

Geochemistry of Hydrothermal Alteration in Volcanic Rocks

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1. Introduction

Hydrothermal alteration is a chemical replacement of the original minerals in a rock by new minerals where a hydrothermal fluid delivers the chemical reactants and removes the aqueous reaction products. An understanding of hydrothermal alteration is of value because it provides insights into the chemical attributes and origins of ore fluids and the physical conditions of ore formation (Reed M. 1997).

Within a mineral deposit, the solution channelways are usually obvious because precipitated minerals and altered wallrocks remain as evidence. The direction in which the solutions flowed, especially in flat-lying deposits, is usually less obvious but in many cases can be inferred from mineral zoning or similar evidence (Skinner B. 1997).

The mobility of major, minor and rare-earth elements (REE) during alteration processes in different environments has been documented by numerous authors and has been used to discriminate the origin of kaolin deposits. (Sturchio et al., 1986; De Groot & Baker, 1992; Gouveia et al., 1993; van der Weijden & van der Weijden, 1995; Condie et al., 1995; Dill et al., 1997, 2000; Galán et al., 1998, 2007; Pandarinath et al., 2008, among others). Terakado & Fujitani (1998) studied the REE and other trace elements in silicstones, alunites and related rocks in order to examine the behaviour of trace elements in the acidic hydrothermal alteration of silicic volcanic rocks. They found that most of the elements such as Na, Fe, Ba and LREE were leached from the silicstones, while HREE, Th, Hf and Zr were retained in the rocks, even under strongly acidic hydrothermal processes. Alunite samples have LREE-enriched and HREE-depleted features. According to Dill et al. (1997), the ratios $TiO_2 + Fe_2O_3$ vs. $Cr + Nb$, Zr vs. TiO_2 and $Ba + Sr$ vs. $Ce + Y + La$ in kaolinities allow discrimination between hypogene and supergene kaolinization processes. The APS-bearing argillaceous zones that formed during supergene processes are significantly enriched in REE relative to hypogene equivalents (Dill, 2000).

Pandarinath et al. (2008) studied the effects of hydrothermal alteration on major, rare-earth, and other trace-element concentrations in rhyolitic rocks of the Los Azufres geothermal field, Mexico. They concluded that the hydrothermal alteration resulted in a decrease in MnO , P_2O_5 , Ta, Rb/Zr and Rb/Nb, and an increase in Zr, Nb and Nb/Y. The greater variances of Y, Ce, Pr, Nd, Sm, Lu and Pb in altered rocks are probably due to hydrothermal

processes, whereas smaller variances of CaO, Sr, Rb/Sr and Rb/Ba in altered rocks suggest that these processes led to more uniform chemical rock compositions. The concentrations of REE were not significantly different between fresh and altered rhyolitic rocks, which implies that either these elements remained immobile or were reincorporated into secondary minerals during the hydrothermal alteration of the rhyolitic rocks.

Papoulis & Tsolis-Katagas (2008) studied kaolin deposits in the western and southern parts of Limnos Island, northeast Aegean Sea, Greece, and they found two types of hydrothermal alteration zones: smectite-illite-halloysite and kaolinite-dickite-rich zones. Mineral assemblages reveal that temperatures ranged from <100°C (smectite-rich and halloysite rich zones) to ~270°C (kaolinite-dickite-rich zones). Limited supergene alteration was observed in the less hydrothermally altered rocks of the illite-rich zones as suggested by the presence of jarosite and pyrite. The development of the various assemblages depends not only on the temperature and composition of the hydrothermal fluids but also on the distance of the rock from the fault or the channel of the ascending hydrothermal fluids. Papoulis et al. (2004) used the K and Na content in a kaolin deposit from Greece to measure the degree of alteration of primary rocks. The positive correlation between Al₂O₃ and LOI and the large negative loadings between SiO₂-Al₂O₃ and SiO₂-LOI indicate that LOI and Al₂O₃ contents increase in the more altered samples.

Ece et al. (2008) studied acid-sulphate hydrothermal alteration in andesitic tuffs in the Biga Peninsula (Turkey), and concluded that changes in the chemical composition of geothermal waters through time and the chemistry of the intermediate products in clay deposits also control the formation of alunite. The main geothermal activity and acidsulphate alterations for the mineralizations of alunite and halloysite occurred after the onset of NAF-related faulting in the Biga Peninsula. The P₂O₅ enrichment in alunite nodules suggests a deep magmatic source for the geothermal waters that passed through the shallow-level granodiorite intrusions.

The minerals that constitute various alteration assemblages depend on: temperature, pressure, primary rock composition, primary fluid composition and the ratio of fluid to rock in the reaction that produced the alteration. (Reed M. 1997).

The aim of the study described in this chapter was to evaluate the relation between the chemical composition of major, minor and trace elements, the stable isotopes in kaolin (O and D) and the mineralogical alteration zonation to confirm the hydrothermal genesis of the deposits, working with volcanic rocks from Patagonia Argentina.

Knowing the genesis of such deposits is crucial in order to establish exploration criteria and evaluate reserves. These Patagonian deposits are derived from Mesozoic rhyolitic and andesitic rocks. There have been several studies aimed at discovering the origin of the primary deposits (Domínguez & Murray, 1995, 1997; Cravero et al., 1991, 2001; Domínguez et al., 2008, Marfil et al., 2005). Most of the studies deal with the mineralogy, chemical composition, the deposit structure and oxygen-deuterium isotopic data.

The deposits examined in this study are located in different areas of Patagonia in the Provinces of Río Negro and Chubut and they are studied by Cravero et al. (2010), Maiza et al. (2009) and Marfil et al. (2005, 2010).

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

Vera 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 altered areas from erosive processes giving rise to smooth elevations in the landscape.

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.

2. Geological setting

The deposits examined in this study are hydrothermal origin, located in the provinces of Río Negro (Blanquita, Equivocada and Loma Blanca mines) and Chubut (Estrella Gaucha mine) (Patagonia, Argentina) (Fig. 1).

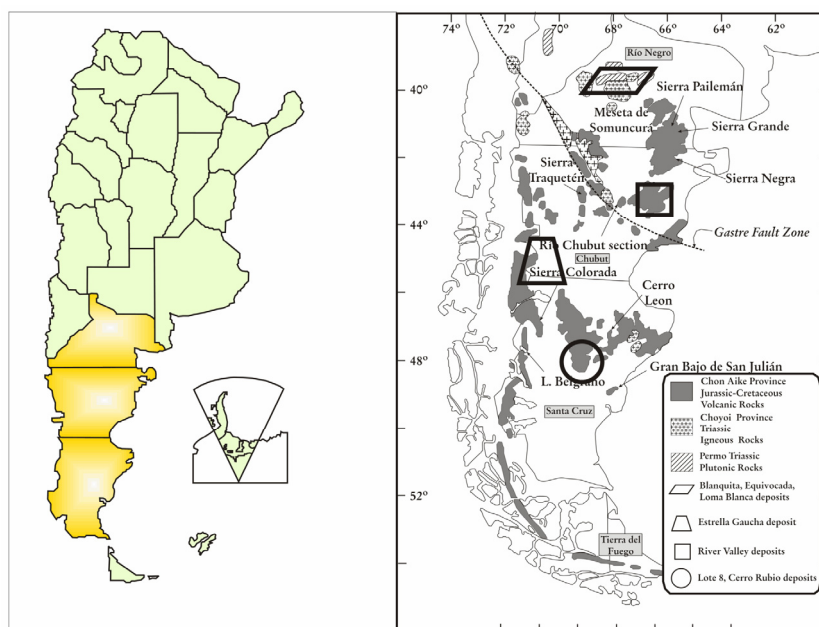


Fig. 1. Localization of the kaolin deposits in a sketch map of Patagonia (Cravero et al. 2010, modified).

In the provinces of Chubut and Santa Cruz there are many kaolin deposits, some of them very extensive, located in the Chubut river valley and lote 8, 18, 19 and Cerro Rubio respectively. These deposits are sedimentary and residual origin, formed from the alteration of volcanic materials, especially Jurassic rhyolitic tuffs.

In the province of Chubut there is another group of kaolin deposit related with hydrothermal alteration. Estrella Gaucha mine is one of them. It is situated in western Chubut Province, 70 km from Alto Río Senguer and 20 km from Aldea Apeleg. It is located at SW from Cerro Bayo at 1620 meters above sea level. Ploszkiewicz & Ramos (1977), found andesites and dacites of Ñirehuao Formation and dacitic ignimbrites of Gato Formation. These volcanic rocks are Cretaceous age. The outcropping rocks in the area studied are conglomeratic sandstones with moderate alteration and stratified. In their composition are common rhyolites, andesites and siliceous sandstones. These rocks are the base of the deposit. Iron oxides are abundant and they are chloritized. The lithic components are selectively altered related with the textures and mineralogical composition. It is possible to observe particles replaced pseudomorphologically by chlorite, kaolinite, alunite and quartz. Some grains conserve the original textures while in others the replacement is massive forming monomineral particles. The mineralization is developed from the alteration of rhyolitic tuffs of the Lower Cretaceous Payaniyeu Formation in contact with tuff sandstone of Apeleg Formation. The relation between both Formations is not clear because the alteration processes developed in the transition zone (Ploszkiewicz & Ramos 1977). The mineralogy consists mainly of dickite with rare alunite and variable amounts of quartz distributed in four alteration zones, from a silicified upper zone, grading downwards to an alunite zone, then a kaolinized zone and, finally, a sericite-chlorite zone (Hayase et al. 1971, Maiza 1972, 1981, Maiza & Hayase 1975 and Maiza et al. 2009). (Fig 2a)

The Chubut River Valley deposits and those of the Santa Cruz province are developed on Jurassic volcanic rocks which are predominantly rhyolitic and form one of the world's most voluminous silicic provinces (Pankurst & Rapela, 1995). It is called Chon-Aike Province (Pankurst et al., 1998), which ranges in age from Early Jurassic to Early Cretaceous. This province comprises several formations that, depending on the geographical locality, receive different names (Marifil and Chon-Aike, among others). In Chubut, the deposits were formed on the Marifil Formation (Malvicini & Llambias, 1974) and are found along the Chubut River in an area of ~60 km². In Santa Cruz, the primary deposits came from the alteration of rhyolitic ash-fall tuffs and ignimbrites of the Chon-Aike Formation which formerly belonged to the Bahía Laura Group) (Domínguez & Murray, 1997; Cravero et al., 2001). In both the Marifil and Chon-Aike rocks, the kaolinized areas have a wide horizontal extension, limited thickness (8-12 m at most) and a downward decreasing degree of alteration. The mineralogical composition is kaolinite with minor halloysite, illite and relict quartz and feldspars (Domínguez & Murray, 1997; Cravero et al., 2001; Domínguez et al., 2008). Table 1 synthesizes the geology and mineralogy of the deposits (Cravero et al. 2010).

Blanquita and Equivocada mines are situated 30 km SE of Los Menucos in the province of Río Negro (Fig. 1). The mineralized zone is distributed along a belt 5 to 8 km wide and 20 km long with an approximate area of 110 km². Kaolinite deposits are enclosed in rhyolitic tuffs of the Sierra Colorada Formation, Triassic to Middle Jurassic in age. Blanquita mine is characterized by the presence of kaolinite and alunite with scarce dickite and pyrophyllite,

whereas in the Equivocada mine, kaolinite is associated with dickite and traces of alunite (without pyrophyllite) (Marfil et al., 2005).

The rhyolitic tuffs, which host most of the kaolinized bodies, were deposited on top of the porphyritic rhyolites. The texture of the tuff is 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 kaolinitization of feldspars and chloritization of amphiboles and biotites (Marfil et al. 2005) (Fig. 2b Blanquita Mine and Fig. 2c Equivocada Mine).

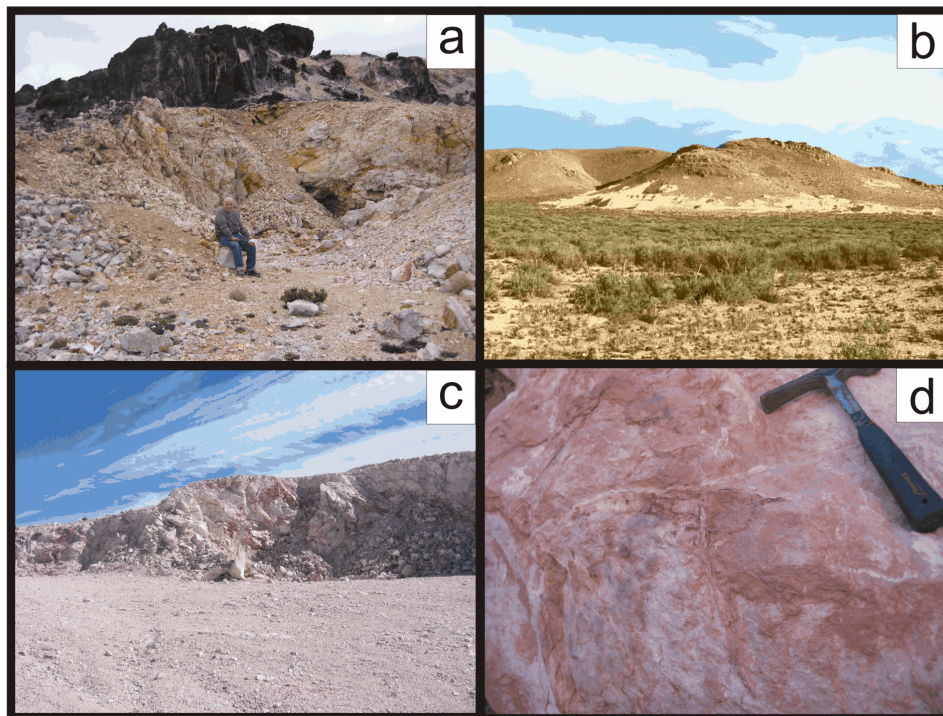


Fig. 2. a. Estrella Gaucha mine (kaolinized zone). b. Blanquita mine. c. Equivocada mine. d. Loma Blanca mine (Advanced argillic alteration zone)

Loma Blanca is situated 70 km NW of Los Menucos (Río Negro Province, Argentina) (Fig. 1). The parent rocks are andesites and their tuffs from the Vera Formation (Lower Triassic) (Los Menucos Group), which lie unconformably on the La Esperanza granite and Colo Niyeu metamorphites. 150 m to the northeast of the deposit there is an outcrop of granite intruded by aplitic dykes. Its geological importance arises from the mineralogy, structure and setting of the strongly mineralized area and its relationship with the different lithologic units (Fig 2d). Hayase & Maiza (1972a) studied the mineralogy of the Loma Blanca deposit using X-ray diffraction (XRD), thermogravimetric (TG) and differential thermal analysis (DTA), and microscopy. They concluded that the deposit was formed by the activity of an acid

Deposit	Host rocks	Mineral association	Age	Origin
Blanquita	Rhyolitic tuffs	Kaolinite ^{***} Alunite ^{**} Dickite [*] Pyrophyllite [*]	Triassic to Middle Jurassic	Hypogene
Equivocada	Rhyolitic tuffs	Kaolinite ^{***} Alunite [*] Dickite ^{**} Natroalunite ^{**}	Triassic to Middle Jurassic	Hypogene
Loma Blanca	Andesites and Andesitic tuffs	Kaolinite ^{***} Alunite ^{**} Dickite ^{**} Pyrophyllite ^{**} Diaspore [*] Illite ^{**} Montmorillonite [*] Chlorite [*]	Lower Triassic	Hypogene
Estrella Gaucha	Rhyolitic tuffs	Dickite ^{***} Alunite [*]	Lower Cretaceous	Hypogene
Chubut River Valley	Rhyolitic tuffs	Kaolinite ^{***} Quartz-Fd ^{**} Illite-halloysite [*]	Lower Jurassic- Lower Cretaceous	Supergene
Santa Cruz	Rhyolitic tuffs	Kaolinite ^{***} Quartz-Fd ^{**} Illite-halloysite [*]	Lower Jurassic- Lower Cretaceous	Supergene

*** Abundant

** Scarce

* Very rare

Table 1. Host-rock composition, alteration mineralogy, age and origin of the Patagonia kaolin deposits (Cravero et al. 2010, modified).

hydrothermal solution or superheated solfatara. They proposed a concentric zonation model. From the parent rock outward, different alteration patterns were recognized: a zone with sericite, chlorite and montmorillonite; a zone with kaolinite and dickite; a zone with dickite, pyrophyllite and alunite-natroalunite; and a zone with quartz, disseminated sulphides and diaspore (Fig. 3). (Marfil et al. 2010). The structure is not clearly exposed due to the scarce outcrops and smooth geomorphical topography covered by recent sediments. Geological evidence from the area indicates the development of tectonic fracturing and differential block movements affecting the heterogeneous volcanosedimentary pile that channelled the hydrothermal solutions responsible for the mineralization. The mineral assemblage, with high-temperature minerals (diaspore, pyrophyllite and dickite), the abovementioned sulphides, the areal structure and favourable lithology related to mineralization processes identify this zone as suitable for metallic mineral prospecting. The floor of the Loma Blanca mine consists of andesite that shows progressive alteration and development of a propylitic zone. Tuffaceous levels are transitionally interlayered; they are affected by tectonics and have developed breccias zones that, owing to their greater

permeability, provide pathways for mineralizing solutions. Towards the top of the mineralized zone, the texture is obliterated due to the intense silicification that has erased the lithological characteristics of the affected rocks (Maiza et al., 2009). The oldest formation in the area is Colo Niyeu, which is a low-grade metasedimentary basement. According to Labudia & Bjerg (1994), it could only be assigned a pre-Permian age. This unit was intruded by different plutonites of the so-called Complejo Plutónico La Esperanza. Close to the deposit, outcrops attributed to the Donosa granite, due to their mineralogical and textural characteristics, were recognized; the age of the intrusion, according to Pankurst et al. (1992), will be Late Permian. Over these formations lie the lithological components of the Los Menucos Group, of Triassic age; they are intruded by andesitic dykes of the Taquetren Formation. The field relations of these units have been obscured by tectonism, covered by recent sediments and masked by the mineralizing process (Marfil et al. 2010).

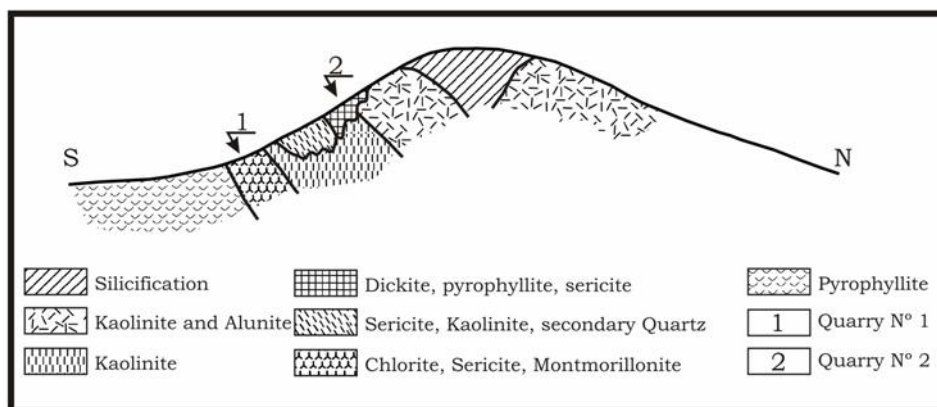


Fig. 3. Scheme of the Loma Blanca mine (Marfil et al. 2010).

3. Methods and instrumentation

The petrographic studies were carried out with an Olympus B2-UMA trinocular petrographic microscope with a built-in Sony 151A video camera, a high-resolution monitor and Image-Pro Plus image processing software were used. The mineralogical composition of bulk samples was determined by XRD, using a Rigaku D-Max III, with Cu-K α radiation and a graphite monochromator operated at 35 kV and 15 mA. The XRD patterns were recorded from 2° to 60° 2 θ . Chemical analyses of bulk samples for major, minor and trace elements were carried out by inductively-coupled plasma mass-spectrometry (ICP). Kaolin samples were selected for H and O isotope, SEM, IR and DTA-TG analyses. Isotope results are presented as % deviation with respect to SMOW. The reproducibility of results is better than $\pm 0.5\%$ for O and $\pm 10\%$ for H.

4. Mineralogical composition

4.1 Estrella Gaucha mine

The mineralogy of the kaolinized zone in this deposit is very simple. The mineral more abundant is dickite, with minor amount of alunite and quartz and scarce pyrophyllite and

diaspore. The presence of dickite was mentioned in other kaolin deposits: Tres Picos Mines (Province of Neuquen) (Hayase & Maiza 1970, Losada et al. 1975), Loma Blanca Mine (Province of Río Negro) (Hayase & Maiza 1972a) and Adelita Mine (Province of Río Negro) (Hayase & Maiza 1972b) but in any case is the more abundant.

In Estrella Gaucha mine dickite is associated with fine size quartz. To the top of the mineralization the more abundant mineral is alunite, with relictic inclusions of dickite, in a 20-30 meters thickness zone. The deposit culminates with a silicified zone with quartz with saccharoidal texture. Massive dickite, constitutes tabular crystals of 200 microns (Fig. 4a). It has parallel extinction (to 4°) and very low birefringence (0.006 to 0.008).

4.2 Blanquita mine

The kaolinization processes have completely obliterated the original textures of the rock, leaving only quartz (Fig. 4b). The mineralogy includes dickite, kaolinite, pyrophyllite, variable amounts of quartz and scarce alunite (Marfil et al. 2005).

4.3 Equivocada mine

The alteration processes is similar to that mentioned in Blanquita mine. It has almost erased the original texture and mineralogy of the tuffs. Only quartz and some biotite remnants are still visible (Fig. 4c). The lithic particles have been pseudomorphically replaced by kaolinite and dickite. The alteration mineralogy consist of a core of alunite grading outwards to an association of kaolinite-illite, illite-zeolite and finally fresh rock (Hayase & Maiza 1970, Marfil et al. 2005). The whole mineralization was later discordantly overprinted by natroalunite (Maiza & Mas 1981).

4.4 Loma Blanca mine

In the propylitic alteration zone the original texture is preserved. Plagioclase (andesine) crystals are altered, mainly to illite and calcite. Chlorite pseudomorphically replaces the mafic minerals, and goethite is formed from the remaining Fe (Fig. 4d). Saccharoidal quartz is found as patches in the groundmass.

In sericitic alteration zone the groundmass is completely argillized with secondary quartz. Iron oxides stain the whole rock. Sericite is the main alteration product. Quartz forms saccharoidal textures where three or more anhedral crystals are grouped. No original minerals are preserved.

In the intermediate argillic alteration the andesitic tuff is completely kaolinized. There is a stockwork of pure dickite veins, where the area between the veins is composed of a quartz-dickite association with variable amounts of illite, and scarce diaspore (Fig. 4e). There are veins of dickite associated with bohemite crystals. Diaspore was identified in silicified zone and is closely related to dickite.

Advanced argillic alteration zone coincides with the greatest mineralization. The texture resembles that of tuff with lithic clasts replaced by natroalunite. There is no relict quartz. The groundmass is an association of quartz-kaolin and metallic minerals. Hydroxides of Al can be recognized in certain areas. Natroalunite is abundant in this area and is associated with dickite and pyrophyllite (Fig. 4f).

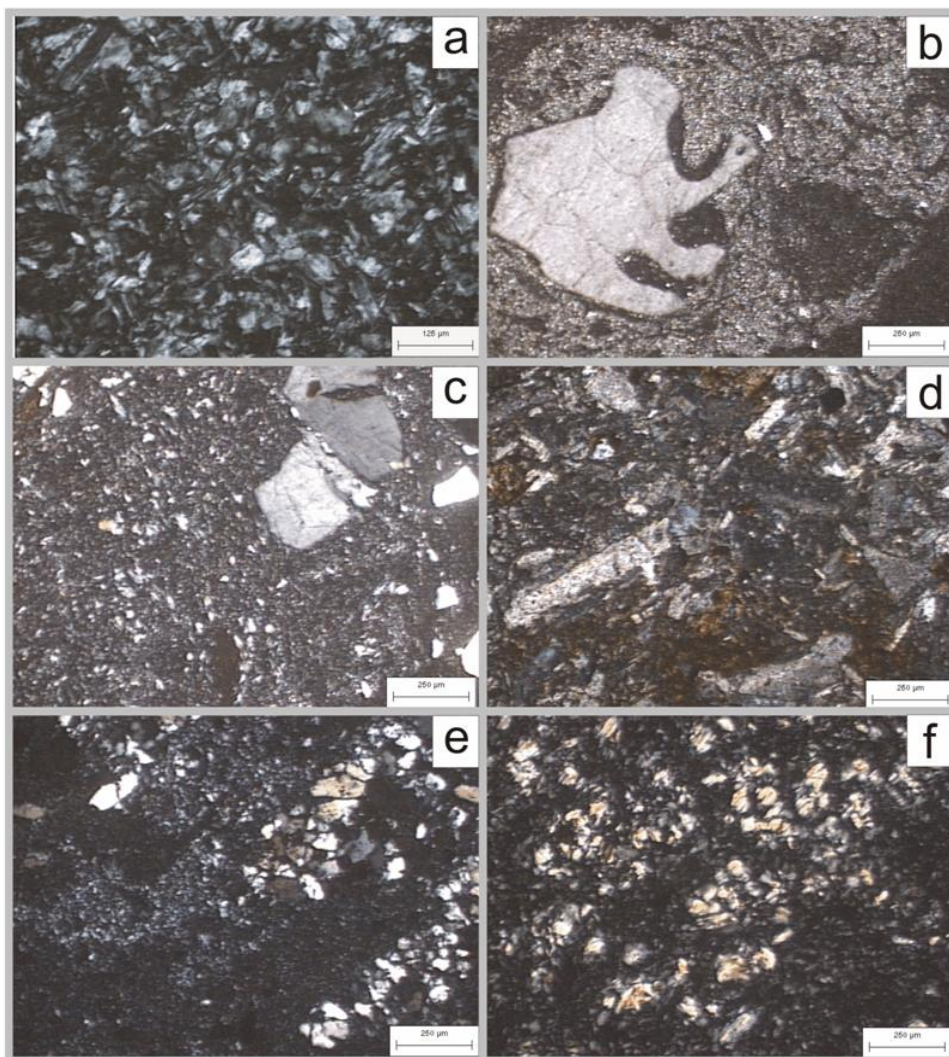


Fig. 4. a. Tabular crystals of massive dickite from Estrella Gaucha mine. b. Blanquita mine.: The kaolinization processes have completely obliterated the original textures of the rock, leaving only quartz. c. Equivocada mine: The original texture and mineralogy of the tuffs have almost erased. d. Propylitic alteration zone in Loma Blanca mine: The original texture is preserved. e. Intermediate argillic alteration: Andesitic tuff completely kaolinized. f. Advanced argillic alteration zone coincides with the greatest mineralization

5. XRD

When kaolinite and dickite are associated, it is very difficult to differentiate them by XRD. The two triplets located between 34° and $40^{\circ}2$, were studied in detail. Dickite appears in

very small proportions compared with kaolinite in the samples Loma Blanca, Blanquita and Equivocada mines while in Estrella Gaucha mine dickite is the predominant mineral. In the last one, dickite with variable amounts of quartz (between 0 to 25 %) was determined. In some samples scarce alunite was identified.

In "Loma Blanca" in the advanced argillic alteration zone, besides alunite-natroalunite, diaspore at the top and pyrophyllite in the highest area of the profile were identified. These minerals are found in isolated masses within the area of greatest hydrothermal activity as relicts of a first stage of higher pressure and temperature. In the propylitic alteration zone, chlorite and scarce illite were identified. Feldspar from the andesitic rock is still present. The predominant alteration mineral is illite together with abundant quartz. In the intermediate argillic alteration zone, kaolinite and quartz reflections were identified. Natroalunite composition was determined by XRD using basal reflections (003, 006 and 009). Maiza & Mas (1980), synthesized the minerals of the series from sericite alteration in a H_2SO_4 solution with varying amounts of KCl and NaCl. They determined the c_0 values in each of the products obtained and checked them by chemical analysis. With these values they fitted a straight line by the least-squares method. The calculated value for natroalunite from Loma Blanca is 16.83 Å, which corresponds to 87% Na. The formula calculated on this basis is $(Na_{0.13}K_{0.87})Al_3(SO_4)_2(OH)_6$. (Marfil et al. 2010).

6. Chemical composition

The kaolinite content in Blanquita, calculated from the mineralogical composition and major element analysis ranges between 27 and 73 % 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 S concentration, 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 can be related to an increase in the degree of alteration of the fresh rock, reaching values close to theoretical ones for pure kaolinite. In these samples, the alkali content is also small (Table 2). The concentration of MnO and MgO in the samples analysed are < 0.01 wt % (Marfil et al. 2005). The trace element contents of kaolinite helps to understand the origin. Kaolinites formed from hydrothermal alteration of acid-type igneous rock show enrichments in S, Ba and Sr, whereas Cr, Nb, Ti and the lanthanides tend to concentrate in kaolinites formed from meteoric processes (Dill et al. 1997). The S contents was determined to ranges from 0.03 to 0.36 wt %, this may reflect the presence of small amounts of alunite in the samples analysed. The Zr and Ti contents show a positive linear correlation with greater values of both elements found in samples from Equivocada mine. The (Ti + Fe) contents are less than 1 wt% and the (Cr + Nb) contents range from 0 and 174 ppm with no significant difference between samples from the two deposits. The (Sr + Ba) concentrations vary between 1000 and 10000 ppm, with the larger values probably related to the presence of trace amount of barite. The Ce + Y + La concentration is also variable (from 3 to 323 ppm). (Fig 5a, b, c and d) (Table 3). (Marfil et al. 2005). The chondrite-normalized REE diagrams are shown in figure 6a and 6b corresponding to Blanquita and Equivocada respectively.

In Loma Blanca mine Fe_2O_3 , CaO, Na_2O and K_2O contents decrease from propylitic to advanced argillic alteration zones, whereas Al_2O_3 and LOI increase in the kaolinite natroalunite zone (Table 2). The percentage of alunite, calculated from the S content, ranges

between 2% and 25%. The sulphur content in some samples is attributed to the sulphides present (covellite, sphalerite and pyrite). Sulphides were identified with a petrographic microscope on polished sections in almost all the samples, so the total percentage of natroalunite is considered to be slightly smaller than the calculated value. Relatively large Ba, Sr, V and Zr contents were observed, mainly in intermediate argillic and advanced argillic zones. Co, Ni, Cu, Zn and Rb are more common in the propylitic zone. Be, Ge, In, Sn, Mo, Nb and Ag are insignificant in all the samples (Table 3). Ba + Sr vs. Ce + Y + La, Fe₂O₃ + TiO₂ vs. Cr + Nb and Zr vs. TiO₂ plots are shown in Fig. 5.

Deposit/samples		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
Blanquita / 18	Average	66.08	22.74	0.28	0.73	0.15	0.06	0.16	0.20	0.16	9.39
	SD	10.31	7.21	0.23	1.78	0.09	0.03	0.07	0.14	0.09	2.97
	Minimum	46.28	10.84	0.11	0.02	0.00	0.01	0.25	0.05	0.03	14.60
	Maximum	84.78	37.21	0.80	6.28	0.23	0.12	0.05	0.64	0.36	4.22
Equivocada/13	Average	60.58	28.19	0.11	0.06	0.02	0.05	0.37	0.25	0.14	10.65
	SD	11.18	8.84	0.07	0.04	0.02	0.04	0.21	0.15	0.09	2.83
	Minimum	45.36	16.13	0.02	0.03	0.00	0.18	0.01	0.01	0.09	14.15
	Maximum	76.25	40.17	0.10	0.18	0.02	0.00	0.58	0.52	0.36	5.98
Loma Blanca/20	Average	58.49	22.20	2.54	0.50	1.22	0.69	0.80	0.28	1.13	11.28
	SD	8.67	7.57	3.02	0.75	1.88	0.76	0.20	0.15	1.49	4.73
	Minimum	34.02	16.25	0.04	0.05	0.09	0.00	0.10	0.17	0.04	5.16
	Maximum	69.18	37.82	9.45	2.86	5.42	3.01	1.12	0.80	3.68	23.03
Estrella Gaucha/9	Average	50.82	42.67	0.05	0.05	0.07	0.02	0.47	0.25	0.12	13.30
	SD	10.23	12.53	0.07	0.01	0.02	0.02	0.34	0.17	0.11	2.66
	Minimum	44.50	20.94	0.01	0.01	0.02	0	0.13	0.07	0.03	8.49
	Maximum	69.06	38.34	0.24	0.06	0.09	0.04	1.08	0.48	0.21	14.92

Table 2. Chemical analysis of major elements on whole rock samples (average weight %).

Deposit/samples		Ba	Sr	Y	Sc	Zr	V	Cr	Ga	Ge	As	Nb	Mo	Ag	La	Ce
Blanquita/ 18	Average	919	1660	4.8	8.9	74.4	107.4	80.3	18	4.7	390.9	5.7	5.8	7.1	35.7	62.4
	SD	2049	906	2.5	3.0	24.6	66.6	43.7	9	2.5	216.4	2.9	4.9	6.5	25.5	57.4
	Minimum	100	335	2	5	33	41	0	10	2	140	0	0	1	9	13
	Maximum	9041	4457	11	17	110	274	170	34	11	707	10	17	21	93	225
Equivocada/ 13	Average	610.4	1540	3.5	6	133.2	83.3	32.3	60.0	2.6	30.8	7.3	2.2	2.1	38.7	67.4
	SD	491.6	1056	1.9	2.2	73.6	59.2	28.9	29.7	1.6	36.4	5.0	2.6	2.0	16.3	32.3
	Minimum	56	32	0	3	11	20	0	0	1	0	0	0	0	1	2
	Maximum	1840	3160	6	11	235	212	90	77	7	107	15	6	6.9	60	118
Loma Blanca/ 20	Average	1122	1867	5.8	7.4	158.4	180.1	26.5	21.2	0.5	10.8	5.1	2.2	2.1	33.3	65.6
	SD	1282	1166	11.2	3.4	46.0	74.55	30.0	5.12	0.6	8.97	1.6	2.6	2.0	18.4	37.6
	Minimum	292	92	0	5	58	109	0	12	0	0	0	0	0	19	203
	Maximum	5990	4765	47	17	272	391	120	32	2	45	7	7	6.9	103	30.0
Estrella Gaucha/ 9	Average	282	1585	2.4	5.7	80.9	285.1	71.1	53.0	4.5	0	3.3	2.0	0	29.2	47.7
	SD	169	1200	2.0	3.1	50.3	128.1	76.7	25.9	1.7	0	2.4	2.4	0	16.5	33.9
	Minimum	72	447	0	2	27	102	0	17	2	0	0	0	0	5	10
	Maximum	563	3845	4	11	166	454	210	90	7	0	6	6	0	58	108

Table 3. Chemical analysis of trace elements (average ppm).

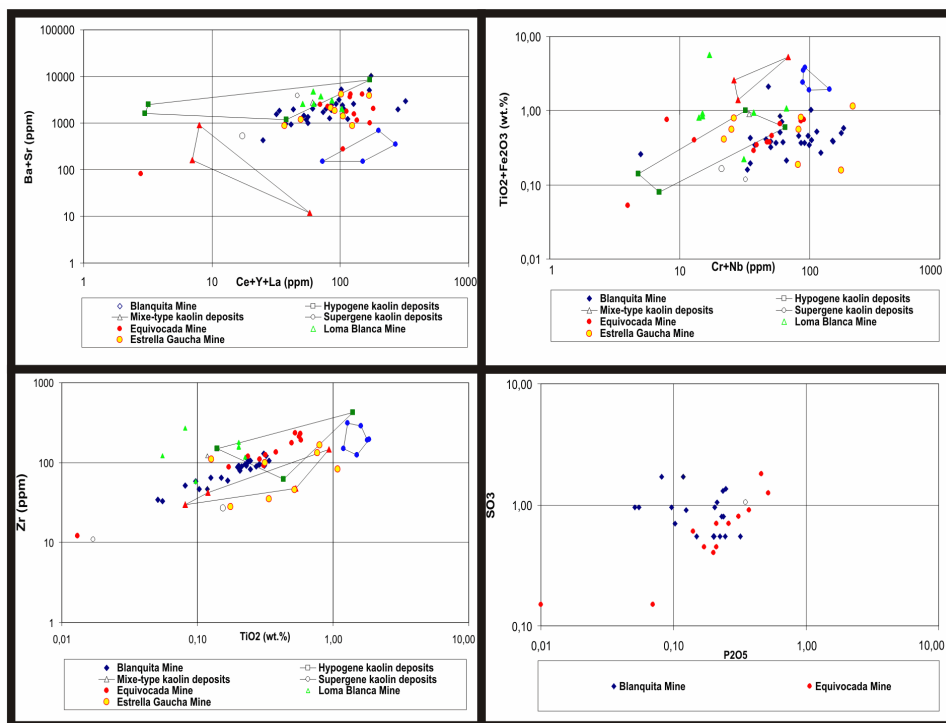


Fig. 5. Data plot from Blanquita, Equivocada, Loma Blanca and Estrella Gaucha mines. a. $(Ba + Sr)$ vs. $(Ce + Y + La)$. b. $(TiO_2 + Fe_2O_3)$ vs. $(Cr + Nb)$ c. Zr vs. TiO_2 . d. SO_3 vs. P_2O_5 from Blanquita and Equivocada mines.

The chondrite-normalized REE diagram according to Boynton, 1984 (in Rollinson, 1992), for the samples of the propylitic and sericitic alteration zones are shown in Fig. 6c and 6d for the samples of intermediate and advanced argillic alteration zones. In the latter, especially in pure kaolin samples, there is marked LREE impoverishment with respect to HREE, especially when compared with the less altered samples. There is no evidence of a positive Ce anomaly, which is typical of the deposits of residual and/or meteoric origin (Cravero et al., 2001). LREE are more abundant than HREE in the intermediate argillic alteration and advanced argillic alteration zones (Marfil et al. 2010).

The results of the chemical analysis of major elements in Estrella Gaucha mine, show that SiO_2 ranges from 44.50 to 69.06 % and Al_2O_3 38.34 to 21.70 %. The SO_3 content (between 0.08 and 0.93 %) was adjudicated to alunite. The alumina amount allowed determining kaolin content between 75 and 100 %. The MnO is less than 0.01 % (Table 2) (Maiza et al. 2009).

The results of trace element contents are shown in Table 3 and plotted in Fig. 5. The content of $TiO_2 + Fe_2O_3$ are lower than 1%wt, $Cr+Nb$ range between 1 and 214 ppm, $Sr+Ba$ between 1.000 and 10.000 while $Ce+Y+La$ is low (15 – 160 ppm). These results are closed with that determined in Blanquita, Equivocada and Loma Blanca mines. The content of As, Rb, Ag, In, Sn, Cs and Bi are insignificant.

In Fig. 6e the chondrite-normalized REE are shown for the samples from Estrella Gaucha. It is possible to observe a LREE impoverishment with respect to HREE, similar to that observed in Blanquita, Equivocada and Loma Blanca mines. Negative Eu anomaly was identified and Ce anomaly was no observed.

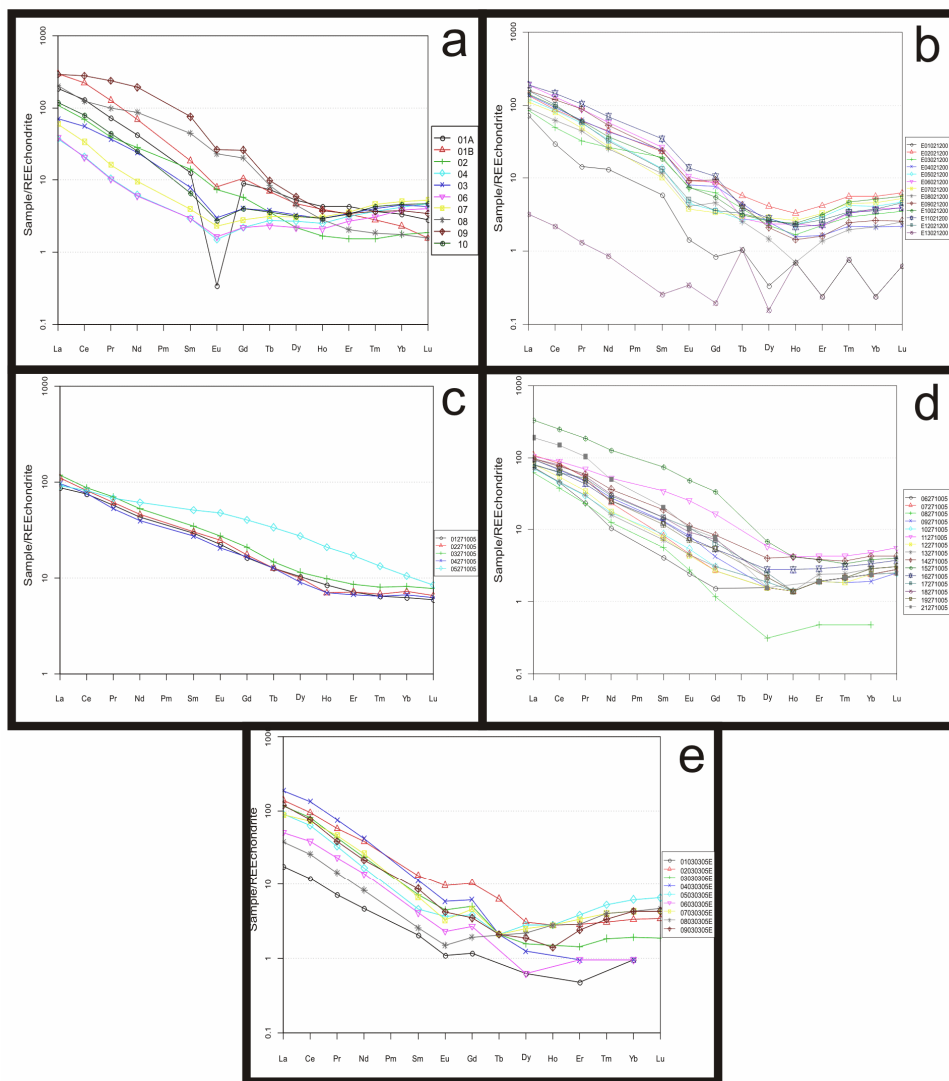


Fig. 6. Chondrite-normalized REE. a. Blanquita mine. b. Equivocada mine. c. Loma Blanca mine: Propylitic and sericitic alteration zones. (d) Loma Blanca mine: Intermediate argillic alteration and advanced argillic alteration zones. e. Estrella Gaucha mine.

7. O and H isotopes

The O and H stable isotope composition of kaolinites samples from the four mines studied are shown in Fig. 7. According to Savin & Lee (1988), the isotopic composition of kaolinite may reflect the geological conditions during its formation, provide the mineral did not suffer isotopic changes after its deposition. Thus, the O isotope composition in kaolinites of sedimentary origin usually varies from +19 to 23 ‰ and kaolinites 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 than the $\delta^{18}\text{O}$ values of the analyzed samples from the four mines, are much lower than those assumed for kaolinite deposit formed under superficial conditions, thus suggesting a different origin for kaolinization fluids (Marfil et al. 2005).

$\delta^{18}\text{O}$ and δD values of kaolinites from Blanquita and Equivocada ranges from +4.8 to +10.3 ‰ and from -88 to -116‰ respectively (Table 4). While the O isotope composition is similar in both deposits, the δD values of Blanquite mine are slightly more negative. (Martil et al 2005). Both $\delta^{18}\text{O}$ 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 Cerro Rubio and La Esperanza deposit in the province of Santa Cruz with kaolinites having $\delta^{18}\text{O}$ and δD values of +24‰ and -98‰ respectively.

Deposit/samples		$\delta^{18}\text{O}_{\text{SMOW}} \text{‰}$	$\delta\text{D}_{\text{SMOW}} \text{‰}$
Blanquita / 6	Average	7.3	-102.8
	SD	2.0	14.5
	Minimum	4.8	-116.6
	Maximum	9.6	-88
Equivocada/6	Average	8.1	-95.9
	SD	2.2	5.0
	Minimum	5.1	-105.1
	Maximum	10.3	-90.0
Loma Blanca/4	Average	11.6	-84
	SD	1.3	0.8
	Minimum	10.4	-85
	Maximum	13.2	-83
Estrella Gaucha/3	Average	15.9	-84.3
	SD	0.3	2.1
	Minimum	15.6	-86
	Maximum	16.1	-82

Table 4. $\delta^{18}\text{O}$ and δD ‰ average of kaolin samples from Blanquita, Equivocada, Loma Blanca and Estrella Gaucha mines.

In Loma Blanca mine $\delta^{18}\text{O}$ values in kaolinites range from 10.8 ‰ to 13.2 ‰ and δD from -83‰ to -85‰ (Table 4). Although these values are within the range of variation for hydrothermal kaolins (Murray & Janssen, 1984), they are larger than those determined for Blanquita and Equivocada mines.

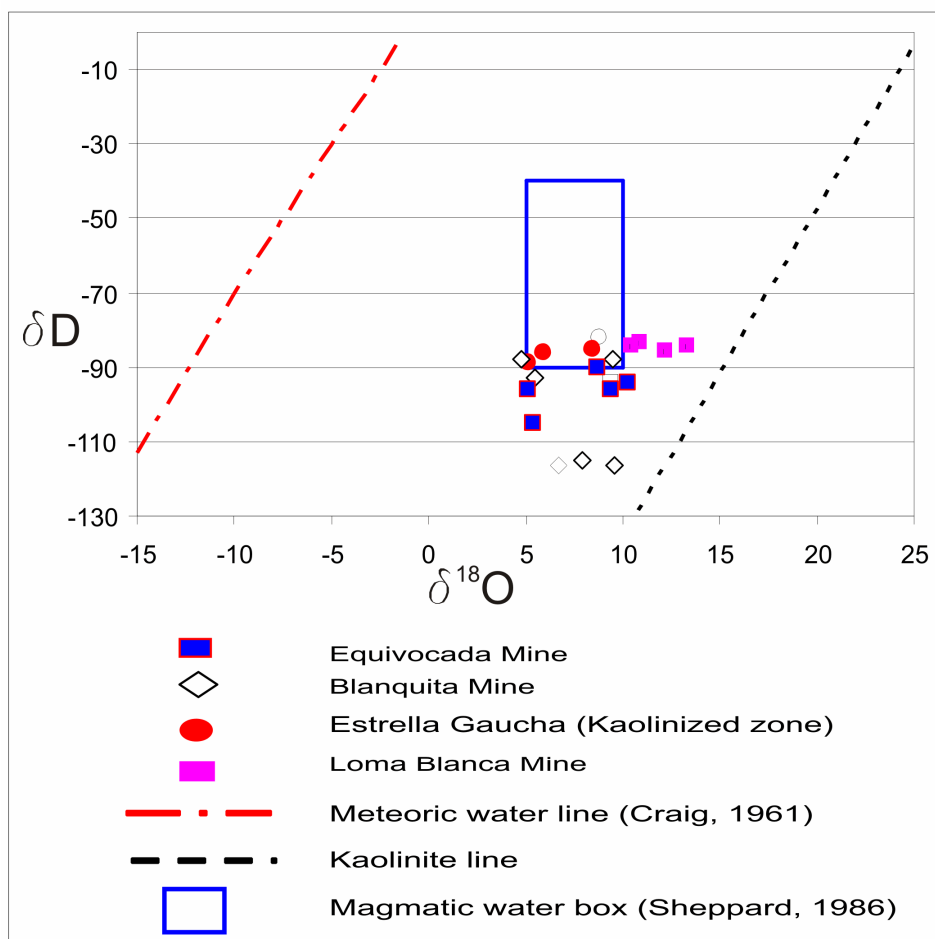


Fig. 7. $\delta^{18}\text{O}$ and δD values in Loma Blanca, Estrella Gaucha, Blanquita and Equivocada kaolins

$\delta^{18}\text{O}$ and δD values of kaolinites from Estrella Gaucha mine range from +5.1 to 8.8 ‰ and from -82 to -89‰ respectively (Table 4). They are similar to that obtained in Blanquita and Equivocada mines. The absence of primary minerals with fluid inclusions, not allowed determining the formation temperature of the deposit. However the presence of diaspore and pyrophyllite in the alteration minerals allows narrow the conditions between 250 and 350 °C, because they are the stability limits of those minerals.

8. Discussion

Dill et al.(1997) used the relationships between SO_3 vs. P_2O_5 , Zr vs. TiO_2 , Ti + Fe vs. Cr + Nb, and Ba + Sr vs. Ce + Y + La to discriminate between kaolin deposits of different origins in Peru. They found that S, Ba and Sr are enriched during hydrothermal alteration, whereas Cr, Nb, Ti and lanthanide elements are concentrated mainly during weathering.

The trace element content and P vs. S, Zr vs. Ti, (Cr + Nb) vs. (Ti + Fe) and (Ce + Y + La) vs. (Ba + Sr) ratios of kaolin samples from the four mines studied do not differ significantly. This suggests that all the deposits might have formed by the same genetic process. However, although the Ti + Fe and Sr + Ba contents indicate a 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 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 (Marfil et al. 2005).

Cravero et al. (2010) compared kaolin deposit from hypogene and supergene origin from Patagonia Argentina. In the hypogene deposits, S, Sr, Pb, V, P₂O₅, and LREE are more abundant, whereas Fe₂O₃, Y, Rb, U, Zr and HREE predominate in the supergene (weathered) deposits. It is important to consider that the samples are altered and the degree of alteration is not the same in all of them. The main alteration products in all the samples are clay minerals of the kaolin group. The approach adopted is to consider that the greater the LOI, the greater the resulting alteration degree. The concentrations of S, Pb and Sr, present only in the hypogene deposits, vary with the degree of alteration, indicating that these elements are mainly concentrated in the clay minerals. Zr does not show a clear behaviour; in the hypogene deposits it appears to be mobile during alteration, whereas under weathering conditions no clear relationship can be established. The V and U contents increase in both types of deposits with the degree of alteration; hence they can be considered to be immobile in both environments. P₂O₅ and S are only present in hypogene deposits and their contents increase with the alteration degree. Y shows no relation with the degree of alteration.

The greater content of HREE in the supergene deposits is more easily explained by considering that these elements are fractionated during alteration in the hydrothermal deposits and remain unchanged during weathering, thereby giving greater values in the supergene deposits, where no fractionation has occurred. Regarding the mobility of elements during hydrothermal alteration, other authors have found different behaviours. In rhyolitic rocks from Yellowstone drill cores, Ti, Al, Fe, Sc, Co, Y, Zr, REE, Hf, Ta and Th remained relatively immobile (Sturchio et al., 1986).

During the hydrothermal alteration of rhyolitic rocks of the Los Azufres geothermal field, Mexico (Pandarinath et al., 2008), REE concentrations were not significantly different between fresh and altered rocks. The immobile role of REE during hydrothermal processes in rhyolitic rocks has been reported by De Groot & Baker (1992). Nevertheless, in the advanced argillic alteration zone of Rangan area (Central Iran), composed mainly of alunite-jarosite and pyrophyllite, LREE are relatively immobile in the rocks of this zone and depleted in LREE and HREE (Parsapoor et al., 2009). These authors considered that this behaviour may be due to the entry of these elements into the lattice of alunite-jarosite. LREE can in fact substitute for K in the large-radius cations (A) of the alunite-jarosite formula. Alunite is a common component of the hypogene deposits studied here.

The samples from Patagonia studied by Cravero et al. 2010 have been taken as representative of the whole altered area, so the element contents do not come from a specific part of the weathering profile; therefore it can be considered that the conservative behaviour of the REE elements arises from the fact that they have fractionation could have occurred within the profile. Another characteristic of the REE that supports a supergene origin is the presence of a Ce anomaly, produced when Ce^{3+} is oxidized to Ce^{4+} . When these data are plotted in the graphical style of Dill et al. (1997, 2000), some of the relationships are not as clear as in their work, except for SO_3 vs. P_2O_5 . Their supergene deposits are characterized by much greater contents of $Ce + Y + La$ than those formed under hypogene conditions, whereas in Patagonia, these values are dispersed. In Peru, supergene kaolins are characterized by large values of both TiO_2 and Zr, whereas in Patagonia only Zr shows the same behaviour. Cr + Nb also show the opposite trend, while in Peru the greatest contents are related to a supergene origin; in Patagonia they are associated with hydrothermal deposits. In both areas, the same behaviour is found for S, P_2O_5 , Ba and Sr, with the greater values being found in the deposits formed in the hypogene environment. The greater amounts of S and V in the hypogene deposits are explained by the presence of minerals such as alunite (sulphate) and mottramite (vanadate).

More information about the formation conditions of the studied deposits can be obtained from their mineralogy. Kaolin deposits of hydrothermal origin are constituted by kaolinite with dickite, alunite and pyrophyllite (Murray, 1984). However, in kaolin deposits of sedimentary origin only kaolinite is present. In the mines studied the presence of dickite, pyrophyllite with alunite and diasporite in Loma Blanca, indicate a hydrothermal origin. In order to estimate the isotopic composition of fluids responsible for the kaolinization process a temperature of 350 °C 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. Numerous authors have synthesized pyrophyllite at temperatures above 260°C (Grim, 1969; Roy & Osborn, 1954; Hemley, 1959; Reed & Hemley, 1967; Tzuzuki & Mizutani, 1971).

The coexistence of pyrophyllite and kaolinite allows us to estimate a maximum temperature of 350°C. Diasporite can be recognized frequently in kaolin deposits of hydrothermal origin. According to Roy & Osborn (1954), the bohemite-diasporite transformation temperature is between 270 and 300°C at 175-1500 atm. water pressure. (Marfil et al. 2010)

A schematic summary of the paragenetic sequence from Loma Blanca mine is given in Table 5. The main Al minerals of higher temperature occur predominantly in the central area below the silicified zone, which is responsible for protecting the deposit from subsequent erosion processes. Dickite and nacrite commonly occur in deposits of hydrothermal origin (Murray, 1984). Numerous authors have synthesized pyrophyllite at temperatures above 260°C (Grim, 1969; Roy & Osborn, 1954; Hemley, 1959; Reed & Hemley, 1967; and Tzuzuki & Mizutani, 1971). The coexistence of pyrophyllite and kaolinite allows us to estimate a maximum temperature of 350°C. Diasporite can be recognized frequently in kaolin deposits of hydrothermal origin. According to Roy & Osborn (1954), the bohemite-diasporite transformation temperature is between 270 and 300°C at 175-1500 atm. water pressure.

Thus, using the O isotope fractionation equation of Shepard & Gilg (1996) indicate that 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. (Marfil et al. 2005).

Mineral	Silicified Zone	Advanced argillic zone	Intermediate argillic zone	Sericitic zone	Propylitic zone
Quartz					
Diaspore					
Natroalunite					
Pyrophyllite					
Dickite					
Kaolinite					
Illite					
Chlorite					

Table 5. Summary of the paragenetic sequence. (Marfil et al. 2010)

9. Conclusions

- The deposits studied consist of a set of irregular bodies and veins developed on tuffs of rhyolitic and andesitic composition.
- The alteration minerals present include kaolinite, dickite, pyrophyllite, alunite, diaspore, illite and chlorite.
- The trace elements contents of the kaolin samples in all the deposits studied 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 volcanic rocks. However the high (Nb + Cr) and (Ce + Y + La) contents do not exclude the presence of kaolinite of residual origin.
- The mineral assemblage (dickite-natroalunitepyrophyllite-diaspore), the alteration zonation pattern, the geochemistry of trace elements, the relation between LREE and HREE and the small $\delta^{18}\text{O}$ values suggest that the deposits studied were formed by hydrothermal processes.
- Mineralization developed in two stages: the first stage, of higher temperature, led to the formation of dickite, pyrophyllite and diaspore. Then the temperature decreased due to contamination with meteoric water, and alunite and kaolinite developed.

- The mineral assemblage allows us to estimate a formation temperature between 270 and 350°C.
- The hypogene deposits are characterized by greater contents of Sr, Pb, V, S and P₂O₅, all of them, apart from V, increasing as alteration proceeds. REE, probably forming part of the alunite structure, are fractionated during alteration.
- The combination of chemical composition, mineralogical association and O and D isotopes data suggest that the deposits studied were formed because the circulation of hydrothermal fluids, discounting superficial processes at low temperatures.

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