

# MINERALOGICAL CHARACTERIZATION OF TOPAZ FROM MIAROLITIC PEGMATITES AND W-BEARING GREISEN IN THE A-TYPE EL PORTEZUELO GRANITE, PAPACHACRA (CATAMARCA PROVINCE)

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## ABSTRACT

The El Portezuelo Granite (Catamarca Province, NW Argentina), probably of Late Devonian or Early Carboniferous age, was emplaced at  $\leq 2$  kbar and displays the chemical characteristics of an A-type granite. It hosts small miarolitic pegmatites and dikes that belong to the NYF petrogenetic family, miarolitic class, miarolitic-REE subclass, with features more similar to those reported for the gadolinite-fergusonite type. Topaz is widespread both in pegmatites and in a W-bearing greisen genetically related to the granite. In pegmatites it occurs as crystals up to over 15 cm long, showing the forms {120} and {041} (dominant), and also {100}, {010}, {001}, {110}, {130}, {230}, {410}, {150}, {340}, {201}, {203}, {011}, {021}, {031}, {111}, {112}, {221}, {223}, and {445}. Crystals are colorless to pale yellow, more rarely brownish or bluish. Electron-microprobe analyses of gemmy crystals from pegmatites and greisen show that topaz is F-rich (between 19.01 and 20.12 wt. % F, most crystals being slightly zoned) and has very low MgO and TiO<sub>2</sub> ( $\leq 0.02$  wt.%), low FeO ( $\leq 0.03$  wt.%), and up to 0.10 wt.% CaO. Refractive indices and unit-cell dimensions reflect the F-rich nature of the studied topaz. This occurrence produces the finest crystals yet known from western South America but probably has no economic potencial as gemstock producer.

Keywords: *Topaz, Miarolitic pegmatites, Greisen, A-type granite, El Portezuelo, Argentina.*

**RESUMEN:** *Caracterización mineralógica de topacio de pegmatitas miarolíticas y un greisen portador de W en el plutón de tipo A El Portezuelo (Granito Papachacra), provincia de Catamarca.* El Granito El Portezuelo (Provincia de Catamarca, Argentina noroccidental), de probable edad devónica superior a carbonífera inferior, se emplazó a  $\leq 2$  kbar y posee las características de un granito de tipo A. Aloja pegmatitas miarolíticas y diques de reducidas dimensiones que pertenecen a la familia petrogenética NYF, clase miarolítica, subclase miarolítica-elementos de tierras raras, con rasgos más similares a los del tipo gadolinita-fergusonita. El topacio está bastante difundido en las pegmatitas y en un greisen portador de W genéticamente relacionado al granito. En pegmatitas se encuentra en cristales que superan los 15 cm, mostrando las formas {120} and {041} (dominantes), y también {100}, {010}, {001}, {110}, {130}, {230}, {410}, {150}, {340}, {201}, {203}, {011}, {021}, {031}, {111}, {112}, {221}, {223} y {445}. Los cristales son incoloros a amarillo pálido, más raramente pardos o celestes. Análisis con microsonda de electrones hechos en cristales de calidad de gema muestran que el topacio es rico en F (entre 19,01 y 20,12% F), y con muy bajo MgO y TiO<sub>2</sub> ( $\leq 0,02$  %), bajo FeO ( $\leq 0,03$ %), y hasta 0,10% de CaO. Los índices de refracción y las dimensiones de la celda unidad reflejan la naturaleza rica en F del topacio estudiado. Esta localidad produce los mejores cristales hasta ahora conocidos del occidente de Sudamérica pero probablemente carece de potencial como depósito de material gemológico. .

Palabras clave: *Topacio, Pegmatitas miarolíticas, Greisen, Granito de tipo A, El Portezuelo, Argentina.*

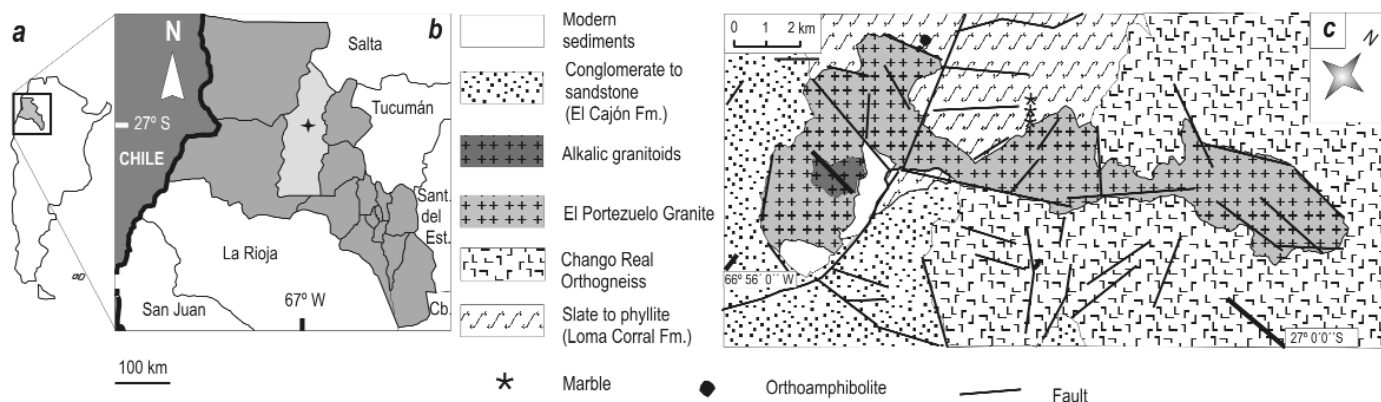
## INTRODUCTION

The El Portezuelo Granite is located in Belén department (Catamarca Province, NW Argentina), slightly East of the intersection of coordinates 67°W and 27°S (Fig. 1). It was emplaced at shallow depth

( $\leq 2$  kbar) and hosts miarolitic cavities, pegmatite pods and small aplite-pegmatite dikes, where topaz is occasionally found. This pluton is very similar to a body located about 15 km due South, called the Altohuasi Granite, and together they are known as Papachacra Granite.

These two plutons produce the best topaz crystals from Argentina and, to the best of our knowledge, of western South America.

It has been known for decades that topaz occurs in this granite (e.g. Llambías 1963), and there are a number of publi-



**Figure 1:** a) Map of the continental portion of Argentina. The square marks the location of map b. b) Departments in Catamarca Province (medium gray). Papachacra is shown as a star inside Belén Department (pale gray). c) Simplified geological map of El Portezuelo Granite and its surroundings.

cations dealing with topaz from Papachacra (e.g. Ávila and Porto 1982, Fuentes and Rossello 1985, Menzies 1995, Peralta *et al.* 1998, Kuck and Saadi 1998, Ávila *et al.* 2004, Saadi 2006). In spite of all this, there are still obscure points about this occurrence, and some mineralogical data (like their chemical composition and unit-cell dimensions) have never been published. Besides, topaz also occurs in a greisen (called Veta Calzada or, less frequently, Piedra Calzada, located at  $27^{\circ}1'33.4''S$ ,  $66^{\circ}53'51.0''W$ ) related to the El Portezuelo pluton; some researchers studied samples from this environment (e.g. Ávila and Porto 1982, Ávila *et al.* 2004) while it is not always clear the provenance (pegmatite vs. greisen) of the specimens studied by other workers.

In this paper we provide morphological, chemical, and crystallographical data, as well as paragenetic information for topaz from El Portezuelo Granite and the Veta Calzada Greisen. Topaz from the Altohuasi pluton is visually indistinguishable from that coming from El Portezuelo Granite, and has not been studied in this contribution.

### Geological setting

El Portezuelo pluton intrudes a low grade (greenschist facies) metapelitic sequence (Loma Corral Formation) and the Chango Real Orthogneiss (Fig. 1). It is elongated in a NE direction; maximum dimensions are  $\sim 16.5$  km by  $\sim 7.5$  km. In

the surroundings of the pluton, the Loma Corral Formation is composed of slate grading to phyllite and minor quartzite and marble lenses. Near the contact with the granite spotted slate is common. Marble is found in a stripe oriented NNW and extending for a few thousand meters. In restricted areas of these marble lenses, fluids emanating from the pluton formed a peculiar type of skarn (termed ribbon rock), composed of finely alternating and contorted bands of opaque (dominated by magnetite partially replaced by hematite) and transparent minerals (mainly fluorite, quartz, amphibole, potassium feldspar and garnet) (García *et al.* 1982).

The Chango Real orthogneiss is a metamorphosed sienogranite to monzogranite (Lazarte 1992). There are also minor outcrops of mafic rocks which are part of the metamorphic sequence (García *et al.* 1981, 1982, García and Rossello 1984). El Portezuelo Granite is intruded by granitoids of alkalic affinity, genetically unrelated to it.

El Portezuelo Granite plots in the syenogranite to monzogranite fields of LeMaitre *et al.* (2002) (according to the data published by Lazarte 1994). It is composed mainly of quartz, K-feldspar and plagioclase ( $An_{12}$  to  $An_0$ ). Accessory species are dark mica (annite-siderophyllite series), fluorite, topaz, zircon, thorite, monazite-(Ce), xenotime-(Y), apatite, magnetite, ilmenite, rutile, uraninite and fe-

rrrocolumbite. Secondary phases include cerianite-(Ce), chamosite, pyrochlore-group minerals and hematite.

El Portezuelo Granite shows the chemical characteristics of low-phosphorus granites as defined by Taylor (1992) and it can be classified as an A-type granite following the criteria exposed by Collins *et al.* (1982) and Whalen *et al.* (1987). A representative analysis of a sample (taken from the Rumi Tucu mine,  $27^{\circ}2'9.7''S$ ,  $66^{\circ}54'57.4''W$ ) is given in table 1.

The age is not well constrained; K-Ar isotopic dating gave a range of ages, the oldest being  $366 \pm 14$  Ma (Rossello *et al.* 2000). A Late Devonian to Carboniferous age is also supported by correlation with similar bodies located in Central and NW Argentina (Lazarte 1994), intruded during a widespread magmatic event that extended to the middle (and probably Early) Carboniferous.

Pegmatites related to the granite belong to the NYF petrogenetic family (so called because they tend to concentrate Niobium, Yttrium and Fluorine) and are representatives of the miarolitic class, miarolitic-rare earth element subclass, with features more similar to those reported for the gadolinite-fergusonite type, according to the criteria suggested by Cerný and Ercit (2005). Most of the topaz comes from miaroles whose zoning matches very well that described by Cerný (2000). These miaroles formed as a result of volatile build-up and fluid exsolution

during the latest stages of melt crystallization.

## EXPERIMENTAL METHODS

Crystallographic forms present in topaz crystals were identified based on measurements on digital pictures taken from conveniently oriented crystals using a binocular microscope, as described by Colombo (2006). Shape V7.0 was used for crystal drawings.

Chemical analyses of topaz were made using an ARL-SEM-Q microprobe at the Earth and Environmental Sciences Department of the University of New Orleans (Louisiana, USA). It was operated at 15 kV acceleration potential, with a beam current of 15 nA, 2  $\mu\text{m}$  beam diameter and 45 s count time. Standards (all K lines) are topaz (Al, Si, F), clinopyroxene (Ca, Mg, Fe), titanite (Ti), rhodonite (Mn) and adularia (K). Background was determined via the MAN method (Donovan and Tingle 1996) using the following standards (and any one of the above, where applicable): hematite, periclase, vanadium(V) oxide, zirconium(IV) oxide, zinc oxide and rutile. Chemical analyses of some pegmatitic and granitic species (plagioclase, mica, tourmaline, chlorite) were made at Brigham Young University (Provo, Utah, USA) with a CAMECA SX 50 microprobe using natural and synthetic standards. Accessory phases in the granite were identified with an Amray 1820 scanning electron microscope (SEM) equipped with EDS. Whole-rock analyses were made on a commercial basis by ActLabs Ltd. (Canada) using a combination of ICP and mass spectrometry.

X-ray diffraction patterns were obtained with an X'Pert Pro diffractometer housed at the Facultad de Ciencias Químicas-INFIQC (Córdoba, Argentina), operating at 40 kV and 40 nA, using  $\text{CuK}\alpha$  radiation. Patterns were measured from  $20^\circ$  to at least  $68^\circ 2\theta$  (and as much as  $120^\circ 2\theta$ ), in steps of  $0.03^\circ 2\theta$  and 1.8 s/step. Unit-cell dimensions were calculated by full-profile fitting method (Le Bail *et al.* 1988) using FullProf software (Rodríguez-Carvajal 2003).

Refractive indices were measured using Cargille liquids and white light.

## Mineralogical description of topaz from pegmatites and greisen related to El Portezuelo pluton

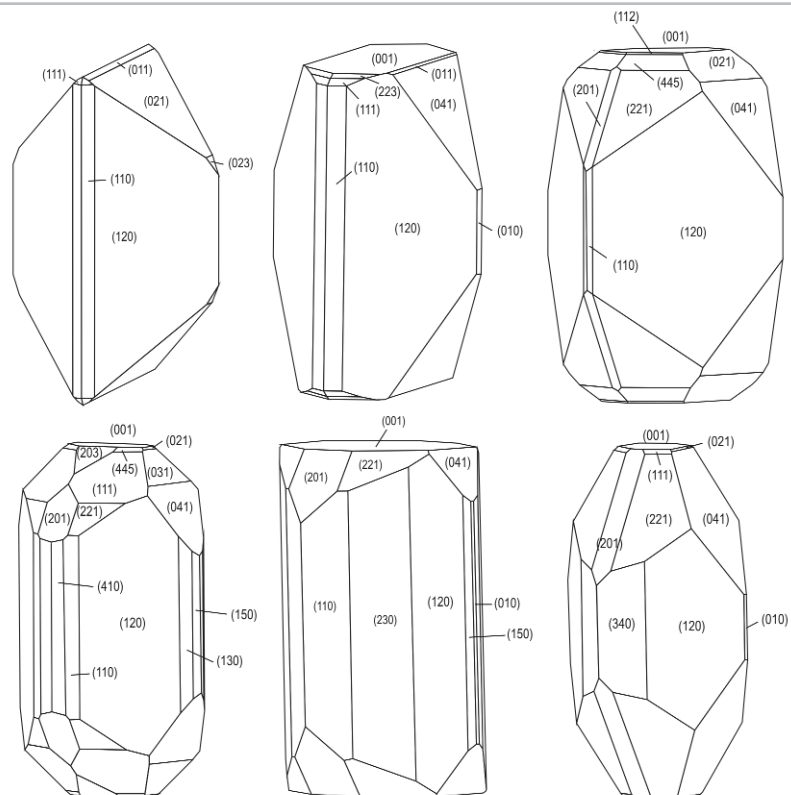
This silicate is an uncommon accessory phase in granite and aplites, where it occurs as anhedral grains, with incipient to advanced alteration to muscovite. Topaz is best developed in miarolitic cavities, where it precipitated late in the paragenetic sequence from a hydrothermal solution. Common associated species include quartz (dark to light smoky or colorless), microcline, albite and strongly zoned mica-group minerals. Less common species are schorl-foitite, bertrandite, chamosite, and florencite-(Ce). Nb-Ta oxides (microlite and other pyrochlore-group minerals, ferrotapiolite and columbite-group species) have not yet been found associated with topaz but occur in nearby pockets. Fluorite, a common species in miaroles, is almost absent in topaz-bearing cavities.

**TABLE 1:** Chemical composition of a representative sample of equigranular medium-grained granite from El Portezuelo pluton\*

	wt. %		ppm
SiO <sub>2</sub>	76.13	Be	12
TiO <sub>2</sub>	0.07	Ba	27
Al <sub>2</sub> O <sub>3</sub>	11.98	Sr	10
Fe <sub>2</sub> O <sub>3</sub> (total)	1.26	Y	79
MnO	0.04	Zr	148
MgO	0.06	Ga	28
CaO	0.41	Rb	545
Na <sub>2</sub> O	3.62	Nb	99
K <sub>2</sub> O	4.92	Sn	4
P <sub>2</sub> O <sub>5</sub>	0.03	Cs	35.3
LOI	0.95	Ce	115.0
Total	99.45	Th	63.4
		U	14.9
ASI	1.00	Hf	7.8
Al	0.94	Ta	15.8

\* (sample 67, Rumi Tucu mine, coord.:  $27^\circ 2' 9.7''\text{S}$ ,  $66^\circ 54' 57.4''\text{W}$ ).

Crystal size ordinarily ranges between 5 mm and 2 cm, but the largest crystal known measures over 15 cm. Topaz displays a short prismatic habit, dominated by the prisms  $\{120\}$  and  $\{041\}$ . Many other forms can be present (figure 2); some of them are  $\{100\}$ ,  $\{010\}$ ,  $\{001\}$ ,



**Figure 2:** Crystal forms and habits of miarolitic topaz from El Portezuelo Granite. The most frequent combination is the one at the upper left corner.

{110}, {130}, {230}, {410}, {150}, {340}, {201}, {203}, {011}, {021}, {031}, {111}, {112}, {221}, {223}, and {445}.

Crystals can be corroded, sometimes strongly, and show the typical striations on [001]. They are frequently transparent and have gem-quality portions.

Color usually ranges from colorless to pale yellow, but it can also be darker brownish yellow or pale blue. Color fades under prolonged exposure to sunlight. Zoning can be present in two different patterns: a bluish core surrounded by brownish sectors, the limits being parallel to {100} (Menzies 1995), or zoning parallel to a {0kl} form (most probably {041}). Some crystals also have terminal faces which are milky due to fluid and solid inclusions (Menzies 1995).

As mentioned before, topaz is also an important rock-forming mineral in greisen outcrops known as Veta Calzada, developed in the contact between granite and slate of the Loma Corral Formation. Topaz occurs as mm-sized anhedral grains in compact greisen, interlocking with quartz and mica, and also as euhedral crystals in flat cavities. Besides quartz and white mica, purple fluorite is a very common associated species. Columbite has been reported from this locality (Ávila and Porto 1982, Ávila *et al.* 2004) but no details were given as to how it was identified. The few reported physical properties are inconclusive, and the density (4.8-5.0 g.cm<sup>-3</sup>, Ávila and Porto 1982) is lower than that of columbite. Strangely, no W-bearing minerals were reported, even though it is well-known that the Piedra Calzada greisen was exploited for tungsten (cf. Soulier 1982). EDS spectra show Fe>>Mn, thus the species is ferberite. An unusual mineral occurring in the Veta Calzada greisen is morinite, NaCa<sub>2</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(F,OH)<sub>5</sub>·2H<sub>2</sub>O (identified using X-ray diffraction and EDS), as one of the components of yellowish massive crusts on quartz and fluorite. This is the first report of the species in Argentina (Colombo 2007).

In open cavities, topaz from the Veta Calzada Greisen usually occurs as crys-

**TABLE 2:** Electron microprobe analyses of topaz (two spots per grain, labelled a and b) from miarolitic cavities and greisen.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	F	H <sub>2</sub> O*	F=O	Corrected total
30-a	32.79	0.01	55.88	0.01	0.00	0.01	0.07	19.60	0.58	8.25	100.69
30-b	32.80	0.01	55.77	0.01	0.00	0.01	0.07	19.89	0.43	8.37	100.62
A1-a	32.70	0.02	55.67	0.00	0.01	0.02	0.01	19.68	0.50	8.28	100.33
A1-b	32.75	0.02	55.60	0.00	0.01	0.01	0.01	19.72	0.47	8.30	100.28
bic-blue-1	32.71	0.01	55.44	0.00	0.00	0.00	0.05	20.05	0.30	8.44	100.12
bic-blue-2	32.69	0.02	55.47	0.01	0.00	0.00	0.03	20.10	0.27	8.46	100.12
bic-brown-1	32.86	0.01	55.79	0.02	0.00	0.00	0.01	19.79	0.48	8.33	100.62
bic-brown-2	32.91	0.01	55.70	0.02	0.00	0.00	0.02	19.81	0.46	8.34	100.58
31-a	33.01	0.02	55.75	0.02	0.00	0.01	0.10	19.45	0.66	8.19	100.82
31-b	33.02	0.01	55.80	0.02	0.00	0.01	0.09	19.56	0.61	8.23	100.89
33-a	32.90	0.01	55.77	0.00	0.00	0.00	0.01	19.76	0.49	8.32	100.62
33-b	32.91	0.01	55.68	0.01	0.00	0.00	0.02	19.47	0.62	8.20	100.50
34-a	32.87	0.00	55.70	0.01	0.00	0.00	0.06	19.89	0.42	8.37	100.58
34-b	32.80	0.01	55.63	0.00	0.00	0.00	0.08	19.54	0.57	8.23	100.41
37-a	32.81	0.02	55.60	0.00	0.00	0.00	0.05	19.29	0.69	8.12	100.33
37-b	32.84	0.02	55.66	0.00	0.00	0.00	0.05	19.41	0.64	8.17	100.44
36-a	33.09	0.00	55.98	0.00	0.00	0.00	0.00	19.01	0.89	8.00	100.96
36-b	32.99	0.00	56.00	0.00	0.00	0.00	0.00	19.08	0.85	8.03	100.89
35-a	32.86	0.02	55.64	0.01	0.00	0.01	0.01	20.01	0.36	8.43	100.51
35-b	32.87	0.02	55.71	0.01	0.00	0.01	0.01	20.00	0.37	8.42	100.59
38-a	32.66	0.01	55.34	0.00	0.00	0.00	0.01	20.12	0.24	8.47	99.91
38-b	32.59	0.01	55.41	0.00	0.00	0.00	0.01	20.09	0.26	8.46	99.91
39-a	32.60	0.02	55.46	0.03	0.00	0.00	0.10	19.98	0.33	8.41	100.10
39-b	32.58	0.01	54.42	0.02	0.00	0.00	0.10	19.92	0.23	8.39	98.91
greisen-a	32.85	0.01	55.78	0.01	0.00	0.00	0.00	19.78	0.48	8.33	100.57
greisen-b	32.84	0.01	55.63	0.00	0.00	0.00	0.00	19.80	0.45	8.34	100.39

bic-blue and bic-brown are parts of the same color-zoned crystal. \*: H<sub>2</sub>O wt. % calculated from (OH) values in table 3.

tals under 15 mm long; the largest crystal known from this place measures 3.3 cm long. Color is pale yellow, rarely with a greenish tinge, to almost colorless, and can be zoned parallel to {100}. It is transparent but macroscopically crystals look translucent due to fractures and irregular, dissolved faces. They always show corrosion on terminal faces, with rounding of crystal edges and a somewhat greasy aspect. Crystals show few crystallographic forms, with dominant {120}, {110} and {041}.

As regards the origin of topaz from the Veta Calzada Greisen, Ávila *et al.* (2004) report an average temperature of ~410-420°C, based on fluid inclusion data. Since no pressure correction was applied, that is a minimum temperature.

When topaz occurs on matrix the geological environment is readily identifiable. When no matrix is present, adhering fragments or inclusions of associated species may give important clues. In the

absence of any other minerals, an informed guess about the provenance of the topaz can be made from crystal morphology: topaz from the greisen does not show complex habits such as those depicted in figure 2 and terminal faces are usually strongly corroded.

### Chemical composition

Eleven samples (one of which is color zoned) of pegmatitic topaz and one from the greisen were selected for electron-microprobe analyses (tables 2 and 3). No zoning was detected in backscattered (BSE) images, so two points were analyzed in each crystal.

Analyzed grains have an Al/Si (in atoms per formula unit, apfu) ratio from 1.990 to 2.009, i.e. very close to the theoretical ratio 2:1 (except for analysis #39-b, which gives 1.969). All pegmatitic crystals are F rich (between 19.01 and 20.12 wt. % F), from 1.816 to 1.951 apfu. Stoichiometric topaz Al<sub>2</sub>SiO<sub>4</sub>F<sub>2</sub> has 20.65 wt.

% F. Most crystals are zoned, with variations of up to 0.35 wt. % F. The high % F (over ~19.5 wt. %) seems typical of NYF pegmatites (cf. Barkley and Wise 2006). Very high F is also characteristic of topaz found in rhyolites (Foord *et al.* 1990). Among the trace elements, Mg, Fe and Ti are at or below the detection limit, Mn was not detected, and Ca reaches up to 0.10 wt. %. No other elements were detected in EDS scans.

There seems to be no relationship between color and chemical composition in the analyzed samples, which is to be expected since yellow and blue color in topaz are due to color centers (Nassau and Prescott 1975).

The F amount of topaz from the Veta Calzada greisen, ~19.79 wt. % F (~1.903 apfu F), lies within the range for pegmatitic topaz. In other respects it is also compositionally similar to the other analyzed grains.

**Unit-cell parameters**

Unit-cell parameters were calculated for 12 topaz samples (table 4). It has long been known that the OH-for-F substitution affects the unit-cell dimensions, and linear regression equations have been proposed to relate unit-cell parameters with F content (e.g. Ribbe and Rosenberg 1971, Wunder *et al.* 1999, Alberico *et al.* 2003). However, the variation does not seem to be strictly linear over the whole OH/(OH+F) range (Wunder *et al.* 1993). Other aspect that further introduces uncertainty is the fact that some authors (e.g. Wunder *et al.* 1999) estimated rather than measured topaz compositions using unit-cell dimensions, and later these composition-cell dimension pairs were used (e.g. by Alberico *et al.* 2003) as if they were independent measurements to calculate regression equations.

In table 5 there is a comparison between the F content as estimated from different equations and the average of two electron-microprobe measurements for each crystal. The F-rich composition of the examined topaz is accurately predicted by these equations; the closest appro-

**TABLE 3:** Formulae based on 3 cations (in atoms per formula unit) of topaz from miarolitic cavities and greisen\*.

	Si	Ti	Al	Fe	Mn	Mg	Ca	F	OH (calc)
30-a	0.996	0.000	2.001	0.000	0.000	0.000	0.002	1.883	0.117
30-b	0.998	0.000	1.999	0.000	0.000	0.000	0.002	1.913	0.087
A1-a	0.997	0.000	2.001	0.000	0.000	0.001	0.000	1.898	0.102
A1-b	0.999	0.000	1.999	0.000	0.000	0.001	0.000	1.903	0.097
bic-blue-1	1.000	0.000	1.998	0.000	0.000	0.000	0.002	1.939	0.061
bic-blue-2	0.999	0.000	1.999	0.000	0.000	0.000	0.001	1.944	0.056
bic-brown-1	0.999	0.000	1.999	0.000	0.000	0.000	0.000	1.903	0.097
bic-brown-2	1.001	0.000	1.997	0.000	0.000	0.000	0.001	1.906	0.094
31-a	1.002	0.000	1.994	0.000	0.000	0.001	0.003	1.867	0.133
31-b	1.001	0.000	1.994	0.000	0.000	0.000	0.003	1.876	0.124
33-a	1.000	0.000	1.999	0.000	0.000	0.000	0.000	1.901	0.099
33-b	1.002	0.000	1.997	0.000	0.000	0.000	0.001	1.874	0.126
34-a	1.000	0.000	1.997	0.000	0.000	0.000	0.002	1.914	0.086
34-b	0.999	0.000	1.998	0.000	0.000	0.000	0.003	1.883	0.117
37-a	1.000	0.000	1.998	0.000	0.000	0.000	0.002	1.860	0.140
37-b	1.000	0.000	1.998	0.000	0.000	0.000	0.001	1.870	0.130
36-a	1.002	0.000	1.998	0.000	0.000	0.000	0.000	1.821	0.179
36-b	1.000	0.000	2.000	0.000	0.000	0.000	0.000	1.828	0.172
35-a	1.001	0.000	1.997	0.000	0.000	0.000	0.000	1.928	0.072
35-b	1.000	0.001	1.998	0.000	0.000	0.001	0.000	1.925	0.075
38-a	1.001	0.000	1.999	0.000	0.000	0.000	0.000	1.950	0.050
38-b	0.999	0.000	2.001	0.000	0.000	0.000	0.000	1.947	0.053
39-a	0.997	0.000	1.999	0.001	0.000	0.000	0.003	1.933	0.067
39-b	1.009	0.000	1.987	0.001	0.000	0.000	0.003	1.951	0.049
greisen-a	0.999	0.000	2.000	0.000	0.000	0.000	0.000	1.903	0.097
greisen-b	1.001	0.000	1.999	0.000	0.000	0.000	0.000	1.909	0.091

\*: (OH) calculated as (2-F) atoms per formula unit.



**Figure 3:** Topaz crystals on smoky quartz and microcline (left crystal ~2 cm long, Renato and Adriana Pagano collection; right crystal ~1 cm long).

**TABLE 4:** Unit-cell dimensions of topaz from miarolitic cavities and greisen.

Sample	Origin	Color	Unit-cell dimensions (Å)		
			a	b	c
30	pegmatite	colorless	4.6493(2)	8.7975(4)	8.3871(3)
31	"	colorless with brown tinge	4.6487(2)	8.7944(5)	8.3901(4)
33	"	very pale blue	4.64792(6)	8.7928(1)	8.38874(7)
34	"	very pale yellow	4.6504(2)	8.7992(4)	8.3877(3)
35	"	very pale brown	4.648(2)	8.7929(4)	8.3913(3)
36	"	colorless with yellow tinge	4.6513(1)	8.801(3)	8.3894(3)
37	"	colorless	4.6481(2)	8.7932(4)	8.3903(3)
38	"	colorless	4.6488(4)	8.7948(9)	8.3911(7)
39	"	colorless	4.6495(2)	8.7969(4)	8.3893(4)
bic. blue	"	very pale blue	4.6504(2)	8.7978(6)	8.3915(4)
bic. brown	"	very pale brown	4.6493(2)	8.7958(4)	8.3903(3)
greisen	greisen	very pale yellow	4.6489(3)	8.7973(4)	8.3858(3)

**TABLE 5:** Wt % F estimated from unit-cell parameters, using the equations listed under this table. Measured wt.% F is an average of 2 electron-microprobe analyses.

Sample	1	2	3	4	5	6	7	Meas. % F
30	19.79	20.62	20.32	19.63	20.53	19.74	20.27	19.74
31	20.10	20.69	20.39	19.78	20.96	19.90	20.70	19.50
33	20.25	20.97	20.67	19.98	21.18	20.10	20.92	19.61
34	19.62	20.35	20.05	19.36	20.29	19.46	20.04	19.72
35	20.24	20.79	20.49	19.96	21.17	20.08	20.91	20.01
36	19.44	20.02	19.72	19.13	20.05	19.23	19.79	19.04
37	20.21	20.82	20.52	19.93	21.12	20.05	20.87	19.35
38	20.06	20.59	20.29	19.76	20.90	19.87	20.64	20.11
39	19.85	20.49	20.19	19.58	20.61	19.69	20.35	19.95
bic blue	19.76	20.19	19.89	19.36	20.49	19.46	20.23	20.08
bic brown	19.96	20.52	20.22	19.63	20.77	19.74	20.51	19.80
greisen	19.81	20.76	20.46	19.73	20.56	19.85	20.30	19.79

Sources and codes of the equations: Ribbe and Rosenberg (1971): 1) %F =  $892.5 - 99.2 * b$ ; 2) %F =  $465.5 - 1.3 * V$ ; Wunder *et al.* (1999): 3) %F =  $564.7 - 1.586 * V$ ; Alberico *et al.* (2003): 4) %F =  $1180.19 - 249.62 * a$ ; 5) %F =  $1237.84 - 138.37 * b$ ; 6) %F =  $1215.87 - 257.27 * a$ ; 7) %F =  $1236.35 - 138.23 * b$ . (a and b are unit-cell dimensions, V is unit-cell volume).

ximations were obtained using equations 4 and 6 of Alberico *et al.* (2003) and equation 1 of Ribbe and Rosenberg (1971). Since most crystals are at least slightly zoned regarding the F content, unit-cell dimensions are necessarily averages, but no peak broadening was observed in X-ray powder patterns.

### Refractive indices

Refractive indices of topaz are also strongly influenced by F-for-OH substitution (Ribbe and Rosenberg 1971). Refractive indices were measured for topaz with the highest and lowest F content (~20.10 wt. % F, sample 38, and ~19.05 wt. % F, sample 36, respectively). Values are:  $\alpha = 1.612(2)$ ,  $\beta = 1.613(2)$ ,  $\gamma = 1.621(2)$  (sample 38) and  $\alpha = 1.619(2)$ ,  $\beta = 1.621(2)$ ,  $\gamma = 1.628(2)$  (sample 36). Refractive indices of one specimen reported by Fuentes and Rossello (1985) overlap with those of the F-richest sample in this study. Regression equations that relate refractive indices and F content have also been proposed. F content estimated from such equations appear in table 6. The best agreement is obtained using the equations of Carman (1981).

### TOPAZ PRODUCTION

Topaz-bearing cavities are not restricted to a given area and they do not follow a pattern; they are particularly abundant in

the southwestern end of the El Portezuelo pluton, especially in an area known as Rumi Tucu mine. Topaz and associated minerals (especially fine microcline and quartz crystals) are collected from weathered granite outcrops mainly for their value as collectibles, and currently there are no systematic or mechanized mining operations. Many topaz crystals show gemmy portions that would afford cut gems up to several carats; however, the pale color (or lack thereof) is a serious commercial drawback. During this study no treatments were made to topaz samples in order to improve the color (but note that, as stated before, color is not stable if exposed to sunlight for long periods). However, even if topaz from this locality showed a favourable color change after an appropriate treatment, the small volume available (considering both the pegmatitic and greisen occurrences), the rather irregular pattern of miarole distribution, the reduced size of the open cavities, and the rough terrain that greatly difficults the use of mechanized equipment, would probably make mining on a larger scale commercially unfeasible.

### ACKNOWLEDGEMENTS

This work would not have been possible without the help of William (Skip) B. Simmons and Alexander U. Falster (Uni-

**TABLE 6:** Wt % F estimated from unit-cell parameters, using the equations listed under this table. Measured wt.% F is an average of 2 electron-microprobe analyses.

Refractive index	1	2	Meas. % F
$\alpha$ (sample 38)	20.93	20.05	20.11
$\alpha$ (sample 36)	19.56	18.66	19.04
$\beta$ (sample 38)	19.39	20.34	20.11
$\beta$ (sample 36)	17.83	18.78	19.04
$\gamma$ (sample 38)	20.13	20.17	20.11
$\gamma$ (sample 36)	18.67	18.70	19.04

Sources and codes of the equations: Ribbe and Rosenberg (1971), column 1: %F =  $-14434 + 18091 * \alpha - 5600 * \alpha^2$ ; %F =  $-15373 + 19232 * \beta - 6007 * \beta^2$ ; %F =  $-10247 + 12847 * \gamma - 4018 * \gamma^2$ ; Carman (1981), column 2: %F =  $-14091.671 + 17669.224 * \alpha - 5530.429 * \alpha^2$ ; %F =  $-14882.367 + 18626.868 * \beta - 5820.051 * \beta^2$ ; %F =  $-9572.430 + 12019.085 * \gamma - 3763.960 * \gamma^2$ .

versity of New Orleans, USA), who made the microprobe analyses. They also informally reviewed an earlier version of the manuscript. We are grateful to Michael Dorais (Brigham Young University, USA) for the microprobe analyses of minerals associated with topaz. Fabián Juárez is gratefully acknowledged for his help during the field work. Most of the data presented here are part of a Ph.D. thesis of the senior author, financed by CONICET. We are also thankful to Michael A. Menzies and Juan Carlos Fuentes for sending copies of their publications. We thank referees M. A. Galliski and C. Herrmann for their comments.

### WORKS CITED IN THE TEXT

- Alberico, A., Ferrando, S., Ivaldi, G. and Ferraris, G. 2003. X-ray single-crystal structure refinement of an OH-rich topaz from Sulu UHP terrane (Eastern China) - Structural foundation of the correlation between cell parameters and fluorine content. *European Journal of Mineralogy* 15: 875-881.
- Ávila, J.C. and Porto, J.C. 1982. Presencia de topacio en el contacto granito-basamento del área de Papachacra, provincia de Catamarca. *Acta Geológica Lilloana* 16: 215-220.
- Ávila, J.C., Fogliata, A.S. and Mas, G. 2004. Topaz of Papachacra, Catamarca, Argentina: Mineralogical Description. 8<sup>o</sup> International Congress of Applied Mineralogy 521-523, Aguas de Lindoia (Sao Paulo).

- Barkley, M. and Wise, M. 2006. F-OH- Substitution and Thermal Effects on the Crystal Structure of Pegmatitic Topaz. 42nd Annual Meeting of the Geological Society of America, Northeast Section, Abstracts with Programs 38(1): 87.
- Carman, M.F. 1981. A spindle stage study of the optical properties of a topaz. *Bulletin de Minéralogie* 104: 742-749.
- Āerný, P. 2000. Constitution, petrology, affiliations and categories of miarolitic pegmatites. In Pezzotta, F. (ed.) *Mineralogy and petrology of shallow-depth pegmatites*. *Memorie della Società Italiana di Scienze Naturale del Museo Civico di Storia Naturale di Milano* 30: 5-12.
- Āerný, P. and Ercit, T.S. 2005. The classification of granitic pegmatites revisited. *Canadian Mineralogist* 43: 2005-2026.
- Collins, W.J., Beams, S.D., White, A. J. R. and Chappell, B.W. 1982. Nature and origin of A-type granites with particular reference to Southeastern Australia. *Contributions to Mineralogy and Petrology* 80: 189-200.
- Colombo, F. 2006. Indexado de cristales usando una cámara fotográfica digital y lupa binocular. 7º Congreso de Mineralogía y Metalogenia, Actas: 51-54, Buenos Aires.
- Colombo, F. 2007. Geología, mineralogía y génesis de granitoides de tipo A y sus pegmatitas asociadas en el plutón compuesto El Portezuelo (Granito Papachacra, provincia de Catamarca). Ph.D. Thesis (unpublished). Facultad de Ciencias Exactas, Físicas y Naturales. Universidad Nacional de Córdoba, 479 p.
- Donovan, J.J. and Tingle, T.N. 1996. An Improved Mean Atomic Number Background Correction for Quantitative Microanalysis. *Journal of Microscopy* 2(1): 1-7.
- Foord, E.E., Jackson, L.L., Taggart, J.E., Crock, J.G. and King, T.V.V. 1990. Environment of crystallization of topaz as inferred from crystal chemistry and infrared spectra (abstract). 15º General Meeting of the International Mineralogical Association, Proceedings 1: 306-307, Beijing.
- Fuentes, J.C. and Rossello, E.A. 1985. Topacios en la provincia de Catamarca, Argentina. *Boletín del Instituto Gemológico Español* VOL. LUME 25-28. LUGAR
- García, H.H. and Rossello, E.A. 1984. Geología y yacimientos minerales de Papachacra, departamento Belén, Provincia de Catamarca. 9º Congreso Geológico Argentino, Actas 7: 245-259, San Carlos de Bariloche.
- García, H.H., Massabie, A.C. and Rossello, E.A. 1981. Contribución a la geología de La Cuesita, departamento Belén, Provincia de Catamarca. 8º Congreso Geológico Argentino, Actas 4: 853-865, San Luis.
- García, H.H., Rossello, E.A. and Massabie, A.C. 1982. El depósito Tiburcio, ejemplo argentino de roca ribbon, Papachacra, Departamento Belén, Prov. de Catamarca, Argentina. 5º Congreso Latinoamericano de Geología, Actas 2: 735-750.
- Kuck, A. and Saadi, J.A. 1998. Les minéraux des pegmatites de Papachacra (Argentine). *Le Règne Minéral* 22: 5-13.
- Lazarte, J.E. 1992. La Formación Chango Real (NW de Sierras Pampeanas, República Argentina), ejemplo del magmatismo paleozoico (Cámbrico?). Diferencias geoquímicas con batolitos ordovícicos. *Estudios Geológicos* 48 (5-6): 257-267.
- Lazarte, J.E. 1994. Geología y geoquímica del Granito Papachacra (¿Carbonífero?), Sierras Pampeanas, Catamarca. *Revista de la Asociación Geológica Argentina* 49(3-4): 337-352.
- Le Bail, A., Duroy, H. and Fourquet, J.L. 1988. Ab-initio structure determination of LiSbWO<sub>6</sub> by X-ray powder diffraction. *Materials Research Bulletin* 23: 447-452.
- Le Maitre, R.W. (Ed.), Streckeisen, A., Zanettin, B., Le Bas, M.J., Bonin, B., Bateman, P., Bellieni, G., Dudek, A., Efremova, S., Keller, J., Lameyre, J., Sabine, P.A., Schmid, R., Sorensen, H. and Woolley, A. R. 2002. *Igneous Rocks: A Classification and Glossary of Terms*. Cambridge University Press. 236 p., Cambridge.
- Llambías, H. 1963. Sobre inclusiones halladas en cristales de inderita, bórax y topacio de la Argentina y consideraciones sobre su empleo como termómetro geológico. *Revista de la Asociación Geológica Argentina* 18(3-4): 129-138.
- Menzies, M.A. 1995. The mineralogy, geology and occurrence of topaz. *The Mineralogical Record* 26: 5-53.
- Nassau, K. and Prescott, B.E. 1975. Blue and Brown Topaz Produced by Gamma Irradiation. *American Mineralogist* 60: 705-709.
- Peralta, E.H., Ovejero, A.I. and Watkins, S.G. 1998. El topacio en aluviones de los ríos Potrero de Gerván, Quebradas del Chiquero y El Cajón, departamento Belén, Catamarca. 10º Congreso Latinoamericano de Geología and 6º Congreso Nacional de Geología Económica, Actas 3: 119-123, Buenos Aires.
- Ribbe, P.H. and Rosenberg, P.E. 1971. Optical and X-ray determinative methods for fluorine in topaz. *American Mineralogist* 56: 1812-1821.
- Rodríguez-Carvajal, J. 2003. FullProf. Software de acceso libre para procesamiento de datos de difracción de rayos X y neutrones (en línea): Laboratoire Leon Brillouin, Powder Diffraction Software Site <<http://www-llbcea.fr/fullweb/fp2k/fp2k.htm>>
- Rossello, E.A., López de Lucchi, M.G. and Osetera, H. 2000. La Formación Papachacra (Belén, Catamarca, Argentina): edades K/Ar y significados tectónicos y metalogénicos. 9º Congreso Geológico Chileno, Actas 1: 360-364, Puerto Varas.
- Saadi, J.A. 2006. Las Piedras Preciosas de la República Argentina. ¿Un recurso mineral desconocido o reservado? Privately published. 183 p., Córdoba.
- Soulier, F.H. 1982. Geología de las manifestaciones de W y Bi de Piedra Calzada, Departamento Belén, provincia de Catamarca. Degree Thesis (unpublished). Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, 42 p.
- Taylor, R.P. 1992. Petrological and geochemical characteristics of the Pleasant Ridge zinnwaldite-topaz granite, southern New Brunswick, and comparison with other topaz-bearing felsic rocks. *The Canadian Mineralogist* 30: 895-921.
- Whalen, J.B., Currie, K.L. and Chappell, B.W. 1987. A-type granites: geochemical characteristics, discrimination and petrogenesis. *Contributions to Mineralogy and Petrology* 95: 407-419.
- Wunder, B., Andrut, M. and Wirth, R. 1999. High-pressure synthesis and properties of OH-rich topaz. *European Journal of Mineralogy* 11: 803-813.
- Wunder, B., Rubie, D.C., Ross II, C.R., Medenbach, O., Seifert, F. and Schreyer, W. 1993. Synthesis, stability, and properties of Al<sub>2</sub>SiO<sub>4</sub>(OH)<sub>2</sub>: A fully hydrated analogue of topaz. *American Mineralogist* 78: 285-297.

Recibido: 18 de febrero, 2008

Aceptado: 2 de marzo, 2009