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1 Yttrium speciation variability in bauxite  
2 residues of various origins, ages and  
3 storage conditions

4

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19 **Abstract**

20

21 Bauxite residues (BRs) are highly alkaline wastes generated during alumina production from  
22 bauxite ore. Billions of tons have been accumulating worldwide for more than 100 years, they are stored  
23 in various forms, and pose environmental and societal issues. At the same time, BRs are promising  
24 secondary sources for the production of critical metals including rare earth elements (REEs). However,  
25 knowledge on REE speciation is lacking, and is consequently an obstacle to the development of large-  
26 scale extraction process.

27 This study analyses the influence of origin of the bauxite ore (lateritic or karstic), the storage  
28 conditions and storage time on the properties of ten BR samples, with a particular focus on the speciation  
29 of yttrium, which is used as a proxy to identify the behaviour of heavy REE.

30 A multi-scale approach linked yttrium speciation and the origin of the bauxite ore whereas no major  
31 variation was observed as a function of storage conditions or ageing of the BRs. Yttrium is mainly found  
32 in the form of xenotime phosphate particles in BRs of lateritic origin, while in karstic BRs, the majority  
33 of yttrium is probably adsorbed or incorporated into other minerals including iron oxyhydroxide and  
34 hydroxyapatite minerals.

# 35 1. Introduction

36

37 The global demand for metals is constantly increasing, both in terms of quantity and diversity  
38 (OECD, 2019; Zepf et al., 2014). This increase is linked to the growth of the world's population and  
39 also to the emergence of new societal needs, which consume large quantities of these resources. This is  
40 particularly true for sectors such as defense and the digital and environmental transition which makes  
41 some metals with specific physico-chemical properties highly strategic (European Commission, 2020;  
42 International Energy Agency, 2021) or even “critical” for a number of non-producing countries (British  
43 Geological Survey, 2015; Grohol & Veeh, 2023; Hatayama & Tahara, 2014; U.S. Geological Survey,  
44 2022).

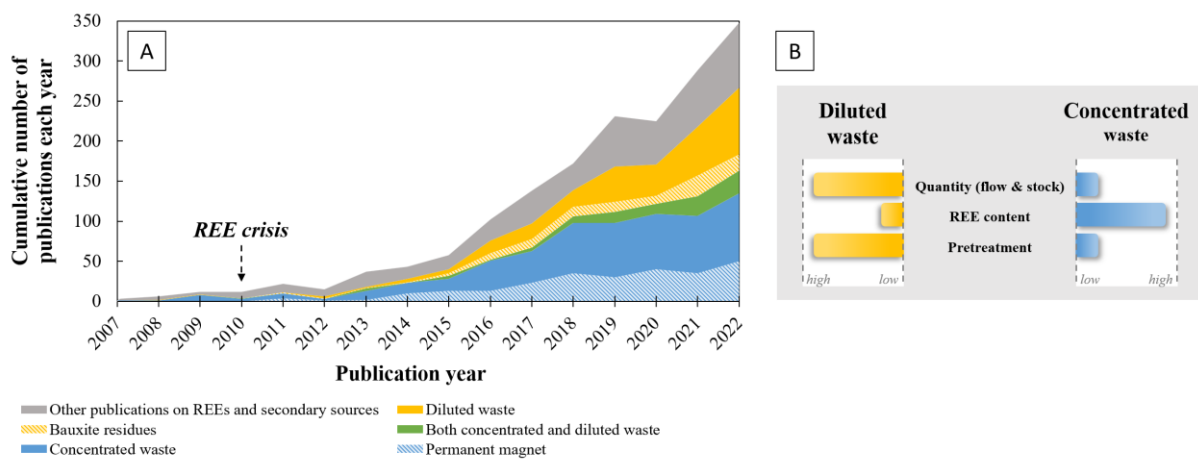
45 Rare earth elements (REEs), considered as one of the most critical elements according to European and  
46 American agencies (Grohol & Veeh, 2023; U.S. Geological Survey, 2022), are the focus of particular  
47 attention. The REE group includes metals from the lanthanide family ( $Z = 57 - 71$ ), as well as yttrium  
48 (Y,  $Z = 39$ ) and scandium (Sc,  $Z = 21$ ) due to their similar physico-chemical properties. REEs are usually  
49 subdivided into two subgroups, light rare earth elements (LREEs), comprising lanthanides from  
50 lanthanum (La,  $Z = 57$ ) to europium (Eu,  $Z = 63$ ) and heavy rare earth elements (HREEs), including Y  
51 and lanthanides from gadolinium (Gd,  $Z = 64$ ) to lutetium (Lu,  $Z = 71$ ). This arbitrary distinction has no  
52 scientific basis because there is no clear physico-chemical separation between these groups, rather a  
53 progressive change in properties and behaviours, including in ionic radii (Gschneidner, 1990). Their  
54 particular electronic configuration gives them specific electromagnetic properties, making them  
55 essential for many applications in electronics, manufacturing, medicine, and renewable energy, among  
56 others (Balaram, 2019). China controls almost the entire REE value chain (Gauß Roland et al., 2021),  
57 making the supply of REEs worldwide extremely vulnerable, as revealed in 2010, when China's quota  
58 policy causes a “REE crisis” in Europe and the US (Chen & Zheng, 2019).

59 Beyond these economic and geopolitical considerations, primary extraction also poses often neglected  
60 environmental and social problems (Eheliyagoda et al., 2020), due to the huge quantities of energy  
61 required and of waste generated (Adewuyi et al., 2020; Farjana et al., 2019), as well as social conflicts  
62 and accidents (Goodland, 2012; Scheidel et al., 2020). All these impacts are further amplified by the  
63 general decline in ore grades (Prior et al., 2012).

64 Faced with the ever-increasing demand for critical metals, the depletion of resources and the  
65 environmental and social crises associated with their extraction, a paradigm shift is urgently needed for  
66 the sustainable production of these metals. In particular, in the context of circular economy, there is a  
67 need to develop processes for extracting metals from secondary sources.

68 Since 2010 and the “REE crisis”, the search for secondary sources of REEs has become a hot research  
69 topic with almost 350 papers published in 2022 whereas before 2010, fewer than 10 papers were  
70 published on this topic per year (**Figure 1 A**). This vast literature can be divided into two main

71 categories. First, papers related to concentrated wastes (i.e. that contain REE concentrations above 1  
 72 wt%), which consist mainly in end-of-life products or product manufacturing scraps, and account for  
 73 the majority of publications. In this category, permanent magnets are the most widely studied followed  
 74 by waste from electrical and electronic equipment (WEEE), batteries, phosphors, catalysts or polishing  
 75 powders (Belfqueh et al., 2022; Ramprasad et al., 2022; Yang et al., 2013). Second, diluted wastes (i.e.  
 76 that contain REE concentration below 1 wt%) are usually more complex matrices (Binnemans et al.,  
 77 2015) that are potentially more difficult to exploit given the low concentrations of REEs but which also  
 78 attract considerable attention. This category includes mining and industrial wastes such as bauxite  
 79 residues (BRs), phosphogypsum, coal fly ash, acid mine drainage, mine tailings or wastewater  
 80 (Binnemans et al., 2015; Dupont & Binnemans, 2015; Hermassi et al., 2022; Peiravi et al., 2021). In this  
 81 category, BRs are one of the most frequently cited and studied as a potential source for REEs (20-35%  
 82 of identified papers in the last five years).



93 **Figure 1:** (A) Evolution of cumulative number of scientific papers containing “rare earth elements” and “secondary  
 94 sources” keywords, from 2007 and 2022, separated into several categories (source Web of Science). The “Concentrated  
 95 waste” category contains the keywords: “magnet”, “WEEE”, “phosphor”, “battery”, “catalyst”, “polishing waste”. The  
 96 “Diluted waste” category contains the keywords: “Bauxite residues”, “phosphogypsum”, “coal fly ash”, “mine drainage”,  
 97 “mine tailings”, “wastewater”. (B) Conceptual scheme of the difference in properties in diluted and concentrated waste.

100 Bauxite residues (BRs), also known as “red mud” when hydrated, are wastes generated during the  
 101 production of alumina using the Bayer process. During this process, the primary bauxite ore, rich in  
 102 aluminium (Al), is digested with concentrated soda under pressure, leaving a highly alkaline and sodic  
 103 residue at the end of the process. BRs are mainly composed of iron oxide but also contain a cocktail of  
 104 toxic and critical metals (Borra et al., 2016; Smith, 2009). REEs, which are naturally present in bauxite  
 105 ore, are concentrated in BRs as a result of the Bayer process and can reach more than 2500 mg/kg (2500  
 106 ppm) (Qu & Lian, 2013; Rayzman, 1998; Wagh & Pinnock, 1987), which makes BRs a potentially  
 107 good secondary source (Deady et al., 2014) with many advantages over concentrated waste (**Figure 1**  
 108 B). First, BRs represent a huge potential reserve of REEs: for every ton of alumina produced, between

109 1 and 2 tons of BRs are generated (Borra et al., 2016). Today, it is estimated that approximately 170 Mt  
110 of BRs are generated each year, i.e. producing a global stockpile exceeding 4 billion tons (Evans, 2016;  
111 International Aluminium Institute, 2023). These stocks are generally easily accessible, as they are  
112 located in storage sites close to alumina plants. Moreover, with their very fine granulometry (Gräfe et  
113 al., 2011), BRs require little grinding pre-treatment, which is often described as the most energy-  
114 consuming stage of the primary extraction processes (Adewuyi et al., 2020).

115 However, although this residue appears to be an interesting alternative for the production of REEs, the  
116 variability of the physico-chemical properties of these residues is an obstacle to the development of a  
117 universal process of REE extraction. Several parameters may cause physico-chemical variations in the  
118 stocks of BRs available worldwide. First, essentially two types of bauxite ores are used as inputs in the  
119 Bayer process: lateritic bauxites, which account for 90% of the mineable reserves, and karstic (or karst)  
120 bauxites (Freyssinet et al., 2005). Both derive from similar processes of alteration and sedimentation  
121 (weathering, transportation and deposition), leading to the formation of an Al-rich ore. The difference  
122 lies in their bedrock lithology: lateritic bauxite deposits overlie aluminosilicate rocks while karstic  
123 deposits overlie carbonate rocks (Bardossy, 1982). Second, differences in the efficiency of the Bayer  
124 process due to different Al mineralogy depending on the type or quality of the bauxite ore and variability  
125 in the implementation of the Bayer process, may result in variable amounts of Al remaining in the mine  
126 tailings. The conditions and time of storage of the residues may also affect their physico-chemical  
127 properties. When not directly discharged into the seas and oceans, BRs are stored in different ways  
128 ranging from dry storage in the open air to storage in the form of sludge in retention ponds (Evans, 2016;  
129 Fourrier, 2020; Power et al., 2011). Aging of BRs can also induce physico-chemical variability since  
130 some residue deposits may be more than 100 years old: the Bayer process was invented at the end of the  
131 19th century (Borra et al., 2016). Consequently, treatment or remediation attempts (cover layers, organic  
132 or inorganic amendment, etc.) have been undertaken at many sites sometimes leading to revegetation of  
133 the site despite particularly hostile conditions for life (Di Carlo et al., 2019).

134 This variability also results in marked differences in chemical composition and mineralogy as reported  
135 in the literature (Borra et al., 2016; Evans, 2016; Ma et al., 2022; Xue et al., 2016). Although the  
136 chemical and mineralogical variability is fairly well documented for major elements such as Fe and Al,  
137 very little information is available on REE speciation (i.e., the chemical environment) in BRs. Also,  
138 most studies that do address REE speciation are based on a microscopic approach (using electron probe  
139 microanalyses (EPMA) or scanning electron microscopy coupled with energy dispersive X-ray  
140 spectrometry (SEM/EDS)) and rely on elemental co-localization to identify REE bearing phases, which  
141 are based on assumptions, rather than on direct speciation analyses (Gentzmann et al., 2021;  
142 Ochsenkiihn-Petropulu et al., 1996; Rivera et al., 2019; Vind et al., 2018). In addition, existing studies  
143 rarely investigate the influence of origin of the bauxite ore, or the time and conditions of storage of BRs.  
144 Indeed, detecting low concentration phases and elements in such complex matrices is far from easy, plus  
145 detailed characterisation of REEs in BRs requires state of the art facilities such as synchrotron sources.

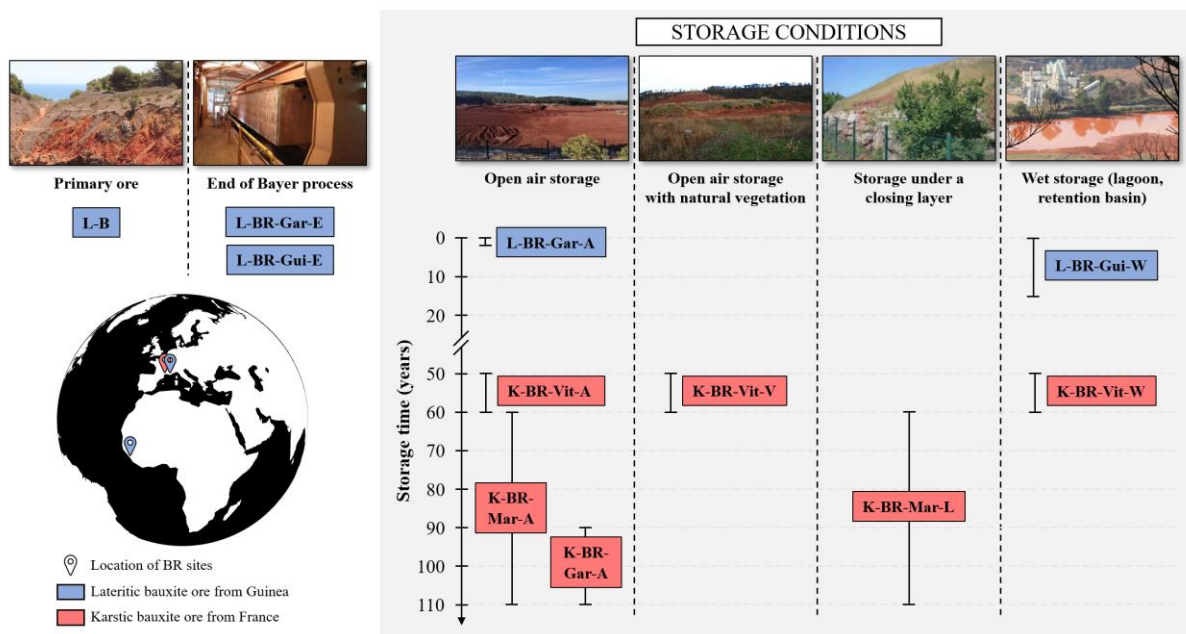
146 In the present study, the physico-chemical properties, chemical composition, mineralogy and yttrium  
147 speciation of ten BR samples with different origins, ages and storage conditions were characterised.  
148 Yttrium was used as a proxy for HREEs thanks to its similar physico-chemical behaviour (Borst et al.,  
149 2020; Lallemand et al., 2022; Pingitore et al., 2014). Improving knowledge of the REE speciation in  
150 BRs and the factors that influence it will pave the way for the development of extraction processes that  
151 account for the specificity of the targeted BRs in terms of origin, storage conditions and time (Dedy et  
152 al., 2014). Such perspectives are discussed in light of our results.

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154 **2. Materials and methods**

155 **2.1. Materials and sampling**

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168 *Sample nomenclature :*  
 169 L/K: lateritic/karstic origin  
 170 B/BR: Bauxite ore/Bauxite residue  
 171 Gar/Gui/Mar/Vit: abbreviations for Gardanne/Guinea/Marseille/Vitrolles collection site  
 172 E/A/V/L/W: end of process/open air storage/open air with vegetation/storage under closing layer/wet storage

170 **Figure 2:** Presentation of the study samples according to the origin of the ore, age, storage conditions and associated  
 171 nomenclature

173 The sample bauxite residues were categorized in two types: those generated from a lateritic-type  
 174 bauxite ore located in Guinea (Boké region), and those generated from a karstic-type bauxite ore located  
 175 in the south of France (Provence region), hereafter referred to respectively as “lateritic BRs” and “karstic  
 176 BRs” for the sake of simplicity. These ten residues were collected from four different tailing sites: three  
 177 in France (Gardanne “Gar”, Vitrolles “Vit”, Marseille “Mar”) and one site in Guinea “Gui” (Fria plant  
 178 site) from three alumina production plants which use the Bayer process. Samples were collected at  
 179 several places: (i) directly at the end of the alumina extraction process (E suffix), after the filter press  
 180 (L-BR-Gar-E) or the last scrubber (L-BR-Gui-E), (ii) from open-air storage sites (A suffix) at the surface  
 181 (maximum 30 cm depth) of the deposits (L-BR-Gar-A, K-BR-Vit-A, K-BR-Mar-A, K-BR-Gar-A), one  
 182 of which in a heavily vegetated area (suffix V) (K-BR-Vit-V), (iii) from a storage site under a vegetated  
 183 capping layer (suffix L), at a depth of 1 m below the surface (K-BR-Mar-L) and (iv) from wet storage  
 184 sites (suffix W) as lagoon or retention basin (L-BR-Gui-W, K-BR-Vit-W). The storage conditions and  
 185 aging times (from 0 to 100 years) of the residues are detailed in **Table 1** and **Figure 2**.

186 The initial lateritic bauxite ore (L-B) sample was supplied by Alteo company, a producer of alumina at  
 187 the Gardanne site which, at that time, used lateritic bauxite ores imported from Guinea. No bauxite ore  
 188 of karstic origin representative of the studied karstic BR samples was used in the present study because



189 either the plant concerned had closed down or the supply had been switched to lateritic bauxite ores, as  
190 was the case in Gardanne between the 1970s and 1990s (Arnaud & Guillon, 1989).  
191 Before the experiments began, all the samples were dried at between 60-70 °C then manually ground to  
192 < 125 µm using an agate mortar and homogenized. The resulting dry materials were stored at ambient  
193 pressure and temperature.

Table 1: Detailed description of the samples cited in this article

Name of sample	Type of sample	Origin of bauxite	Plant	Sampling location	Storage conditions	Some known detailed conditions	Storage time
<b>L-B</b>	Bauxite ore	Lateritic (Guinea)	/	*	/	/	/
<b>L-BR-Gui-E</b>	Bauxite residue	Lateritic (Guinea)	Fria plant (Guinea)	At the plant (end of process)	End of Bayer process (after the last scrubber)	/	/
<b>L-BR-Gui-W</b>	Bauxite residue	Lateritic (Guinea)	Fria plant (Guinea)	Dote dam, Guinea	Wet storage (Tropical climate)	/	~0-15 years***
<b>L-BR-Gar-E</b>	Bauxite residue	Lateritic (Guinea)	Gardanne plant (France)	At the plant (end of process)	End of Bayer process (after the filter press)	/	/
<b>L-BR-Gar-A</b>	Bauxite residue	Lateritic (Guinea)	Gardanne plant (France)	Gardanne tailing site (Mange-Garri)	Storage in the open air (Mediterranean climate)	Occasional watering / BR was mixed with compost at this location	~1 year
<b>K-BR-Gar-A</b>	Bauxite residue	Karstic (France)	Gardanne plant (France)	Gardanne tailing site (Mange-Garri)	Storage in the open air (Mediterranean climate)	Occasional watering / soil amendment in the 1960's / light vegetation cover	~ <b>90</b> -110 years**
<b>K-BR-Mar-A</b>	Bauxite residue	Karstic (France)	Saint-Louis-les-Aygalades plant (France)	Marseille tailing site (La Delorme)	Storage in the open air (Mediterranean climate)	/	~ <b>60</b> -110 years**
<b>K-BR-Mar-L</b>	Bauxite residue	Karstic (France)	Saint-Louis-les-Aygalades plant (France)	Marseille tailing site (La Delorme)	Storage under closing layer (Mediterranean climate)	Backfill layer and vegetation (capping layer)	~ <b>60</b> -110 years**
<b>K-BR-Vit-A</b>	Bauxite residue	Karstic (France)	Saint-Louis-les-Aygalades plant (France)	Vitrolles tailing site (Griffon)	Storage in the open air (Mediterranean climate)	Presumed landfill (sewage sludge spreading)	~ <b>50</b> -60 years**
<b>K-BR-Vit-V</b>	Bauxite residue	Karstic (France)	Saint-Louis-les-Aygalades plant (France)	Vitrolles tailing site (Griffon)	Storage in a heavily vegetated area (Mediterranean climate)	Vegetation cover / backfills presence / presumed landfill	~ <b>50</b> -60 years**
<b>K-BR-Vit-W</b>	Bauxite residue	Karstic (France)	Saint-Louis-les-Aygalades plant (France)	Vitrolles tailing site (Griffon)	Wet storage, in a retention basin (Mediterranean climate)	Presumed landfill and backfills presence	~ <b>50</b> -60 years**

\* Supplied by Alteo, the company that currently manages the Gardanne plant.

\*\* Uncertainty concerning the time of use of the storage site. Dry samples collected on the surface and therefore considered to be young (in **bold** in the table).

\*\*\* Difficult to determine the exact age of storage of liquid samples in the dam because of potential transfer between young and old residues. Liquid samples collected on the surface can be considered to be relatively young (0-15 years) compared to the age of the dam (40 years).

## 194 **2.2. Characterisation of the samples**

### 195 **2.2.1. pH and conductivity**

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197 For pH and electrical conductivity measurements, aqueous suspensions with a 1/5 solid/liquid  
198 ratio (1 g of material in 5 mL of distilled water) were prepared according to ISO 10390:2021.  
199 Measurements were made at 20 °C with two replicates after 2 h of stirring and 24 h of decantation.

### 200 **2.2.2. Chemical composition**

201 Preparation and bulk chemical analyses were conducted at CEREGE (France). The samples  
202 were digested by alkaline fusion using 100 mg of sample mixed with 500 mg of previously dried flux  
203 (49.5% lithium tetraborate, 49.5% lithium metaborate, 1% LiBr) and placed in an oven (Malvern  
204 Panalytical Claisse LeNeo) to undergo specific high refractory material digestion (up to 1050 °C for 22  
205 min). The resulting fusion pearl was immediately dissolved in 40 mL of nitric acid (3-4 wt%). After  
206 appropriate dilution in distilled water, trace elements (<1000 µg/L) were analysed by inductively  
207 coupled plasma mass spectrometry (ICP-MS, Perkin Elmer 300X quadrupole) and major elements  
208 (>1000 µg/L) were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES  
209 Perkin Elmer Optima 4300 DV).

210 Three replicates were made of each analysis, and the results (concentration in mg/kg dry weight) are  
211 expressed along with the average and the standard deviation of the three samples.

### 212 **2.2.3. Mineralogy**

213 Mineralogy was performed by X-ray diffraction (XRD) at 40 kV and 40 mA on a PANalytical  
214 X'Pert Pro (Malvern Panalytical, UK) diffractometer equipped with a rear monochromator and a cobalt  
215 anticathode ( $\lambda = 1.79 \text{ \AA}$ ) at CEREGE (France). Powder samples were deposited on low background  
216 silicon plates with a drop of ethanol and scanned from 5 to 75° (2 $\theta$ ) with a step size of 0.033° and a total  
217 counting time of 3 h. The sample was rotated at 15 rpm during analysis to improve the statistics. Phase  
218 identification was performed using the X'pert Highscore plus software (Malvern Panalytical) with the  
219 PDF-2 ICDD (International Center for Diffraction data, Powder Diffraction Files 2) and COD  
220 (Crystallography Open Database).

### 222 **2.2.4. Microscale observations**

223 Microscale observations were performed using a Quattro S Environmental Scanning Electron  
224 Microscope (ThermoFisher) coupled with a XFlash6 / 100 Energy Dispersive X-ray Spectrometer with  
225 Quantax 400 software (Bruker) (SEM/EDS) (ICSM, France). The L-BR-Gui-E and K-BR-Mar-A  
226 powder samples were embedded in resin (Araldite 2020) and then polished (using silicon carbide and  
227 diamond) with oil. The cross-sections were then coated with carbon, and copper tape was used to ensure  
228 good conduction during microscopy. Series of elemental distribution maps (12×12 and 15×15, ×500  
229 magnification) were first recorded (30 kV, 200 keps, 20 min for each) to locate particles or grains  
230 containing Y over a large area (6-8 mm<sup>2</sup>). Once the particles were identified, EDS point analyses (15

231 kV, 100 kcps, 1 min), as well as EDS elemental maps of the selected areas (12 kV, 50 kcps, 20 min)  
232 were performed. Finally, quantitative-EDS elemental maps were performed to avoid interference  
233 between elements. These maps were produced by integrating 8×8 pixels from the qualitative EDS maps  
234 to increase the counting statistics and reduce calculation time.

235

### 236 **2.2.5. Yttrium speciation by X-ray absorption spectroscopy (XAS)**

237 XAS spectra at Y K-edge (17.038 keV) were recorded at the European Synchrotron Radiation  
238 Facility (ESRF, Grenoble, France) on beamline BM30 (CRG-FAME beamline) (Chaurand et al., 2025).

239 Incoming photon flux energy was modulated using a Si(220) double crystal monochromator and  
240 higher harmonics were suppressed using Rh-curved mirrors. The data were collected in the step-by-step  
241 mode with a beam size of 200×150 μm.

242 Samples of bauxite ore and BRs were prepared as pure pellets (~30 mg), and model compounds were  
243 prepared as pellets diluted with polyvinylpyrrolidone (PVP). For the latter, the dilution ratio with PVP  
244 was calculated to obtain an optimal  $\Delta\mu_{theoretical}$  of 1 with ABSORBIX software (v3.02) (Michalowicz  
245 et al., 2009).

246 During the experiment, incoming X-ray beam energy was calibrated and regularly checked using a  
247 reference metal foil of Y. Each sample was measured in an He cryostat at 10-20 K to prevent beam  
248 damage. Spectra were obtained in fluorescence mode for bauxite ore and BR samples (average of 3 to 9  
249 scans depending on the signal to noise ratio), and in transmission mode for model compounds (1 to 3  
250 scans), except for the Y-doped hematite model compound which was run in fluorescence mode due to  
251 the relatively low concentration of Y. XAS spectra (XANES and EXAFS) were recorded from 16.85 to  
252 17.58 keV ( $k = 12 \text{ \AA}^{-1}$ ) with an energy step of 5 eV between 16.85 and 17 keV (1s counting time), of  
253 0.5eV from 17 to 17.085 keV and a  $k$  step of 0.05  $\text{\AA}^{-1}$  from 17.085 to 17.58 keV. Calibration, merging  
254 and normalization were performed with XAS-Viewer software (Larch, v0.9.65) (Newville, 2013).

255

256 A library of Y reference compound spectra was used to identify Y species in bauxite ore and BRs  
257 (Couturier et al., 2022). The library consisted of commercial references (purity >99.9%): yttrium oxide  
258 ( $\text{Y}_2\text{O}_3$ ; Acros Organics), yttrium carbonate ( $\text{Y}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ ; Alfa Aesar), yttrium phosphate  
259 ( $\text{YPO}_4 \cdot x\text{H}_2\text{O}$  Alfa Aesar) hereafter “medium crystallized xenotime  $\text{YPO}_4$ ” or “mcx $\text{YPO}_4$ ”, but also  
260 synthesized references (see protocols and XRD in SI): yttrium hydroxide ( $\text{Y}(\text{OH})_3$ ), yttrium phosphate  
261 ( $\text{YPO}_4$ ) with different phase and crystallinity (churchite, low and high crystallized xenotime), Y-  
262 adsorbed on montmorillonite ( $(\text{Na,Ca})_{0,3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ ), Y-doped Calcite ( $\text{CaCO}_3$ ), Y-  
263 doped hematite ( $\text{Fe}_2\text{O}_3$ ), low and high crystallized Y-doped hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ).

264 Linear combination fitting (LCF) of the XANES region was performed from 17000 to 17220 eV with a  
265 maximum of three components (adding a fourth component did not improve fits) using XAS Viewer  
266 software (Larch, v0.9.65) (Newville, 2013). The reduced-chi-square value ( $\chi_{red}^2$ ), which accounts for  
267 degrees of freedom in the fit, was used to compare the relative quality of two fits that use the same

268 interval but a potentially different number of variables. A change between two fits is considered  
269 statistically significant when the ratio of their two reduced-chi-square is greater than two standard  
270 deviations, according to the reference (Kelly et al., 2008). In our case, this criterion was used to identify  
271 all fits that were significantly identical to the best fit, which were then defined as "good fits". The value  
272 of the criterion was 1.185 and was obtained with the number of points in the fitting interval ( $N = 237-$   
273  $239$ ) and the number of variables in the fit ( $V = 3-4$ ).

### 274 3. Results and discussion

#### 275 3.1. pH and electrical conductivity

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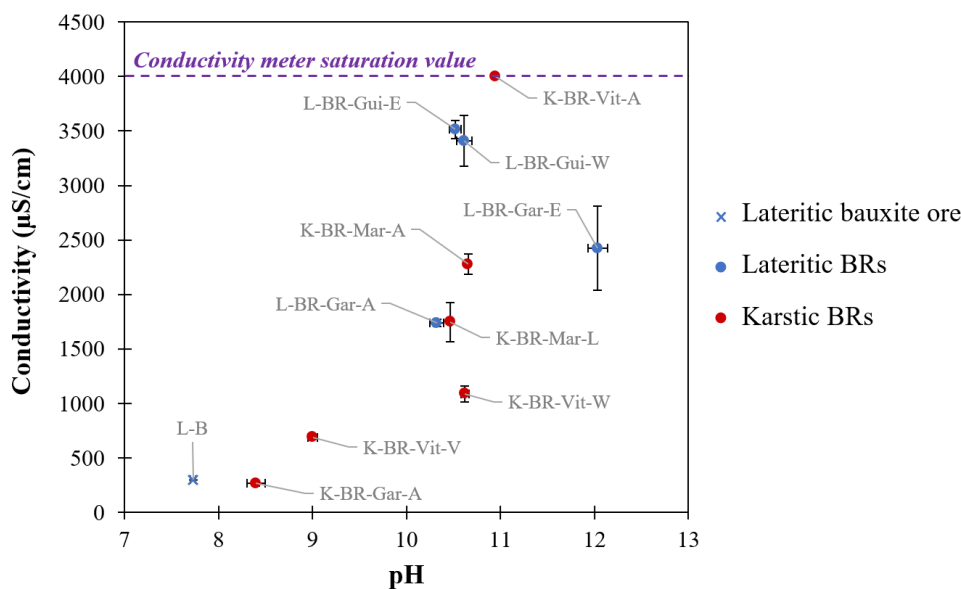
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289 **Figure 3:** Conductivity of all the samples as a function of pH (solid/liquid ratio = 1/5, 20 °C) (blue = lateritic-type, red =  
290 karstic-type).

291

292 pH and conductivity varied widely among the samples (**Figure 3, Table S1**). The bauxite ore  
293 sample (L-B) had an almost neutral pH and very low conductivity (<300 µS/cm), whereas the BRs had  
294 alkaline pH ranging from 8.4 to 12, and strongly varying conductivity, i.e. from 266 µS/cm to >4 mS/cm  
295 (saturation value). The high variability observed is nevertheless consistent with that reported in the  
296 literature (Gräfe et al., 2011; Snars & Gilkes, 2009).

297 The alkaline nature and high conductivity of BRs are due to the contact between bauxite ore and  
298 concentrated soda during the Bayer process. In addition to solubilizing Al, excess OH<sup>-</sup> and Na<sup>+</sup> ions in  
299 the residue are responsible for the high pH and conductivity (Di Carlo et al., 2019; Gräfe et al., 2011).  
300 Many parameters can influence both pH and conductivity of the BRs. During the Bayer process, the  
301 concentration of the NaOH solution, the quality of the washing steps or the inclusion of a filtration step  
302 determine the alkalinity and salinity of the BR at the outlet of the plant, among other things (Power et  
303 al., 2011). During storage, locally strong increases in pH and conductivity can occur at the surface of  
304 the deposit, resulting in the formation of efflorescence (Di Carlo et al., 2019; Wu et al., 2020), mainly  
305 in the form of a thin white layer composed of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. This phenomenon has already been  
306 observed at the Vitrolles site (Fourrier, 2020) and may explain the high conductivity of K-BR-Vit-A.  
307 However, a decrease in pH and conductivity is most often observed as a function of the storage time of  
308 the deposit. The decrease is related to the leaching of alkaline soluble compounds by natural weathering  
309 (mainly rainfall), to the slow carbonation of BRs by atmospheric CO<sub>2</sub> or even to the activity of  
310 microorganisms and plants (Cusack et al., 2019; Di Carlo et al., 2019; Khaitan et al., 2010; Kong, Guo,

311 et al., 2017; Macías-Pérez et al., 2022; Zhu et al., 2016). This aging effect was particularly visible in the  
312 oldest sample, K-BR-Gar-A. Organic, inorganic, acidic or seawater amendments also lead to the  
313 neutralization of BRs, which is one of the most desired effects when the aim is remediation or use of  
314 these wastes around the world (Fourrier et al., 2021; Jones et al., 2012; Khaitan et al., 2009, 2010;  
315 Klauber et al., 2011; Kong, Li, et al., 2017; Menzies & Kopittke, 2021; Wong & Ho, 1991).  
316 Neutralization of BRs is the main factor that enables the natural establishment of micro-organisms and  
317 vegetation (Di Carlo et al., 2019; Santini & Fey, 2013; Xue et al., 2016), as can be seen at the K-BR-  
318 Gar-A and L-BR-Vit-V sites.

319 The age or storage conditions of the BRs thus appear to have an influence on their pH and conductivity,  
320 but many other parameters also come into play, making it difficult to make clear correlation, especially  
321 when the history of operations at the site is difficult to trace.

322

323 **3.2. Chemical composition**

324

325 **Table 2:** Chemical composition by mass of major elements (Fe, Al, Ti, Si, Ca), Y and sum of all REEs (including Y and Sc)  
 326 present in our samples, obtained by ICP-MS and ICP-OES after alkaline fusion (3 replicates).

Sample	Fe (wt%)	Al (wt %)	Ti (wt %)	Si (wt %)	Na (wt %)	Ca (wt %)	Y (mg/kg)	ΣREEs (mg/kg)
L-B	14.51 ± 0.08	23.11 ± 0.04	1.57 ± 0.01	1.00 ± 0.01	0.01 ± 0.02	0.00 ± 0.01	34 ± 2	218 ± 6
L-BR-Gui-E	31.24 ± 0.11	8.05 ± 0.14	3.26 ± 0.08	2.02*	1.94 ± 0.03	1.16 ± 0.09	102 ± 2	562 ± 15
L-BR-Gui-W	32.33 ± 1.34	8.73 ± 0.35	3.40 ± 0.18	2.31*	1.98 ± 0.12	1.46 ± 0.11	101 ± 6	563 ± 25
L-BR-Gar-E	31.48 ± 0.45	5.56 ± 0.11	4.74 ± 0.10	1.97 ± 0.02	2.23 ± 0.09	4.28 ± 0.09	118 ± 0	727 ± 4
L-BR-Gar-A	31.90 ± 0.23	6.49 ± 0.03	5.15 ± 0.04	1.92 ± 0.02	2.54 ± 0.04	2.82 ± 0.04	123 ± 2	778 ± 13
K-BR-Gar-A	28.47 ± 0.65	8.97 ± 0.06	2.37 ± 0.03	3.13 ± 0.06	1.28 ± 0.04	3.53 ± 0.05	226 ± 4	1792 ± 24
K-BR-Mar-A	29.43 ± 1.01	5.60 ± 0.17	4.08 ± 0.14	3.20 ± 0.11	3.06 ± 0.15	4.45 ± 0.02	226 ± 8	2261 ± 74
K-BR-Mar-L	39.02 ± 0.13	6.22 ± 0.03	4.52 ± 0.02	2.76 ± 0.01	2.34 ± 0.02	0.85 ± 0.01	265 ± 10	2702 ± 128
K-BR-Vit-A	25.31 ± 0.51	9.92 ± 0.15	2.70 ± 0.04	3.67 ± 0.07	5.91 ± 0.27	1.85 ± 0.04	219 ± 2	1924 ± 18
K-BR-Vit-V	21.64 ± 0.28	7.96 ± 0.05	2.47 ± 0.02	5.25 ± 0.03	3.04 ± 0.06	5.01 ± 0.04	184 ± 1	1549 ± 11
K-BR-Vit-W	20.80 ± 0.06	7.78 ± 0.03	2.47 ± 0.01	5.88 ± 0.02	3.79 ± 0.22	6.01 ± 0.02	199 ± 3	1668 ± 7

327 \* Silicon was only measured in one replicate of L-BR-Gui-E and L-BR-Gui-W samples.

328

329 The chemical composition of the samples is listed in **Table 2** (additional elements are reported  
 330 in **Table S2**). The bauxite ore sample (L-B) mainly contained aluminium (Al, 23.1 wt%) and iron (Fe,  
 331 14.5 wt%) while BR samples mainly contained Fe (20-39 wt%), Al (5-10%), silicon (Si, 2-6 wt%) and  
 332 titanium (Ti, 2-5 wt%). The main difference in composition between bauxite ore and the BR samples  
 333 was due to Al extraction during the Bayer process. The Bayer process was also at the origin of the non-  
 334 negligible sodium content (Na, 1.3-5.9 wt%) and calcium content (Ca, 0.8-6.0 wt%) in the BRs, whereas  
 335 these elements were not present in the L-B sample. The presence of Na is due to digestion of bauxite  
 336 ore with caustic soda (NaOH) and the presence of Ca to the addition of lime (CaO, Ca(OH)<sub>2</sub>) during  
 337 preliminary desilication and causticization (Borra et al., 2016; Smith, 2009).

338 Among the minor elements, the amount of total REEs (including Y and Sc) in the L-B sample  
 339 was 218 mg/kg while total REE contents in BRs ranged from 562 to 2702 mg/kg. The enrichment of the  
 340 REE content in BRs is specific to the Bayer process, as these elements are not released by soda during  
 341 the process and are consequently concentrated in the residues. Individually, REE concentrations agree  
 342 with their natural occurrence, ranked in decreasing order: Ce, followed by Y, La, Nd and Sc and the  
 343 other REEs (**Table S2**).

344 Despite the significant differences between the BR samples considered in the present study, in terms of  
 345 their ore origin, storage conditions, ages, as well as pH and conductivities, variations in the  
 346 concentrations of the major elements remain limited compared to the variety of compositions reported  
 347 in the literature (Binnemans et al., 2015; Evans, 2016; Gräfe et al., 2011; Khairul et al., 2019; Snars &



348 Gilkes, 2009; Xue et al., 2016). In particular, no correlation was found between the variations in the  
349 concentration of these elements and their storage time, thereby confirming some findings reported in the  
350 literature (Cusack et al., 2019). However, some slight variations in the composition of BRs can be  
351 explained by the history of activities at the storage site concerned or during the implementation of the  
352 Bayer process. To give an example, aerial image archives have proven the presence of construction site  
353 landfills in the lower part of the Vitrolles tailing site over the last 30 years, which correspond to the areas  
354 where the K-BR-Vit-V and K-BR-Vit-W were sampled (Fourrier, 2020). The addition of Si and Ca rich  
355 materials is probably responsible for lower concentrations of Fe, Al and Ti and higher concentrations of  
356 Si and Ca compared to the K-BR-Vit-A sample, which was collected from the upper part of the same  
357 tailing site and has never been in contact with these landfills. However, the difference in Al content  
358 between L-BR-Gui-E (8.0 wt%) and L-BR-Gar-E (5.6 wt%) could also be due to differences in the  
359 quality of the ore and/or in the performance of the Bayer process.

360 In contrast to major elements, the origin of the bauxite ore has a strong influence on REE content in BRs  
361 ( $657 \pm 112$  mg/kg ( $n = 4$ ) for lateritic BRs and  $1983 \pm 429$  mg/kg ( $n = 6$ ) for karstic BRs). Indeed, karstic  
362 bauxites are known to have higher concentrations of REEs than lateritic bauxites (Binnemans et al.,  
363 2015; Borra et al., 2016; Vind et al., 2018), and can reach 1000 mg/kg or more (Liu et al., 2016; Mondillo  
364 et al., 2019). This difference has been widely reported and is usually attributed to the "pH-barrier" of  
365 the underlying alkaline carbonate rock that tends to favour REE concentration in karstic bauxites  
366 (Gentzmann et al., 2021). Consequently, the difference is carried over to the BRs with concentrations  
367 of up to 2702 mg/kg in the K-BR-Mar-L sample, which is more than ten times the average for the earth's  
368 crust ( $\sum$ REEs  $\approx 240$  mg/kg) (Haynes, 2014). The high REE contents in BRs originating from karstic  
369 bauxite ores make them promising secondary sources of REEs for the future. In comparison, some  
370 natural deposits currently being exploited for their REEs contain less than 1 wt% REEs (Davris et al.,  
371 2017; Huang et al., 2021; M. Y. H. Li et al., 2019).

372 The specific karstic/lateritic signature in terms of the chemical compositions of BRs can be also  
373 observed in other elements. For example, P, Cr, V, Ga are more abundant in lateritic BRs, while Si, Mg,  
374 Mn, Sr, Ni, Pb, As, Co are present at higher concentrations in karstic BRs. Finally, among the elements  
375 present in the BRs (**Table S2**), we also noted the presence of significant quantities of Ti (up to >5 wt%),  
376 Mg (up to >3000 mg/kg in karstic BRs), Zr (up to >2000 mg/kg), P (up to >2000 mg/kg in lateritic BRs),  
377 V (up to >1500 mg/kg in lateritic BRs), Cr (up to >1500 mg/kg in lateritic BRs), Mn (up to >800 mg/kg  
378 in karstic BRs), Sr (up to >400 mg/kg in karstic BRs), Ni (up to >300 mg/kg in karstic BRs), which are  
379 also considered as critical elements by the European Commission or the USGS (Grohol & Veeh, 2023;  
380 U.S. Geological Survey, 2022), and for which the possibility to use BRs as a secondary source remains  
381 to be investigated.

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### 3.3. Chondrite-normalized REE profiles

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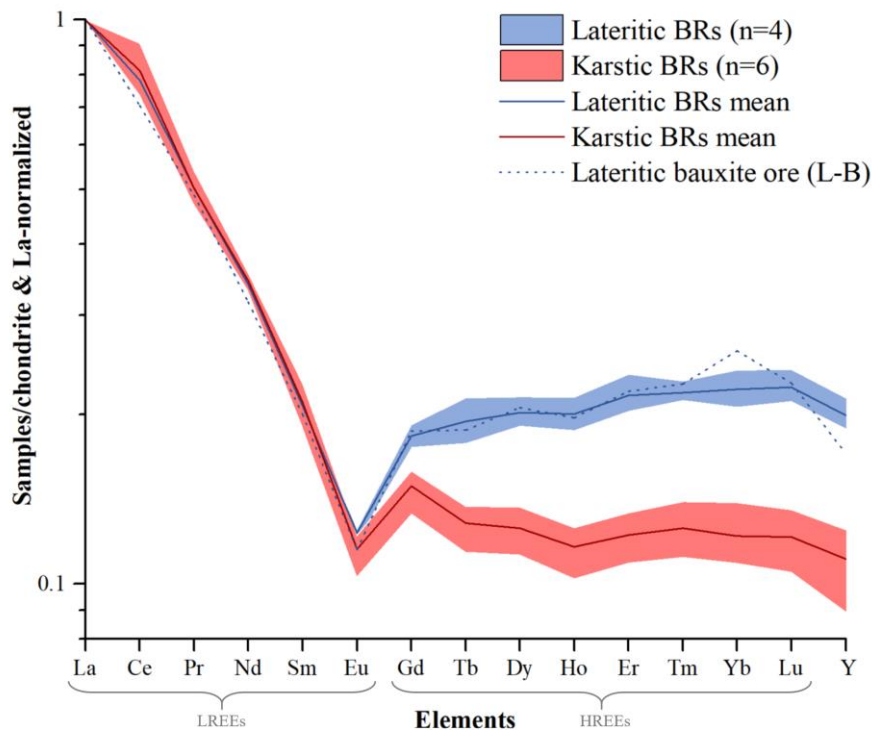
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**Figure 4:** Patterns of chondrite and lanthanum-normalized rare earth elements in all the bauxite residue samples studied here, separated according to the origin of the ore. The normalized spectrum of lateritic bauxite ore sample is plotted for the purpose of comparison. The normalized values come from (Taylor & McLennan, 1985)

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For a more in-depth analysis of the observed differences between lateritic and karstic BRs with respect to REEs, chondrite-normalized REE profiles are plotted by normalizing each REE content by the corresponding value in the chondrites (Taylor & McLennan, 1985), (**Figure 4, Table S3**). In order to compare samples independently of their total REE content, the REE profiles are also normalized by the lanthanum value for each sample.

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All the BRs showed dominance of LREEs over HREEs, which decreased with an increase in Z, as often reported for bauxites in the literature [69], [70]. The Ce and Eu anomalies, defined as the  $\frac{Ce_N}{\sqrt{(La_N * Pr_N)}}$  and  $\frac{Eu_N}{\sqrt{(Sm_N * Gd_N)}}$  ratios also presented similar values (1.0 to 1.3 and 0.6 to 0.7 respectively), when we compared BR compositions (**Table S4**). Interestingly, a difference appeared in the behaviour of HREEs depending on the origin of the bauxite ore. Evidence for a relative enrichment of HREEs, also visible on Y, was found in lateritic BRs compared to in karstic BRs. This variation can be characterised by the value of the slope of the REE pattern, defined as the ratio of normalized  $La_N/Lu_N$  values, which is lower for lateritic BRs (4.2 to 4.7) than for karstic BRs (7.4 to 9.5) (**Table S4**). It is also important to note that the lateritic bauxite ore sample (L-B) followed the same pattern as the lateritic BRs despite a 2 to 4 times lower REE concentration. This supports the conclusion that the differences observed in the HREEs are characteristic of the origin of the bauxite ore, as, when we compared the

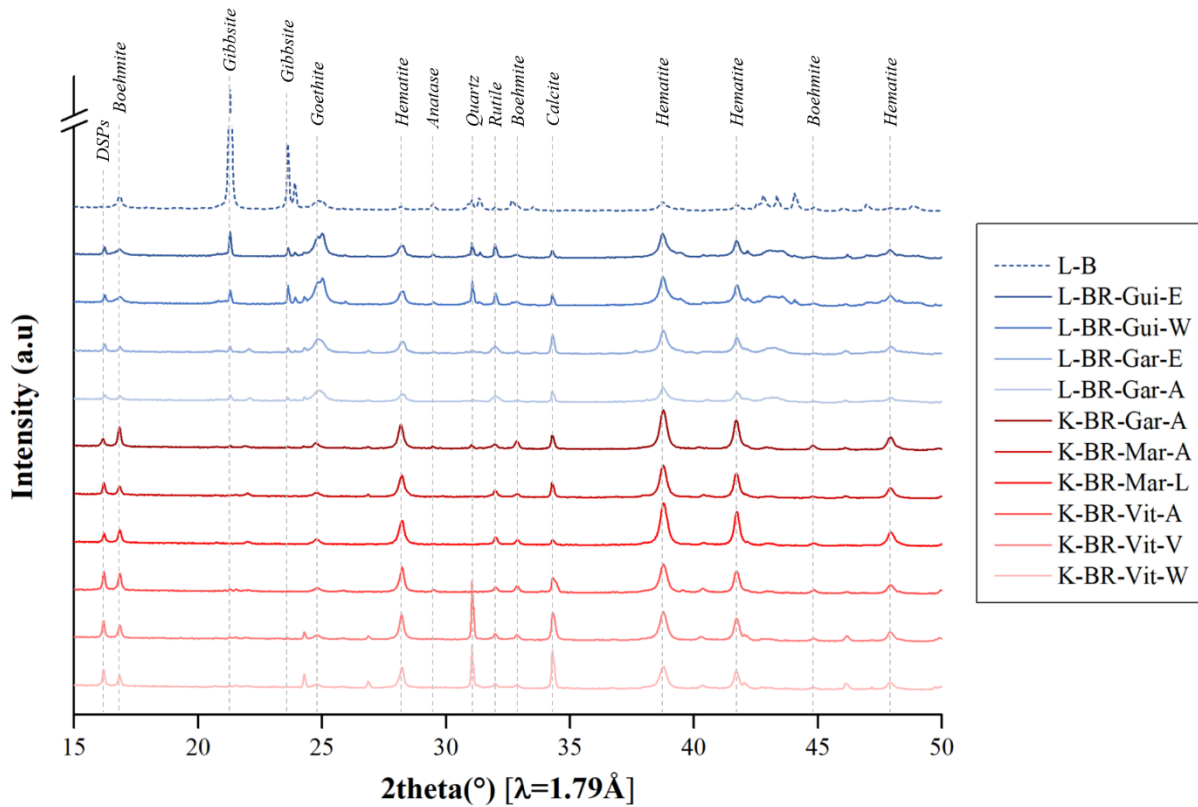
420 REE profiles of L-B and lateritic BRs, the Bayer process had no effect on the relative proportions of the  
421 REEs.

422 Differences in REE patterns may be the signature of different speciation (Bea, 1996). **Figure 4** suggests  
423 that HREEs bearing phases in BRs differ depending on the origin of the bauxite ore. This hypothesis  
424 was reinforced by further analysis of the chemical data. For example, the scatterplot between P and  
425 HREEs shows that HREEs concentration is correlated with the concentration of P in lateritic BRs,  
426 whereas no correlation was apparent in karstic BRs (*Figure S2*). To identify the HREE-bearing phases  
427 and the potential association of HREEs with P in the BRs, the mineralogy of the samples was next  
428 examined from a macroscopic and microscopic perspective, as described in the following sections.

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### 3.4. Mineralogy



**Figure 5:** X-ray diffraction patterns of the studied bauxite ore (L-B) and bauxite residue samples sorted by origin of the ore (blue = lateritic-type, red = karstic-type). Identification of the main peaks of the major phases. DSPs: desilication products

The X-ray diffraction (XRD) patterns are reported in **Figure 5**. In agreement with the elemental composition, the mineralogy of the lateritic bauxite ore sample (L-B) was dominated by Al phases, mostly in the form of gibbsite ( $\text{Al}(\text{OH})_3$ ). Gibbsite is known to be the main Al phase in lateritic bauxites characterised by weathering under a tropical climate (Baïoumy, 2016; Bhukte et al., 2020; De Oliveira et al., 2016; Negrão & Costa, 2021; Sidibe & Yalcin, 2018; Vind et al., 2018), although diaspore ( $\text{AlO}(\text{OH})$ ) may be encountered in certain cases (Gu et al., 2013). Also, karstic bauxites (not studied here) often contain boehmite ( $\text{AlO}(\text{OH})$ ) as the main Al phase (Kloprogge et al., 2002; Mondillo et al., 2019; Radusinović & Papadopoulos, 2021; Reinhardt et al., 2018) even if gibbsite or diaspore phases are the main phases in some non-Mediterranean karstic bauxites (Z. Li et al., 2013; Torró et al., 2017). The effect of the Bayer process transforming bauxite ore into BR is clearly visible on XRD diffractograms. The majority of the Al phases contained in L-B were extracted showing the Fe phases to be predominant in BRs as hematite ( $\text{Fe}_2\text{O}_3$ ) or goethite ( $\text{FeO}(\text{OH})$ ). The decrease in the Al phase in the BRs also brought out minor Ti phases, such as anatase or rutile ( $\text{TiO}_2$ ), and Si, as quartz ( $\text{SiO}_2$ ) which were masked in L-B due to the limit of detection of this technique ( $\approx 1$  wt%). Similarly, calcite ( $\text{CaCO}_3$ ) and aluminosilicate phases (cancrinite, sodalite, vishnevit) corresponding to desilication products

468 (Gräfe et al., 2011; Radomirovic et al., 2013; Senaputra et al., 2012) were observed in the XRD patterns  
469 of BRs. These results are consistent with data reported in the literature (Evans, 2016; Gentzmann et al.,  
470 2021; Khairul et al., 2019; Klauber et al., 2011).

471 The mineralogy of all the BR samples was relatively similar, except for some slight variations that  
472 mainly depended on the origin of the bauxite ore. Gibbsite (main peak at  $\theta = 21.3^\circ$ ) was not observed  
473 from the XRD pattern of karstic BRs. The intensity of the boehmite-related peak (main peak at  $\theta =$   
474  $16.9^\circ$ ) was more intense in the XRD pattern of karstic BRs than in the XRD pattern of lateritic BRs,  
475 confirming reports on karstic bauxites in the literature (Kloprogge et al., 2002; Mondillo et al., 2019;  
476 Radusinović & Papadopoulos, 2021; Reinhardt et al., 2018). Iron-containing phases were present as a  
477 mixture of hematite and goethite, but relatively speaking, the intensity of hematite peaks was far greater  
478 than that of the goethite peaks in karstic BRs. The intensity of the aluminosilicate peak (main peak at  $\theta$   
479  $= 16.2^\circ$ ) was also greater in karstic BRs.

480 In agreement with the chemical composition, the effect of construction site backfill during storage of K-  
481 BR-Vit-V and K-BR-Vit-W is visible here due to more intense quartz ( $\theta = 31.0^\circ$ ) and calcite peaks ( $\theta =$   
482  $34.3^\circ$ ) on the diffraction patterns. Similarly, we attribute the higher gibbsite and quartz peaks in L-BR-  
483 Gui-E and L-BR-Gui-W, compared to the other lateritic BRs on the diffractograms, to the quality of the  
484 ore or to the performance of the Bayer process. Indeed, the bauxite ore used at Fria plant is reputed to  
485 be of lower quality than that used at the Gardanne plant, due to its higher silica content, which hampers  
486 aluminium extraction.

487 The structural analysis performed by XRD revealed differences in the mineralogy of the major phases  
488 of BRs depending on the origin of the bauxite ore, but no other drastic mineralogical variation were  
489 found related to the age or storage conditions of the BRs. However, other characterisation techniques  
490 are needed to investigate the possible REE phase differences mentioned earlier in more detail3.3.

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### 3.5. Microscopic and macroscopic evidence of speciation

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#### 3.5.1. SEM/EDS observations

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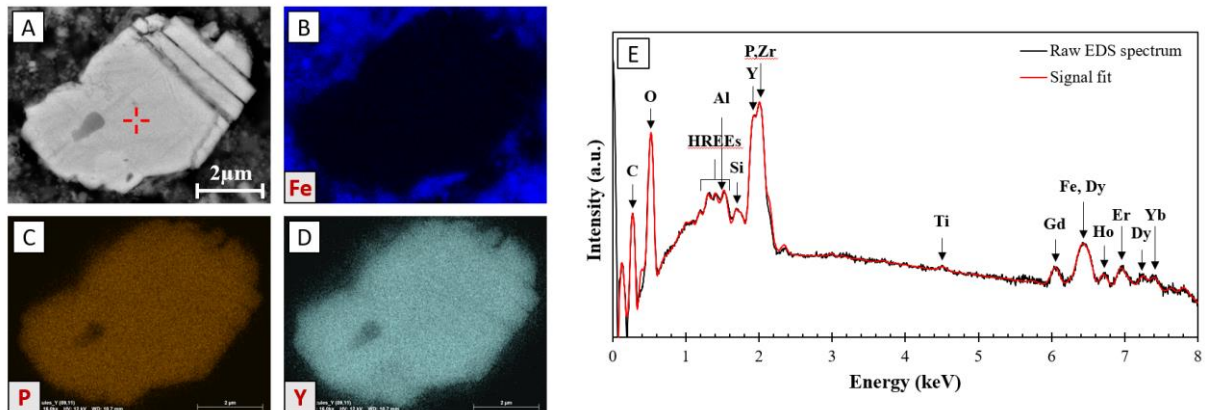
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**Figure 6:** (A) SEM image (BSE detector) of an yttrium particle found in samples L-BR-Gui-E as an example of lateritic bauxite residue (magnification  $\times 4000$ ) and associated quantitative EDS elemental maps showing the spatial distribution for (B) iron (C) phosphorus and (D) yttrium (12 kV, 50 kcps, 20 min). (E) EDS spectrum associated to the micro-analysis performed with the incident beam centered at the red cross position on (A) (15 kV, 100 kcps, 1 min).

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Scanning electron microscopy (SEM) observations coupled with energy dispersive X-ray spectroscopy (EDS) were performed on L-BR-Gui-E and K-BR-Mar-A BRs, as these two samples were assumed to be representative of lateritic and karstic BRs, respectively (**Figure 6** and **Figure S3**). In order to identify the occurrence of these particles in the samples in a representative way, a series of elemental distribution maps (magnification  $\times 500$ ) were performed on large regions of interest (6-8 mm<sup>2</sup>) for both samples. The analytical conditions chosen allowed the identification of particles with a diameter as small as 500 nm.

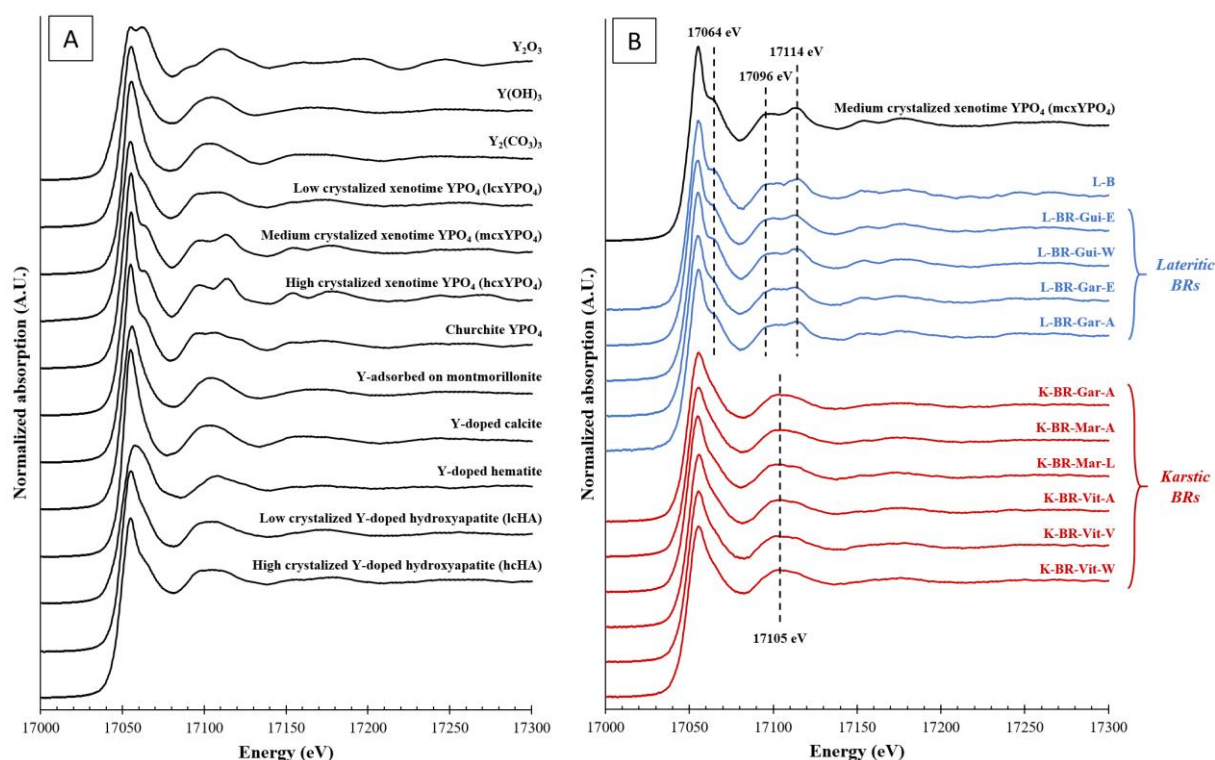
In both cases, Y-rich particles were found, co-localized with similar elements. Yttrium was found co-localized with other HREEs (Gd, Dy, Ho, Er, Yb), which supports the classification of Y as HREEs and validates using it as a proxy for HREEs (Borst et al., 2020; Lallemand et al., 2022; Pingitore et al., 2014). EDS elemental maps show that Y and HREEs are always associated with phosphorus (P), but not associated with major elements (Fe, Al, Ti, Ca < 3 at%) (**Figure 6** B, C and D). Moreover, the local chemical micro-analyses show P/HREEs atomic ratios close to 1 and Y/O atomic ratios between 0.15 and 0.25, suggesting the presence of xenotime (YPO<sub>4</sub>) or churchite (YPO<sub>4</sub>·2H<sub>2</sub>O) phases. In rare cases, Si and Zr can also be associated (>3 at%), suggesting traces of zircon (ZrSiO<sub>4</sub>) associated with xenotime, as well as with Fe from the surrounding matrix. These results are in good agreement with microscopic observations reported in the literature on BRs and bauxites (Lallemand et al., 2022; Z. Li et al., 2013; Mordberg et al., 2001; Radusinović & Papadopoulos, 2021; Reinhardt et al., 2018; Rivera et al., 2019; Vind et al., 2018). All these studies show that Y is found as xenotime or churchite phosphate particles

529 in BRs, as in bauxites, regardless of the origin of their geological ore, although Y has also been detected  
530 in mixed phases of REEs in Greek BRs (Vind et al., 2018).

531 Based on this local probe technique, it seems that Y speciation does not differ as a function of the lateritic  
532 or karstic origin of the samples and cannot confirm our hypothesis that there is a difference in HREE  
533 mineralogy between lateritic and karstic BRs based on REE patterns. However, scanning large sample  
534 areas (6-8 mm<sup>2</sup>) indicated approximately twice as many particles present in the L-BR-Gui-E sample  
535 than in the K-BR-Mar-A sample (2.4 and 1.3 particles/mm<sup>2</sup> respectively) while the Y content was twice  
536 lower in the L-BR-Gui-E sample than in the K-Mar-A sample (102 and 226 mg/kg respectively).

537 Additionally, while in both samples, most of the particle diameters were smaller than 5 µm, several large  
538 particles were found in L-BR-Gui-E, including one particle with a 50 µm diameter (**Table S5** and **Table**  
539 **S6**). This suggests that most of the Y in the K-BR-Mar-A sample is not detectable by SEM and,  
540 according to the P vs HREE scatterplot (**Figure S2**), is probably not associated with P. X-ray absorption  
541 spectroscopy (XAS) was performed at bulk scale to specifically characterise the atomic environment of  
542 Y species in all the samples, including the phosphate phases and other potential Y-bearing phases not  
543 detected by SEM analysis (Y-minerals and absorbed species).

### 3.5.2. X-Ray absorption spectroscopy measurements at Y K-edge



**Figure 7:** (A) Stacking of Y K-edge XANES spectra of the model yttrium compounds used in the study. (B) Stacking of Y K-edge XANES spectra of all the studied samples sorted by origin of the ore (blue = lateritic-type, red = karstic-type). Spectra of crystallized  $\text{YPO}_4$  xenotime model compound is plotted for the purpose of comparison. The main features of the spectra are identified by the dashed lines.

The X-ray Absorption Near Edge Structure (XANES) spectra of the model compounds are shown in **Figure 7 A**. Among them, the xenotime  $\text{YPO}_4$  compounds show a clearly identifiable structure consisting of a shoulder after the white line at 17064 eV and a double feature at 17096 eV and 17114 eV that is repeated at 17153 and 17178 eV, these structures being more pronounced with higher crystallization. The churchite  $\text{YPO}_4$  spectrum shows a slightly different structure with three features instead of two between 17090 and 17130 eV, allowing the xenotime to be differentiated from churchite using XAS measurements. The spectra of Y-doped hematite and  $\text{Y}_2\text{O}_3$  are also very specific and easily identifiable. Conversely, high-crystallized Y-doped hydroxyapatite (hcHA), which is a calcium phosphate, shows very similar characteristics to those of low crystallized xenotime  $\text{YPO}_4$  (lcxYPO<sub>4</sub>). None of the other model compound spectra show a very specific signature but consist in a single oscillation centered around 17105 eV and little or no post-white line shoulder, making identification of the presence of these phases potentially difficult.

The Y speciation in the samples studied here can be categorised in two types of signals mainly correlated with the origin of the bauxite ore (**Figure 7 B**).



580 Visually, the speciation of Y in samples of lateritic origin is very similar to a xenotime phase. Indeed,  
581 linear combination fitting (LCF) of the results of the XANES region (17000 to 17220 eV) confirmed  
582 these observations with the strong presence (>34% in all best fits) of medium-crystallized xenotime  $\text{YPO}_4$   
583 ( $\text{mcxYPO}_4$ ) (*Table S7*). For example, the best fit for L-BR-Gui-E consisted in a mixture comprising  
584 57% medium-crystallized xenotime  $\text{YPO}_4$  ( $\text{mcxYPO}_4$ ) and 35% hcHA with a very good match ( $\chi^2 = 0.02$ )  
585 (*Figure 8 A*).

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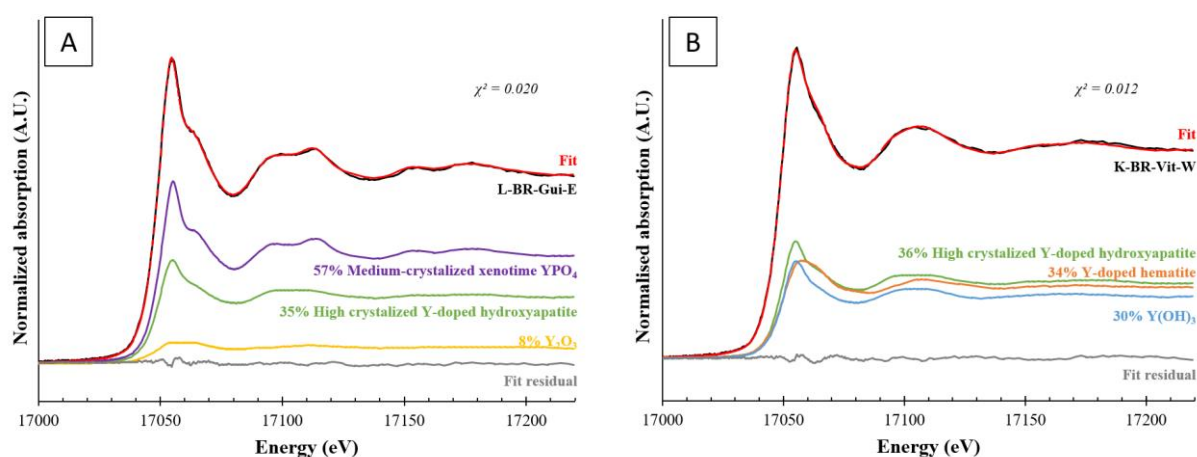
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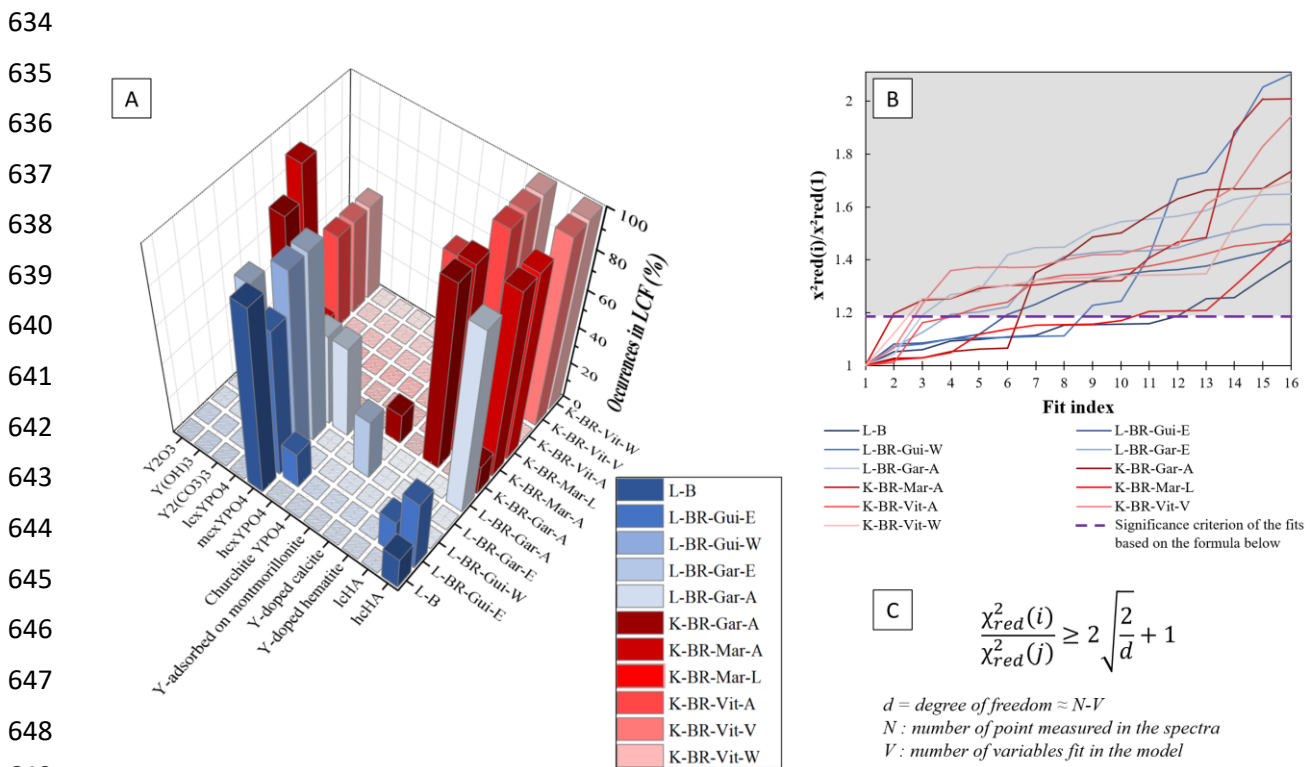
**Figure 8:** Best linear combination fitting (LCF) XANES analysis results for (A) L-BR-Gui-E, as an example of lateritic samples and (B) K-BR-Vit-W, as an example of karstic samples. Fits were performed with Larch software (17000-17220 eV, with a maximum of 3 components).

*Figure 9* is a statistical study of the LCF results to compare samples with different noise levels and to obtain statistically relevant results. In *Figure 9 A*, the percentages of occurrence of the main model compounds (with an arbitrary threshold of 25% in the fit) in all the good fits (i.e., all fits that do not statistically differ from the best fit) are plotted for each sample. A quality criterion (*Figure 9 C*), based on reduced chi-square value ( $\chi_{red}^2$ ), was used to determine the number of significantly good fits for each sample (*Figure 9 B*) (see section 2.2.5). Indeed, in the case of a noisy spectrum, a large number of combinations of model compounds can correctly fit the experimental data, as is the case of L-B sample with 11 fits (fit n°1 to fit n°11 in the white area) considered to be good. Thus, it does not seem reasonable to rely only on the best fit.

Our statistical study confirmed that xenotime  $\text{YPO}_4$  appears in 100% of good fits of all lateritic samples in the form of  $\text{mcxYPO}_4$  or less often in the form of  $\text{hcxYPO}_4$ . With the exception of the strong presence of hcHA in L-BR-Gar-A good fits, as well as  $\text{Y}(\text{OH})_3$ , which was present in the majority of L-BR-Gar-E good fits, no other model compounds appear significantly in the good fits of lateritic samples. These results confirm and complement the results of the study by (Lallemant et al., 2022) who proposed

616 speciation of Y as a mixed amorphous and crystalline xenotime phosphate based on the same lateritic  
 617 material (L-BR-Gar-E).

618  
 619 The speciation of Y in samples of karstic origin clearly differs from speciation in samples of lateritic  
 620 origin, but is also more difficult to identify than in lateritic ones. Visually, the XANES signals do not  
 621 reveal a specific structure or if they do, only tenuously. The LCF results of the XANES region showed  
 622 no clear predominance (**Table S7**), as illustrated by the best fit for K-BR-Vit-W, consisting, with a very  
 623 good match ( $\chi^2 = 0.01$ ) of a mixture of 36% highly crystallized hydroxyapatite (hcHA), 34% Y-doped  
 624 hematite and 30% Y(OH)<sub>3</sub> (**Figure 8 B**). Our statistical study nevertheless showed that only hcHA, Y-  
 625 doped hematite, Y(OH)<sub>3</sub> and to a lesser extent, Y-adsorbed on montmorillonite, are present in the good  
 626 fits of karstic BRs (**Figure 9 A**). In none of the cases, do the xenotime YPO<sub>4</sub> compounds stand out, in  
 627 contrast to in the samples of lateritic origin. To be consistent with XAS responses, Y in karstic BRs  
 628 could be adsorbed or incorporated into one or more mineral phases, as is the case for Sc in BRs  
 629 (Gentzmann et al., 2021). However, Sc speciation is known to diverge from that of other REEs  
 630 (Horowitz, 1975; Suss et al., 2018; Vind et al., 2018), so extrapolation to Y behaviour is not feasible.  
 631 For example, in their study, Gentzmann et al. show that the geological origin of the ore implies only  
 632 minor changes in the distribution of Sc in the host mineral phases, which is not the case for Y  
 633 (Gentzmann et al., 2021).



653 normalized by the best fit for each sample and significance cut-off criterion. Fits present in the grey area differ significantly  
654 from the best fit. (C) Significant criterion formula between two fits,  $i$  and  $j$  according to the reference (Kelly et al., 2008).

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656 Yttrium speciation in the BRs probed by bulk XANES analysis is mainly influenced by the  
657 origin of the bauxite ore and tend to corroborate the differences between the lateritic and karstic BRs  
658 suggested by the REE patterns, contrary to the microscopic approach. In all samples of lateritic origin,  
659 Y was mainly found in the form of xenotime  $YPO_4$ , which could be distinguished from churchite  $YPO_4$ ,  
660 confirming the microscopic observations. Given that  $YPO_4$  xenotime particles were also found in karstic  
661 BRs using microscopic observation methods, but that the XANES signal indicates that the majority of  
662 Y is not in xenotime or churchite phosphate form, we can assume that Y is present in several phases in  
663 the karstic BRs. Pellet heterogeneity was also investigated by examining each XANES spectrum  
664 collected at different locations in the sample pellet before averaging, confirming the presence of rare  
665  $YPO_4$  particles in karstic BRs (2 out of 27 scans collected) resulting in noisier, more intense spectra and  
666 exhibiting the xenotime  $YPO_4$  features (**Figure S4**). However, the majority of Y in karstic BRs is  
667 probably incorporated in small quantities in other mineral phases (iron oxyhydroxide, hydroxyapatite)  
668 or adsorbed on the surface of other minerals, which would explain why they are not easily detectable by  
669 SEM-EDS (below the limit of detection).

670 However, no variability in Y speciation was detected linked to the storage conditions of the  
671 tailings, nor their aging time for a given origin.

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## 673 **4. Perspectives**

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675 The information obtained in this study is crucial for the use of BRs as a secondary source of REEs,  
676 particularly for the design and implementation of selective recovery processes.

677 First, HREE solubility probably differs as a function of origin. Indeed, the observed difference in  
678 speciation may affect HREE recovery yields depending on the origin of the bauxite ore. A comparative  
679 study of the dissolution behaviour of HREEs from these different BRs is needed to validate this  
680 hypothesis. The solubility of HREEs was found to be very low for lateritic BRs (Lallemand et al., 2022)  
681 because of the very low solubility of xenotime. Given the higher REE content in karstic BRs than in  
682 lateritic BRs and the difference in HREE speciation, it would be interesting to test and compare similar  
683 recovery approaches. Second, the marked variability of BR storage conditions and durations does not  
684 appear to have a significant effect on HREE speciation which should consequently facilitate the  
685 treatment of tailings stored in different conditions and for different storage times at large scales.

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687 Although origin appears to be the only parameter that affects HREE speciation, we recall that some  
688 geographical disparities may also exist due to variations in the bedrock lithology of a given origin  
689 (lateritic or karstic). In our case, bauxites ore from all lateritic BR samples came from the Boké region  
690 in Guinea (West Africa) and bauxite ore from all the karstic BR samples came from the region of  
691 Provence (South of France). Therefore, to extrapolate these results worldwide, it is crucial to study  
692 potential geological differences, including HREE speciation, for a given origin in other geographical  
693 regions of the world, such as China, Australia, Brazil or India, which are the main generators of BRs at  
694 the present time. In addition, some alumina production sites use a mixture of lateritic and karstic bauxites  
695 as ore input, e.g., at the Aluminium of Greece plant (Vind et al., 2018). In these cases, it would be  
696 impossible to address the link between the origin of the ore and HREE speciation in the BRs.

697 Finally, a complete understanding of REE speciation in BR remains to be achieved for LREEs, for  
698 which no clear speciation has been assigned to date.

## 699 **5. Conclusion**

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The aim of this study was to perform a multi-scale characterisation of different bauxite residues (BRs) as a function of origin of the ore, of the storage conditions and storage time, with a particular focus on the speciation of Y as a proxy of the behaviour of heavy rare earth elements (HREEs). We have shown that some physico-chemical properties of BRs, such as pH, conductivity or chemical composition of major elements, vary with the storage conditions and storage time and may partially explain the marked variability of physico-chemical properties of BRs reported in the literature. More interestingly, this study has shown that other properties of the BRs, such as the mineralogy of the major phases as well as the chemical composition and speciation of the HREEs varied with the origin of the bauxite ore but were not influenced by the storage conditions or by the age of the BRs. Notably, and to our knowledge, for the first time, we were able to link the origin of the bauxite ore, lateritic or karstic, and the speciation of Y. In the case of lateritic BRs, HREEs are mostly present in the form of pure and crystallized phosphate particles (xenotime). In karstic BRs, HREEs are mainly present in a more complex speciation, probably adsorbed or incorporated in other minerals, including iron oxyhydroxide and hydroxyapatite minerals, although some xenotime phosphate particles were also detected (< 25%). Only the complementarity use of macroscopic, microscopic and spectroscopic approaches enabled us to reach a full understanding of Y speciation in these complex residues. The present study thus paves the way for a study of the potential of BRs for the selective recovery of HREEs in a circular economy context. Our results also underline the importance of considering BRs produced in different parts of the world not as a single material but as incorporating certain disparities as a function of the origin of the ore that may require a range of different extraction processes. It is true for REEs but also for other critical elements including vanadium for example for which such eventual disparities are not documented today.

## 735 **Declaration of Competing Interest**

736 The authors declare that they have no known competing financial interests or personal relationships that  
737 could have appeared to influence the work reported in this paper.

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## 739 **Data Availability**

740 Data will be made available on request.

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## 753 **Supporting information**

754 Supplementary data associated with this article can be found in the online version at  
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