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Stable isotope constraints on the origin of kaolin deposits from Variscan granitoids of Galicia (NW Spain)

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ABSTRACT

Kaolinite-rich fractions of <45, <2 and <1 μm size from deposits of Galicia (NW Spain) at Ramón-Fazouro and Nuevo Montecastelo to the north, Vimianzo, Barilongo and Lendo in the center, and Santa Tecla to the south show significant ranges in $\delta^{18}O$ from 16.5 to 22.4‰ and in δD from −99 to −40‰. These widely spread values question a single crystallization process as no statistically significant overall correlation between $\delta^{18}O$ and δD can be obtained. The analytical spread is such that 11 of the 43 analyzed separates plot below the kaolinite weathering line, and one at the line separating the supergene from hypogene evolution field. Noteworthy for this wide scatter is the fact that some separated size fractions, especially from Ramón-Fazouro deposit contain also up to 65% halloysite, as well as varied amounts of contaminating minerals generally considered as relicts from parental igneous rocks, such as quartz, illite (=muscovite) and feldspars. However, the addition of these minerals does not appear to significantly bias the isotopic data of the <2 μm size fractions. Mean values for the <1 μm kaolin fractions of the five deposits for which there is more than a single sample have linearly correlated $\delta^{18}O$ and δD values with a best-fit line: $\delta D = 8.75\ \delta^{18}O - 248$ ($R = 0.896$, $n = 5$, >95%) rather similar to the kaolinite weathering line of $\delta D = 7.5\ \delta^{18}O - 220$. However, the overall spread of values and particularly those for coarser material, together with occurrences of halloysite, strongly suggest that higher temperature process(es) also occurred.

Kaolinite, and also likely halloysite, crystallized from waters, whose $\delta^{18}O$ values were of meteoric signature from about −5 to −1‰, at temperatures ranging from about 20 °C to 50 °C. The higher crystallization temperatures, especially at the sedimentary Lendo deposit, imply fluids at higher temperatures than during a climatic-controlled weathering process, probably of a low-temperate hydrothermal character with a fluid isotopically close to meteoric origin. However, interaction with fluids at higher temperatures and with higher $\delta^{18}O$ cannot be ruled out, because the relatively wide ranges of kaolin $\delta^{18}O$ and δD values are difficult to reconcile with a narrow range of $\delta^{18}O$ and δD for the interacting parental fluids. The most likely scenario for the kaolinite and halloysite precipitation is then a two-stage process of interaction with meteoric waters at close Earth-surface temperature, but with one of the two episodes occurring at temperatures slightly above those of weathering processes even under tropical conditions. There is no compelling evidence for an episode of significantly high temperature, such as in most hydrothermal fluid–rock interactions, but a low-temperature episode of about 50 °C cannot be ruled out unequivocally, especially for the <2 μm material. Following local continental weathering, percolation of meteoric waters at temperatures up to ~50 °C, and even higher, through the granitoids and felsites could have favored halloysite crystallization and affected the isotopic composition of earlier precipitated kaolinite.

1. Introduction

Northwestern Spain is characterized by large-scale kaolinization of Variscan granitoids in the northern Iberian Massif (Galán and Martín-Vivaldi, 1975a, 1975b). Extensive mineralogical and geochemical studies of this alteration process have shown that the deeply weathered rocks are dominated by well-ordered kaolinite with minor amounts of quartz, K-feldspar, micas, together with gibbsite and halloysite locally, and minute amounts of rutile, ilmenite, zircon and monazite. It is generally agreed that these kaolin deposits are mainly of supergene origin, and that they formed by extensive replacement of feldspars, predominantly plagioclase, in equilibrium with meteoric waters at temperatures of about 20 °C (Galán et al., 2007, 2010, 2013).

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The Variscan Iberian Massif of northwestern Spain was subjected to orogenic episodes between Late Devonian and Late Carboniferous times. As part of the northwestern massif, some of the constitutive rocks were also affected by later regional metamorphic and/or magmatic events (Pérez-Estaún et al., 1991). This complex evolutionary history could have developed hydrothermal activity triggering migration of acidic fluids that could have favored crystallization of kaolinite, as has been suggested in SW England granites in relation with the formation of the Plymouth Basin (Psyrillos et al., 2003). In fact, some granitic massifs of Galicia are affected by late and post-magmatic hydrothermal alteration, with albitization, muscovitization, greisenization, and kaolinization developing locally at variable scales (Galán and Martín-Vivaldi, 1975a; Mangas and Arribas, 1991). In such exposures, deeply kaolinized rocks with networks of quartz veins occasionally containing disseminated Sn-W mineralization pass laterally and suddenly into unaltered rocks, thus providing reliable evidence for hydrothermal alteration (Lageat et al., 2001). The timing of this hydrothermal alteration is uncertain and difficult to document, because the altered rocks were often affected by later meteoric weathering, but it may be assumed in a first approximation that it is closely linked to the late cooling stages of the Variscan granitoids.

Because detailed information about their stable isotope systematics is lacking, the origin of the largest kaolin deposits of Galicia is still under debate, as kaolinite could have formed by either weathering reactions (supergene kaolins), hydrothermal alteration during the late stages of pluton cooling (hydrothermal kaolins), or a combination of both (Murray, 1988). As a late low-temperature hydrothermal impact not related to pluton cooling cannot formally be discarded, the purpose of the present study is then an evaluation of the potential origins of kaolin minerals from six important kaolin deposits of the Galician region in NW Spain, on the basis of a stable isotope investigation with complementary mineralogical and chemical characteristics. The study was also an occasion to compare the isotopic signatures of the constitutive kaolin minerals with those of other West-European Variscan deposits, in Portugal (Bobos and Gomes, 1998), Brittany (Boulvais et al., 2000), and southwestern England (Sheppard, 1977; Psyrillos et al., 2003).

2. Geological setting

Galicia belongs to the Iberian Massif, which represents one of the largest exposures of the European Variscan orogen that developed during the Devono-Carboniferous collision of the Gondwana, Armorica and Laurentia cratons (Matte, 1991). The northwestern Iberian Massif is classically subdivided into two tectono-stratigraphic zones (Julivert et al., 1972): the West Asturian-Leonese Zone (WALZ) and the Central Iberian Zone (CIZ). The WALZ exposes Precambrian to Devonian metasediments that were strongly folded and foliated by three successive tectono-thermal phases (Pérez-Estaún et al., 1991) broadly coeval with various episodes of regional metamorphic and magmatic events. Northern CIZ comprises the complexes of the so-called Galicia-Trás-Os-Montes Zone (Farias et al., 1987), an allochthonous crustal block that was thrust over the CIZ. The deformation phases in the CIZ are comparable to those of the WALZ. The geology of the Variscan foldbelt of Galicia has been described in detail, and the salient stratigraphic, structural and petrographic features can be found in comprehensive review publications (e.g. Martínez-Catalán et al., 1997; Pérez-Estaún and Bea, 2004).

Variscan granitoids make up almost half of the present-day outcrops in Galicia (Fig. 1), with large volumes of granite extensively kaolinized (Galán and Martín-Vivaldi, 1975b; Wilson, 1998). These granitoids were traditionally grouped into two series based on their mineral and chemical compositions (Capdevila and Floor, 1970): the alkaline and per-aluminous two-mica granites and leucogranites, and the calc-alkaline granitoids consisting predominantly of biotite-bearing granodiorites. According to their structural characteristics, these granitoids can be divided into syntectonic and post-tectonic types (Corretge et al., 1990). The origin of the granitoids is generally agreed to have resulted from a partial melting of crustal protoliths (Ortega and Gil-Ibarguchi, 1990). Strike-slip fault systems affecting the Galicia region favored formation of small Tertiary NW–SE oriented basins that evolved independently, influenced by local tectonic structures (Cabrera et al., 1996). Economically workable secondary kaolin deposits also resulted from this tectonic and sedimentary evolution.

Endogenous features of Late Variscan activity largely controlled the present-day landforms, although a dense network of faults and fractures was generated by the subsequent Alpine tectonic activity. During Mesozoic and Cenozoic times, the region was subjected to extensive denudation (Vidal-Romaní et al., 2014), and consequently the root zones of most granites were exposed at the current erosion level; hence mostly intrusive rocks outcrop in the region. As most of the hypogene kaolin deposits were presumably removed by erosion, this could be a plausible argument to explain the scarce evidence for hydrothermal kaolinization. Once exhumed, the granites, their host rocks and associated sediments were deeply weathered under tropical conditions during the Tertiary period, while subjected also to periglacial conditions during several well-defined cold periods in the Pleistocene (Blanco-Chao et al., 2003). At the present-day, weathering of granitic rocks occurs under humid (average rainfall of 1400 mm/year) and temperate (mean annual temperature of 12 °C) conditions that promote the formation of well-drained and highly leached soils with kaolinite and gibbsite, as well as kaolin deposits containing allophane and halloysite, together with disordered kaolinite (Galán et al., 2010). Apparently, intense kaolinization occurred during post-Alpine weathering periods that overprinted and even obliterated most of the earlier deposits, and therefore could have biased the original signatures and the indices of hydrothermal activity. However, renewed tectonic activity occurred in NW Galicia during the Alpine orogenesis with hydrothermal mineralization along E-W fractures. Some of these features were very rich in kaolinite, such as at Lage in La Coruña province (Parga Pondal et al., 1953; Galán and Martín-Vivaldi, 1975a).

3. Sampling and analytical methods

3.1. Sampling information

Several kaolin deposits representing primary and secondary types were selected for this study at Ramón-Fazouro and Nuevo Montecastelo near the town of Burela to the north of Galicia, Vimianzo, Barilongo and Lendo in the center, the latter being the only secondary deposit hosted by sediments, and Santa Tecla to the south at the boundary with Portugal (Fig. 1). Some aspects of the different deposits, as well as the sample locations in the profiles, are illustrated in Fig. 2.

The Ramón-Fazouro deposit in the Lugo province is the largest kaolin deposit in Spain (Fig. 2A). It has been mined by ECESA for more than half a century for the manufacture of high-quality ceramics, especially porcelain ware. The kaolin material is a mixture of kaolinite and halloysite, sometimes with minor allophane (Galán et al., 2013). This valuable deposit is spatially and genetically related to felsites and a swarm of quartz-porphyry dykes that intruded Lower Cambrian metasediments. Four types of kaolin outcrops were identified in the deposit: massive, or associated to felsites, quartzites and metapelites. It is unclear if extensive kaolinization resulted from chemical weathering, whether some hydrothermal auto-metamorphic alteration occurred first, or if it resulted from combination of the two processes. In any case, a folding of the series led to an apparently chaotic kaolin distribution, with a weathering episode superimposed on any earlier hydrothermal transformation. The nearby Nuevo Montecastelo deposit extends over more than 50 m below the surface, providing access to large-scale weathering of Variscan post-tectonic granitoids (Fig. 2B). Kaolin developed in two-mica leucogranites and alkali feldspar granites that belong to a complex, heterogeneous pluton intruding an Early