

Statistical analysis of geochemical data: a tool for discriminating between kaolin deposits of hypogene and supergene origin, Patagonia, Argentina

Presented at the XIV International Clay Conference, Castellaneta Marina, Italy, June 2009

F. CRAVERO^{1,*}, S. A. MARFIL^{1,2} AND P. J. MAIZA¹

¹Departamento de Geología, INGEOSUR, UNS-CONICET, Universidad Nacional del Sur. San Juan 670. 8000 Bahía Blanca, Argentina, and ²CIC de la Provincia de Buenos Aires, Argentina

(Received 15 September 2009; revised 10 November 2009; Editor: John Adams)

ABSTRACT: The numerous kaolin deposits located in Patagonia, Argentina, have been formed by hypogene or supergene processes. The primary origin has been established from O¹⁸ and D isotopic composition of the main minerals, kaolinite and/or dickite, and from the behaviour of certain elements during the alteration. The aim of this paper was to find if there is a tool, other than oxygen-deuterium data, to establish the origin of the Patagonian kaolin deposits. To handle the large number of variables per sample, a statistical multivariate study was used. The Principal Component method defines, on one hand the variables that better characterize each deposit and, on the other hand, the correlation between them. Fifty seven elements were considered and those that were not explained using these two components (which represent 75% of the total variance of the model) were discarded. As a result, the contents of Fe₂O₃, P₂O₅, LOI, Sr, Y, Zr, V, Pb, Hf, Rb, S and REE were used and the results show that the two components separate the deposits into two fields that are consistent with the process of formation. The first component indicates that Fe₂O₃, Y, Rb, U and HREE are more abundant in the supergene deposits, whereas, Sr, Pb, S and V are more abundant in the hypogene deposits. The second component shows that S, P₂O₅ and the LREE are enriched in the hydrothermal deposits, whereas Zr is more abundant in those formed under weathering conditions.

KEYWORDS: kaolin deposits, statistical analysis, geochemical data, Patagonia, Argentina.

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.*, 2007;

Pandarínath *et al.*, 2008, among others). In Patagonia, southern Argentina, kaolins of different origins are an important natural resource. Primary and sedimentary deposits, the former being supergene or hypogene in origin, have been documented. These Patagonian deposits are derived from Mesozoic rhyolitic rocks.

There have been several studies aimed at discovering the origin of the primary deposits (Domínguez & Murray, 1995, 1997; Cravero *et al.*, 2001; Domínguez *et al.*, 2008). Most of the studies deal with the mineralogy, the deposit structure, etc., but the most conclusive evidence is

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

DOI: 10.1180/claymin.2010.045.2.183

based on oxygen-deuterium isotopic data. Each type of deposit has been studied separately. All the published and unpublished geochemical data (which largely belong to the aforementioned authors) have been gathered in order to make a comprehensive study. Because of the large amount of data, a statistical method was chosen to prove if the primary origin of these deposits can be discriminated from the behaviour of certain elements. Because of the large amount of data a multivariate statistical method, Principal Components Analysis (ACP), was used to determine which elements better characterize the deposits. ACP is a statistical technique which permits a reduction in the number of variables to a smaller number, losing as little information as possible.

No references exist in the literature about statistical methods used the way we are proposing here. The Principal Component method has been used, on the other hand, to correlate the properties of a clay with its mineralogical and chemical composition (Galán *et al.*, 1998).

GEOLOGICAL SETTING

The kaolin deposits examined in this study are located in four areas of Patagonia (Fig. 1), the Blanquita and Equivocada mines in the Province of Río Negro, the Estrella Gaucha mine and River Valley deposits in the Province of Chubut, and Lote 8 and Cerro Rubio in the Province of Santa Cruz. The Blanquita and Equivocada mines are situated 30 km SE of Los Menucos. 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. The 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 Estrella Gaucha deposit is located in western Chubut Province, 70 km from Alto Río Senguier and was formed from the alteration of rhyolitic tuffs of the Lower Cretaceous Payaniyeu Formation. 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. The study focused on the kaolinized zone (Maiza *et al.*, 2009)

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 (Pankhurst & Rapela, 1995). It is called Chon-Aike Province (Pankhurst *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 (Marfil and Chon-Aike, among others). In Chubut, the deposits were formed on the Marfil 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 (Dominguez & Murray, 1997; Cravero *et al.*, 2001). In both the Marfil 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 quite simple – kaolinite with minor halloysite ± illite and relict quartz and feldspars (Dominguez & Murray, 1997; Cravero *et al.*, 2001; Dominguez *et al.*, 2008). The Equivocada and Blanquita mines and Estrella Gaucha are hypogene deposits, formed from hydrothermal waters (Marfil *et al.*, 2005; Maiza *et al.*, 2009), whereas the River Valley deposits and those in Santa Cruz Province were formed by meteoric waters in a supergene environment (Cravero *et al.*, 1991). Table 1 synthesizes the geology and mineralogy of the deposits.

MATERIALS AND METHODS

The chemical analysis of 57 kaolin samples from the four locations was used: the data are from published papers dealing with the genesis of the deposits (Marfil *et al.*, 2005; Maiza *et al.*, 2009; Cravero *et al.*, 2001; Dominguez *et al.*, 2008) and from unpublished data provided by the senior author. The study was carried out on 31 major, minor and trace elements (Tables 2, 3 and 4) from the 57 samples.

Principal Components Analysis consists of a simplification of the structure of the variables, reducing their number while retaining as much

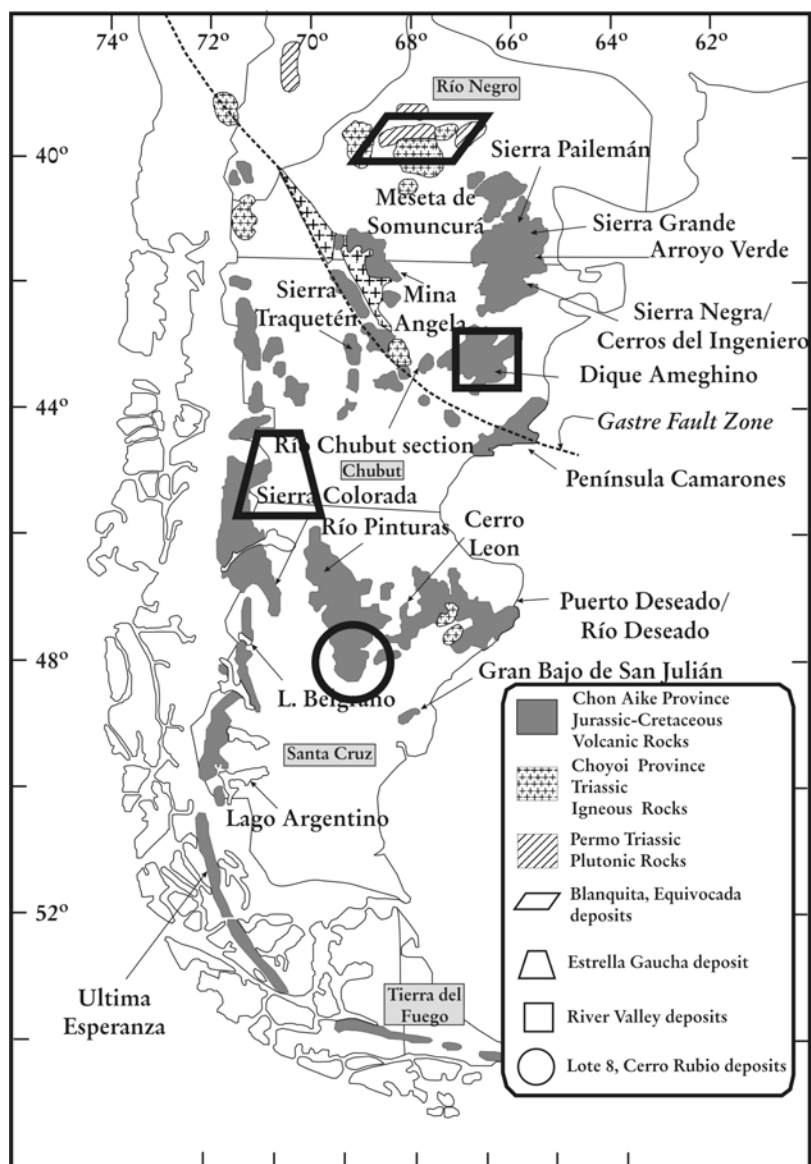


FIG. 1. Localization of the kaolin deposits in a sketch map of Patagonia (after Pankhurst *et al.*, 1998).

information as possible. The new components are the result of a linear combination of the original variables and are mutually independent. This method is useful when a large degree of correlation exists between the variables, indicating that there is redundant information; therefore, a few components can explain the whole variability. In order to select the useful components, the first to be considered is

one which comprises the greatest proportion of the original variability; the second should comprise the greatest variability not considered in the first component and so on.

An initial 57×31 (samples \times variables) matrix was transformed in another matrix with a correlation of the variables. A correlation matrix was then used to impart the same weight to all variables, as

TABLE 1. Host-rock composition, alteration mineralogy, age and origin of the Patagonia kaolin deposits.

Deposit	Sample ID	Host rocks	Mineral association	Age	Origin
Blanquita	B	Rhyolitic tuffs	Kaolinite*** Alunite ** Dickite* Pyrophyllite *	Triassic to Middle Jurassic	Hypogene
Equivocada	E	Rhyolitic tuffs	Kaolinite*** Alunite* Dickite**	Triassic to Middle Jurassic	Hypogene
Estrella Gaucha	EG	Rhyolitic tuffs	Dickite*** Alunite*	Lower Cretaceous	Hypogene
Chubut River Valley	CH	Rhyolitic tuffs	Kaolinite*** Quartz-Fd** Illite-halloysite*	Lower Jurassic- Lower Cretaceous	Supergene
Santa Cruz	SC	Rhyolitic tuffs	Kaolinite *** Quartz-Fd** Illite-halloysite*	Lower Jurassic- Lower Cretaceous	Supergene

*** Abundant

** Scarce

* Very rare

the data had been obtained in two different units (% and ppm). Then each component was calculated as the algebraic addition of each correlation variable

multiplied by each variable. Two types of plots are useful to visualize the data obtained. In a variable plot (Fig. 2), the length of the vector implies the

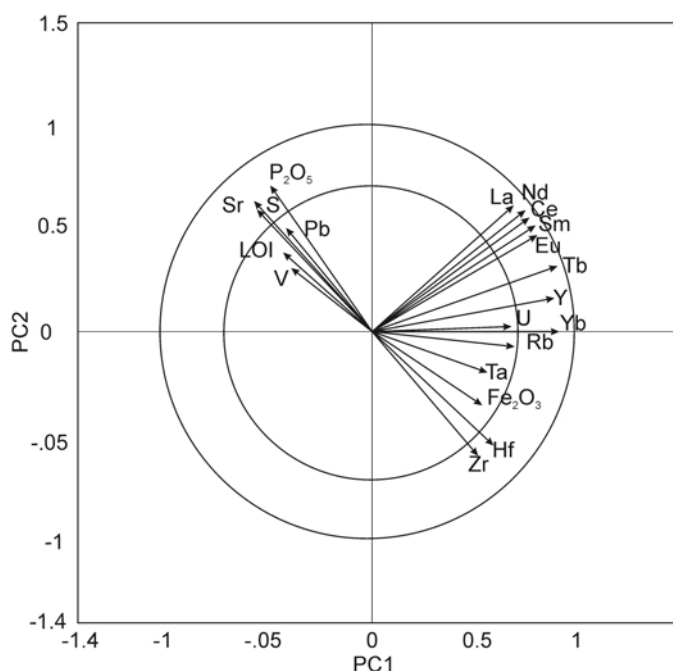


FIG. 2. Correlation of the variables in the first two components.

TABLE 2. Chemical analysis of major elements on whole-rock samples from kaolin deposits (wt.%).

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI
SC1	55.49	26.83	2.53	0.18	0.23	0.21	0.09	0.60	0.04	12.84
SC2	76.84	12.03	1.48	0.18	0.23	0.32	0.33	0.16	0.04	8.71
SC3	66.29	17.67	1.93	0.18	0.25	0.48	0.1	0.45	0.02	10.8
SC4	67.78	19.09	1.08	0.09	0.03	1.30	0.14	0.44	0.02	10.76
SC5	59.43	25.05	1.27	0.05	0.05	0.41	0.04	0.38	0.03	11.84
SC6	64.63	20.72	1.16	0.22	0.18	0.51	0.07	0.47	0.02	10.94
SC7	73.23	14.22	1.06	0.09	0.06	0.71	7.47	0.16	0.03	2.60
SC8	62.07	27.41	0.36	0.07	0.09	0.04	0.22	0.22	0.03	10.48
SC9	56.84	26.56	0.25	0.01	0.03	0.39	7.81	0.14	0.06	6.80
SC10	65.51	17.74	2.71	0.71	0.55	0.36	1.26	0.27	0.02	10.74
CH1	74.71	15.51	1.34	0.17	0.12	0.13	1.09	0.23	0.02	5.98
CH2	72.31	16.22	1.51	0.04	0.05	0.73	2.54	0.22	0.03	5.89
CH3	73.56	15.92	1.46	0.06	0.14	0.58	0.29	0.22	0.02	7.40
CH4	77.48	15.08	0.59	0.09	0.10	0.01	0.61	0.16	0.03	5.93
CH5	71.21	18.69	1.27	0.20	0.14	0.01	1.32	0.36	0.03	6.92
CH6	63.88	21.84	1.42	0.36	0.28	0.12	2.69	0.339	0.06	8.51
CH7	67.66	20.66	0.83	0.26	0.33	0.10	0.29	0.410	0.05	9.20
E1	45.36	40.17	0.10	0.08	0.06	0.09	0.00	0.017	0.35	14.21
E2	50.22	35.90	0.22	0.00	0.05	0.03	0.06	0.237	0.37	13.08
E3	55.94	32.05	0.03	0.00	0.06	0.02	0.04	0.318	0.31	11.37
E4	60.56	27.71	0.07	0.00	0.06	0.05	0.18	0.308	0.46	10.70
E5	76.44	16.13	0.18	0.02	0.05	0.03	0.01	0.578	0.21	6.45
E6	69.19	21.72	0.17	0.02	0.05	0.03	0.03	0.494	0.17	8.35
E7	70.76	20.82	0.15	0.01	0.06	0.02	0.01	0.575	0.07	7.89
E8	51.86	34.52	0.09	0.00	0.06	0.02	0.06	0.289	0.26	12.76
E9	52.06	33.98	0.12	0.00	0.12	0.02	0.06	0.171	0.52	12.93
E10	76.25	16.87	0.24	0.02	0.06	0.00	0.04	0.524	0.21	6.18
E11	60.34	31.49	0.02	0.02	0.18	0.00	0.09	0.381	0.20	5.98
E12	71.81	16.04	0.04	0.00	0.03	0.00	0.06	0.564	0.14	11.47
E13	46.75	39.07	0.04	0.02	0.05	0.02	0.01	0.013	0.01	14.15
B1	55.23	22.56	0.73	0.16	6.28	0.23	0.08	0.118	0.23	13.48
B2	56.84	24.38	0.66	0.08	4.85	0.19	0.05	0.055	0.28	12.84
B3	66.55	23.15	0.40	0.05	0.29	0.19	0.02	0.097	0.25	9.38
B4	63.60	26.10	0.18	0.04	0.11	0.15	0.03	0.202	0.08	9.87
B5	70.69	20.15	0.17	0.02	0.08	0.23	0.02	0.225	0.12	8.09
B6	73.43	18.44	0.26	0.04	0.08	0.26	0.07	0.201	0.07	7.32
B7	72.32	18.51	0.32	0.08	0.19	0.32	0.12	0.201	0.09	7.58
B8	46.28	37.21	0.43	0.04	0.11	0.17	0.08	0.081	0.64	14.60
B9	58.24	29.46	0.25	0.15	0.12	0.17	0.06	0.205	0.33	11.48
B10	73.92	16.76	0.80	0.03	0.70	0.17	0.06	0.230	0.17	7.24
B11	60.29	28.37	0.11	0.03	0.07	0.09	0.04	0.103	0.18	10.99
B12	84.78	10.84	0.14	0.01	0.04	0.06	0.01	0.247	0.10	4.22
B13	79.53	14.40	0.11	0.00	0.04	0.05	0.01	0.237	0.12	5.59
B14	82.86	11.14	0.13	0.00	0.02	0.05	0.03	0.235	0.05	4.51
B15	63.46	25.86	0.06	0.03	0.09	0.19	0.08	0.212	0.27	10.01
B16	65.37	24.98	0.07	0.01	0.06	0.06	0.10	0.125	0.17	9.26
B17	56.60	31.36	0.11	0.03	0.06	0.07	0.03	0.051	0.24	11.91
B18	61.42	27.28	0.11	0.00	0.04	0.00	0.12	0.150	0.24	10.79
EG1	46.09	38.59	0	0.01	0.03	0.02	0.02	0.154	0.07	14.18
EG2	44.79	37.76	0.07	0.06	0.12	0.09	0.005	1.078	0.21	14.92
EG3	44.74	38.12	0.04	0.06	0.14	0.1	0.04	0.521	0.28	15.13
EG4	44.5	38.34	0.01	0.05	0.13	0.09	0.03	0.176	0.48	15
EG5	44.78	38.05	0.01	0.04	0.05	0.07	0.005	0.795	0.21	14.64
EG6	69.06	20.94	0.07	0.05	0.04	0.07	0.005	0.338	0.12	8.49
EG7	50.37	34.60	0.03	0.05	0.06	0.07	0.07	0.127	0.2	13.6
EG8	68.1	21.70	0.02	0.05	0.06	0.06	0.02	0.769	0.12	8.86
EG9	44.93	37.51	0.24	0.05	0.19	0.07	0.005	0.316	0.56	14.88

Ref.: SC = Santa Cruz deposits, CH = Chubut River Valley deposits, B = Blanquita mine, E = Equivocada mine (Río Negro deposits), EG = Estrella Gaucha deposit.

TABLE 3. Chemical analysis of minor and trace elements (ppm).

Sample	Ba	Sr	Zr	V	Nb	Pb	Zn	S	As	Cr	Rb	Sc	Th
SC1	14	22	322	32	14.0	18	14	115	3	7	18	19.0	11.2
SC2	210	31	104	7	6.0	9	23	25	1	1	32	6.7	17.5
SC3	26	26	314	33	18.0	30	15	25	1	9	16	18.9	30.9
SC4	37	6	222	106	11.0	10	8	730	3	12	10	18.0	12.7
SC5	18	10	284	50	18.0	9	5	25	1	1	7	16.1	12.7
SC6	17	18	240	130	14.0	11	8	185	9	11	7	17.1	18.0
SC7	1160	34	119	6	12.0	38	115	25	7	0	362	4.5	18.6
SC8	18	9	114	24	10.0	28	17	25	3	0.5	17	11.1	16.4
SC9	343	15	230	33	20.0	12	8	25	6	1	270	22.7	39.6
SC10	418	68	144	26	9.0	27	131	55	6	1	125	4.8	20.2
CH1	70	11	262	11	0.0	20.0	50.0	180	3	6	133	5	31
CH2	168	9	160	34	0.0	23.0	32.0	430	9	3	94	4	34
CH3	23	11	170	46	0.0	33.0	23.0	440	10	3	18	5	30
CH4	40	10	160	22	10.0	12.0	21.0	150	4	19	64	5	41
CH5	13	10	327	70	13.0	11.0	49.0	110	8	14	90	8	34
CH6	192	24	122	57	18.9	63	73	0	9	0	119	7	29.2
CH7	93	34	126	113	21.5	35	64	0	0	0	46	9	25.4
E1	481	3360	17	75	4.3	1320	0	2100	44	28	0	3	2.6
E2	567	3035	123	220	6.6	1600	0	1800	7	44	0	11	13.7
E3	777	1695	129	161	6.7	1840	0	1600	11	32	0	8	9.0
E4	1778	2433	93	120	13.1	1880	0	3600	10	34	0	4	13.0
E5	724	1068	185	77	0.0	1360	0	1400	12	90	0	6	15.3
E6	229	762	163	32	14.6	456	0	900	103	44	0	7	24.2
E7	51	228	228	41	9.4	129	0	300	11	77	0	8	15.8
E8	682	1566	115	24	2.8	1170	0	1400	107	46	0	5	10.6
E9	1044	3154	87	21	12.0	1560	0	2500	52	25	0	5	16.2
E10	347	1229	227	24	8.4	562	0	900	29	0	0	6	16.9
E11	953	1066	132	113	13.1	1050	0	800	15	0	0	7	15.7
E12	202	933	207	121	0.0	240	0	1200	0	0	0	5	12.4
E13	58	25	22	110	4.4	33	0	300	0	0	0	3	1.5
B1	9041	1300	47	274	3.9	1600	0	3400	213	55	4	7	34.3
B2	488	1509	33	126	2.5	1420	0	1900	166	58	0	7	64.0
B3	1067	1479	58	82	4.0	2680	0	1900	295	170	4	17	10.4
B4	372	1441	87	48	8.3	556	0	1100	701	42	0	7	6.5
B5	824	882	95	98	8.4	363	0	1100	181	142	0	7	6.8
B6	180	1390	88	71	7.7	641	0	1100	624	74	0	8	6.8
B7	214	1213	92	140	9.5	1910	175	1100	707	103	0	9	8.7
B8	676	4457	52	249	3.0	3040	0	3400	650	56	0	10	14.0
B9	1010	1929	79	76	9.2	2150	0	1900	585	88	0	7	21.1
B10	714	1293	91	100	8.6	526	0	1600	172	93	0	5	15.5
B11	203	2315	47	78	2.0	1590	0	1500	686	64	0	12	7.9
B12	90	1083	105	43	6.0	770	0	500	293	145	0	7	7.2
B13	265	1716	101	62	6.0	951	0	1000	503	93	0	8	7.4
B14	100	335	110	26	6.0	609	0	300	215	85	0	5	6.6
B15	432	1603	90	122	9.0	3230	0	1500	243	113	0	12	6.5
B16	235	1023	65	72	3.0	1560	0	900	140	32	0	9	6.8
B17	140	3009	34	118	0.0	1700	0	1400	445	33	0	12	14.3
B18	485	1898	65	163	5.0	2960	0	2700	218	0	0	11	11.6
EG1	72	447	27	454	0.5	2.5	15	300	2.5	10	1	2	1.7
EG2	174	694	83	323	4.0	38	15	700	2.5	210	1	9	5.9
EG3	303	1087	46	302	2.0	14	15	1000	2.5	80	1	6	5.8
EG4	563	3334	28	272	0.5	17	15	2100	2.5	80	1	3	9.3
EG5	517	1565	166	484	6.0	19	15	1000	2.5	80	1	11	7.0
EG6	174	1007	35	272	2.0	7	15	700	2.5	10	1	2	3.7
EG7	307	1525	110	129	5.0	21	15	1000	2.5	170	1	6	11.8
EG8	121	760	133	102	6.0	12	15	600	2.5	20	1	7	5.0
EG9	308	3845	100	228	5.0	22	30	3700	2.5	20	1	5	14.4

TABLE 4. Chemical analysis of REE (ppm).

Sample	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
SC1	2.5	7	2	0.4	0.3	0	0.8	0.13
SC2	66.0	133	57	10.8	2.5	1.1	1.8	0.25
SC3	18.5	58	17	3.4	0.9	0	1.6	0.25
SC4	3.3	10	2	0.8	0.3	0	1.3	0.18
SC5	10.2	33	10	1.9	0.8	0.6	1.6	0.23
SC6	2.9	10	2	0.9	0.4	0.6	3.6	0.50
SC7	28.4	66	24	5.1	0.6	0.6	3.7	0.57
SC8	31.1	52	18	3.4	0.5	0	2.2	0.34
SC9	113	325	108	20.8	3.3	3.0	11.8	1.77
SC10	46.7	86	28	5.0	0.9	0.8	4.5	0.63
CH1	46.4	78.0	35.0	5.2	0.6	0.8	3.9	0.6
CH2	66.7	96.0	47.0	7.8	1.0	0.9	3.1	0.5
CH3	73.4	123.0	55.0	8.4	0.9	1.3	3.6	0.5
CH4	60.0	106.2	39.0	5.1	0.7	0.6	3.0	0.5
CH5	55.0	84.0	37.0	5.0	0.7	1.0	4.6	0.7
CH6	243	339	210	37.2	4.96	3.3	5.8	0.77
CH7	119	290	87.6	16.2	2.70	2.4	6.6	1.02
E1	22.5	23.7	7.9	1.1	0	0	0	0
E2	42.6	70.0	26.7	4.5	0.67	0.3	1.2	0.20
E3	26.3	39.8	15.9	3.7	0.54	0.2	0.7	0.11
E4	43.0	74.9	26.1	4.7	0.59	0.2	0.4	0.07
E5	37.7	69.1	20.4	2.7	0.33	0.1	0.9	0.15
E6	59.8	106	34.8	5.2	0.78	0.1	0.8	0.13
E7	34.8	64.9	16.1	2.0	0.28	0.1	1.0	0.17
E8	28.3	49.9	15.3	2.3	0.30	0.1	0.5	0.08
E9	49.6	95.6	31.7	4.6	0.67	0.2	0.6	0.08
E10	44.3	79.0	22.0	3.6	0.55	0.2	1.1	0.18
E11	59.2	118	42.1	6.7	1.02	0.2	0.8	0.13
E12	49.6	82.0	19.6	2.6	0.37	0.2	0.8	0.15
E13	1.0	1.8	0.5	0	0.00	0	0	0
B1	58.3	106.0	25.2	2.5	0.00	0.3	0.7	0.09
B2	93.2	179.8	41.7	3.6	0.59	0.3	0.5	0.05
B3	33.9	55.7	16.9	2.8	0.54	0.2	0.4	0.06
B4	11.5	17.1	3.7	0.6	0.11	0.1	0.9	0.15
B5	22.0	45.2	14.4	1.5	0.22	0.2	0.9	0.14
B6	12.0	16.7	3.6	0.6	0.12	0.1	0.8	0.13
B7	18.6	27.4	5.8	0.8	0.17	0.2	1.1	0.17
B8	63.1	100.3	52.3	8.7	1.70	0.4	0.4	0.05
B9	90.8	225.4	116.1	14.7	1.95	0.5	0.8	0.11
B10	36.7	63.7	15.1	1.3	0.20	0.2	1.0	0.15
B11	20.0	40.5	14.1	2.1	0.39	0	0.4	0.06
B12	17.6	33.6	10.5	1.4	0.24	0.1	0.6	0.11
B13	16.1	24.2	6.2	1.0	0.16	0	0.6	0.10
B14	8.9	13.0	3.2	0.5	0.09	0	0.6	0.1
B15	25.6	31.2	8.4	1.6	0.32	0.1	0.6	0.09
B16	30.7	48.9	16.4	2.3	0.38	0.1	0.5	0.07
B17	44.6	50.2	9.1	1.3	0.26	0.1	0.5	0.07
B18	36.5	44.7	7.8	1.4	0.30	0.2	0.6	0.09
EG1	5.5	9.8	2.8	0.4	0.08	0	0.2	0
EG2	43.5	76.4	23.3	2.6	0.71	0.3	0.7	0.11
EG3	36.3	66.2	14.3	1.4	0.33	0.1	0.4	0.06
EG4	58.3	108	25.5	2.2	0.43	0.1	0.2	0.04
EG5	28.2	51.2	10.2	0.9	0.27	0.1	1.3	0.21
EG6	15.8	31.4	8.4	0.8	0.17	0	0.2	0
EG7	27.4	59.2	15.9	1.3	0.24	0.1	0.9	0.14
EG8	11.8	21.1	5	0.5	0.11	0	0.9	0.15
EG9	37.3	61	13	1.7	0.31	0.1	0.9	0.14

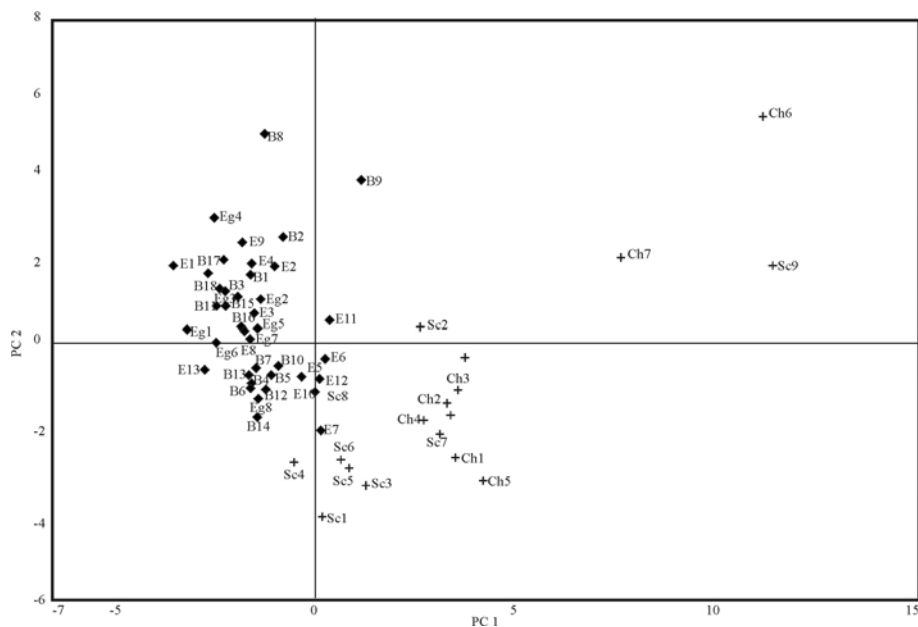


FIG. 3. PC1 (First Principal Component) and PC2 (Second Principal Component) plotted on a PCA score plot.

amount by which each variable loads on a component (maximum 1) and the angle between the variables indicate the degree of correlation between two variables, i.e. 90° means no correlation at all. In a PCA score plot (Fig. 3), each point represents the load that each sample has of PC1 and PC2.

RESULTS

After considering all the elements, those that were not explained in the first two components (which represent 75% of the total variance of the model) were discarded. Therefore, only the contents of Fe_2O_3 , P_2O_5 , Sr, Y, Zr, V, Pb, Hf, Rb, S, REE and LOI were used because the other elements did not show any variability. The variance percentage associated with each Principal Component is shown in Table 5. The first three components

represent 75% of the total variance. Although S is represented in both first two components, it has been taken into account for discussion because of its geological relevance.

Table 6 shows that the first component is given by S, Y, Rb, U and REE (mainly HREE) vs. Pb, V, S and LOI, which represents 48% of the total variance of the model, showing that these elements are related. The second component is mostly given by the relation P_2O_5 , Sr, S and LREE vs. Zr and Hf and represents 20% of the total variance. The third component is given by the V content and represents only 7% of the total variance. This small value led the authors to work only on the plot of the first two components, which have a large percentage of the reconstruction of each variable. The reconstruction percentages of each variable using the first two components are: Fe_2O_3 , 44.57; P_2O_5 , 75.75; LOI, 75.87; Sr, 78.94; Y, 84.92; Zr, 61.54; V, 68.44; Pb,

TABLE 5. Associated variance.

Component no.	I	II	III	IV	V	VI
Associated variance (%)	0.46946	0.67552	0.74853	0.81267	0.86277	0.90080

TABLE 6. Correlation between variables and the first two components.

Variable	Component 1 (PC1)	Component 2 (PC2)
Fe ₂ O ₃	0.52175	-0.4146
P ₂ O ₅	-0.43969	0.70501
LOI	-0.41634	0.41995
Sr	-0.54209	0.64081
Y	0.89916	0.11383
Zr	0.48109	-0.66005
V	-0.38404	0.36618
Pb	-0.38162	0.48881
S	-0.56588	0.62711
Hf	0.57246	-0.61863
Rb	0.68776	-0.11654
Ta	0.55466	-0.25442
U	0.69106	-0.03697
La	0.73491	0.58200
Ce	0.79078	0.53670
Nd	0.78945	0.52321
Sm	0.83440	0.47802
Eu	0.83193	0.44835
Tb	0.92888	0.27155
Yb	0.92042	-0.04125
Lu	0.91151	-0.06522

61.59; S, 72.30; Hf, 66.57; Rb, 49.12; Ta, 63.36; U, 53.44; La, 89.02; Ce, 91.31; Nd, 90.63; Sm, 92.90; Tb, 88.83; Eu, 93.96; Yb, 86.87 and Lu, 84.92.

Figure 2 shows the correlations between the variables and the load that each variable has of the components. Figure 3 shows the scores for each sample where component 1 has been defined by the equation: $Y1 = 0.53847Fe_2O_3 - 0.49379P_2O_5 - 0.43854LOI - 0.58991Sr + 0.89141Y + 0.50830Zr - 0.39873V - 0.42028Pb - 0.56588S + 0.59761Hf + 0.69089Rb + 0.56032Ta + 0.68598U + 0.69995La + 0.75799Ce + 0.75993Nd + 0.80784Sm + 0.80875Eu + 0.91275Yb + 0.91107Lu$ (Table 5). Therefore, positive values for PC1 (component 1) correspond to the greatest contents of Y, Rb, U and REE (mostly HREE), and are consistent with the Chubut River Valley and Santa Cruz kaolin deposits (supergene deposits). Samples with negative values of PC1 have greater contents of Pb, V, S and Sr, and correspond to the Blanquita, Equivocada and Estrella Gaucha deposits (hypogene deposits).

The variables of the second component (PC2) do not correlate with those of the first component and show that P₂O₅, S and LREE are enriched in the

hypogene deposits, and Zr in the supergene deposits.

DISCUSSION

The statistical analysis discriminates between two groups of kaolin deposits in Patagonia: Those with positive values of the first Principal Component (Chubut River Valley and Santa Cruz deposits) and those with negative values in the first Principal Component, (Río Negro deposits and Estrella Gaucha).

Oxygen and deuterium isotopic compositions (Fig. 4), determined in whole-rock samples, clearly show that the Chubut River Valley and Santa Cruz deposits were formed in a supergene environment under the influence of meteoric waters, and that the Río Negro Province and Estrella Gaucha deposits were formed in a hypogene environment by hydrothermal processes. Consequently, the discrimination made by the Principal Components is in agreement with the hypogene and supergene origin of the deposits.

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. Although S is represented in the two first components, the load is in the first component, where it represents almost 50% of the total variance. Moreover, S in both components is associated with the hypogene deposits.

To understand these results, 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. Figure 5 shows the relation between LOI and the elements found in this work as characteristics of each type of deposit. Moreover, La_N/Yb_N are considered instead of the elements alone, so in this case, only the LREE/HREE relation is considered and not the individual amount itself, which can be very variable and could lead to misinterpretation.

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

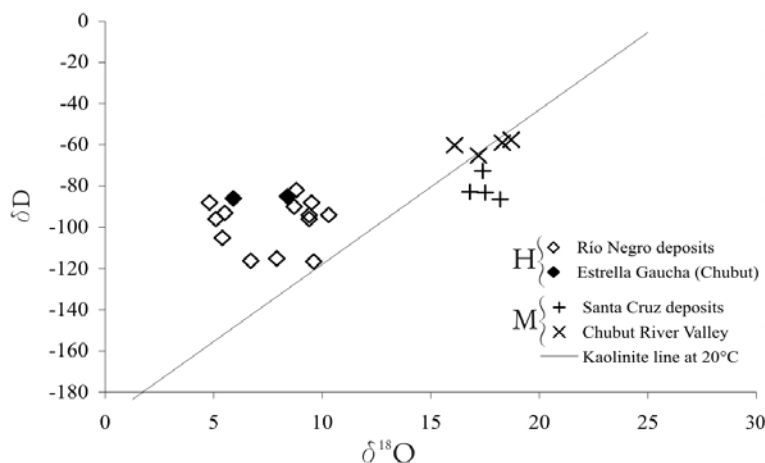


FIG. 4. Oxygen and deuterium isotope data for the Patagonia kaolin deposits.

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. P_2O_5 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.

When the La_N/Yb_N relation is plotted against LOI, those samples from supergene deposits show little variation with the degree of alteration, in contrast to those from hypogene alteration where this relation increases as the alteration progresses. From these data, it is considered that there is fractionation of REE during hydrothermal alteration, resulting in a depletion of HREE. No clear trend is found under weathering conditions. The greater content of HREE in the first Principal Component and its relation with 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. Figure 6, where the most altered samples of each type of deposits are plotted, clearly shows this trend.

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 MREE 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 Blanquita deposit showed the greatest alunite content (Table 1) and these samples are also plotted in Fig. 6.

Nesbitt (1979) showed that whilst the REE are mobilized during weathering, they are precipitated at the site of weathering. Gouveia *et al.* (1993) found that during supergene processes HREE contents decrease, especially in the middle and top of the weathering profile developed on granitic rocks, whereas van der Weijden & van der Weijden (1995) observed no systematic trends in REE behaviour during the weathering of granitoids in central Portugal. Condie *et al.* (1995) reported that Rb, Zr, Sc, Cr, Co, Hf, Nb, Ta, Y, Th, U and REE are concentrated in the upper parts of a weathering profile developed on a granodiorite. Galán *et al.* (2007) found that variable amounts of Si, Na, Ca,

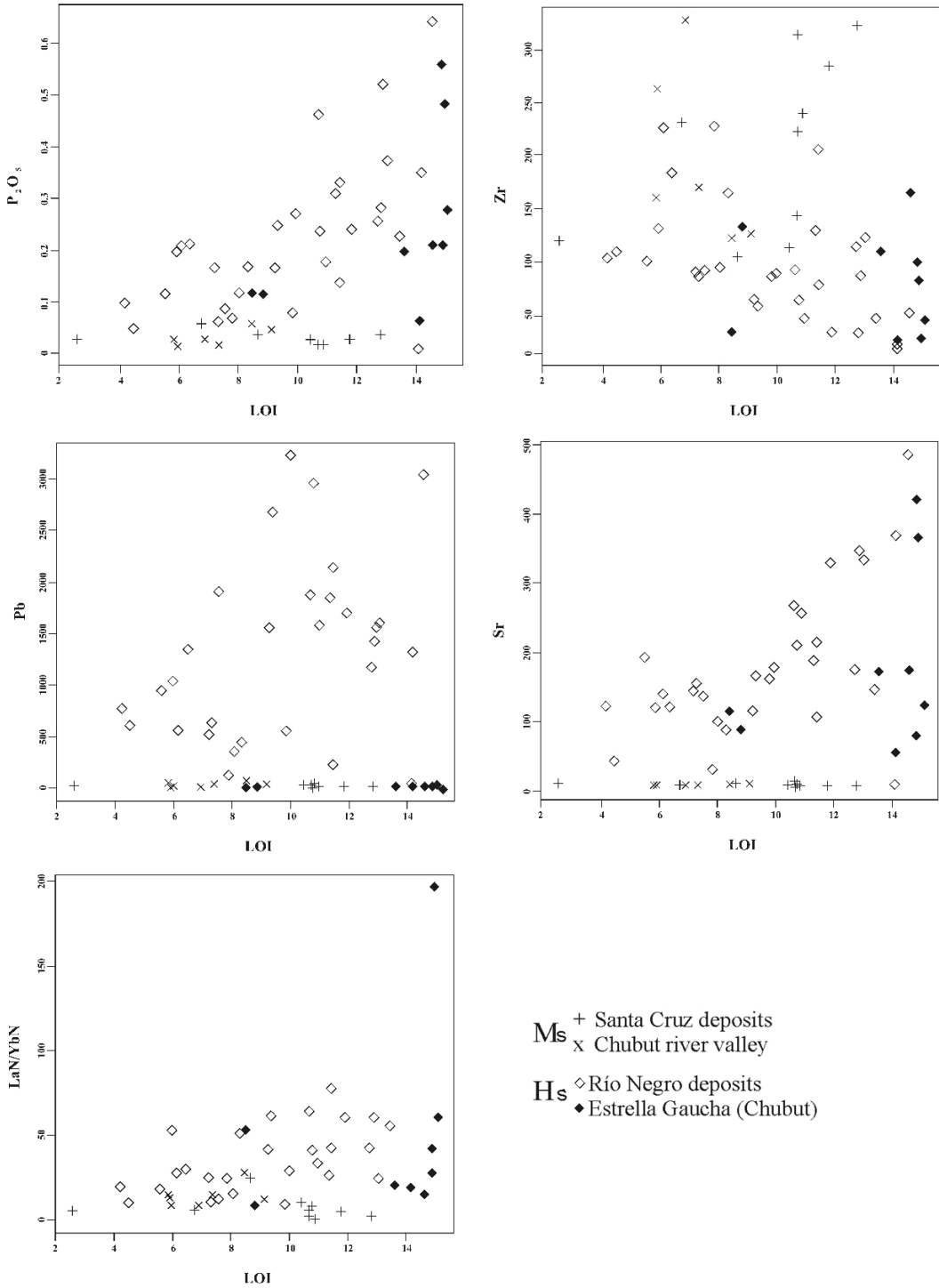


FIG. 5. Relation between LOI (as a degree of alteration) and different elements.

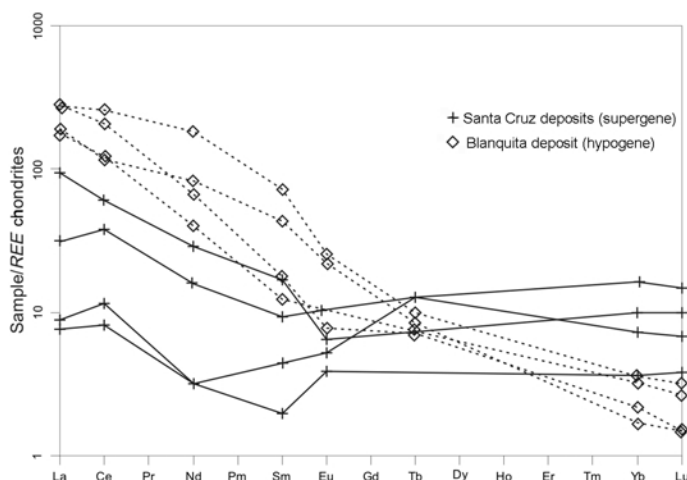


FIG. 6. *REE*/chondrite for the Blanquita (hypogene) and Santa Cruz (supergene) deposits.

K, Rb, Cs, Ba, U and P were lost from the weathering profiles of granitic rocks in Spain, whereas Al, Fe, Ti, Zr, Th, Hf and *REE* were concentrated in the residual kaolin.

In this study the samples 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 remained at the weathering site, although some 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+} (Fig. 6)

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.

When the data found here are plotted in the graphical style of Dill *et al.* (1997, 2000), some of the relationships are not as clear as in their work (Fig. 7), 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 character-

ized 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).

CONCLUSIONS

(1) The Principal Components method has discriminated between two types of kaolin deposits in Patagonia, Argentina, that have been regarded as hypogene and supergene in origin.

(2) The supergene deposits of Patagonia are characterized by greater contents of Fe_2O_3 , Y, Zr, Rb, U and *REE*. The *REE* have not undergone any fractionation during the weathering process.

(3) The hypogene deposits are characterized by greater contents of Sr, Pb, V, S and P_2O_5 , all of them, apart from V, increasing as alteration proceeds. *REE*, probably forming part of the alunite structure, are fractionated during alteration.

(4) From all the elements that the statistical method discriminates as being more abundant in each type of deposit, the relationship SO_3 vs. P_2O_5

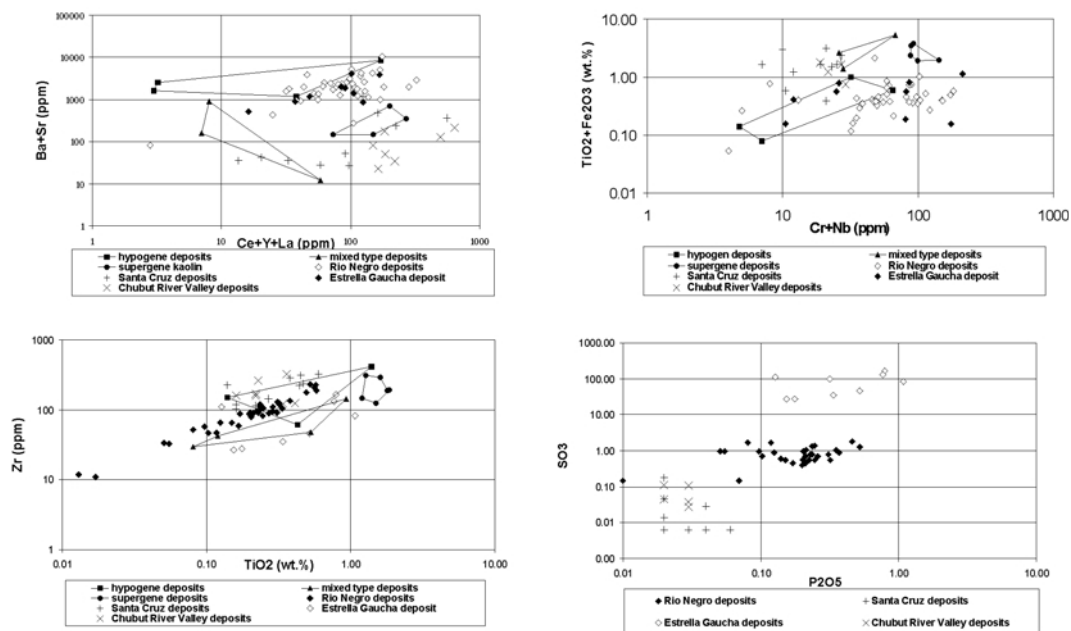


FIG. 7. Data plotted after Dill *et al.* (2000) graphics, where fields were defined for hypogene, supergene and mixed type kaolin deposits in Peru.

as established by Dill *et al.* (1997, 2000) and REE behaviour seem to be the most representative.

(5) When substantial chemical data but no isotopic data are available, this method is suitable for a first approach to discriminating different populations. Subsequently, the data found need to be analysed in geological terms.

ACKNOWLEDGMENTS

The authors thank the Department of Geology – UNS, Comisión de Investigaciones Científicas, CONICET, and Mr Rodolfo Salomón for their helpful support during the research. They are indebted to Dr Maria Cristina Gómez for her critical review; also to the reviewers, especially Dr H. Dill, for constructive comments.

REFERENCES

- Condie K.C., Dengate J. & Cullers R.J. (1995) Behavior of rare earth elements in a paleoweathering profile on granodiorite in the Front Range, USA. *Geochimica et Cosmochimica Acta*, **59**, 279–294.
- Cravero M.F., Domínguez E. & Murray H.H. (1991) Valores δO^{18} y δD n caolinitas, indicadores de un clima templado moderado durante el Jurásico Superior-Cretácico Inferior de la Patagonia, Argentina. *Revista Asociación Geológica Argentina*, **46**, 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.
- De Groot P. & Baker J.H. (1992) High element mobility in 1.9–1.86 Ga hydrothermal alteration zones, Bergslagen, central Sweden: relationships with exhalative Fe-ore mineralizations. *Precambrian Research*, **54**, 109–130.
- 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. *Mineralium Deposita*, **32**, 149–163.
- Dill H.G., Bosse H.R. & Kassbohm J. (2000) Mineralogical and chemical studies of volcanic-related argillaceous industrial minerals of the Central American Cordillera (western El Salvador). *Economic Geology*, **95**, 517–538.
- Domínguez E. & Murray H.H. (1995) Genesis of the Chubut river valley kaolin deposits, and their industrial applications. Pp. 129–134 in:

- Proceedings of the 10th International Clay Conference, 1993* (G.J. Churchman, R.W. Fitzpatrick & R.A. Eggleton, editors) CSIRO Publishing, Melbourne, Australia.
- Domínguez E. & Murray, H.H. (1997) The Lote 8 Kaolin Deposit, Santa Cruz, Argentina. Genesis and paper industrial application. Pp. 57–64 in: *Proceedings of the 11th International Clay Conference* (H. Kodama, A.M. Mermut & J.K. Torrance, editors) Ottawa, Canada.
- Domínguez E., Iglesias C. & Dondi M. (2008) The geology and mineralogy of a range of kaolins from the Santa Cruz and Chubut Provinces, Patagonia (Argentina). *Applied Clay Science*, **40**, 124–142.
- Galán E., Aparicio P., González I. & Miras A. (1998) Contribution of multivariate analysis to the correlation of some properties of kaolin with its mineralogical and chemical composition. *Clay Minerals*, **33**, 66–75.
- Galán E., Fernández-Caliani J.C., Miras A., Aparicio P. & Márquez M.G. (2007) Residence and fractionation of rare earth elements during kaolinization of alkaline peraluminous granites in NW Spain. *Clay Minerals*, **42**, 341–352.
- Gouveia M.A., Prudencio M.I., Figueiredo M.O., Pereira L.C.J., Waerenborgh J.C., Morgado I., Pena T. & Lopes A. (1993) Behavior of REE and other trace and major elements during weathering of granitic rocks, Évora, Portugal. *Chemical Geology*, **107**, 293–296.
- Maiza P., Marfil S., Cardellach E. & Zunino J. (2009) Geoquímica de la zona caolinizada de Mina Estrella Gaucho (Prov. de Chubut, Argentina). *Revista de la Asociación Geológica Argentina*, **64**, 426–432.
- Malvicini L & Llambías E. (1974) In: 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*, 649–662.
- Marfil S.A., Maiza P.J., Cardellach E. & Corbella M. (2005) Origin of kaolin deposits in the 'Los Menucos', Río Negro Province, Argentina. *Clay Minerals*, **40**, 283–293.
- Nesbitt H.W. (1979) Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature*, **279**, 206–210.
- Pandarínath K., Dulski P., Torres Alvarado I.S. & Verma S.P. (2008) Element mobility during the hydrothermal alteration of rhyolitic rocks of the Los Azufres geothermal field, Mexico. *Geothermics*, **37**, 53–72.
- Pankhurst R.J. & Rapela W. (1995) Production of Jurassic rhyolite by anatexis in the lower crust of Patagonia. *Earth and Planetary Science Letters*, **134**, 23–26.
- Pankhurst R.J., Leat P.T., Sruoga P., Rapela C.W., Márquez M., Storey B.C. & Riley T.R. (1998) The Con Aike province of Patagonia and related rocks in West Antarctica: A silicic large igneous province. *Journal of Volcanology and Geothermal Research*, **81**, 113–136.
- Parsapoor A., Kahlili M. & Mackinzadeh H.A. (2009) The behaviour of trace and rare earth elements (REE) during hydrothermal alteration in the Rangan area (central Iran). *Journal of Asian Earth Sciences*, **34**, 123–134.
- Sturchio N.C., Muehlenbchs K. & Meitz M. (1986) Element redistribution during hydrothermal alteration of rhyolite in an active geothermal system: Yellowstone drill cores Y-7 and Y-8. *Geochimica et Cosmochimica Acta*, **50**, 1619–1631.
- van der Weijden C.H. & van der Weijden R.D. (1995) Mobility of major, minor and some redox-sensitive trace elements and rare-earth elements during weathering of four granitoids in central Portugal. *Chemical Geology*, **125**, 149–167.