–39.

KELLER, P.C. (1983): The Capão topaz deposit, Ouro Preto, Minas Gerais, Brazil. Gems and Gemology 19, 1, 12–20.

KONNO, H. and AKIZUKI, M. (1982): Fluorine determination in topaz and relation between fluorine content and 2V value of topaz. N. Jb. Mineral. Mh. 10, 465–470.

NALINI JR., H.A. (1993): Análise estrutural descritiva e cinemática do flanco sul e terminação periclinal do anticlinal de Mariana e adjacências, região sudeste do Quadrilátero Ferrífero, MG, Brasil. Diss. Mestrado, UFMG, Belo Horizonte, 134 pp.

OLSEN, D.R. (1971): Origin of topaz deposits near Ouro Preto, Minas Gerais, Brazil. Econ. Geol. 66, 627–631.

OLSEN, D.R. (1972): Origin of topaz deposits near Ouro Preto, Minas Gerais, Brazil – A reply. Econ. Geol. 67, 120–121.

PETROV, I., SCHMETZER, K. and BANK, H. (1977): Orangefarbene Topaskristalle von Saramenha bei Ouro Preto, Minas Gerais, Brasilien. Aufschluss 28, 219–222.

PIRES, F.R.M. (1989): Equilibrio no sistema SiO_2-Al_2O_3-H_2O aplicado aos depósitos de topázio e cianita de Ouro Preto, Q.F., Minas Gerais. An. 5° Simp. Geol. Núcleo Minas Gerais, 1° Simp. Geol. Núcleo Brasília, SBG, 36–40.

PIRES, F.R.M., FREITAS, C.O., PALERMO, N. and SARCIÁ, M.N.G. (1983): Geologia e gênese dos depósitos de topázio do distrito de Ouro Preto, Minas Gerais, Brazil. An. 2° Simp. Geol. de Minas Gerais, Belo Horizonte, 2, 283–296.

POTY, B., LEROY, J. and JACHIMOVICZ, L. (1976): Un nouvel appareil pour la mesure des températures sous le microscope: l'installation de microthermometrie CHAIXMECA. Soc. Fr. Mineral. Cristallogr. Bull. 99, 2/3, 182–186.

RAGER, H., SCHOTT, S., SCHÜRMANN, K. and TARAN, M. (2001): Untersuchungen zur Farbe von Imperial-Topas aus Minas Gerais, Brasilien. Ber. Deut. Mineral. Ges., Bheft Eur. J. Mineral. 13 (1), p. 148.

RAMBOZ, C., PICHAVANT, M. and WEISBROD, A. (1982): Fluid immiscibility in natural processes: Use and misuse of fluid inclusion data. II. Interpretation of fluid inclusion data in terms of immiscibility. Chem. Geol. 37, 29–48.

RIBBE, P.H. and ROSENBERG, P.E. (1971): Optical and X-ray determinative methods for fluorine in topaz. Am. Mineral. 56, 1812–1821.

ROEDDER, E. (1984): Fluid inclusions. Reviews in Mineralogy 12, 644 pp.

ROLFF, A. (1971): Brazilian Imperial Topaz. Lapidary J. 25, 1556–1562.

ROSENBERG, P.E. (1967): Variations in the unit-cell dimensions of topaz and their significance. Am. Mineral. 52, 1890–1895.

SAUER, D.A., KELLER, A.S. and McCLURE, S.F. (1996): An update on Imperial Topaz from the Capão Mine, Minas Gerais, Brazil. Gems and Gemology 32, 4, 232–241.

SCHOBBENHAUS, C., CAMPOS, D.A., DEZER, G.R. and ASMUS, H.E. (coord.) (1984): Geologia do Brasil – Tex-

to explicativo da mapa geológico do Brasil e da área oceânica adjacente incluindo depósitos minerais, escala 1:2.500.000. Brasília, DNPM, 501 pp.

SCHWARZ, D. (1997): Brasilien: Das Land der Topase. In: WEISE, Ch. (ed.): Topas. Ein prachtvolles Mineral, ein lebhafter Edelstein. Extralapis 13, 46–53.

SHEPHERD, T.J., RANKIN, A.H. and ALDERTON, D.H.M. (1985): A practical guide to fluid inclusion studies. Blackie and Sons, London, 239 pp.

DA SILVA, J.C. and FERREIRA, C.M. (1987): Gemas do Brasil (Gems of Brazil). São Bernardo do Campo, 130 pp.

SOOM, M., ARMBRUSTER, Th. and STALDER, H.A. (1988): OH-rich topaz from alpine fissures in Triassic dolomites near Lugnez, Graubünden (Mesozoic cover of Gotthard Massif, Swiss Alps). Schweiz. Mineral. Petrogr. Mitt. 68, 141–155.

SPEAR, F.S. (1993): Metamorphic phase equilibria and pressure-temperature-time paths. Min. Soc. Am. Spec. Publ., Book Crafters, Chelsea, USA, 799 pp.

VON SPIX, J.B. and VON MARTIUS, C.F.P. (1831): Reise in Brasilien. Lindauer, München, 300 pp.

THOMAS, R. (1982): Ergebnisse der thermobarogeochemischen Untersuchungen an Flüssigkeitseinschlüssen in Mineralen der postmagmatischen Zinn-Wolfram-Mineralisation des Erzgebirges. Freiberger Forschungshefte, C370, 855 pp.

THOMPSON, A.B. and TRACY, M.J. (1979): Model systems for anatexis of pelitic rocks II. Facies series melting and reactions in the system $CaO-KAlO_2-NaAlO_2-Al_2O_3-SiO_2-H_2O$. Contrib. Mineral. Petrol. 70, 429–438.

WIRTH, R. and WUNDER, B. (2000): Characterization of OH-containing phases by TEM using electron energy-loss spectroscopy (EELS): Clinohumite-OH, chondrodite-OH, phase A, and the (F,OH)-solid solution series of topaz. J. Trace and Microprobe Techniques 18, 35–49.

WUNDER, B., RUBIE, D.C., ROSS II, C.R., MEDENBACH, O., SEIFERT, F. and SCHREYER, W. (1993): Synthesis, stability, and properties of $Al_2SiO_4(OH)_2$: A full hydrated analogue of topaz. Am. Mineral. 78, 285–297.

WUNDER, B., ANDRUT, M. and WIRTH, R. (1999): High-pressure synthesis and properties of OH-rich topaz. Eur. J. Mineral. 11, 803–813.

ZHENG, Y.-F. and SIMON, K. (1991): Oxygen isotope fractionation in hematite and magnetite: A theoretical calculation and application to geothermometry of metamorphic iron-formations. Eur. J. Mineral. 3, 877–886.