Geochemistry of hydrothermal kaolins in the SE area of Los Menucos, Province of Río Negro, Argentina

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Rhyolitic tuffs of the Sierra Colorada Fm (Triassic – Middle Jurassic) accommodate remarkable argillaceous mineralization with a zonation characterized by strong silicification at the upper levels, kaolinite, dickite and alunite at the intermediate levels, and sericitization at the bottom, where relicts of the original texture of the rock can be recognized.

The alteration process has wholly obliterated the original texture. Relicts of embayed quartz, phantoms of mafic minerals, defined by the precipitation of iron oxides, and feldspar pseudomorphically replaced by almost pure kaolinite and dickite with crystals that can be up to 70 μm in size, can be recognized.

Ore samples taken from a quarry about 15 meters in width were analyzed by XRD, TG-DTA, IR, SEM,EDAX and ICP. These methods allowed the identification of dickite, kaolinite and alunite occurrence.

Rare earth elements (REE) were analyzed showing a marked Eu negative anomaly, but no Ce anomaly, which would be typical of sedimentary deposits.

There is a close spatial relationship between kaolinite and dickite crystallization, which is concentrated at the intermediate levels. Alunite distribution is being concentrated at the most permeable sections.

The presence of dickite and alunite, the textures and values of REE support a hydrothermal origin. Ore-bearing fluids reached a quite acid pH, determined by the presence of alunite and temperatures of about 250°C, which allowed dickite crystallization.

1. INTRODUCTION AND GEOLOGIC SETTING

In this work kaolin mineralization, whose petrographic and mineralogical characteristics had been described by Maiza (1972) and Maiza et al. (1975), was studied. Its aim was to support the hydrothermal origin of the deposit based on a geochemical analysis.

An assemblage of vulcanites and tuffs and scarce clastic sedimentary rocks overlie the Mesozoic basement. The volcanic complex starts with a mesosiliceous lithology (mainly

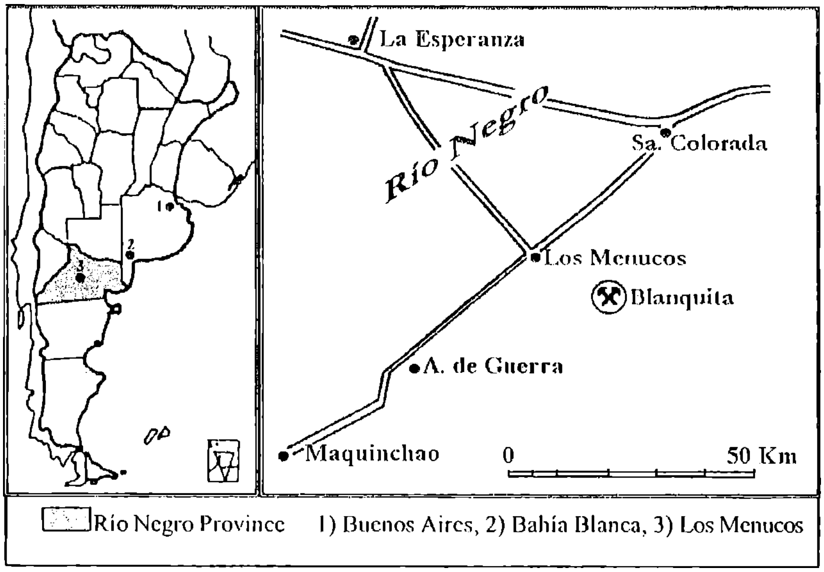

Figure 1: Location map.

andesites), defined as Los Menucos Formation. This formation is overlain by a sandy tuffaceous sequence rich in fossils, called Flora de Dicroidium Fm. It ends with a series of rhyolitic flows, ignimbrites and tuffs called Sierra Colorada Formation. This assemblage was subsequently termed Marifil Complex (Cortés 1981).

Blanquita is one of the main quarries of the so-called Blanquita - Don Sergio area. It is located at 30 km SE of the locality of Los Menucos (Province of Río Negro - Argentina). (Figure 1).

The kaolin mineralization occurs in rhyolitic tuffs from the Sierra Colorada Formation, of Triassic – Middle Jurassic age. The kaolinized zone lies between two impermeable rhyolitic flows that control the alteration process, with silicification in the upper rhyolite and weak argillization in the lower one.

The volcanic complex has undergone randomly oriented faults, although in Mina Blanquita it occurs in a predominantly NE – SW structure. This cracking developed a number of higher temperature centers in the area where kaolin enrichment occurs and are characterized by a mineralogy of dickite well crystallized kaolinite, alunite and pyrophyllyte.

In nearby regions it is possible to recognize fluorite veins, silicified structures with evidence of sulfides and dikes of andesitic-trachytic-rhyolitic lithologic composition, of uncertain age, though attributed to Late Mesozoic.

The mineralized area is about 5 to 8 km wide by approximately 20 km long and covers about 100 km^2. Furthermore, in the region of Los Menucos there are other two areas with similar characteristics but with lower temperature mineralogies. They are the so-called Adelita – Fortuna and Aguada de Guerra areas (5 km and 45 Km south of Los Menucos, respectively). In all the cases the rock that accommodates the mineralization is a rhyolitic tuff whose upper levels are silicified. These levels have protected the kaolinized areas.

Blanquita is an open pit quarry and its irregular shape indicates the presence of iron, the main impurity that has limited the exploitation of the kaolin ore.

Work was carried out at the upper part of the deposit, at a 15-meter high quarry. Marfil et al. (1999) identified dickite and alunite associated with kaolinite that had not been mentioned before.

2. MATERIALS AND METHODS

Eighteen (18) samples were collected from a quarry 15 meters in width. Vertical and horizontal sampling was performed.

Petrographic and mineralogical characteristics were studied using a petrographic microscope, X-ray diffraction, SEM, TG - DTA and IR. Determinations were performed on bulk samples on a Rigaku X-ray diffractometer D-Max III - C with Cu Kα radiation and a graphite monochromator at 35 kV and 15 mA; a scanning electron microscope JEOL JSM; a Rigaku simultaneous thermoanalyzer and a Perkin Elmer infrared spectrometer 599-B, with a scanning range between 4000 and 200 cm^{-1}. Chemical analysis of major and trace elements were performed by ICP in ACTLABS (Canada).

3. RESULTS

3.1 PETROGRAPHY AND MINERALOGY

Kaolinized bodies are emplaced within a rhyolitic tuff overlying porphyritic rhyolites with microcrystalline matrices, with abundant quartz, sanidine, plagioclase, hornblende and biotite (Figure 2a). Alteration is moderate, with sericitized and kaolinized feldspars and chloritized amphiboles and biotites. Zeolites are common in the matrices (Figure 2b). The tuffaceous level is of varying texture, from very fine-grained tuffs to conglomeratic types.

It is possible to observe strongly kaolinized zones obliterating textures where only original quartz and relict forms of tuffaceous components can be detected.

The upper level is a rhyolite with a felsic matrix, with relict volcanic glass, locally silicified with scarce phenocrysts. Cracked embayed quartz and scarce pseudomorphically replaced feldspar are identifiable (Figure 2c).

SEM observations showed large dickite crystal bundles in a well-crystallized kaolinite matrix (Figure 2d).

X-ray diffraction indicated that the samples are composed mainly of kaolin minerals (kaolinite - dickite), with varying amounts of quartz and scarce alunite. The latter was identified in the samples with higher kaolin minerals content. The richest zone is the upper-middle level of the profile.

The quarry mineralogy, determined by XRD, is shown in Figure 3. Samples 12, 13 and 14 correspond to a strongly silicified zone and sample 10 to the upper level of the sampled profile.

IR and TG -DTA were used to characterize the kaolin-group minerals. The infrared spectrum showed absorption bands at 3.698 cm^{-1}, 3.658 cm^{-1} and 3.620 cm^{-1} that are related to the H-O-H bond typical of kaolinite and dickite.

The differential thermal analysis showed an endothermic peak at 585°C related to kaolinite, with an inflection of the curve at 665°C due to the presence of dickite. The exothermic peak appears at 990°C.

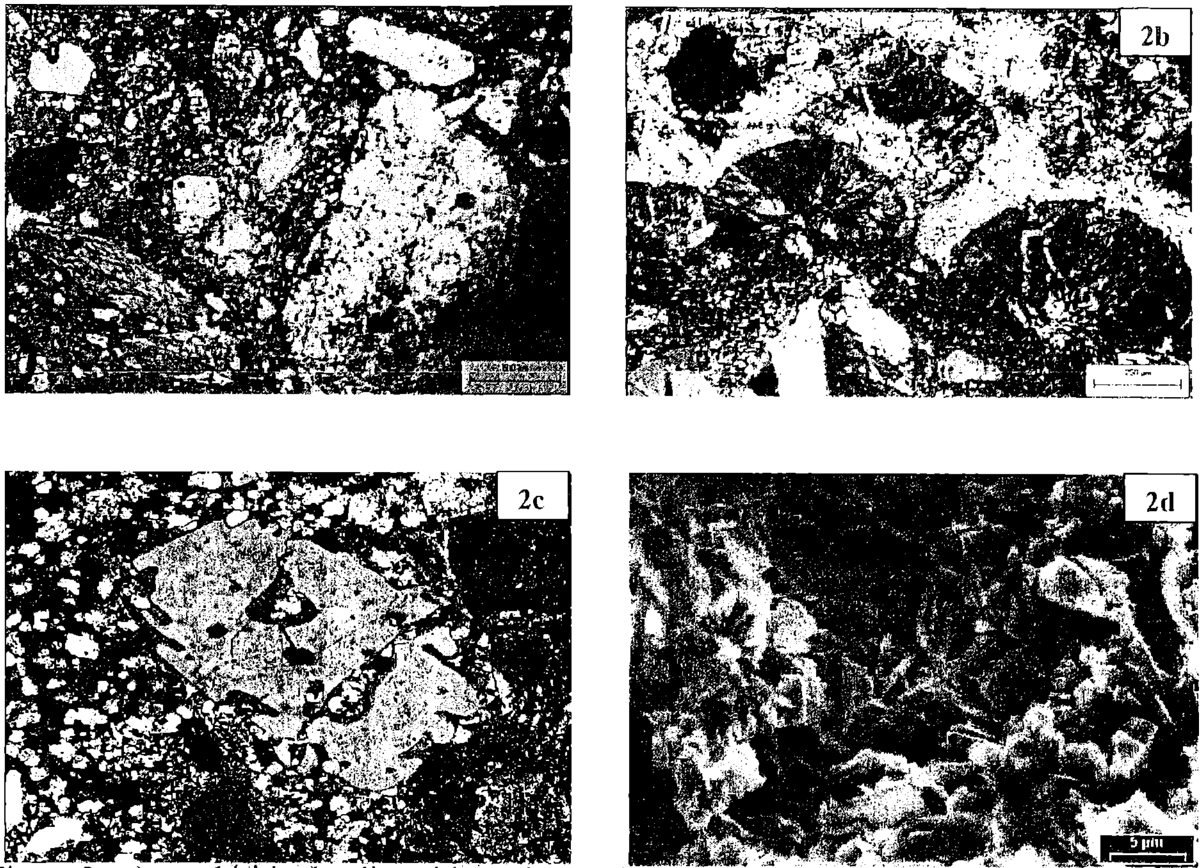

Figure 2. a) porphiritic rhyolite with moderate alteration, b) zeolites in the matrix, c) cracked embayed quartz, d) large dickite crystals in a kaolinite matrix.

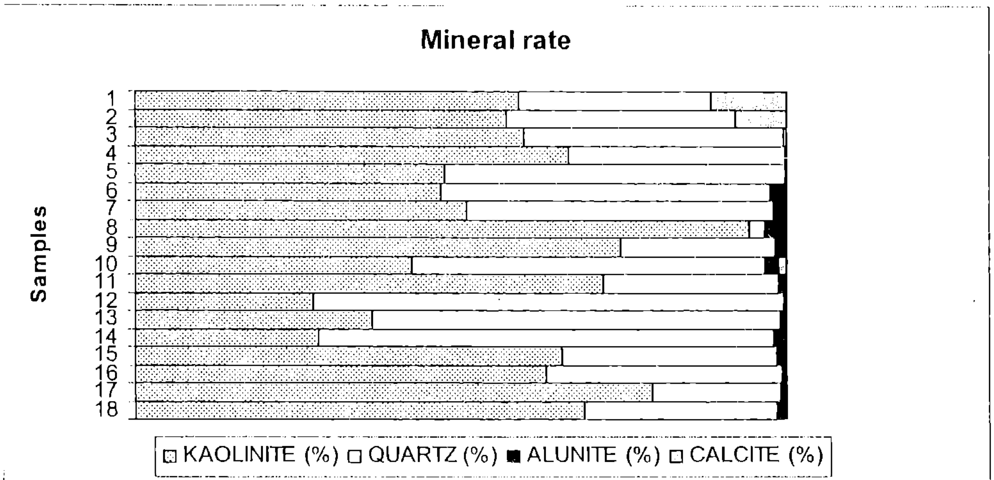

Figure 3: Quarry mineralogy.

3.2. CHEMICAL ANALYSIS

3.2.1 Major elements

From the analysis of major elements (Table 1) the kaolin minerals (kaolinite + dickite) content is calculated to range between 27 and 73 %. The samples with higher silica content correspond to the silicified zone. Sulfur allowed us to estimate an alunite content that varies between 0.3 and 2.1 %, which is closely linked to the most intense kaolinization.

Although major elements cannot be used as a guide to determine the source of mineralization, the increase in alumina content, which is close to theoretical values for pure kaolinite, and the decrease in alkalis are closely related to increased alteration.

Table 1. Chemical analysis of major elements on a whole rock (%).

Sample	$Si0_2$	Al_2O_3	Fe_20_3	MnO	MgO	Ca0	Na_2O	K_2O	TiO_2	P_2O_5	S	LOI
01	55.23	22.56	0.73	0.007	0.16	6.28	0.23	0.08	0.118	0.23	0.34	13.48
02	56.84	24.38	0.66	0.002	0.08	4.85	0.19	0.05	0.055	0.28	0.19	12.84
03	66.55	23.15	0.40	0.004	0.05	0.29	0.19	0.02	0.097	0.25	0.19	9.38
04	63.60	26.10	0.18	-	0.04	0.11	0.15	0.03	0.202	0.08	0.11	9.87
05	70.69	20.15	0.17	0.002	0.02	0.08	0.23	0.02	0.225	0.12	0.11	8.09
06	73.43	18.44	0.26	0.002	0.04	0.08	0.26	0.07	0.201	0.07	0.11	7.32
07	72.32	18.51	0.32	0.002	0.08	0.19	0.32	0.12	0.201	0.09	0.11	7.58
08	46.28	37.21	0.43	0.002	0.04	0.11	0.17	0.08	0.081	0.64	0.34	14.60
09	58.24	29.46	0.25	0.002	0.15	0.12	0.17	0.06	0.205	0.33	0.19	11.48
10	73.92	16.76	0.80	0.002	0.03	0.70	0.17	0.06	0.230	0.17	0.16	7.24
11	60.29	28.37	0.11	0.002	0.03	0.07	0.09	0.04	0.103	0.18	0.15	10.99
12	84.78	10.84	0.14	0.002	0.01	0.04	0.06	0.01	0.247	0.10	0.05	4.22
13	79.53	14.40	0.11	0.002	-	0.04	0.05	0.01	0.237	0.12	0.10	5.59
14	82.86	11.14	0.13	0.002	-	0.02	0.05	0.03	0.235	0.05	0.03	4.51
15	63.46	25.86	0.06	0.002	0.03	0.09	0.19	0.08	0.212	0.27	0.15	10.01
16	65.37	24.98	0.07	-	0.01	0.06	0.06	0.10	0.125	0.17	0.09	9.26
17	56.60	31.36	0.11	-	0.03	0.06	0.07	0.03	0.051	0.24	0.14	11.91
18	61.42	27.28	0.11	-	-	0.04	-	0.12	0.150	0.24	0.27	10.79

3.2.2 Trace elements

The results from trace elements for the analyzed samples are shown in Table 2 where their high content in Ba, Sr and As is apparent.

Table 2: Chemical analysis of trace elements (ppm).

Sample	Ba	Sr	Y	Sc	Zr	V	Cr	Ga	Ge	As	Nb	Mo	Ag
01	9041	1300	11	7	47	274	55	14	2	213	4	4	2
02	488	1509	10	7	33	126	58	12	2	166	3	5	1
03	1067	1479	3	17	58	82	170	13	3	295	4	17	6
04	372	1441	5	7	87	48	42	17	11	701	8	3	4
05	824	882	5	7	95	98	142	13	5	181	8	15	3
06	180	1390	5	8	88	71	74	14	6	624	8	6	1
07	214	1213	5	9	92	140	103	20	8	707	10	9	11
08	676	4457	6	10	52	249	56	34	4	650	3	0	0
09	1010	1929	7	7	79	76	88	28	5	585	9	4	3
10	714	1293	5	5	91	100	93	22	2	172	9	9	1
11	203	2315	2	12	47	75	64	26	9	686	2	3	21
12	90	1083	3	7	105	41	145	11	4	293	6	11	16
13	265	1716	4	8	101	57	93	12	4	503	6	7	16
14	100	335	3	5	110	28	85	10	3	215	6	6	12
15	432	1603	5	12	90	126	113	16	3	243	9	5	5
16	235	1023	3	9	65	67	32	14	3	140	3	0	12
17	140	3009	3	12	34	111	33	21	6	445	0	0	11
18	485	1898	2	11	65	164	0	27	4	218	5	0	5

3.2.3 Rare earths

The behavior of rare earth elements (REE) during the interaction of hydrothermal solutions with the country rock is not well known.

Michard (1989), concludes that hydrothermal solutions have low REE concentrations, about $5x10^2$ to 10^6 times less than the country rock. Therefore such hydrothermal activity will not vary the REE content of the solid unless the hydrothermal solution-country rock relation is very high. Furthermore, she noted that REE concentrations in hydrothermal fluids increase with the decrease in pH, regardless of the rock type or temperature. In this work it is also noted that Eu anomalies are restricted to high temperature solutions, rich in chlorides and with acid pH.

Chondrite-normalized results from samples of a cross section, following Boynton, (1984) (Rollinson H., 1992), are plotted and compared with fresh rock data in Figure 4.

REE are impoverished with respect to the country rock, with marked parallelism in element distribution. There is a small Eu negative anomaly. Although Ce behavior in marine environments is well known, Eu positive anomalies have been identified in weathering profiles related to laterites, (Rankin et al., 1976). Cravero et al. (2001) have detected a Ce positive anomaly in kaolin deposits in the Provinces of Chubut and Santa Cruz (Argentina) of sedimentary origin. No Ce anomaly is present in the analyzed samples from Blanquita.

4. DISCUSSION

Dill et al. (1997) discriminated between hypogene and supergene kaolinization using the relations between several elements present in kaolin (P vs. S, Zr vs. Ti, Cr + Nb vs. Ti + Fe, and Ce + Y + La vs. Ba + Sr). S, Ba and Sr are appreciably enriched in the kaolins developed during hydrothermal alteration, whereas Cr, Nb, Ti and lanthanide elements are concentrated mainly during weathering.

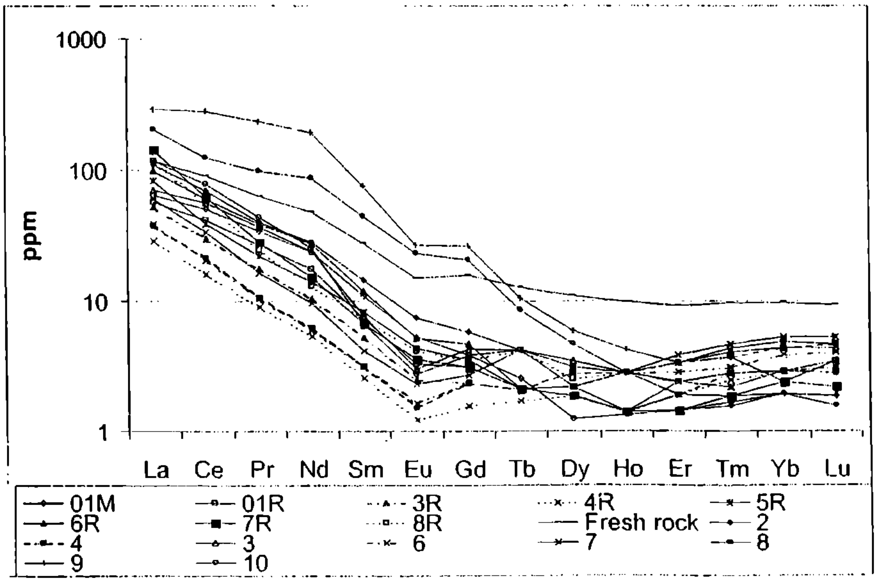

Figure 4: Chondrite-normalized REE profiles.

Dill et al. (2000) used binary diagrams to distinguish the origin of kaolin deposits for diagnostic major and trace elements. The results obtained for Zr versus Ti suggest that titanium is released from primary minerals during hypogene and supergene kaolinization. However, Ti concentration is much more effective during supergene kaolinization. By plotting Cr + Nb versus Ti + Fe contents it can be observed that kaolin deposits of supergene origin have high Cr and Nb values, while these values are low in hypogene type deposits. By plotting Ba + Sr versus Ce + Y + La contents, the authors observed that supergene deposits contain high amounts of Ce + Y + La, whereas hypogene deposits exhibit high Ba + Sr contents.

The results from Blanquita samples are plotted in the graphs shown in Figure 5. By a comparison with data published by Dill (2000), their hypogene origin becomes apparent.

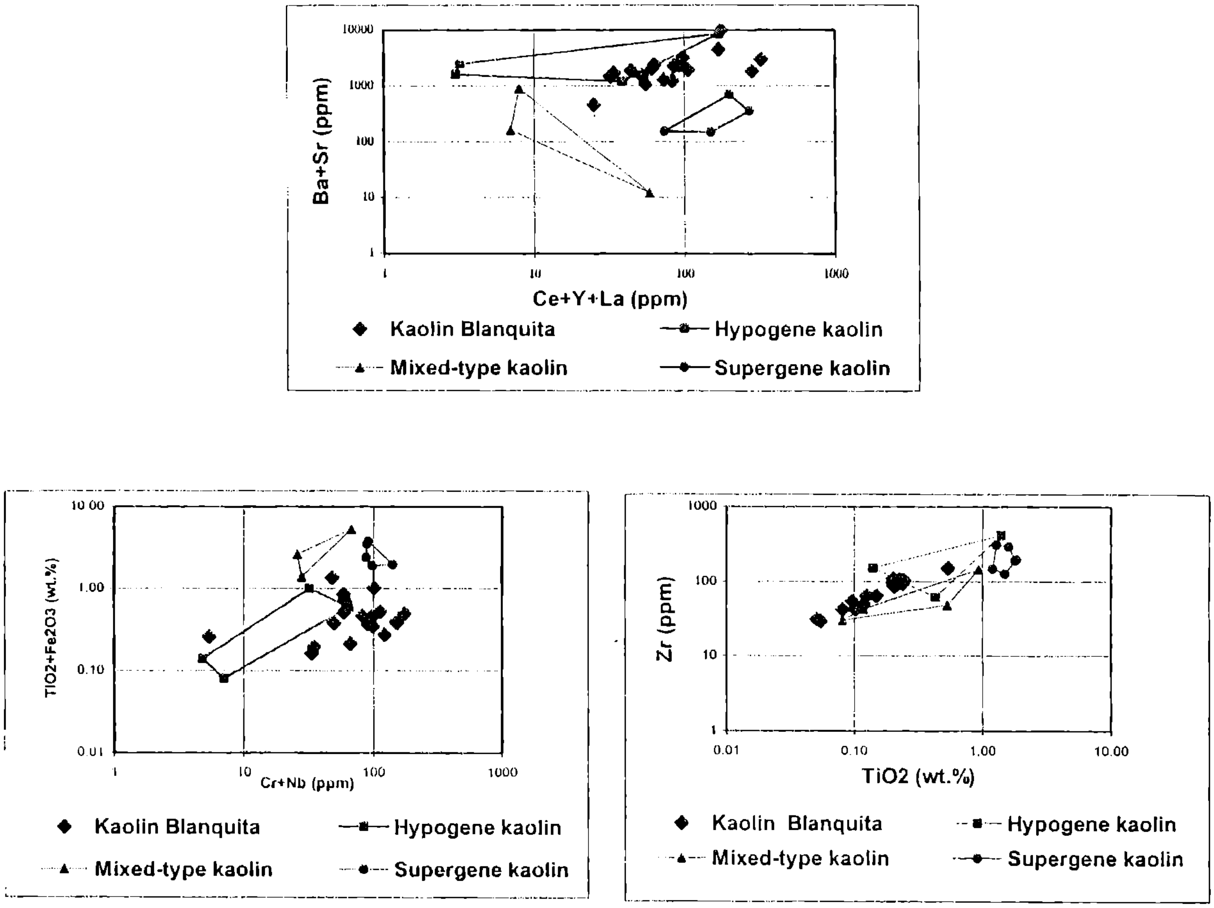

Figure 5: Cross plots to discriminate hypogene and supergene kaolin using major and trace element contents. a: Ba + Sr vs. Ce + Y + La. b: TiO_2 + Fe_2O_3 vs. Cr. c: Zr vs. TiO_2 (Dill et al. 2000).

CONCLUDING REMARKS

- The presence of well crystallized alunite, dickite and kaolinite, replacing feldspars, mafic minerals and rock matrix, and their arrangement in high purity veinlets give clear evidence for the development of hydrothermal activity.
- The ore shoot structure and heterogeneous mineralization relate the kaolinization process to the endogenous environment.
- Alunite-dickite association leads to an acid environment and temperatures above 270°C (Maiza, 1972).
- The high Sr, Ba and As contents and the low Ce content are clear indicators of hypogene origin for the mineralization of Mina Blanquita.
- The low $TiO_2 + Fe_2O_3$ vs. Cr + Nb relations and the Zr - TiO_2 relation contribute to support hydrothermal origin (Dill 2000).

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