XRS

X-ray fluorescence analysis applied to geochemistry of quartz in Argentina[†]

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The growing demand for high-purity quartz in the international market led to the systematic investigation of the geochemical quality of this mineral in deposits Argentina. This study is a contribution to the scarce information on the geochemistry of quartz in Argentina. A total of 525 multielemental chemical analyses were performed with XRF spectrometry in less than 3 months. SiO₂ concentration was calculated by difference from XRF impurity determinations. As a result of this study, 36 sites over 141 sampled deposits were identified as being of desirable quality. Low-Z oxides, considered critical impurities for quartz, were determined by atomic absorption spectrometry, only in samples of these selected sites, because of high XRF detection limits. The analytical results allowed the classification of the quality of quartz according to its environment and geological genesis. It could be determined that better purity quartz corresponds to veins far away from the Achala and Alpa Corral batholith and occurs in metamorphic rocks, followed by pegmatitic quartz from inside the batholith and lastly by quartz of well-known hydrothermal origin. Copyright © 2005 John Wiley & Sons, Ltd.

INTRODUCTION

The main objective of this research was to establish a map of the quality of quartz from different types of deposits, the geological settings where they occur and the approximate size of the sampled deposits in Argentina. The sampling was carried out in deposits of different geological settings, so that data on pegmatitic quartz associated with batholith and granitic intrusions, non-granitic-related deposits intruded in metamorphic rocks and hydrothermal deposits emplaced within and outside the granitic complexes were obtained. The sampling sites were located with handheld GPS (Global Positioning System) and a mining file was made, stating all the geological and mineralogical aspects of interest. The field sampling was carried out very carefully to avoid contamination with other substances. For that reason, blocks of quartz of up to 0.2 m³ were hammered and fresh chips were collected.

Geological samples were introduced into a rigid quality protocol to reproduce identical steps during throughout

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the 6 months of the field campaign. All the samples were analysed by x-ray fluorescence (XRF) spectroscopy in a first step. Samples from selected deposits having higher SiO₂ concentrations calculated by difference of XRF impurities were complementarly analysed by atomic absorption spectrometry (AAS) to determine Na₂O, MgO and K₂O. For these elements XRF shows limits of quantification (near three times the limit of detection) higher than expected and our quantification method produced uncertainties near the realistic limit of application. These AAS determinations were taken into account to re-calculate the SiO₂ concentrations by difference. The average flux of analysis performed was 15 samples per day of quartz, feldspars and granitoids (these two last not included in this work), determining 28 elements per sample. This work demonstrated the suitability of wavelength-dispersive (WD) XRF analysis considering the automation of the sample changer of our spectrometer.

The goal of this project was to carry out the most complete characterization so far of silicate rocks performed in the centre of Argentina. In this work the competitiveness of quantitative XRF for prospective mining studies was confirmed as the main analytical technique because it is a simple and fast technique giving satisfactory results for an initial characterization of industrial mineral deposits. The analyses relative cost of XRF analyses is very advantageous in comparison with AAS, ICP and other chemical techniques. The reproducibility, detection limits and accuracy obtained

by XRF spectrometry for silicates were satisfactory for the purposes of the project.

GEOLOGICAL SETTING AND SAMPLING

Prior to starting the sampling, a complete bibliographical research on the quartz, feldspar, granites and mica deposits of Córdoba was carried out, and the regional distribution of claims of these minerals registered in the Córdoba Mining Department was taken into account. This work led to a first general idea about the distribution of the deposits of interest, of which 48% of the quartz deposits are situated south of the 32°S parallel, 44% are between the 32° and 31°S parallels and only 8% north of the 31°S parallel. The explanation of this circumstance lies in the regional geology of Córdoba Hills (Fig. 1). The regional geology south of the 32°S parallel is composed of medium-to high-grade metamorphic rocks (gneisses and anatexites), which do not host abundant pegmatitic deposits. The deposits are nearly pure quartz veins in the south of the batholith and muscovite-bearing pegmatites in the north. The influence of the Achala batholith is remarkable between the 32° and 31°S parallels, and most of the quartz sampled in this area is related to this batholith. Here, zoned pegmatites frequently rich in feldspar and muscovite apart from quartz are predominant. North of the 31°S parallel the quartz deposits are very scarce, since the main geological units are metamorphic and migmatitic complexes, poor not only in pegmatites but also in hydrothermal veins.

In order to discriminate genetically the different types of quartz as regards their purity, a systematic sampling was performed, taking into account the host rock and the petrology of the regional environment.

Quartz of pegmatites related to granitic intrusions

Most of these types of deposits are located in the Achala batholith (Fig. 1, type 4). Within the Achala batholith, the most interesting deposits are located in two main groups:[1]

1. The first group is located northeast of the batholith. The pegmatites are predominantly zoned, egg or cupola shaped, with massive quartz or quartz microcline cores. The intermediate zones are coarse-to very coarse-grained and are composed of quartz, blocks of microcline, albite and muscovite. They show beryl, apatite, triplite, columbo-tantalite, biotite and garnet as accessory minerals and topaz in some deposits. The host rocks are medium- and coarse-grained porphyritic granites.
2. The second group comprises many small-to medium-sized deposits located on the western slope of the Achala batholith. The pegmatites are tabular and zoned with intermediate zones of coarse to very coarse grain composed of blocks of perthitic microcline, plagioclase and muscovite. Crystals of beryl, triplite, apatite and rarely topaz, amblygonite, columbo-tantalite, Fe and Mn secondary phosphates are present. The host rocks are medium-and coarse-grained porphyritic granites. These pegmatites may have been formed by crystallization in closed chambers of remnant fluids of the host granites.
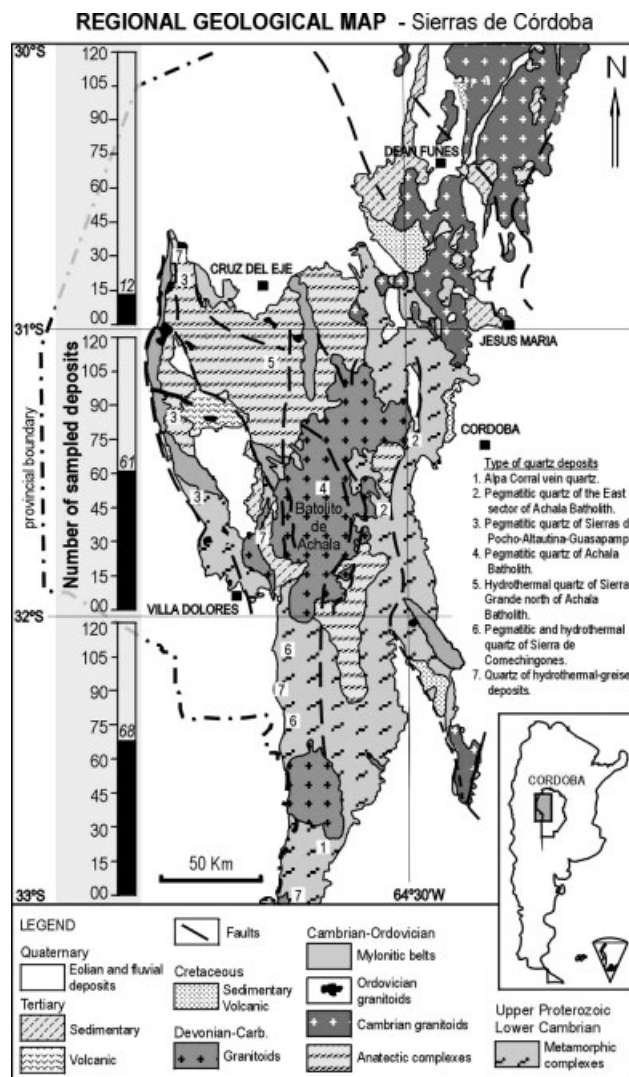

Figure 1. Regional geological map of the Córdoba hills (Sierras de Córdoba), where the quantity and type of sampled deposits are shown.

These fluids were enriched with volatile and incompatible elements during fractional crystallization.

Quartz of pegmatites not directly related to granitic intrusions

These pegmatites are described separately since, from geological evidence[2] (occurrence, deformation degree, age) they may not be directly related to the magmatism that originated the great batholiths of the Córdoba Hills; within this group the main districts are shown in Fig. 1, type 3. A genetic relation between these deposits and the Achala batholith cannot be established, because the pegmatites are concordant with the foliation of the metamorphic basement, they are folded, and with strong internal deformation. These events are prior to the intrusion of said batholith. The pegmatites are zoned, with intermediate zones of plagioclase or microcline, quartz and muscovite (of commercial size) with tourmaline, garnet, beryl, apatite and biotite as accessories.

Mica and uranium-bearing pegmatites

This zone is referred to in Fig. 1 as type 6. The pegmatites emplaced here have stromatitic migmatites and mylonitic gneisses as host rocks,[3] in a migmatic belt in the east; further south medium-grade metamorphic rocks outcrop (gneisses, micaschists and amphibolites) that are the east boundary of mylonitic gneisses. The pegmatites of the district are generally zoned, tabular to lens-shaped, 100–200 m fone and 5–10 m wid. In the bodies external zones composed of plagioclase–quartz–muscovite, with scarce accessories (tourmaline, apatite, and zircon), can be distinguished.

The muscovite usually appears as strips up to 0.3 m wide, which have been mined. The intermediate zones are composed of coarse-grained microcline–plagioclase–quartz–muscovite, in some cases with good-quality mica. Among the accessories are garnet, apatite, beryl, triplite, columbo-tantalite, uraninite, gahnite, some sulfides and secondary uranium minerals. The cores are composed of white quartz, in many cases of saccharoidal type; they usually present foliation with muscovite developed on the planes. In certain deposits, zoned pegmatites are not observed and the bodies are composed of pure white quartz, generally saccharoidal, with muscovite as the main accessory.

Mica-bearing pegmatites of the eastern sector of the Achala Batholith

These pegmatites are represented in Fig. 1 as type 2. The host rocks of the pegmatites are medium to high-grade metamorphic rocks (gneisses and migmatites), affected by mylonitic belts in the south. Tabular to lens-shaped zoned pegmatites are very common. In these bodies the external zones are usually well developed and are composed of plagioclase–quartz–muscovite with garnet and biotite as accessories. The muscovite, of commercial grade, forms belts located in the boundaries or the centre of the zone. The intermediate zones do not appear in all the bodies; they are medium-to very coarse-grained, with perthitic microcline–quartz–plagioclase–muscovite with scarce garnet and beryl as accessories. Quartz and perthitic microcline or quartz in large masses, with rare muscovite forms the cores.

Other types of quartz

Alpa corral vein quartz (Fig. 1 type 1)

Geologically this region is constituted by medium-grade metamorphites (gneisses and amphibolites) and mylonites. In general, these deposits are coarse-grained pure quartz veins, with scarce accessories such as muscovite and iron oxides. The veins are small, and only exceptionally exceed 100 m long and 10 m wide.

Hydrothermal quartz (quartz–sericite greisen type)

Within the Córdoba Hills there are bodies of hydrothermal quartz (Fig. 1, type 7), which are characterized by its high tonnage and medium-to low-quality quartz. These deposits are generally associated with regional faults within granitic plutons. Zones of siliceous breccias cemented by white massive or vuggy quartz are developed in these faults and in some parts they form monomineral veins; the breccia clasts are generally sericitized. The bodies are hundreds of meters long and vary in width, but they do not generally go over 50 m. The mineralogy of the bodies is simple since the quartz is associated with sericite and iron oxides. These deposits are the result of filling of open cavities from hydrothermal fluids of meteoric origin, with formation temperatures that range from 300 to 400 °C.

Hydrothermal quartz of north of Achala Batholith (Fig. 1, type 5)

A metamorphic–migmatitic complex constituted essentially by cordieritic migmatites, gneisses, schists and amphibolites forms the region.

GEOCHEMICAL CONSIDERATIONS

Up to now, quartz deposits have been classified genetically, and they have been described according to their geological setting and their typology. Nevertheless, and due to the relevance of geochemical data in this work, a classification based on the content of SiO_2 is proposed. The main accompanying cations determined by XRF were Al, Fe and Ti, with Cr as a trace element. This classification is directly related to the quality of the raw material (quartz) and strongly correlated with the geological classification given in the previous section. Table 1 shows the highest concentration values of minor elements associated with silicon in quartz identified from the whole analysed samples. These maximum values occur essentially in quartz of hydrothermal–greisen deposits and are substantially lower in the other categories of deposits. Concerning trace elements, concentrations were insignificant in almost all samples, but a small number of samples reached maximum values, as shown in Table 2. Sn, W, As and Co were not detected.

This understanding aims to generate new trends in exploration based on the geology and geochemistry of the deposits.

Table 1. Highest concentrations of minor elements analysed by XRF for quartz

Analyte	Concentration (%)	Analyte	Concentration (%)
Al_2O_3	0.85	K_2O	0.46
Fe_2O_3	0.71	Na_2O	0.076
TiO_2	0.060	P_2O5	0.21
MgO	0.13	S	0.058
MnO	0.020	C1	0.090
CaO	0.89	F	0.97

Table 2. Maximum concentrations of trace elements analysed by XRF for quartz

Analyte	Concentration (ppm)	Analyte	Concentration (ppm)
Rb	180	Ba	41
Cu	180	Sr	25
Y	99	Cs	21
Cr	71	V	6
Pb	65	Ni	5
Zn	56		

EXPERIMENTAL

Preparation of XRF samples

The samples of rocks were taken by the expert geologist co-authors of this work. They arrived at CEPROCOR with an average particle size of 2 cm free of external contamination. Part of this material was crushed using a tungsten carbide (W_2C) hammer, reducing the granulometry to 0.5 cm. The W_2C was used to minimize the contamination of critical elements, such as those present in stainless-steel dispositives. A 20 g amount of this mass was ground in a zirconium alloy disk-mill for 7 min. This material was sieved in a plastic sieve of 325 mesh. Finally, 8 g of this powder were mixed with 2 g of microwax binder and pressed at 25 tons in a matrix of 40 mm diameter. The pressed pellet samples obtained after different experimental tests were very stable, without surface or border failures. A numerical code was applied to each pressed pellet sample and correlated with the original raw material storage package and also with the powder recipient before blending. A database computer program saved each code with information about geological setting, the analytical procedure and the post-analysis location of the XRF disk, powder and original raw material for control.

Instrumental

A 4 kW power Bruker SRS 3400 spectrometer was used to measure XRF intensities. The x-ray tube has a thin Be window (75 μm) to optimize the detection limit. The spectrometer includes six Bragg analyser crystals, OVOB, OVOC, OVO55, PET, LIF 200 and LIF 220, allowing it to measure elements from B up to U. For Si the measurement method uses the PET crystal, setting the operational tube parameters at 30 kV and 130 mA. AAS measurements were carried out with a Seiko SAS 7500 Instrument of CEPROCOR.

Measurements and quantification

The XRF quantification method used in this work was designed to determine the most significant chemical components for quartz such as SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, MnO, CaO, K_2O, Na_2O, P_2O_5, S, Cl and elements that normally have low concentrations such as F, Ba, Sr, Rb, Y, Pb, Zn, Sn, W, Cu, V, As, Cr, Ni, Co and Cs. Quantification was carried out by comparison with certified standards and secondary standards made by mixing certified standards and high-purity oxides. The calibration straight line for each analyte was fitted using a set of standards that covered the main concentration range. Silicon was determined by difference. Figure 2 shows the detection limit as a function of analyte

atomic number in a quartz matrix. Detection limits were determined using the quantification method of this work. It can be seen this parameter is optimized for metals.

A total of 525 quartz samples were measured and quantified for all the above oxides and elements. The results obtained allow us to do a preliminary XRF selection of quartz samples (corresponding to 36 georeferenced sites) containing highest values of SiO_2. These samples were separated and sent for a complementary AAS analysis of Mg, Na and K owing to the high XRF detection limits. Finally, these AAS determinations were merged with XRF concentrations of the other elements, allowing us to recalculate by difference the SiO_2 concentration. Table 3 shows the results of chemical analysis for four quartz samples taken arbitrarily as an illustration. The elements not present in the analysis were not detected by XRF. Determination of Rb by AAS was performed for geological purposes not related to this work.

CONCLUSIONS

The results for the 525 samples analysed allowed us to make a geochemical ordering of quartz according to purity. This classification matched very well the geological categorization of quartz deposits. Figure 3 shows how the decreasing order SiO_2 concentration allows to group quartz in seven regional areas in good agreement with the geological genetics of the deposits setting. These areas are (1) Alpa Corral vein quartz, covering highest
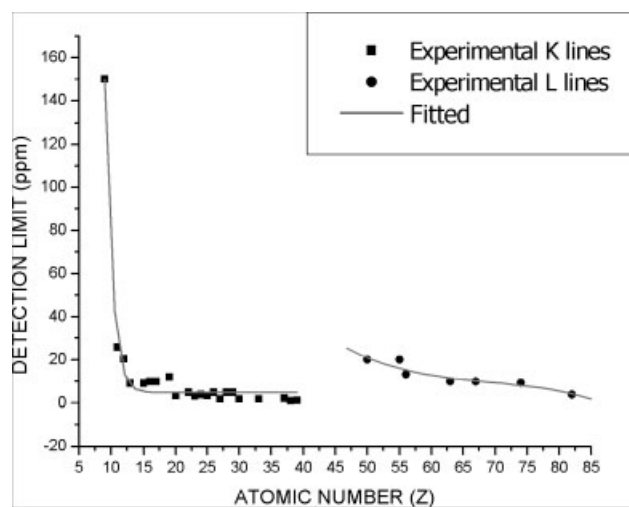

Figure 2. XRF detection limit as a function of analyte atomic number in a quartz matrix.

Table 3. Analysis of four quartz samples taken arbitrarily as an illustration

Sample	SiO_2 (%) (by difference)	Sr (ppm) (XRF)	Rb (ppm) (AAS)	Zn (ppm) (XRF)	TiO_2 (ppm) (XRF)	Al_2O_3 (ppm) (XRF)	Fe_2O_3 (ppm) (XRF)	MgO (ppm) (AAS)	CaO (ppm) (XRF)	Na_2O (ppm) (AAS)	K_2O (ppm) (AAS)
Q19	99.96	<LOQ[a]	0.42	3	<LOQ	<LOQ	23	98	18	133	98
Q30	99.97	4	0.11	<LOQ	<LOQ	21	34	109	<LOQ	98	16
Q40	99.97	<LOQ	0.29	3	<LOQ	50	33	55	<LOQ	62	29
Q134	99.97	4	0.15	<LOQ	14	<LOQ	29	91	15	46	34

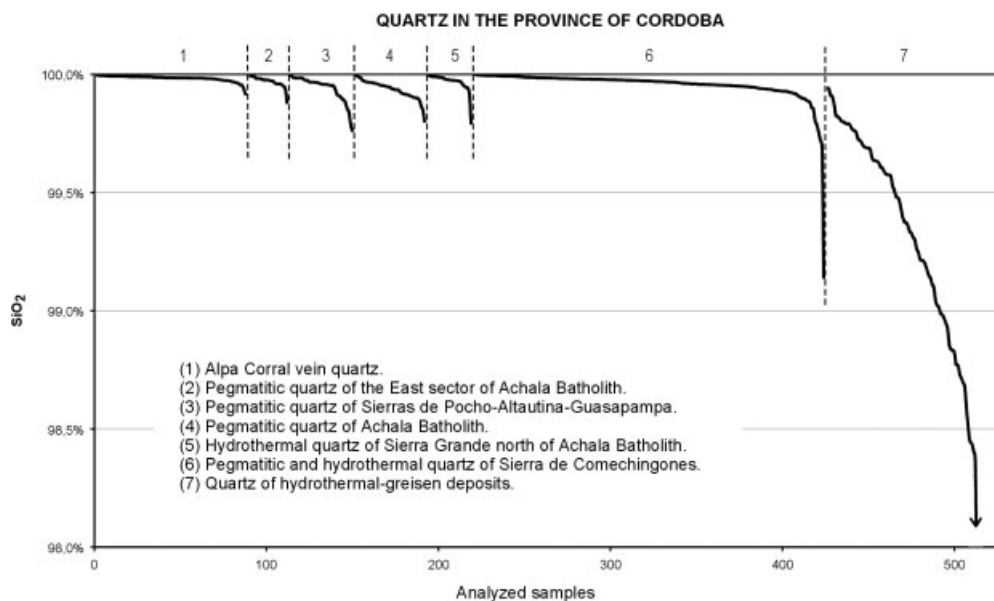[a] LOQ, limit of quantification for XRF.

Figure 3. Geochemical discrimination of quartz according to purity and geological setting of the deposits.

purity quartz in the central region of Argentina with average values of 99.97% for SiO_2, (2) pegmatitic quartz of the east sector of Achala Batholith, with an average concentration of 99.95%, (3) pegmatitic quartz of Sierras de Pocho–Altautina–Guasapampa, average value of 99.92%, (4) pegmatitic quartz of Achala Batholith, average value of 99.92%, (5) hydrothermal quartz of Sierra Grande north of Achala Batholith, average value of 99.95%, (6) pegmatitic and hydrothermal quartz of Sierra de Comechingones, average value of 99.94% and (7) quartz of hydrothermal–greisen deposits, having an average of 99.26% SiO_2, determining the lowest quality of quartz.

In the Sierras de Córdoba, good-quality quartz has been found. As a result of the studies performed on 141 quartz deposits sampled in the Province of Córdoba, 36 sites have been identified where the content of $SiO_2 \approx 99.97\%$. This highest purity quartz occurs mainly south of parallel 32 °S, in deposits of the Sierra de Comechingones (Fig. 1, types 1 and 6). The hosting deposits have been called here Alpa Corral quartz veins, the metamorphic basement being its host rock.

The quartz deposits located in the Achala Batholith have higher values of Al_2O_3 and in general all the quartz of pegmatitic origin are more impure. The content of Fe_2O_3 is low in almost all the quartz analysed, except those of the hydrothermal–greisen type, where there is an increase not only of Fe_2O_3, but also of Al_2O_3.

WDXRF has been demonstrated to be an excellent high-performance analytical technique for major, minor and trace elements in geochemical quartz mapping, except for low-Z oxides. The accuracy reached in the determination of oxides and trace elements was satisfactory for the purpose of this work aimed at obtaining a first geochemical distribution of quartz in Argentina. The geochemical information obtained in this work was sent to our regional and national authorities as a contribution to improving the industrial applications of quartz.[4]

Acknowledgements

REFERENCES

1. Gay HD, Sfragulla J. *I Reunión de Mineralogía y Metalogeni*. Instituto de Recursos Minerales, Universidad Nacional de La Plata: Argentina, Publication No. 2, 1992; 137–146.
2. Bonalumi A, Sfragulla JA, Simian G, Juri E, Sánchez J. *Unpublished report*, Dirección de Geología, Promoción e Industrias Mineras, Córdoba, Argentina, 1999; 1–22.
3. Galliski MA. '*Recursos Minerales de la República Argentina*, Instituto de Geología y Recursos Minerales–SEGEMAR, Anales 35, Zappettini EO (Ed), Buenos Aires, 1999; 361–364.
4. Bonalumi A, Sfragulla J, Pérez D, Rubio M, Guereschi A, López A, Gozalvez M. In *VII Argentinean Congress on Economics Geology*, Vol. 2. Asociación Argentina de Geólogos Economistas: Salta, Argentina, 2001; 97–109.