

Origin of kaolin deposits in the ‘Los Menucos’ area, Río Negro Province, Argentina

S. A. MARFIL^{1,2,*}, P. J. MAIZA^{1,3}, E. CARDELLACH⁴ AND M. CORBELLA⁴

¹*Departamento de Geología, Universidad Nacional del Sur, San Juan 670, 8000 Bahía Blanca, Argentina,*

²*Investigador Independiente Comisión de Investigaciones Científicas de la Provincia de Bs. As., Argentina,*

³*Investigador Principal CONICET,* ⁴*Departamento de Geología, Universidad Autónoma de Barcelona, 08193 Bellaterra, Spain*

(Received 17 November 2004; revised 26 January 2005)

ABSTRACT: Kaolinite deposits, hosted by rhyolitic tuffs, are found in the SE of the ‘Los Menucos’ area (Province of Río Negro, Argentina). The most representative examples are from the Blanquita and Equivocada mines. To discover the origin of these deposits, a mineralogical, geochemical (major and trace element) and stable isotope study (O and H) of kaolinite was carried out. Mineralogically, Blanquita mine is characterized by the presence of dickite, kaolinite, alunite and pyrophyllite, whereas in Equivocada mine, kaolinite is accompanied by dickite and traces of alunite (without pyrophyllite). The trace element contents and ratios of kaolin samples (P vs. S, Zr vs. Ti, (Cr + Nb) vs. (Ti + Fe), and (Ce + Y + La) vs. (Ba + Sr)) suggest that they formed from the hydrothermal alteration of the enclosing rhyolites although a possible contribution of kaolinite from residual processes cannot be discounted. $\delta^{18}\text{O}$ values of kaolinite range from +4.8 to +10.3‰, and δD varies from –88 to –116‰. The presence of pyrophyllite in Blanquita mine suggests temperatures of formation >350°C. The calculated isotopic composition of the fluid in equilibrium with kaolinite at 350°C varies from +3.6 to +9.2‰ for O and from –74 to –103‰ for H. These values are compatible with fluids of magmatic origin or with fluids of surficial origin isotopically equilibrated with a rhyolitic magma at high temperatures. The isotope composition of kaolinite from the Blanquita and Equivocada mines is clearly different from kaolinite of residual origin from deposits in the Chubut and Santa Cruz provinces. The isotopic signature has proved to be a useful tool in discriminating between different genetic processes in the formation of kaolin deposits.

KEYWORDS: kaolin deposits, stable isotopes, trace elements, Argentina.

In Argentina, the most important kaolin deposits are found in the Santa Cruz and Chubut provinces (Fig. 1). Based on geochemical (trace element and stable isotopes) data, Cravero *et al.* (2001) suggested that these deposits are of residual and sedimentary origin, developed during the meteoric alteration of rhyolitic tuffs of Middle to Upper Jurassic age.

The Río Negro province is another region with significant potential as a kaolin producer. The most important known deposits are the Blanquita and Equivocada mines which are located in the Los Menucos area (Fig. 1). Unlike the Santa Cruz and Chubut deposits, the processes that led to the formation of these kaolin deposits are not well known.

From a genetic point of view, kaolin deposits can be classified in two broad groups: primary, of hydrothermal and residual origin, formed *in situ* by the alteration of crystalline rocks, and secondary, of

* E-mail: smarfil@uns.edu.ar

DOI: 10.1180/0009855054030172

sedimentary origin, usually produced from the deposition of kaolinite formed elsewhere (Murray, 1988). Although deposits of primary origin are more common, in many cases it is difficult to know what was the original process that led to the formation of a kaolin deposit as some hydrothermal and residual processes may develop under similar *P-T* conditions.

The combination of geochemical (major and trace element contents) and stable isotope (O and H) data from kaolin samples may provide information to help determine the genesis of the deposits. According to Dill *et al.* (1997) the P/S , Zr/Ti , $(Cr + Nb)/(Ti + Fe)$ and $(Cr + Y + La)/(Ba + Sr)$ ratios in kaolinites may discriminate between hypogenic and supergenic kaolinization processes. The stable isotope composition of kaolinites may also help to understand their origin, provided that the mineral retained the isotopic composition attained during formation (Savin & Lee, 1988; Sheppard & Gilg, 1996).

In the present work a mineralogical, geochemical (minor and trace element analysis) and stable isotope study was carried out on samples from the Blanquita and Equivocada mines in order to establish the conditions of formation and the origin of these deposits. Knowing the genesis of such deposits is crucial in order to establish exploration criteria and evaluate reserves. Finally, we compare our data with those of the known deposits from the Chubut and Santa Cruz provinces.

GEOLOGICAL SETTING AND MINERALOGY

The Blanquita and Equivocada mines are situated 30 km to the SE of Los Menucos (Fig. 1). The mineralized area is distributed along a belt 5–8 km wide and 20 km long with an approximate area of 110 km².

Geologically, the area is characterized by the presence of a set of volcanic rocks and tuffs with minor clastic sediments that overlie a basement of Mesozoic age, essentially constituted by granites. At the base, the volcanic complex is composed of andesites, which is known as the Los Menucos formation. This complex is followed by a succession of sandstone tuffs, rich in fossil plants (Dicroidium Flora formation) and finally by a suite of ignimbritic tuffs and flows known as the Sierra Colorada formation, deposited at the top of the series. The age of this volcano-sedimentary complex ranges from Triassic to Middle Jurassic.

Kaolinite deposits are enclosed in rhyolitic tuffs of the Sierra Colorada formation. An important silicification, developed at the top of the formation, seems to have protected the kaolinized areas from erosive processes giving rise to smooth elevations in the landscape (Fig. 2).

In the Blanquita mine area, the volcanic complex has been affected by several fracture events, developing a dominant structure trending NE–SW. Kaolinite mineralization appears as

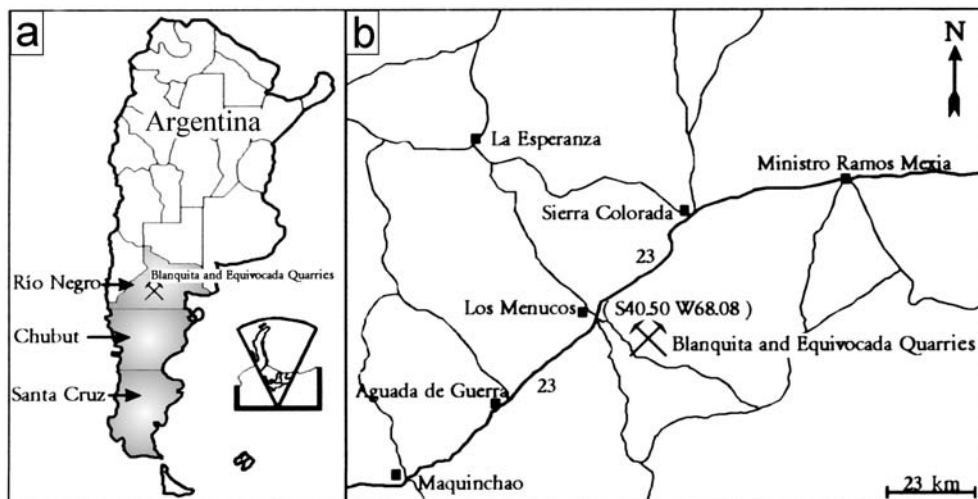


FIG. 1. Locations of the studied deposits.

irregular bodies spatially related to the fracture system. They are limited by two levels of rhyolitic lavas that apparently control the alteration processes that produced the silicification on the hangingwall rhyolite and a weak argillization on the footwall rhyolite (Maiza, 1972; Marfil *et al.*, 2000; Maiza *et al.*, 2003). The main mining work is currently situated at the top of the outcrop and has a front ~15 m thick.

The Equivocada mine has been exploited in two areas. The older workings were developed along a N145°/155° fracture. The morphology of the mineralized body is vein-like and was mined through an open pit. The present study was carried out along the current mining works, situated ~300 m to the NW and 40 m above the old workings.

Around these mineralizations, there are some small fluorite and sulphide-quartz veins, as well as dykes of andesitic, trachytic and rhyolitic composition, probably of Mesozoic age (Manera, 1972; Vallés, 1975; Malvicini & Valles, 1984). The possible relationship between these hydrothermal episodes and the kaolinization processes is not known.

Other smaller kaolinite deposits are known in the region. The most interesting are those at Adelita-Fortuna and Aguada de Guerra, situated 5 and 45 km south of Los Menucos, respectively. The geological setting is very similar to that of the

Equivocada and Blanquita mines although the mineralogy is different and they were not studied in the present work. The abundant kaolinite occurrences enhance the economic potential of the whole area.

SAMPLING AND ANALYTICAL METHODS

Eighteen samples from the Blanquita mine (abandoned quarry) and 13 from the Equivocada mine (currently active workings) were collected. A petrographical and mineralogical study of the samples was performed using polarized light microscopy and X-ray diffraction (XRD). Major, minor and trace elements were analysed by inductively coupled plasma spectrometry.

Twelve kaolinite samples (six from Blanquita and six from Equivocada) were selected for H and O isotope analysis. Because kaolinite isotope results can be affected by the presence of other phyllosilicates such as illite or illite-smectite (Harris *et al.*, 1999), only fractions of grain sizes between 2 and 0.2 μm were analysed, having previously been separated by standard centrifuge methods.

Stable isotope analyses were carried out at the LIE (University of Salamanca, Spain) and at the Activation Laboratories Ltd. (ACTLABS, Canada). The D/H ratios were determined following the method of Jenkin (1988). Kaolinite samples were

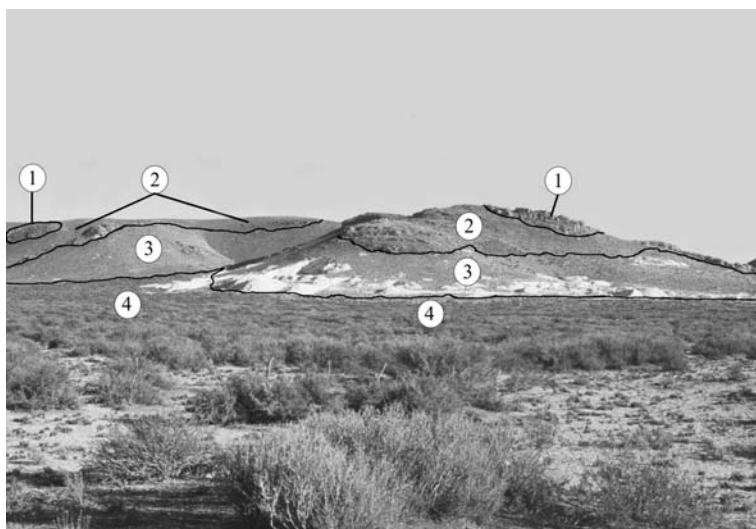


FIG. 2. General view of the Blanquita mine area. (1) rhyolite; (2) silicified zone; (3) kaolinized zone; (4) sericitized and chloritized zone; (2 + 3 + 4 = rhyolitic tuff).

heated up to 1500°C in Pt crucibles. Evolved H₂O was converted to H₂ in the presence of U. Oxygen was extracted by reaction of kaolinite with ClF₃ according to the method of Clayton & Mayeda (1963). Samples were pre-heated overnight at 110°C to eliminate absorbed water. The O and H isotope compositions were measured in a VG Sira II mass spectrometer. Results are presented as ‰ deviation with respect to SMOW. Reproducibility of results is better than ±0.5‰ for O and ±10‰ for H.

Petrography and mineralogy

The rhyolitic tuffs, which host most of the kaolinized bodies, were deposited on top of porphyritic rhyolites. The tuff is texturally variable, from fine-grained up to agglomerate levels, and shows a microcrystalline matrix with abundant quartz, sanidine, plagioclase, hornblende and biotite. Alteration is moderate with sericitization and kaolinization of feldspars and chloritization of amphiboles and biotites. Zeolites are also present in the matrix.

In some areas of the Blanquita mine, the kaolinization processes have completely obliterated the original textures of the rock, leaving only quartz and relicts of the tuffaceous components (Fig. 3a). The mineralogy, determined by XRD (Maiza, 1972; Marfil *et al.*, 2000), includes dickite, kaolinite, pyrophyllite, variable amounts of quartz and scarce alunite.

Similarly, in the Equivocada mine, alteration processes have almost erased the original texture and mineralogy of the tuffs. Only quartz and some

biotite remnants are still visible. The lithic clasts have been pseudomorphically replaced by kaolinite and dickite. The alteration mineralogy consists of a core of alunite grading outwards to an association of kaolinite-sericite, sericite-zeolite (Fig. 3b) and finally fresh rock (Hayase & Maiza, 1970). The whole mineralization was later discordantly overprinted by natroalunite (Maiza & Mas, 1981). The XRD analysis showed that the collected samples included kaolinite, quartz and minor amounts of alunite.

Chemical composition of kaolin

The kaolinite content of the samples, calculated from the mineralogical composition and major element analysis (Tables 1 and 2), ranged between 27 and 73% in Blanquita, and between 40 and 97% in Equivocada. Samples with a greater silica content correspond to the silicified zone of the deposits. The alunite content, estimated from the S concentration of the samples, varied from 0.3 to 2.1% in both deposits, the larger contents being related to the more intense kaolinization. On the other hand, an increase in the alumina content of the samples can be correlated to an increase in the degree of alteration of the fresh rock, reaching values close to theoretical ones for pure kaolinite (sample 08 in Blanquita and sample 01 in Equivocada). In these samples, the alkali content is also small. The concentrations of MnO and MgO in the samples analysed are <0.01 wt.%.

The trace element contents of kaolinite are presented in Tables 3 and 4. Kaolinites formed from hydrothermal alteration of acid-type igneous

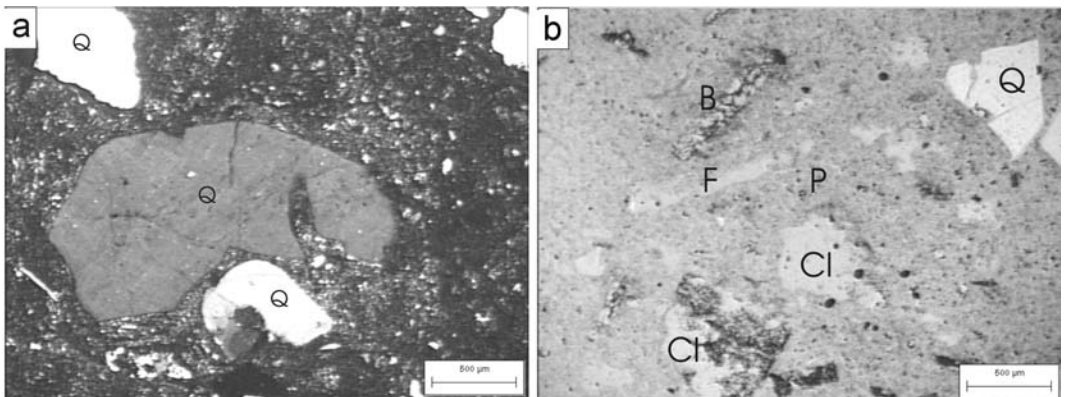


FIG. 3. Thin sections of altered tuff. (a) Kaolinized tuff from Blanquita mine. (Q: quartz crystals with cracks and embayments.) (b) Kaolinized tuff from Equivocada mine. (B: biotite, P: kaolinized matrix, Q: quartz, Cl: lithic clast, F: feldspar).

TABLE 1. Chemical analysis (wt.%) of major elements for whole-rock samples from the Blanquita mine.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	S	LOI
01	55.23	22.56	0.73	6.28	0.23	0.08	0.118	0.23	0.34	13.48
02	56.84	24.38	0.66	4.85	0.19	0.05	0.055	0.28	0.19	12.84
03	66.55	23.15	0.40	0.29	0.19	0.02	0.097	0.25	0.19	9.38
04	63.60	26.10	0.18	0.11	0.15	0.03	0.202	0.08	0.11	9.87
05	70.69	20.15	0.17	0.08	0.23	0.02	0.225	0.12	0.11	8.09
06	73.43	18.44	0.26	0.08	0.26	0.07	0.201	0.07	0.11	7.32
07	72.32	18.51	0.32	0.19	0.32	0.12	0.201	0.09	0.11	7.58
08	46.28	37.21	0.43	0.11	0.17	0.08	0.081	0.64	0.34	14.60
09	58.24	29.46	0.25	0.12	0.17	0.06	0.205	0.33	0.19	11.48
10	73.92	16.76	0.80	0.70	0.17	0.06	0.230	0.17	0.16	7.24
11	60.29	28.37	0.11	0.07	0.09	0.04	0.103	0.18	0.15	10.99
12	84.78	10.84	0.14	0.04	0.06	0.01	0.247	0.10	0.05	4.22
13	79.53	14.40	0.11	0.04	0.05	0.01	0.237	0.12	0.10	5.59
14	82.86	11.14	0.13	0.02	0.05	0.03	0.235	0.05	0.03	4.51
15	63.46	25.86	0.06	0.09	0.19	0.08	0.212	0.27	0.15	10.01
16	65.37	24.98	0.07	0.06	0.06	0.10	0.125	0.17	0.09	9.26
17	56.60	31.36	0.11	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

rocks show enrichments in S, Ba and Sr, whereas Cr, Nb, Ti and the lanthanides tend to concentrate in kaolinites formed from superficial (meteoric) processes (Dill *et al.*, 1997). P vs. S, Zr vs. Ti, (Cr + Nb) vs. (Ti + Fe), and (Ce + Y + La) vs. (Ba + Sr) plots are shown in Fig. 4.

The S content varies from 0.03 to 0.36 wt.% and the P₂O₅ content from 0.01 to 0.64 wt.% (Fig. 4a); this may reflect the presence of small amounts of alunite in the samples analysed. The Zr and Ti contents (Fig. 4b) show a positive linear correlation with greater values of both elements found in

samples from the Equivocada mine. The (Ti + Fe) contents are <1 wt.% and the (Cr + Nb) contents range from 0 to 174 ppm with no significant differences between samples from the two deposits (Fig. 4c). The (Sr + Ba) concentrations vary between 1000 and 10,000 ppm, with the larger values probably related to the presence of trace amounts of baryte (Fig. 4d). The (Ce + Y + La) concentration is also variable, from 3 to 323 ppm. Figure 4 illustrates that, from minor and trace element concentrations, kaolin samples from both deposits are almost indistinguishable.

TABLE 2. Chemical analysis (wt.%) of major elements for whole-rock samples from the Equivocada mine.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	S	LOI
01	45.36	40.17	0.10	0.06	0.09	0.00	0.017	0.35	0.21	14.21
02	50.22	35.90	0.22	0.05	0.03	0.06	0.237	0.37	0.18	13.08
03	55.94	32.05	0.03	0.06	0.02	0.04	0.318	0.31	0.16	11.37
04	60.56	27.71	0.07	0.06	0.05	0.18	0.308	0.46	0.36	10.70
05	76.44	16.13	0.18	0.05	0.03	0.01	0.578	0.21	0.14	6.45
06	69.19	21.72	0.17	0.05	0.03	0.03	0.494	0.17	0.09	8.35
07	70.76	20.82	0.15	0.06	0.02	0.01	0.575	0.07	0.03	7.89
08	51.86	34.52	0.09	0.06	0.02	0.06	0.289	0.26	0.14	12.76
09	52.06	33.98	0.12	0.12	0.02	0.06	0.171	0.52	0.25	12.93
10	76.25	16.87	0.24	0.06	0.00	0.04	0.524	0.21	0.09	6.18
11	60.34	31.49	0.02	0.18	0.00	0.09	0.381	0.20	0.08	5.98
12	71.81	16.04	0.04	0.03	0.00	0.06	0.564	0.14	0.12	11.47
13	46.75	39.07	0.04	0.05	0.02	0.01	0.013	0.01	0.03	14.15

TABLE 3. Chemical analysis (ppm) of trace elements in samples from the Blanquita mine.

Sample	Ba	Sr	Y	Sc	Zr	V	Cr	Ga	Ge	As	Nb	Mo	Ag	La	Ce
01	9041	1300	11	7	47	274	55	14	2	213	4	4	2	58	106
02	488	1509	10	7	33	126	58	12	2	166	3	5	1	93	180
03	1067	1479	3	17	58	82	170	13	3	295	4	17	6	34	56
04	372	1441	5	7	87	48	42	17	11	701	8	3	4	12	17
05	824	882	5	7	95	98	142	13	5	181	8	15	3	22	45
06	180	1390	5	8	88	71	74	14	6	624	8	6	1	12	17
07	214	1213	5	9	92	140	103	20	8	707	10	9	11	19	27
08	676	4457	6	10	52	249	56	34	4	650	3	0	0	63	100
09	1010	1929	7	7	79	76	88	28	5	585	9	4	3	91	225
10	714	1293	5	5	91	100	93	22	2	172	9	9	1	37	64
11	203	2315	2	12	47	75	64	26	9	686	2	3	21	20	41
12	90	1083	3	7	105	41	145	11	4	293	6	11	16	18	34
13	265	1716	4	8	101	57	93	12	4	503	6	7	16	16	24
14	100	335	3	5	110	28	85	10	3	215	6	6	12	9	13
15	432	1603	5	12	90	126	113	16	3	243	9	5	5	26	31
16	235	1023	3	9	65	67	32	14	3	140	3	0	12	31	49
17	140	3009	3	12	34	111	33	21	6	445	0	0	11	45	50
18	485	1898	2	11	65	164	0	27	4	218	5	0	5	36	45

O and H isotopes

The O and H stable isotope composition of 12 kaolinite samples is shown in Table 5. $\delta^{18}\text{O}$ and δD values of kaolinites range from +4.8 to +10.3‰ and from -88 to -116‰, respectively. While the O isotope composition is similar in both deposits, the δD values of Blanquita mine are slightly more negative. Both the $\delta^{18}\text{O}$ and δD values are clearly different from those reported by Cravero *et al.* (1991) in kaolinites from deposits of residual origin in the Santa Cruz and Chubut provinces ($\delta^{18}\text{O}$ from

+16.5 to +18.8‰ and δD from -57.5 to -86.5‰). In a later paper, Cravero *et al.* (2001) presented additional data from the Cerro Rubio and La Esperanza deposits in Santa Cruz province with kaolinites having $\delta^{18}\text{O}$ and δD values of +24‰ and -98‰, respectively.

According to Savin & Lee (1988), the isotopic composition of kaolinite may reflect the geological conditions during its formation, provided the mineral did not suffer isotopic changes after its deposition. Thus, the O isotope composition in

TABLE 4. Chemical analysis (ppm) of trace elements in samples from the Equivocada mine.

Sample	Ba	Sr	Y	Sc	Zr	V	Cr	Ga	Ge	As	Nb	La	Ce
01	455	3160	0	3	11	73	28	74	2	44	4	23	24
02	548	2890	6	11	119	212	44	81	7	7	7	43	70
03	749	1600	4	8	124	152	32	86	4	11	7	26	40
04	1840	2430	3	4	92	118	34	121	2	10	13	43	75
05	742	1060	5	6	191	73	90	60	2	12	0	38	69
06	233	695	4	7	176	25	44	30	2	103	15	60	106
07	57	278	5	8	229	40	77	27	2	11	9	35	65
08	696	1520	2	5	110	20	46	74	3	107	3	28	50
09	1080	3160	3	5	87	20	25	73	2	52	12	50	96
10	343	1240	5	6	235	21	0	31	1	29	8	44	79
11	932	1040	4	7	135	108	0	73	4	15	13	59	118
12	204	926	4	5	211	116	0	26	2	0	0	50	82
13	56	31	0	3	12	105	0	28	1	0	4	1	2

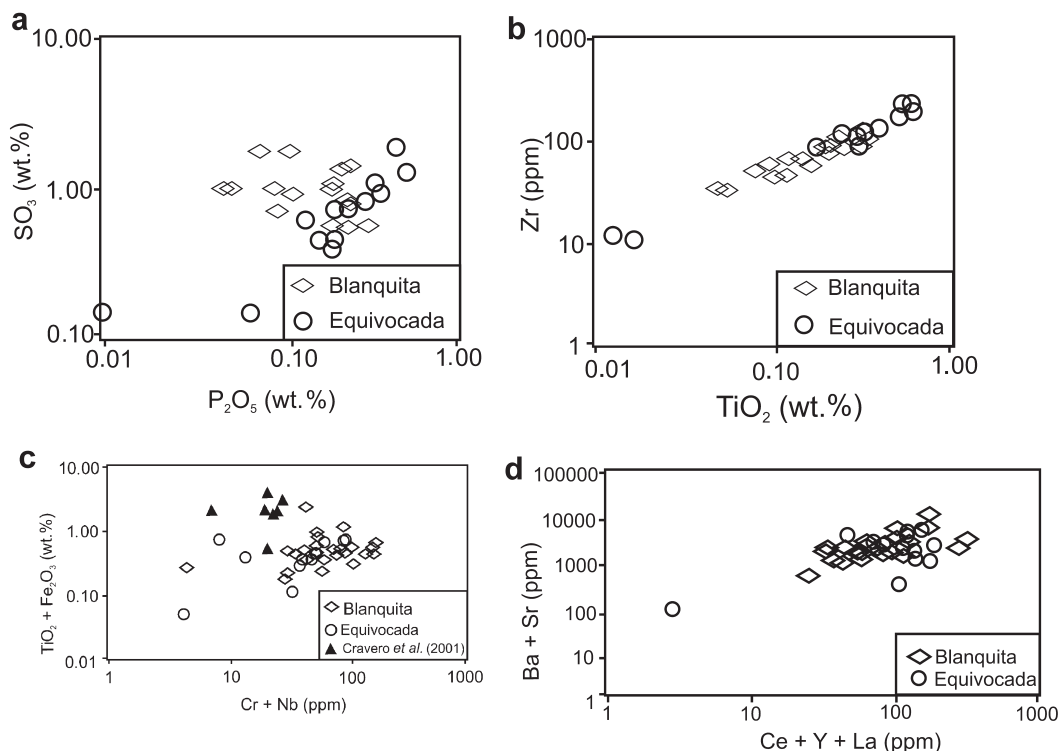


FIG. 4. (a) SO_3 vs. P_2O_5 data plot of samples from Blanquita and Equivocada mines. (b) Zr vs. TiO_2 data plot of samples from Blanquita and Equivocada mines. (c) $(\text{TiO}_2 + \text{Fe}_2\text{O}_3)$ vs. $(\text{Cr} + \text{Nb})$ data plot of samples from Blanquita and Equivocada mines and from Chubut and Santa Cruz kaolin deposits (Cravero *et al.*, 2001). (d) $(\text{Ba} + \text{Sr})$ vs. $(\text{Ce} + \text{Y} + \text{La})$ data plot of samples from Blanquita and Equivocada mines.

kaolinites of sedimentary origin usually varies from +19 to +23‰ and kaolinite from residual deposits has a $\delta^{18}\text{O}$ between +15 and +19‰ (Murray &

Janssen, 1984); these values are compatible with a meteoric origin at temperatures between 20 and 25°C. It is important to note that the $\delta^{18}\text{O}$ values of

TABLE 5. $\delta^{18}\text{O}$ and δD ‰ of kaolinite samples from the Blanquita (BL) and Equivocada (E) mines.

Sample	$\delta^{18}\text{O}_{\text{SMOW}}$	$\delta\text{D}_{\text{SMOW}}$	$\delta^{18}\text{O}(\text{fluid}-350^\circ\text{C})^*$	$\delta\text{D}(\text{fluid}-350^\circ\text{C})^*$
BL-0800	6.7	-116.3	6.3	-103
BL-0899	9.6	-116.6	9.2	-104
BL-0817	7.9	-115.1	7.5	-102
BL-0100	4.8	-88.0	4.4	-75
BL-0499	5.5	-93.0	5.1	-80
BL-0999	9.5	-88.0	9.1	-75
E-01	9.4	-94.2		
E-03	5.4	-105.1		
E-13	9.4	-96.2		
E-02	5.1	-96.0		
E-08	8.7	-90.0		
E-09	10.3	-94.0		

* Calculated from the fractionation equation of Sheppard & Gilg (1996)

the analysed samples (from +4.8 to +10.3‰) are much lower than those assumed for kaolinite deposits formed under superficial conditions, thus suggesting a different origin for the kaolinization fluids.

DISCUSSION

The trace element content and P vs. S, Zr vs. Ti, (Cr + Nb) vs. (Ti + Fe), and (Ce + Y + La) vs. (Ba + Sr) ratios (Fig. 4) of kaolin samples from Blanquita and Equivocada mines do not differ significantly. This suggests that both deposits might have formed by the same genetic process. However, although the (Ti + Fe) and (Sr + Ba) contents indicate a possible hypogenic origin (Dill *et al.*, 1997), the presence of large (Cr + Nb) and (Ce + Y + La) concentrations in some samples could indicate the presence of kaolinite of supergenic origin as well.

Titanium may be released from a primary mineral in the parent rock (e.g. biotite) during either hypogenic or supergenic kaolinization. However, as supergenic alteration seems to be more efficient, the Ti content in kaolinite has been used to discriminate between the two processes (Dill *et al.*, 1997). Because it behaves as a geochemically immobile element in superficial conditions, Zr is also a good indicator of the degree of meteorization of the parent rock. Consequently, kaolin samples with high Ti and Zr contents point to a superficial environment of formation.

Compared to hypogenic deposits, kaolin deposits of supergenic origin usually present higher concentration of Nb and Cr ((Cr + Nb) > 100 ppm). This is due to the concentration of Nb in Ti-bearing minerals and to the substitution of Ti in TiO₂ and of Fe in goethite by Cr during supergenic kaolinization. On the other hand, as Ti and Fe tend to concentrate preferentially in supergenic kaolin, the amount of (Ti + Fe) present in this type of deposit is usually > 1 wt.% (Dill *et al.*, 1997). The (Cr + Ni) vs. (Ti + Fe) ratios represented in Fig. 4c, show that most of the samples analysed plot below the values discussed above, i.e. they plot within the theoretical field for kaolinites of hypogenic origin.

The high Sr and Ba concentrations ((Sr + Ba) between 1000 and 10,000 ppm) are probably caused by the presence of baryte, a mineral usually found in kaolin deposits of hypogenic origin (Dill *et al.*, 1997). However, trace elements such as Ce, Y and La usually concentrate in kaolinite of supergenic

origin. In our case, the (Ce + La + Y) contents in the samples analysed are variable, reaching up to 550 ppm in the Blanquita mine (Fig. 4d and Table 3). Therefore, considering the trace element geochemistry, the wide range in and the large (Ce + Y + La) and (Nb + Cr) contents, especially in the Blanquita mine, this kaolinite is interpreted as the result of a mixture of kaolinites of hypogenic and supergenic origin in both deposits.

Although the (Ti + Fe) content in samples from the Blanquita and Equivocada mines is smaller than those reported by Cravero *et al.* (2001) in kaolinites of supergenic origin from Cerro Rubio (Santa Cruz Province, Patagonia) (see Fig. 4c), the (Cr + Nb) concentrations are similar. This implies that, in the studied deposits, the trace and minor elements content of kaolinites alone is not an adequate tool to discriminate definitively between hypogenic and supergenic processes and additional data are needed.

More information about the formation conditions of the studied deposits can be obtained from their mineralogy. Kaolin deposits of hydrothermal (primary) origin are constituted by kaolinite with minor amounts of halloysite, dickite and nacrite (Murray, 1988). However, in kaolin deposits of sedimentary (secondary) origin, dickite is uncommon. If this is the case, the presence of dickite in Equivocada and Blanquita would suggest a hypogenic origin with temperatures of formation between 100 and 400°C (Hanson *et al.*, 1981). This temperature range is compatible with the presence of pyrophyllite in the Blanquita mine as its lower temperature of formation is ~350°C with an upper stability limit of kaolinite (Spear, 1993).

In order to estimate the isotopic composition of fluids responsible for the kaolinization process a temperature of 350°C for Blanquita mine was assumed. Higher temperatures would not be reasonable as kaolinite coexists with pyrophyllite, and lower values would not be compatible with the presence of pyrophyllite. Thus, using the O isotope fractionation equation of Sheppard and Gilg (1996), the calculated $\delta^{18}\text{O}$ of the hydrothermal fluid in equilibrium with kaolinite in Blanquita mine, would have a value between +3.6 and +9.2‰. The δD of the fluid at the same temperature, calculated from the equation of Gilg & Sheppard (1996), would vary from -74 to -103‰. These values indicate that the O and H isotope composition of the fluids involved in the kaolinization process are of magmatic origin or of superficial origin but

isotopically equilibrated with magmatic rocks at magmatic temperatures. In any case, the calculated isotopic composition of fluids discards the involvement of meteoric waters at low temperatures. The present-day isotope composition of meteoric waters in the area is $\delta^{18}\text{O}$ of -7 to -6% and δD of -44 to -34% . These values do not differ significantly from the estimated isotope composition of meteoric waters during the Upper Jurassic–Lower Cretaceous ($\delta^{18}\text{O}$: -5.6 to -8.9% and δD : -28.4 to -58.25%), estimated by Cravero *et al.* (1991) from the isotope composition of residual kaolinite in deposits of the Chubut and Santa Cruz provinces.

Calculation of the isotope composition of fluids during kaolinite formation in the Equivocada mine is difficult. The absence of pyrophyllite in the deposit does not constrain the temperature as it only indicates that kaolinite formed below 350°C . As isotope fractionations are very sensitive to small changes in temperature, any assumed value would be of dubious value. However, similar geochemical and isotopic compositions of kaolinite from the two studied deposits seem to indicate that fluids in Equivocada mine might have a similar origin although the kaolinization process took place at lower temperatures.

The isotope composition of analyzed kaolinites, the calculated composition of fluid in equilibrium with kaolinite from Blanquita mine at 350°C and the kaolinite line corresponding to equilibrium with local meteoric water at 20°C are shown on a $\delta^{18}\text{O}/\delta\text{D}$ plot in Fig. 5. The isotope composition of the samples plots far from the kaolinite line. Kaolinites and calculated isotopic composition of fluids in equilibrium with the Blanquita mine kaolinites at 350°C plot close or within the magmatic water field, suggesting a magmatic origin for the hydrothermal fluids and reinforcing the hypothesis of a hypogenic origin for this deposit. The similar isotope signatures of Equivocada mine kaolinites suggest a related origin.

It is also important to note that $\delta^{18}\text{O}$ and δD of kaolinite vary in each deposit studied. These variations might be explained by any of the following reasons: (1) changes in temperature during the kaolinization processes; (2) changes in the isotopic composition of hydrothermal fluids during kaolinite precipitation; and (3) changes in the water:rock ratio during the alteration process. From the available data it is not possible to know which of these factors was dominant; moreover, a simultaneous effect cannot be discounted.

The $\delta^{18}\text{O}$ of sedimentary kaolinite from the Neuquén, Chubut and Santa Cruz provinces ranges from 16.1 to 18.8‰ (Cravero & Dominguez, 1999). These values are clearly greater than those obtained in samples from the Equivocada and Blanquita mines and confirm a different origin. These important differences demonstrate that, compared with the results obtained from minor and trace element chemistry of kaolin samples in the present case, the isotope composition of kaolinite allows a better discrimination between different genetic origins.

The combination of mineralogical, trace element and isotope data suggests that the kaolin deposits of the Los Menucos area (Blanquita and Equivocada mines) formed as a result of the circulation of hydrothermal fluids at elevated temperatures ($\geq 350^\circ\text{C}$) in the Blanquita mine, as reflected by the presence of pyrophyllite, and at lower temperatures (possibly 200°C ?) in the Equivocada mine. Mineralogical zoning in the Equivocada mine would be compatible with this model, where changes in pH and/or temperature of fluids would sequentially produce alunite, kaolinite and finally sericite. Compared with other kaolin deposits in Argentina (Cravero *et al.*, 2001), the ^{18}O -depleted

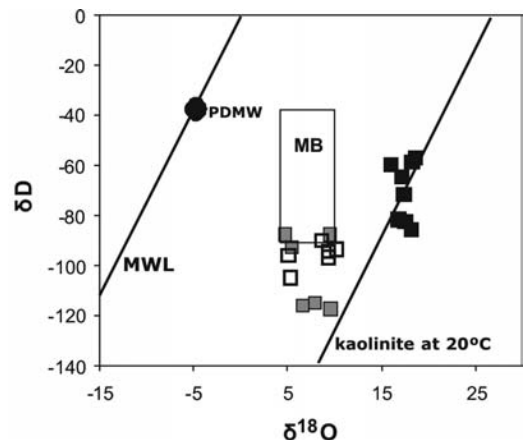


Fig. 5. $\delta^{18}\text{O}$ - δD plot with the isotopic composition of the kaolinites analysed. Open squares: Blanquita mine data. Grey squares: Equivocada mine data. Black squares: Chubut and Santa Cruz deposit data (Cravero *et al.*, 2001). MWL: meteoric water line. PDMW: present day meteoric water. MB: magmatic box; assumed isotopic composition for magmatic waters (Sheppard, 1986). Kaolinite at 20°C line: isotopic composition of kaolinite in equilibrium with meteoric water at 20°C .

values of kaolinite from the Los Menucos area could be explained by a different genetic process involving fluids at higher temperatures.

The occurrence of hydrothermal events in the region is also proven by the presence of fluorite and Pb-Cu-Zn veins (Labudia & Hayase, 1975). Fluorite veins are hosted by rhyolites presenting an alteration mineralogy with sericite, carbonates, silica and kaolinite (Labudia & Hayase, 1975). According to Manera (1972) and Hayase & Manera (1973), homogenization temperatures of fluid inclusions in fluorite are between 150 and 240°C (without correction for pressure). The presence of kaolinite and the formation temperatures of these veins suggest a possible relationship between fluorite-base metal veins and the studied kaolinite deposits of the area. In this case, kaolinite occurrences could be used as a prospecting tool for other types of mineral deposits in the region.

CONCLUSIONS

Mineralogical, geochemical and isotope study of the kaolin deposits of the Blanquita and Equivocada mines led to the following results: (1) The kaolinite deposits of the Blanquita and Equivocada mines consist of a set of irregular bodies and veins developed on tuffs of rhyolitic composition. (2) The clay minerals present in the Blanquita mine include dickite, kaolinite, alunite and pyrophyllite with a zonal distribution of these minerals. Alunite tends to be found in the core and kaolinite in the outer margins of the bodies. In the current mining works of Equivocada mine, kaolinite is accompanied by dickite and small amounts of alunite (without pyrophyllite). (3) The trace element contents of the kaolin samples in both deposits are very similar. Most of the comparative diagrams (P vs. S, Zr vs. Ti, (Cr + Nb) vs. (Ti + Fe), and (Ce + Y + La) vs. (Ba + Sr) suggest that kaolinite formed from hydrothermal alteration of rhyolites. However, the high (Nb + Cr) and (Ce + Y + La) contents do not exclude the presence of kaolinite of residual origin. (4) $\delta^{18}\text{O}$ of kaolinite ranges from +4.8 to +10.3‰ and δD from -88 to -116‰, values far from those reported by Cravero *et al.* (1999) in deposits of residual origin from the Chubut and Santa Cruz provinces. As the presence of pyrophyllite in the Blanquita mine indicates temperatures of formation of at least 350°C, the calculated isotope composition of fluids in equilibrium with kaolinite varies from +3.6 to +9.2‰ for O and from -74 to

-103‰ for H. These values are compatible with hydrothermal fluids of magmatic origin or with fluids of superficial origin isotopically equilibrated with the magmatic rocks at high temperatures. (5) The combination of trace element and O and H isotope data suggests that kaolinite deposits of the Los Menucos area formed because of the circulation of hydrothermal fluids, discounting superficial processes at low temperatures. The deposits studied might be related to larger hydrothermal systems that would have also caused the precipitation of fluorite and base metal veins in the district as described by Labudia & Hayase (1975). If this hypothesis is correct, kaolinite occurrences might be useful in prospecting mineralized vein systems in the area. (6) Compared to the other techniques used, isotope analysis (O and H) has proved to be the best method to characterize the genetic processes in kaolinite formation.

ACKNOWLEDGMENTS

The authors wish to thank the Comisión de Investigaciones Científicas, the Departamento de Geología de la UNS and CONICET for their support during the research.

REFERENCES

- Clayton R.N. & Mayeda T.K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, **27**, 43–52.
- Cravero F. & Dominguez E. (1999) Origin of sedimentary kaolin in the Neuquén basin, Argentina as determined by oxygen isotopes. *Periodico di Mineralogia*, **68**, 213–222.
- Cravero F., Dominguez E. & Murray H. (1991) Valores δO^{18} y δD en caolinitas indicadoras de un clima templado-húmedo para el Jurásico superior-Cretácico inferior de la Patagonia. *Revista de la Asociación Geológica Argentina*, XLVI (1-2), 20–25.
- Cravero F., Domínguez E. & Iglesias C. (2001) Genesis and applications of the Cerro Rubio kaolin deposit, Patagonia (Argentina). *Applied Clay Science*, **18**, 157–172.
- Dill H., Bosse R., Henning H. & Fricke A. (1997) Mineralogical and chemical variations in hypogene and supergene kaolin deposits in a mobile fold belt the Central Andes of northwestern Peru. *Mineralia Deposita*, **32**, 149–163.
- Gilg H. & Sheppard S. (1996) Hydrogen isotopic fractionation between kaolinite and water revisited.

- Geochimica et Cosmochimica Acta*, **60**, 529–533.
- Hayase K. & Maiza P. (1970) Génesis del yacimiento de caolín 'Mina Equivocada' Los Menucos, Prov. de Río Negro, República Argentina. *Revista de la Asociación Argentina de Mineralogía Petrología y Sedimentología I*, (1–2), 33–34.
- Hayase K. & Manera T. (1973) A statistical analysis of experimental data on filling temperature of fluid inclusions in fluorite from fluorite deposits of Patagonia Argentina. *Mining Geology, Japan*, **23**, 1–2.
- Hanson R.F., Zamora R. & Keller W.D. (1981) Nacrite, dickite and kaolinite in one deposit in México. *Clays and Clay Minerals*, **29**, 451–453.
- Harris C., Compton J.S. & Bevington S. (1999) Oxygen and hydrogen isotope composition of kaolinite deposits, Cape Peninsula, South Africa: low temperature, meteoric origin. *Economic Geology*, **94**, 1353–1366.
- Jenkin G.R.T. (1988) *Stable isotope studies in the Caledonides in SW Connemara, Ireland*. PhD thesis, University of Glasgow, UK.
- Labudia C. & Hayase K. (1975) Relaciones entre las rocas y las mineralizaciones de Pb-Cu-Zn, fluorita y caolín de los alrededores de Los Menucos, Prov. de Río Negro, Argentina. *Sexto Congreso Geológico Argentino, Actas, Bahía Blanca*, III, pp. 69–80.
- Maiza P. (1972) *Los yacimientos de caolín originados por la actividad hidrotermal en los principales distritos caoliníferos de la Patagonia, República Argentina*. Tesis Doctoral, Universidad Nacional del Sur, Argentina.
- Maiza P. & Mas G. (1981) Presencia de natroalunita en Mina Equivocada, Río Negro. Su significado. *VIII Congreso Geológico Argentino, San Luis, Actas*, IV, pp. 285–292.
- Maiza P.J., Pieroni D. & Marfil S.A. (2003) Geochemistry of the hydrothermal kaolins in the SE area of Los Menucos. Prov. de Río Negro. *A Clay Odyssey – Proceedings of the 12th International Clay Conference, Argentina, 2001*. Elsevier, Amsterdam, pp. 123–130.
- Malvicini L. & Vallés J.M. (1984) Metalogénesis. Capítulo III-5. Geología y recursos naturales de la Provincia de Río Negro. *Relatorio del IX Congreso Geológico Argentino, San Carlos de Bariloche, Río Negro, Argentina*, pp. 649–662.
- Manera T. (1972) *La mineralización de los yacimientos de fluorita de la Provincia de Río Negro*. Tesis Doctoral, Universidad Nacional del Sur, Bahía Blanca, Argentina.
- Marfil S.A., Pieroni D. & Maiza P.J. (2000) Dickita y alunita en mina Blanquita, Los Menucos (Provincia de Río Negro). *V Congreso de Mineralogía y Metalogenia. MINMET 2000, La Plata, Argentina*, pp. 281–286.
- Murray H.H. (1988) Kaolin minerals: their genesis and occurrences. Pp. 67–89 in: *Hydrous Phyllosilicates (Exclusive of Micas)* (S.W. Bailey, editor). Reviews in Mineralogy, **19**, Mineralogical Society of America, Washington, D.C.
- Murray H. & Janssen J. (1984) Oxygen isotopes – indicators of kaolin genesis? *Proceedings of the 27th International Geological Congress*, **15**, 287–303.
- Savin S.M. & Lee S. (1988) Isotopic studies of phyllosilicates. Pp. 189–223 in: *Hydrous Phyllosilicates (Exclusive of Micas)* (S.W. Bailey, editor). Reviews in Mineralogy, **19**, Mineralogical Society of America, Washington, D.C.
- Sheppard S.M.F. (1986) Characterization and isotopic variations in natural waters. *Stable Isotopes in High-Temperature Geological Processes* (J.W. Valley, H.P. Taylor, Jr. & J.R. O'Neil, editors). Reviews in Mineralogy, **16**, Mineralogical Society of America, Washington, D.C.
- Sheppard S.M.F. & Gilg H.A. (1996) Stable isotope geochemistry of clay minerals. *Clay Minerals*, **31**, 1–24.
- Spear F.S. (1993) *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*. Monograph 1, Mineralogical Society of America Memoir, Washington, D.C., 799 pp.
- Vallés J.M. (1975) Contribución a la metalogénesis de la Provincia de Río Negro. *Actas del Sexto Congreso Geológico Argentino, Bahía Blanca, Argentina*, pp. 179–200.