Applied Clay Science 131 (2016) 44–47

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Note

Genesis and mining potential of kaolin deposits in Patagonia (Argentina)

Eduardo Domínguez [a], Michele Dondi [b], Ricardo Etcheverry [c], Clemente Recio [d], Claudio Iglesias [e]

[a] Departamento de Geología, Universidad Nacional del Sur — CONICET, Bahía Blanca, Argentina
[b] Instituto CNR-ISTEC, Faenza, Italy
[c] Instituto Recursos Minerales (UNLP-CICBA) – CONICET, La Plata, Argentina
[d] Servicio General de Isótopos Estables de la Universidad de Salamanca, Salamanca, Spain
[e] Piedra Grande SAMICAyF, Pto Madryn, Chubut, Argentina

ARTICLE INFO

Article history:
Received 24 July 2015
Received in revised form 22 December 2015
Accepted 29 December 2015
Available online 14 January 2016

Keywords:
Kaolin
Isotopes
Genesis
Resources

ABSTRACT

Kaolin occurs in Patagonia as residual (weathering or hydrothermal) deposits at the surface of an extended Jurassic rhyolite province or in the upper sedimentary Cretaceous or Danian–Paleocene layers. On the same paleogeographic surface, numerous epithermal Au–Ag lodes occur, making kaolin genesis a crucial point in mining exploration. The weathering or sedimentary genesis of some deposits (Puma, Súper, FPS, Espingarda and Marta) was confirmed through clay isotope results. The origin of some corrective clays (Bajo Grande and White Bentonite) was analyzed and compared with that of one sample from Ukraine and one from a hydrothermal deposit in Furtei, Sardinia, Italy. In Patagonia, the residual and sedimentary kaolin deposits have resources of over 12 million tons. The identified hydrothermal deposits have more limited resources, due to their strong mineralogical zonation, which requires their selective "pocket" kaolin exploitation. The Patagonian region is the southernmost part of a continent where a Gondwana paleosurface of Late Mesozoic age developed on Jurassic rhyolite volcanic units. This surface is exposed along tens of thousands square kilometers in the cratonic units of northern and southern Patagonia, having a strong potential for finding new kaolin or epithermal precious metal deposits.

1. Introduction

The Patagonian residual kaolin deposits occur over a paleosurface of an extended Jurassic rhyolite province named Bahía Laura Group (Lesta and Ferello, 1972), or Marifil Formation (Malvicini and Llambías, 1974) outcropping in two cratonic areas: Macizo del Deseado and Somuncura. The sedimentary ball clays, derived from kaolinized volcanic parent rocks, occur in the Cretacic Baquero Formation (Archangelsky, 1967); or in the Danian–Paleocene Salamanca Formation (Lesta and Ferello, 1972).

Even today a controversy exists about the origin and significance of these kaolin deposits. After a pioneering isotopic work, Murray and Jansend (1984) found that several kaolin deposits were residual, and afterwards many studies confirmed that kaolinite was formed by weathering in a warm climate along the Late Jurassic time (Cravero et al., 1991; Cravero et al., 2001). On the same paleosurface, many epithermal precious metal deposits with hydrothermal kaolinite alteration have been discovered and in some cases, kaolin has been exploited (Fig. 1). In the Río Negro Province, the kaolin hydrothermal genesis has been confirmed (Blanquita, Equivocada; Marfil et al., 2005) and in the same area, other kaolin manifestations were linked to a high sulfidation system (C° La Mina; Ducart et al., 2006).

The relationship between kaolinite deposit genesis and potential resources is not easily found in the literature. Only the USGS Deposit Models, with frequency tonnage figures, can be used for estimating the potential resources for residual, hydrothermal or sedimentary deposits (Hosterman and Orris, 2000; Hosterman, 2000).

The purpose of this study was to confirm, by stable isotopes data, the weathering-sedimentary kaolin genesis of some of the major Patagonian kaolin deposits used due to their ceramic properties (Dondi et al., 2008; Zanelli et al., 2011). The local industry needs around 300,000 t per year. Other corrective clays and one of clearly hydrothermal genesis were studied for comparison. An additional purpose of this work was to establish the relationship between kaolin genesis and the potential deposit resources. The early field estimation of a weathering or hydrothermal genesis is significant in terms of exploration strategies.

2. Geology of deposits

The residual (weathering or hydrothermal) sedimentary kaolin deposits are found in a wide variety of Jurassic volcanic rocks and their overlapping sedimentary Cretaceous or Paleocene layers are in an area of more than 500,000 km^2 in more than 200 mines in the Santa Cruz, Chubut and Río Negro provinces (Fig. 1).

http://dx.doi.org/10.1016/j.clay.2015.12.031

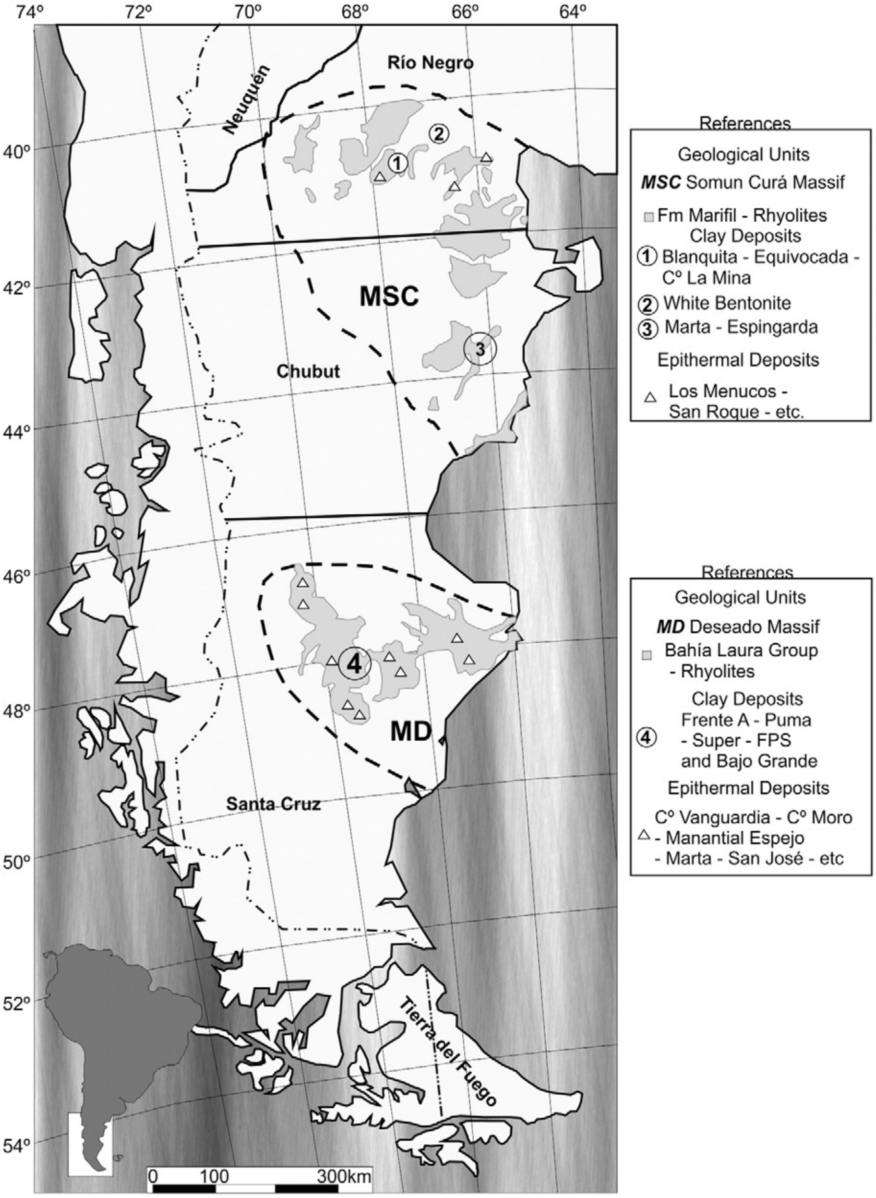

Fig. 1. Distribution of kaolin and epithermal deposits in the Patagonian Gondwana rhyolitic paleosurface. Map modified from Fernández et al. (2008).

The geology, mineralogy, and kaolin properties of the major deposits Frente A, Súper, FPS, Espingarda, Marta, and Bajo Grande were described in detail by Domínguez et al. (2008 and 2010) and Dondi et al. (2008). The White Bentonite corrective clay deposit is located in a sedimentary layer belonging to the Neuquén Group (Cretaceous) in the Río Negro province. Bentonite forms extended lens up to 2.5 m thick between sands, silts, and tuffs. Mineralogically, the material is composed of montmorillonite, and opal-CT, although small amounts of volcanic fragments, glass shards, quartz, albite, and biotite are also present (Vallés and Impiccini (2003)). The Ukrainian clay comes from the Miocene sedimentary deposits of the Donetsk basin (O'Driscoll, 1998) and it consists mainly of poorly ordered kaolinite, interstratified illite/smectite and a low quartz content (Zanelli et al., 2015). The hydrothermal kaolin comes from the gold deposit of Furtei, Sardinia, Italy. The exploited kaolin forms a tabular body 15 m in thickness developed in a volcanic sequence. Currently, it is not industrially used, and details of its geology and mineralogy can be found in Ruggieri et al. (1996) and Simeone et al. (2005).

3. Materials and methods

Samples of sedimentary (Puma, Frente A, Súper), residual (Espingarda, Marta) kaolin deposits along with high plasticity corrective clays were analyzed (Bajo Grande, White Bentonite). One sample from Ukraine (sedimentary) and one from Furtei, Sardinia (hydrothermal) were used for comparison. The samples were taken by a combination of channel and chip methods at the working fronts.

For isotopic determinations, the <2 μm fraction was concentrated by centrifugation and its purity was controlled by X-ray diffraction and the water released during the hydrogen extraction. The sample purity is as follows: In Frente A the kaolinite content is over 96% with 4% quartz; in Espingarda, Super, and Puma is over 99%; in Furtei is over 98% with 2% quartz; in Marta is over 90% with 9% interstratified (Ie) I/Sm clays and 1% quartz; in Ukrania is over 74% with 23% Ie–I/Sm and 3% quartz; in FPS is over 32% with 68% Sm; and in Bajo Grande and Bentonita Blanca the smectite content is over 98% with 2% kaolinite.

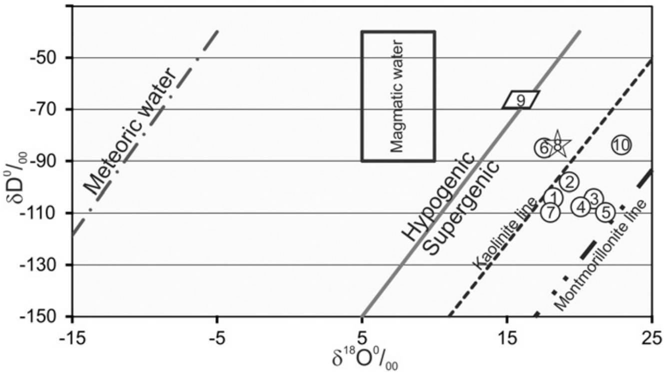

Fig. 2. A) Plot of δD‰ and $\delta^{18}O$‰ clay isotope from Patagonian deposits along with kaolin from the Ukraine and Furtei deposits. Meteoric water line from Craig (1961); and kaolinite–montmorillonite, from Savin and Epstein (1970). Analyzed deposits: 1 Frente A — Sedimentary (Sed); 2 Súper — Sed; 3 FPS — Sed; 4 Puma — Sed; 5 Bajo Grande — weathering (Wa); 6 Marta — Wa; 7 White Bentonite — Wa; 8 Ukraine — Sed; 9 Furtei — Hydrothermal; 10 Espingarda — Wa.

The oxygen was extracted by fluorination according to Clayton and Mayeda (1963), charged following Friedman and Gleason (1973) using ClF_3 as reactant (Borthwick and Harmon, 1982). The samples were outgassed at 200 °C under vacuum for 2 h. Oxygen was converted to CO_2 by reaction with spectrographic graphite heated by a platinum resistance. The isotopic relations were measured with a SIRA II-VG-Isotech device. Deuterium was extracted from samples previously outgassed for 15 h at 140 °C under vacuum. The extraction line was constructed following Godfrey (1962) and Jenkin (1988). The water released was reduced to H_2 by reaction with warm U (800 °C). The D/H relationships were determined by a SIRA II spectrometer. The isotopic determinations were expressed on SMOW conventional. The reproducibility was 0.8% for O and 2% for D. The NSB-30 value was O 5.1 and D-66.7.

The resource figures based on detailed geologic information and more than 7000 m of core drillings made in 46 mines were taken from the work of Domínguez et al. (2013).

4. Results

All the Patagonian kaolin deposits studied have isotope values that plot in the supergene kaolinite field near the kaolinite line from Field and Fifarek (1985) (Fig. 2). The Puma, Frente A, FPS, Bajo Grande and White Bentonite deposits are located in the field between the kaolinite and montmorillonite lines. In all cases, the sample location is attributed to the contribution of traces of interstratified smectite or illite/smectite contents in the analyzed samples. All data are similar to previously published values. The sedimentary Ukrainian clay has values compatible with a weathering origin. The only exception is the Furtei hydrothermal kaolinite that plots in the hypogenic–supergenic limit. Its $\delta^{18}O$ is similar to the values found by Simeone et al. (2005).

The weathering and sedimentary kaolin deposits lie along the flatlands over the paleosurface and have a short range of kaolinite oxygen isotopic variation in the different outcrops. Their field outcrops are extended horizontally (Fig. 3). Each deposit has resources between 5000 and 3,000,000 tons, totalizing more than 12,000,000 tons (Domínguez et al., 2013).

The hydrothermal kaolin deposit outcrops at the top or in the slope of hills associated with quartz veins or some type of silicification (Fig. 3). They show a more complex and variable mineralogy, and their oxygen isotopic values have strong vertical variations (Marfil et al., 2005). The resource evaluation in these deposits is difficult and usually selective "pocket" exploitation is needed due to their strong lateral and vertical mineralogical zonations.

5. Conclusions

New isotopic results confirm that the main Patagonian kaolin mineralization was formed by weathering or later sedimentary processes. The total resources, over 12,000,000 tons, are in agreement with the figures taken from the USG Models. The hydrothermal deposits have less and more irregular kaolin resources and are currently inactive.

The Patagonian region was part of the southernmost Gondwana continent where a paleosurface, developed on Jurassic rhyolite volcanic units during Late Mesozoic time, is exposed over tens of thousands square kilometers (Bétard et al., 2014). During this time, the climate was wet and warm, allowing the development of extensive chemical

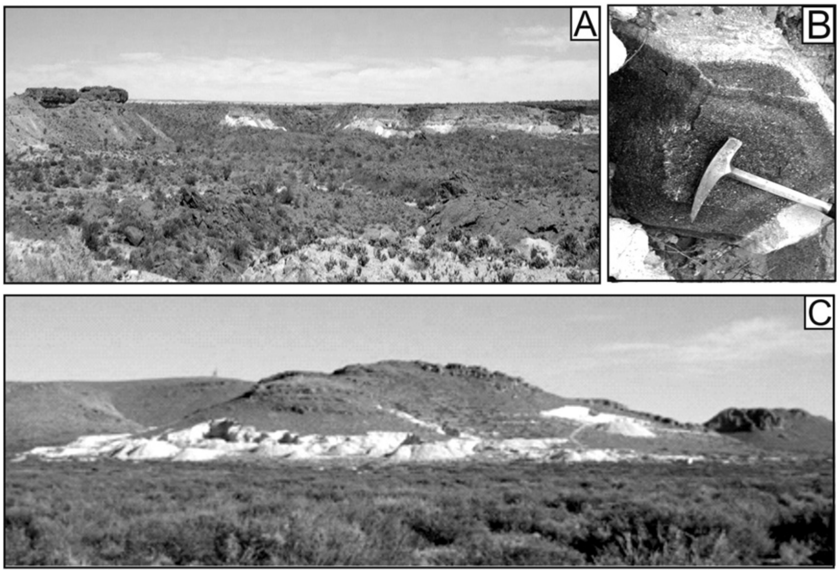

Fig. 3. A) View of the residual kaolin paleosurface at the Cerro Alto deposit in Chubut (43° 30.5′ S, 65°58.9′ W). The kaolin at the top of Jurassic rhyolites is covered by Danian–Paleocene clays and sandstones. B) Characteristic spheroidal weathering at the extraction bottom. C) View of hydrothermal kaolin extraction fronts at the Blanquita deposit with a quartz vein and silicified rocks at the top of the hill (40°50′ S; 68°.08′ W).

weathering. This paleosurface has a strong potential for finding new kaolin and precious metal mineralizations.

Acknowledgments

The authors would like to thank CONICET-Argentina/CNR-Italy that funded this work through the International Cooperation Agreement 2013–2014.

References

Archangelsky, S., 1967. Estudio de la Formación Baqueró, Cretacico Inferior de Santa Cruz, Argentina. Revista del Museo de La Plata, Paleontología 5, 57–63.

Bétard, F., Peulvast, J.P., Rabassa, J., Aguilera, E., 2014. Meso-Cenozoic Paleotopographies and Paleolandscapes in the Deseado Massif (Santa Cruz Province, Argentina). In: Rabassa, J., Ollier, C. (Eds.), Gondwana Landscapes in southern South America — Argentina, Uruguay and Southern BrazilEarth System Sciences 15. Springer, p. 498.

Borthwick, J., Harmon, R.S., 1982. A note regarding CLF$_3$ as alternative to BrF$_5$ for oxygen isotope analysis. Geochim. Cosmochim. Acta 46, 1665–1668.

Clayton, R., Mayeda, T., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotope analysis. Geochim. Cosmochim. Acta 27, 43–52.

Craig, H., 1961. Isotope variations in meteoric waters. Science 133, 1702–1703.

Cravero, M.F., Domínguez, E., Murray, H.H., 1991. Valores δO18 y δD en caolinitas, indicadores de un clima templado moderado durante el Jurásico Superior-Cretácico Inferior de la Patagonia, Argentina. Revista de la Asociación Geológica Argentina, XLVI 1-2, 20–25.

Cravero, M.F., Domínguez, E., Iglesias, C., 2001. Genesis and application of the Cerro Rubio kaolin deposit, Patagonia (Argentina). Appl. Clay Sci. 18, 157–172.

Domínguez, E., Iglesias, C., Dondi, M., 2008. The geology and mineralogy of a range of kaolins from the Santa Cruz and Chubut Provinces, Patagonia. Appl. Clay Sci. 40, 124–142.

Domínguez, E., Iglesias, C., Dondi, M., Brendel, M., 2013. Arcillas y caolines de Chubut y Santa Cruz. Geología, propiedades cerámicas, recursos y perspectivas. Actas 10° Congreso de Geología Económica, pp. 74–86 (San Juan).

Dondi, M., Iglesias, C., Domínguez, E., Guarini, G., Raimondo, M., 2008. The effect of kaolin properties on their behavoir in ceramic processing as illustrated by a range of kaolins the Santa Cruz and Chubut Provinces, (Argentina). Appl. Clay Sci. 40, 143–158.

Ducart, D.F., Crosta, A.P., Souza Filho, C.R., Coniglio, J., 2006. Alteration mineralogy at the Cerro la mina epithermal prospect, Patagonia, Argentina: field mapping, short-wave infrared spectroscopy, and ASTER images. Econ. Geol. 101, 981–996.

Fernández, RR; Blesa, A; Moreira, P; Etcheveste, H; Mykietiuk, K; Andrada de Palomera, P.A; and Tessone, M; 2008. Los depósitos de oro y plata vinculados al magmatismo Jurásico de la Patagonia: Revisión y Perspectivas para la Exploración. Rev. Asoc. Geol. Argent. Vol 63, N° 4, 665–681.

Field, C.W., Fifarek, R.H., 1985. Light stable isotope systematics in the epithermal environment. Rev. Econ. Geol. 2, 99–125 (Chapter 6, Economic Geology).

Friedman, I., Gleason, J.D., 1973. Notes on the bromine pentafluoride technique of oxygen extraction. Journal of research U.S. Geophys. Surv. 1 (6), 679–680.

Godfrey, J.D., 1962. The deuterium content of hydrous minerals from the East-Central Sierra Nevada and Yosemite National Park. Geochim. Cosmochim. Acta 26, 1215–1254.

Hosterman, J., 2000. In: Stoeser, D.B., Hearn, W.D. (Eds.), Preliminary Descriptive Model for Residual KaolinMineral Deposit Models 2000. US Geological Survey (DDS-064, version 1.0).

Hosterman, J.W., Orris, G.J., 2000. In: Stoeser, D.B., Hearn, W.D. (Eds.), Preliminary Descriptive Model of Hydrothermal KaolinMineral Deposit Models 2000. US Geological Survey (DDS-064, version 1.0).

Jenkin, G.R.T., 1988. Stable isotope studies in the calidonides of SW. Connemara, Ireland (PhD Thesis) Univ of Glasgow.

Lesta, P., Ferello, R., 1972. Región Extraandina de Chubut y norte de Santa Cruz. In: Leanza, A.F. (Ed.), Geología Regional Argentina. Academia Nacional de Ciencias, Córdoba, pp. 601–653.

Malvicini, L., Llambías, E., 1974. Geología y génesis del depósito de manganeso de Arroyo Verde, provincia de Chubut. Quinto Congreso Geológico Argentino, Buenos Aires, Argentina, Actas II, pp. 185–221.

Marfil, S.A., Maiza, P.J., Cardellach, E., Corbella, M., 2005. Origin of kaolin deposits in the 'Los Menucos', Río Negro Province, Argentina. Clay Miner. 40, 283–293.

Murray, H.H., Janssen, J., 1984. Oxygen isotopes indicators of kaolin genesis? Proceedings of the 27th International Geological Congress 15, pp. 287–303

O'Driscoll, M.J., 1998. Ukraine's minerals. Industrial Minerals 373, 21–43.

Ruggieri, G., Lattanzi, P., Luxoro, S., Dessì, R., Benvenuti, M., Tanelli, G., 1996. Geology, mineralogy and fluid inclusions data of the Furtei high sulfidation gold deposit, Sardinia, Italy. Econ. Geol. 92, 1–19.

Savin, S.M., Epstein, S., 1970. The oxygen and hydrogen isotope geochemistry of clay minerals. Geochim. Cosmochim. Acta 34, 35–42.

Simeone, R., Dilles, J.H., Padalino, G., Palomba, M., 2005. Mineralogical and stable isotope studies of kaolin deposits: shallow epithermal system of western Sardinia, Italy. Econ. Geol. 100, 115–130.

Valles, J.M., Impiccini, A., 2003. White bentonite from Patagonia, Rio Negro Province, Argentina. 2001. A Clay OdysseyProceedings of the 12th International Clay Conference, Bahia Blanca, Argentina. Elsevier, pp. 331–337.

Zanelli, C., Guarini, G., Raimondo, M., Dondi, M., Iglesias, C., Domínguez, E.A., Ullmann, R., 2011. Improving the technological performances of Argentinian ball clays: A case study from Patagonia, Argentina. Cfi/DKG, Ceramic Forum International 88 (8–9), E1–E4.

Zanelli, C., Iglesias, C., Domínguez, E., Gardini, D., Guarini, G., Raimondo, M., Dondi, M., 2015. Mineralogical composition of Ukrainian ball clays as a key to understand their technological properties. Appl. Clay Sci. 108, 102–110.