Comparison of Three Approaches for Bioleaching of Rare Earth Elements from Bauxite

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Abstract: Approximately 300 million tonnes of bauxite are processed annually, primarily to extract alumina, and can contain moderate rare earth element (REE) concentrations, which are critical to a green energy future. Three bioleaching techniques (organic acid, reductive and oxidative) were tested on three karst bauxites using either *Aspergillus* sp. (organic acid bioleaching) or *Acidithiobacillus ferrooxidans* (reductive and oxidative bioleaching). Recovery was highest in relation to middle REE (generally Nd to Gd), with maximum recovery of individual REE between 26.2% and 62.8%, depending on the bauxite sample. REE recovery occurred at low pH (generally < 3), as a result of organic acids produced by *Aspergillus* sp. or sulphuric acid present in *A. ferrooxidans* growth media. Acid production was seen when *A. ferrooxidans* was present. However, a clear increase in REE recovery in the presence of *A. ferrooxidans* (compared to the control) was only seen with one bauxite sample (clay-rich) and only under oxidative conditions. The complex and varied nature of REE-bearing minerals in bauxite provides multiple targets for bioleaching, and although the majority of recoverable REE can be leached by organic and inorganic acids, there is potential for enhanced recovery by bioleaching.

Keywords: bioleaching; bauxite; rare earth elements; Turkey; *Aspergillus* sp.; acidophile; *Acidithiobacillus ferrooxidans*
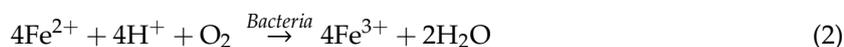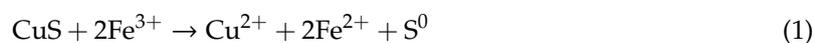
1. Introduction

The rare earth elements (REE) are widely used in a range of modern technologies, which is driving a steady increase in demand, particularly for the most critical REE, such as neodymium (Nd) and praseodymium (Pr) [1]. China dominates the primary global production of the REE (over 71% of global production in 2018 [2]), primarily from carbonatite and ion adsorption deposits [3]. In recent years, there has been significant interest in developing alternative REE resources, and one area of research has focused on the recovery of the REE from bauxite [4].

Bauxite is the primary source of aluminium globally, with an annual production of approximately 326 Mt in 2018 (the last year for which data are available) [2]. Bauxites are subdivided into three types [5]: (1) lateritic bauxite deposits, derived from in situ weathering of aluminosilicate rocks; (2) Tikhvin-type deposits, deposited on aluminosilicate rocks of no genetic relation, and (3) karst bauxite deposits. Karst bauxite deposits occur in the karst topography of limestone and dolomite and comprise aluminosilicate residues transported from either proximal or distal locations, undergoing lateritic weathering [5]. Of the karst bauxite types, the "Mediterranean type" is of interest in this study due to its REE content. During bauxitisation, authigenic REE-bearing minerals can be formed, the most common of which is hydroxylbastnäsite-(Nd) (Nd (CO$_3$)(OH)) [6]. Bauxites from the Southern

Apennines (Italy) and Nurra (Sardinia) contain authigenic high-Ce, Ca-bearing fluorcarbonate minerals ($REE_2Ca(CO_3)_3F_2$) [7,8]. Karst bauxites host on average 600 mg·kg^{-1} total REE, while the waste product (red mud, generated by the Bayer process of producing alumina from bauxite) shows up to a two-fold increase in REE concentration, with on average 1000 mg·kg^{-1} total REE [9]. Due to the large-scale nature of alumina production, the production of REE as by-products from bauxite is potentially a rapid way to develop an alternative source of REE.

Bioleaching is a low-energy approach that is being explored in various ores and materials, and it can be divided into three main approaches:

(1) Oxidative leaching by aerobic autotrophs: Current commercial biomining and bioleaching operations typically target sulphide ores for the recovery of metals such as copper, nickel and uranium by oxidative leaching or oxidative beneficiation [10]. Oxidative leaching relies upon acidophilic, chemoautotrophic prokaryotes (such as *Acidithiobacillus ferrooxidans*) respiring aerobically. The release of copper into the solution occurs through an indirect oxidation process (redoxolysis) via biogenic ferric iron (Fe^{3+}) by *A. ferrooxidans* and is presented in Equation (1). The role of microorganisms is to regenerate ferric iron (Equation (2)) and sulphuric acid (Equation (3)) to allow the copper reaction to continue.

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^0 \tag{1}$$

$$4Fe^{2+} + 4H^+ + O_2 \overset{Bacteria}{\rightarrow} 4Fe^{3+} + 2H_2O \tag{2}$$

$$2S^0 + 3O_2 + 2H_2O \overset{Bacteria}{\rightarrow} 2H_2SO_4 \tag{3}$$

For non-sulphide bearing ores, sulphuric acid generated by the microbial oxidation of added elemental sulphur (S^0) (Equation (3)) can result in acid dissolution (acidolysis) of iron hydroxide minerals (Equation (4)) to release the target metal.

$$FeOOH + 2H^+ \rightarrow Fe^{3+} + OH^- + H_2O \tag{4}$$
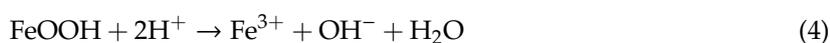
The biogenic production of sulphuric acid from elemental sulphur has been demonstrated as an indirect mechanism for enhancing the leaching of material other than sulphidic ore, e.g., limonitic ore [11] or metallurgic slag [12].

The final pH of the combined sulphur oxidation (acid production) and iron hydroxide acid dissolution, which is an acid consuming reaction, is dictated by the kinetics of each reaction [11].

(2) Reductive leaching by anaerobic autotrophs: More recently an alternative biomining technique using these same acidophilic organisms respiring anaerobically has been proposed (Equations (5) and (6)). "Biomining in reverse gear" exploits the fact that certain microbes, particularly *A. ferrooxidans*, can reduce an oxidised ore in the absence of oxygen [13]. This reductive leaching approach has been applied to the solubilisation of nickel and copper from laterites [14,15] and cobalt from limonites [11]. Microbial reductive leaching operates at a temperature of ~30 °C and requires the addition of an electron donor such as elemental sulphur.

$$6Fe^{3+} + S^0 + 2H_2O \overset{Bacteria}{\rightarrow} 6Fe^{2+} + 8H^+ + SO_4^{2-} \tag{5}$$

$$6FeOOH + S^0 + 10H^+ \overset{Bacteria}{\rightarrow} 6Fe^{2+} + SO_4^{2-} + 8H_2O \tag{6}$$

Equation (6) is a highly acid-consuming reaction.

(3) Organic acid leaching from aerobic heterotrophs: Organic acid bioleaching relies on the fact that microbially-produced organic acids (for example, gluconic acid production by *Aspergillus* species [16]) have the potential to dissolve mineral matrices via acidolysis [17], but laboratory observations have not yet been converted into commercial operations. In addition to acid production, the formation of metal ligand complexes can improve the stability of metals in the solution and cause the fractionation of REE (complexolysis) due to the increasing stability of heavy REE-organic ligand complexes [18].

REE are currently not commercially produced via bioleaching, but there is extensive research in this area focusing on the potential of microbially-produced organic acids to leach REE from a wide range of materials, including raw materials and waste streams [19–22]. Reported REE recoveries from geological material are highly variable and can include all REE, selected REE or total REE; 80% Lu from Chinese red mud [23], 86% total REE from carbonaceous shales [24] and 80% La from ion adsorption deposits [16]. Several studies have looked into the REE recovery by organic acid leaching of the phosphate mineral monazite with variable leaching extent, from 0.13% to 60.6% [25–28]. Leaching of the REE fluorcarbonate mineral bastnäsite was less successful, with only up to 0.08% detectable in the leaching solution [29]. One study has considered bioreductive dissolution for leaching REE from monazite [30], leaching up to 8% La with *A. thiooxidans*. The red mud tailings from the processing of bauxite have been a target for the bioleaching of REE, focusing on organic acid bioleaching with heterotrophic bacteria and fungi [23,31–33], and one recent study demonstrates the ability of microalgae to accumulate REE (plus Y and Sc) in quantities of up to 54.5 mg·kg^{-1} of dry biomass from red mud [34]. To date, unprocessed bauxite has not been targeted for REE bioleaching.

Microbial processes have been implicated in the formation of bauxite, both during the weathering of the parent rock and the subsequent maturation of the bauxite, by enhancing the removal of iron and silica [35]. This has led to some research into the potential of bio-beneficiation of bauxite by various heterotrophic bacteria [36–39] and fungi [40,41] under aerobic or anaerobic conditions. To explore the potential of bioleaching for the recovery of REE from bauxite in this study, three karst bauxite samples were selected, as they showed a range of REE-bearing mineral phases and varied chemical composition. Data from a sequential extraction of these materials indicated that the REE in these bauxites were held in organic acid soluble, reducible and oxidisable fractions. Therefore, we applied the three bioleaching methods outlined above (organic acid, reductive and oxidative) to the three selected karst bauxites to ascertain the suitability of the different approaches.

2. Materials and Methods

2.1. Materials

Three karst, "Mediterranean type" bauxite samples from Turkey were used in these experiments; these were collected from deposits in the Seydişehir region during a 2014 sampling campaign. These deposits have been mined as the feedstock for alumina production since the 1970s and are hosted in Cretaceous limestone and dolomitic limestone and overlain by Paleocene and Eocene limestone and sandstone (Figure 1). They have previously been investigated for their REE content, and the total REE content of the Mortaş bauxite ranges between 282 and 986 mg·kg^{-1}, depending on the bauxite layer [42].

The three samples selected for this study are referred to as low-Ca, high-Ca and clay-rich bauxite and are described in Section 3.1.
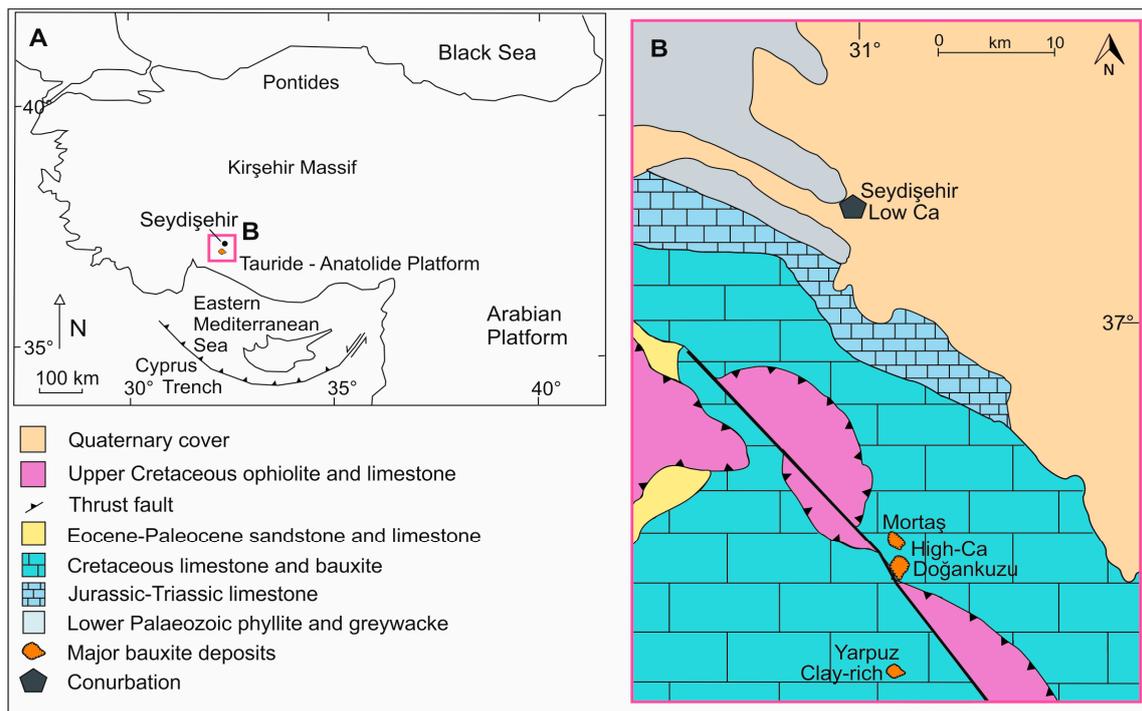
Figure 1. (**A**) Location of bauxite samples and (**B**) the regional geological setting. Adapted after [9].

2.2. Material Characterisation

2.2.1. Scanning Electron Microscopy (SEM) Analysis

Qualitative chemical analysis of the REE-bearing phases was performed using a FEI Quanta 600 scanning electron microscope (Oxford Instruments) with energy dispersive X-ray spectroscopy (SEM-EDS). The SEM was operated under low vacuum (0.98 torr) at a 20 kV accelerating voltage, with the optimal analytical working distance of 10 mm and an X-ray detector take-off angle of 45°.

Polished thin sections were used to assess the REE-bearing phases under SEM. Locating the REE-bearing phases in these samples was achieved using the feature analysis function of the SEM INCA™ software.

2.2.2. Sequential Chemical Extraction

Sequential extraction provides information on the leachable elements of the bauxite under different conditions. Table 1 summarises the steps and nominal target phases. Sequential extraction was completed on 1 g ball milled bauxite (<0.53 μm). All steps were agitated and performed at room temperature with 40 mL fluid, unless otherwise stated. Step 1 was shaken for one hour and steps 2 and 3 for 16 h. Step 4 was performed in several stages, firstly with 10 mL hydrogen peroxide at room temperature for one hour before raising the temperature to 85 °C for one hour. Volume was reduced to 3 mL before the addition of 10 mL of hydrogen peroxide at 85 °C for a further hour. Volume was then reduced to 1 mL and cooled to room temperature. A total of 50 mL ammonium acetate was then added and the experiment incubated for 16 h. After leaching, the fluids were filtered through a 0.45 μm filter and acidified (1% HNO_3) before element analysis by ICP-MS (Agilent 8900 ICP-QQQ). Solid bauxite was prepared by NaOH fusion prior to mixed acid digestion for ICP-MS.

Table 1. Steps for sequential extraction.

Step	Reagent	Fraction Label	Nominal Target Phase(s)
Step 1	1 M MgCl$_2$ (pH 7.0)	Water soluble	Soluble and exchangeable cations
Step 2	0.11 M acetic acid	Acid soluble	Carbonates
Step 3	0.5 M hydroxylammonium chloride (pH 1.5)	Reducible	Fe-Mn oxyhydroxides
Step 4	9.8 M hydrogen peroxide then 1 M ammonium acetate (pH 2.0)	Oxidisable	Organic matter and sulphides

2.3. Bioleaching Experiment Setup

Three bioleaching processes were tested. All bioleaching tests used a two-stage process. Stage 1 allowed for the measurement of microbial growth and any associated changes in media and was carried out in the absence of bauxite. In stage 2, the bauxite was mixed with the media, for a leaching stage lasting 7 days (Table 2). Bioleaching was conducted in acid-washed conical flasks with 40 mL fluid and 1 g milled (<53 μm) bauxite. All bioleaching processes were tested in triplicate for each bauxite sample and were compared to an uninoculated control, also tested in triplicate.

Table 2. Summary of bioleaching set up conditions.

Mechanism	Organism	Medium	Stage 1: Growth	Stage 2: Leaching
Organic acid bioleaching	*Aspergillus* sp.	Sucrose-rich medium	Aerobic	Aerobic
Reductive bioleaching	*A. ferrooxidans*	Basal salts medium plus sulphur	Aerobic	Anaerobic
Oxidative bioleaching	*A. ferrooxidans*	Basal salts medium plus sulphur	Aerobic	Aerobic

Organic acid bioleaching: Organic acids were produced by a laboratory strain of *Aspergillus* sp. isolated from Madagascan lateritic soils [16]. *Aspergillus* sp. was grown aerobically at 25 °C, 175 rpm for 7 days in sucrose-rich media (L^{-1}): sucrose (140 g), (NH$_4$)$_2$SO$_4$ (2.5 g), K$_2$HPO$_4$ (0.5 g), MgSO$_4$·7H$_2$O (0.25 g), ZnSO$_4$·7H$_2$O (1.3 mg) and FeSO$_4$·7H$_2$O (0.5 mg). The starting pH of the media was 7.4, reaching pH 2.04 at the end of stage 1 (Table 3). No pH adjustments were made after the addition of the bauxite. Biomass was removed by filtering through sterile cheesecloth before adding to bauxite. This was intended to remove the majority of the biomass but not remove all viable material. The removed biomass had a dry weight of 11.4 g·L^{-1}. Leaching (stage 2) was conducted at room temperature (approximately 21 °C), shaking at 175 rpm. After leaching, the fluids were filtered through a 0.45 μm filter and acidified (1% HNO$_3$) before element analysis by ICP-MS (Agilent 7500CX series).

Table 3. Characterisation of fluids at the end of stage 1 before the addition of any bauxite.

Leaching Fluid	Microorganism	pH	Total Fe (mg·L^{-1})	Reduced Fe as % of Total Fe	Al (mg·L^{-1})	TREE * (μg·L^{-1})
Organic acid leaching	*Aspergillus* sp.	2.04	0.352	n.d.	< d.l	6.44
	Uninoculated	7.37	0.37	n.d.	< d.l	0.00
Reductive and oxidative leaching	*A. ferrooxidans*	1.82	113	0.0	< d.l	0.275
	Uninoculated	1.89	50.6	89.9	0.490	0.401

* excluding Ce: TREE—total rare earth element; n.d. not determined; d.l.—detection limit.

Reductive and oxidative bioleaching: *A. ferrooxidans* (DSM-14882) was purchased from DSMZ (Braunschweig, Germany) and was initially grown according to their recommendations, i.e., statically under aerobic conditions at 25 °C in Leptospirillum medium (DSMZ medium 882). The culture was spun down and resuspended in basal salt media (L^{-1}): MgSO$_4$·7H$_2$O (500 mg), (NH$_4$)$_2$SO$_4$ (450 mg), Na$_2$SO$_4$·10H$_2$O (150 mg), KH$_2$PO$_4$ (50 mg), KCl (50 mg) and Ca(NO$_3$)$_2$·4H$_2$O (14 mg), FeSO$_4$·7H$_2$O (280 mg), 1 mL SL-10 trace element solution [43] and pH adjusted to 1.8 with H$_2$SO$_4$. The pH of this media remained at 1.8 after stage 1 and Fe^{2+} from the basal salt media dropped to 0% of total Fe (Table 3). Initial iron concentration was higher in the inoculated tests due to some carry over from the initial growth medium. All results are corrected for starting iron and other elemental concentrations. To test reductive leaching, cultures were moved to an anaerobic cabinet overnight, prior to the addition

of bauxite. Elemental sulphur was added to concentration 1.25% solid to liquid ratio in both conditions. Due to the high carbonate content of the high-Ca and clay-rich bauxite samples, the pH was adjusted after sample addition to enable further activity for *A. ferrooxidans*; 400 μL of 5 M H_2SO_4 was added to the high-Ca bauxite and 600 μL 5 M H_2SO_4 was added to the clay-rich bauxite. The pH values, without additional acid, were 6.62 and 6.74, respectively. The acid was added to inoculated and uninoculated controls. Leaching was conducted at 25 °C without shaking. After leaching, the fluids were filtered through a 0.45 μm filter and acidified (1% HNO_3) before element analysis by ICP-MS (Agilent 7500CX series). Reduced iron (Fe^{2+}) and total iron in the fluid were measured in separate subsamples. Reduced iron was measured using a final concentration of 0.1% 2,2'-bipyridyl; absorbance was measured after a minimum of 10 min of incubation at 520 nm with analytical triplicates (Bio-Rad Laboratories iMark Microplate Absorbance Reader). Absorbance was compared to the standard curve of 0, 0.05, 0.2, 0.5 and 2 mM Fe^{2+}. Total iron was measured by adding ascorbic acid to the final concentration of 0.67% and incubated at room temperature for at least 1 h before the addition of bipyridyl. Absorbance was measured at 520 nm and again compared to the standard curve, as above. Comparison of the absorbance of reduced iron to total iron was used to calculate the percentage of reduced iron.

3. Results

3.1. Materials

3.1.1. Mineralogy

The three samples selected for this study are referred to as low-Ca, high-Ca and clay-rich bauxite; these can be distinguished by bulk chemistry (Table 4 and Figure 2) and mineralogy (Table 5 and Figure 3).

Table 4. Major element and total REE (TREE) composition of bauxites used in this study.

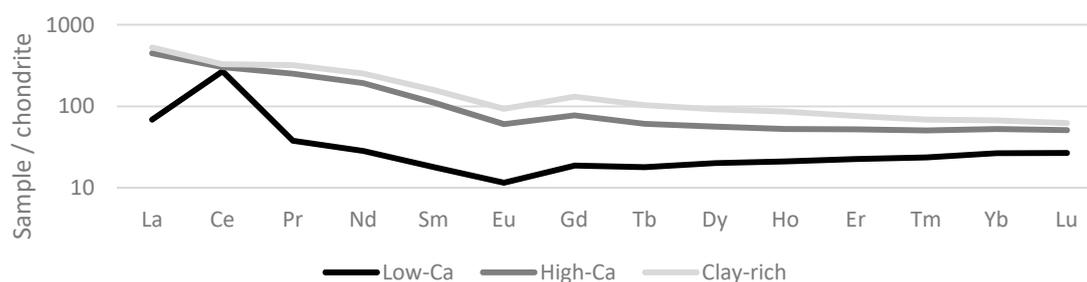| Bauxite	Al g·kg⁻¹	Fe g·kg⁻¹	Si g·kg⁻¹	Ti g·kg⁻¹	Ca g·kg⁻¹	TREE mg·kg⁻¹
Low-Ca	296	109	32.1	13.4	0.537	221
High-Ca	241	99.1	23.9	11.9	64.1	477
Clay-rich	176	119	12.7	8.9	132	583

Figure 2. Chondrite normalised [44] pattern of REE elements for each of the bauxites tested.

Table 5. REE-bearing phases present in the bauxite samples used in this study, identified from thin sections.

Sample	Alteration	CaCO₃	Cerianite	Fluorcarbonate	Xenotime	Fe Oxide Phases *	Other REE Phases—Unidentified
Low-Ca	Fresh	Limited CaCO₃ phases	X		X	X	X
High-Ca	Fresh	Visible clasts of limestone		X		X	X
Clay-rich	Altered	Veinlets of secondary CaCO₃	X			X	X

* Fe oxide mineral phases are likely to be goethite and hematite; these were analysed using SEM-EDS analysis and were not individually identified.
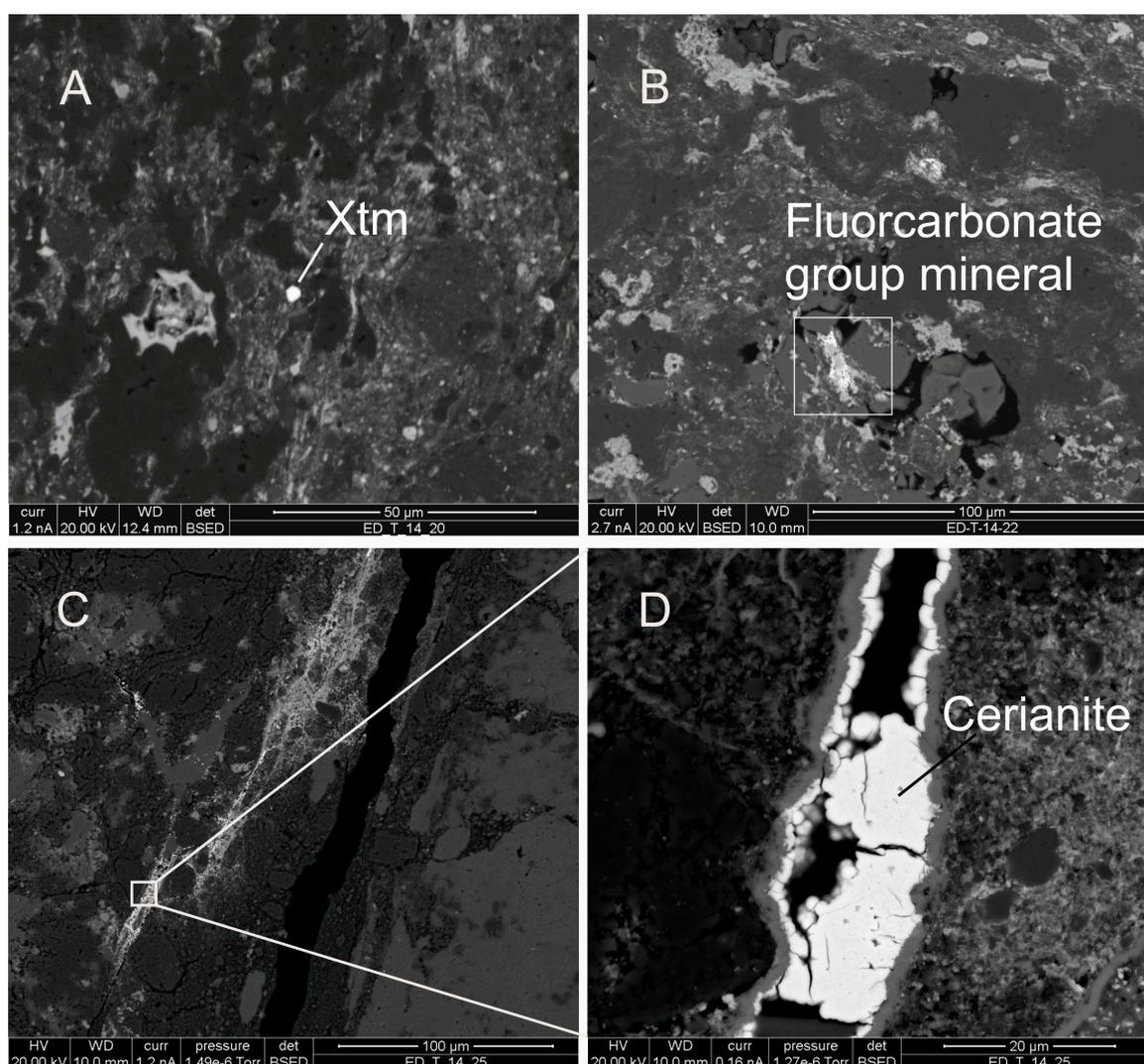
Figure 3. (**A**) Low-Ca bauxite—xenotime (Xtm) in the matrix; (**B**) High-Ca bauxite—interstitial fluorcarbonate; (**C**) Clay-rich bauxite—framboidal cerianite infill along fractures; (**D**) Clay-rich bauxite—framboidal cerianite in fractures.

The chondrite-normalised pattern of the REE in the low-Ca bauxite differs from the high-Ca and clay-rich bauxites in that it has a large positive Ce anomaly and there is only minor enrichment in light REE (Figure 2). High-Ca and clay-rich bauxites show similar chondrite normalised REE patterns with no Ce anomaly.

The karst bauxites in this region are dominated by boehmite, hematite, goethite, diaspore and anatase [45]. The presence of REE-bearing phases in each of the bauxite samples was confirmed using SEM. Clear examples of cerianite ($(Ce,Th)O_2$), fluorcarbonates ($REE(CO_3)F$) and xenotime ($Y(PO_4)$) were identified (Figure 3), and the petrographic analysis is summarised in Table 5.

In the low-Ca sample, both authigenic and detrital REE minerals are present. Xenotime occurs as a rare, disseminated, likely detrital, heavy REE-bearing phase (Figure 3A). Secondary (authigenic) platy and botryoidal cerianite are both present. Cerianite also occurs as amorphous Ce-rich oxides, both disseminated in the matrix of the bauxite and in fractures.

The high-Ca bauxite contains small clasts of the contact limestone. The dominant REE phases in this sample are REE-bearing fluorcarbonates, present in the matrix of the bauxite. These occur as fibrous minerals infilling pore space (Figure 3B). Detrital REE minerals were not identified.

The clay-rich bauxite is heavily altered to clay-rich phases and contains veinlets of secondary calcite. The iron oxy-hydroxides contain numerous impurities (including Si, Ti, Al, Ca), which could indicate a mixture of iron oxide and clay minerals. The sample is conspicuously porous, with an almost spongy texture. Cerianite, which dominates the REE budget in this sample, is present mainly as framboidal clusters along fracture and micro-crack fillings (Figure 3C,D). It also occurs in the microporous matrix, which is dominated by various aluminium oxides and iron oxyhydroxide.

3.1.2. Sequential Extraction

REE in detrital minerals are not thought to be leached out during Steps 1 to 4; therefore, the term non-detrital is used to refer to the REE recovered throughout the sequential extraction steps. Minimal REE were recovered during step 1 (exchangeable) of the sequential extraction of all three bauxites, with a maximum recovery of 0.16% (Figure 4). The highest REE recovery was observed during step 3 (reducible) for all bauxites. For the low-Ca and high-Ca bauxites, recovery during step 3 was greater than during step 2, which in turn was greater than during step 4 (reducible > acid soluble > oxidisable). For the clay-rich bauxite, there was similar recovery in steps 2, 3 and 4 (acid soluble, reducible and oxidisable). The overall trend and amount of leaching of REE from non-detrital minerals varied for each bauxite, and these are described in the subsequent section in the context of the REE recovery of the different bioleaching techniques.
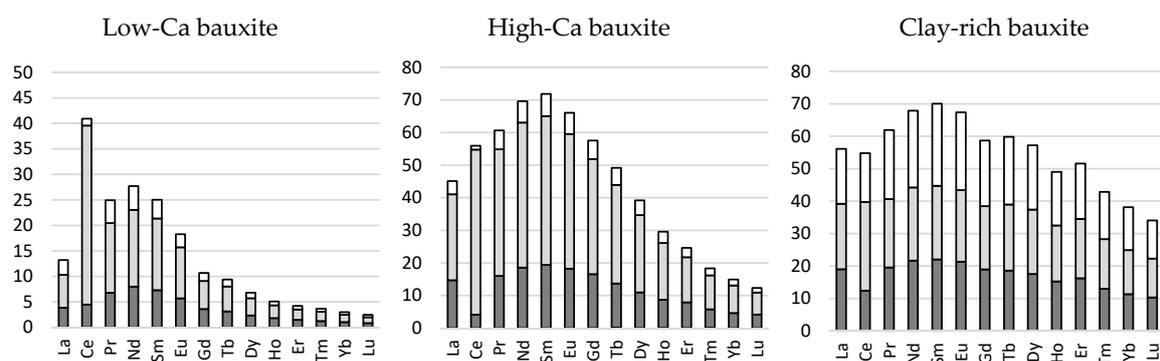

Figure 4. Recovery (%) of individual REE using sequential extraction. Leaching from step 1 exchangeable (magnesium chloride) is not visible; step 2, dark grey—acid soluble (acetic acid); step 3, pale grey—reducible (hydroxylamine hydrochloride); step 4, white—oxidisable (hydrogen peroxide).

3.2. Bioleaching Experiment

Chemical analysis (ICP) results from the leaching experiments and the original solid material are provided in Table S1.

3.2.1. Low-Ca Bauxite

REE recovery from the non-detrital minerals, as shown by the sequential extraction data, ranged from 2.5% Lu to 40.9% Ce, indicating that light to middle REE (Ce to Sm) are relatively more leachable than the heavy REE (Figure 4). The very low heavy REE recovery seen in sequential extraction is consistent with the presence of detrital xenotime in thin section; xenotime is enriched in heavy REE compared to light REE [46]. Bioleaching of low-Ca bauxite by all approaches showed REE recovery similar in extent and trend to the sequential extraction data, including the highest recovery of Ce to Sm (Figure 2). This suggests that all bioleaching methods successfully release the REE from the non-detrital minerals. Sequential extraction data also indicated higher recovery of Ce over the other REE in this bauxite, up to 40.9%. Cerium frequently behaves differently to other REE, forming cerianite (CeO$_2$) [47], as confirmed in thin section (Figure 3C,D). Higher recovery of Ce over the other REE is also seen in the bioleaching approaches. However, a lower recovery of Ce compared to the other

bioleaching methods is shown by the oxidative leaching in the presence of *A. ferrooxidans*, suggesting that some cerianite is not dissolved.

During the organic acid bioleaching, the pH decreased from 2.32 to 1.73 (Table 6), indicating the ongoing production of organic acids. The pH also decreased in the uninoculated controls, from 7.41 to 5.29, potentially due to the stimulation of the natural microbial community, but this did not result in any significant REE leaching (maximum 1.1% La).

Table 6. Changes in pH, iron, aluminium and TREE concentrations and percentage of reduced iron in final solutions for low-Ca bauxite during organic acid, reductive and oxidative leaching and uninoculated controls. Initial pH was recorded after 1 h and the final pH was recorded at the end of 7 days of leaching. Total REE (TREE) excludes Ce, due its different behaviour during leaching compared to other REE. Characterisation of starting fluid conditions is shown in Table 3. Errors are one standard deviation of triplicate experiments.

Bioleaching Technique	Microorganism	pH		Change in Total Fe (mg·L^{-1})	Reduced Fe as % of Total Fe	Change in Al (mg·L^{-1})	Change in TREE * (μg·L^{-1})
		Initial	Final				
Organic acid leaching	*Aspergillus* sp.	2.32 ± 0.02	1.73 ± 0.05	16.0 ± 5.8	n.d.	139 ± 11	170 ± 8
	Uninoculated	7.41 ± 0.02	5.29 ± 1.41	0.287 ± 0.365	n.d.	1.21 ± 1.75	6.93 ± 12.0
Reductive leaching	*A. ferrooxidans*	1.88 ± 0.02	2.01 ± 0.02	16.2 ± 3.7	90.3 ± 0.3	125 ± 1	199 ± 1
	Uninoculated	1.94 ± 0.02	2.19 ± 0.01	4.54 ± 0.57	85.7 ± 1.1	124 ± 4	189 ± 0
Oxidative leaching	*A. ferrooxidans*	1.80 ± 0.03	1.85 ± 0.01	8.50 ± 0.87	2.24 ± 1.23	125 ± 4	203 ± 2
	Uninoculated	1.86 ± 0.06	2.24 ± 0.01	2.24 ± 1.23	84.3 ± 1.5	130 ± 4	202 ± 1

n.d. not determined; * excludes Ce.

During the reductive and oxidative bioleaching, the presence of *A. ferrooxidans* gave similar REE recovery to the uninoculated controls, with the exception of Ce (Figure 5). A small increase, up to 1.4% (Nd), in the amount of individual REE recovered during reductive leaching compared to uninoculated controls was observed; however, further analyses would be required in order to test the significance.
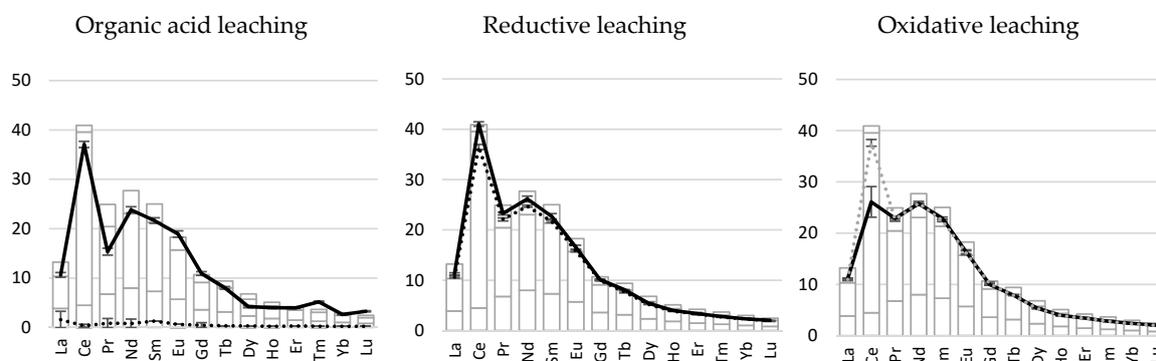

Figure 5. Recovery (%) of individual REE from low-Ca bauxite for each of the leaching techniques tested. Solid lines represent inoculated tests and dotted lines are uninoculated controls. Error bars are plus or minus one standard deviation of triplicate experiments. Bar charts show sequential extraction data, as in Figure 4.

The leaching behaviour of major elements could provide insights into the main host mineral phases releasing REE into solution. Aluminium was abundant in all solutions except for the uninoculated organic acid leaching, in accordance with the pH-dependent solubility of Al hydroxides and oxides. There were minimal changes in Al leached in the presence or absence of *A. ferrooxidans*. In contrast, leaching of iron was more variable. In the presence of *A. ferrooxidans,* more iron was dissolved during reductive and oxidative leaching compared to the controls (Table 6). The greatest increase in iron is seen during reductive leaching, indicating the enhancement of reductive dissolution by *A. ferrooxidans*. Despite the enhanced dissolution of iron during both reductive and oxidative bioleaching compared to the uninoculated controls, this is not reflected in an increase in REE recovery. Furthermore, the percentage of reduced iron is considerably lower in the presence of *A. ferrooxidans*

(2.24%) compared to the uninoculated control (84.3%), indicating that *A. ferrooxidans* is using reduced iron as an electron donor.

3.2.2. High-Ca Bauxite

Sequential extraction data indicated the greatest REE recovery in relation to middle REE (Nd to Eu) for high-Ca bauxite. REE recoveries were higher than in the low-Ca bauxite, with 12.3% Lu to 71.8% Sm recovered from non-detrital minerals. Recovery of Ce is similar to the adjacent REE. This is consistent with the absence of cerianite in thin section. REE recovery was low during organic acid bioleaching, whereas substantial REE recovery occurred during reductive and oxidative bioleaching. This trend was similar to that of the sequential extraction, with the maximum recovery of Nd to Gd (Figure 6). However, the recovery of individual REE during bioleaching was lower (up to 14.5% Nd) than REE recovered from non-detrital minerals via sequential extraction.
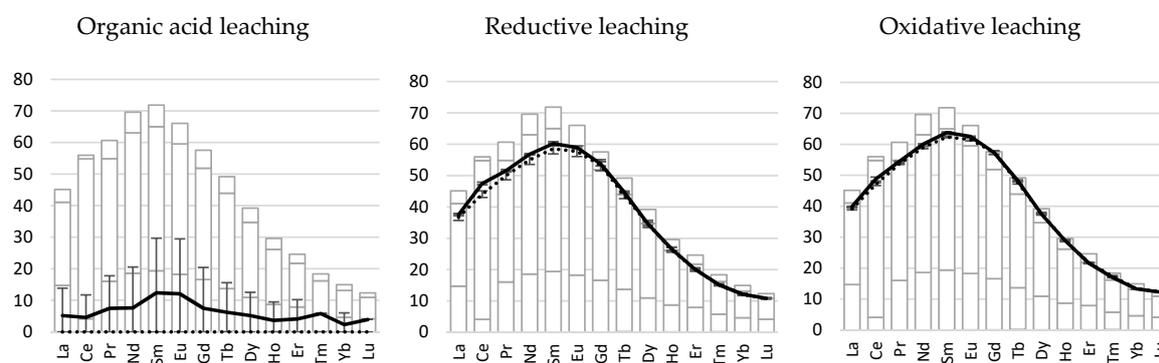

Figure 6. Recovery (%) of individual REE from high-Ca bauxite for each of the leaching techniques tested. Solid lines represent inoculated tests and dotted lines are uninoculated controls. Error bars are plus or minus one standard deviation of triplicate experiments. Bar charts show sequential extraction data, as in Figure 4.

In the organic acid bioleaching, which had the lowest REE recoveries of all the bioleaching, the replicates were highly variable, with two having REE recovery rates of <1% for each of the individual elements, and the third replication recovery at between 3.9% and 24.6% depending on the element. The pH of the organic acid microbial leaching solution increased from 2.04 to 7.16 after mixing with high-Ca bauxite, before reducing to 2.18 after 7 days (Table 7). However, there is no clear relationship between final pH and REE recovery, as the replicate with highest REE recovery had the highest pH of the three replicates. Oxidative bioleaching had the highest REE recovery, up to 4.41% (for Eu) greater than reductive bioleaching (Figure 6). The pH at the beginning and end of oxidative bioleaching was slightly lower than for the reductive bioleaching (final pH 1.68 for oxidative leaching compared to 1.81 for reductive leaching). Only a minimal increase in REE recovery was seen in the presence of *A. ferrooxidans* under reductive and oxidative leaching compared to the uninoculated control. The greatest difference was observed during the reductive leaching of the light REE. The final pH was slightly lower in the presence of *A. ferrooxidans* during oxidative and reductive leaching. More iron was leached during oxidative leaching than during reductive leaching, in both the uninoculated controls and the presence of *A. ferrooxidans*. The proportion of reduced iron was lower when *A. ferrooxidans* was present (especially notable during the oxidative leaching). REE recovery was higher during oxidative leaching, with the presence of *A. ferrooxidans* having enhanced REE recovery further. The difference observed for the REE is not seen in the leaching of total iron (the data points lie within experimental error).

Table 7. Changes in pH, iron, aluminium and TREE concentrations and percentage of reduced iron in final solutions for high-Ca bauxite during organic acid, reductive and oxidative leaching and uninoculated controls, recorded after 1 h and then at the end of 7 days of leaching. The initial pH for reductive and oxidative leaching was measured after the addition of H_2SO_4. This was required in order to reduce the pH to within the growth range for *A. ferrooxidans*, following pH increase caused by carbonate dissolution. Characterisation of starting fluid conditions is shown in Table 3. Errors are one standard deviation of triplicate experiments.

Bioleaching Technique	Microorganism	pH		Change in Total Fe (mg·L^{-1})	Reduced Fe as % Total Fe	Change in Al (mg·L^{-1})	Change in Total REE (µg·L^{-1})
		Initial	Final				
Organic acid	*Aspergillus* sp.	7.16 ± 0.08	2.18 ± 0.44	20.1 ± 10.7	n.d.	53.7 ± 5.2	626 ± 1042
leaching	Uninoculated *	7.96 ± 0.01	7.66 ± 0.11	<d.l.	n.d.	0.015 ± 0.001	<d.l.
Reductive	*A. ferrooxidans*	1.72 ± 0.01	1.81 ± 0.01	8.05 ± 2.23	68.6 ± 12.1	55.9 ± 0.9	5556 ± 77
leaching	Uninoculated	1.75 ± 0.02	1.93 ± 0.03	12.1 ± 2.0	72.4 ± 0.6	59.3 ± 1.8	5394 ± 90
Oxidative	*A. ferrooxidans*	1.61 ± 0.02	1.68 ± 0.01	24.5 ± 8.5	2.58 ± 1.20	64.4 ± 2.9	6062 ± 50
leaching	Uninoculated	1.57 ± 0.09	1.75 ± 0.03	31.0 ± 0.6	58.4 ± 3.1	60.5 ± 1.8	5787 ± 169

* duplicates only; n.d. not determined; d.l. detection limit.

3.2.3. Clay-Rich Bauxite

Like the other bauxites, the sequential extraction data suggest that the highest REE recovery would be in relation to middle REE (Nd to Eu). This recovery trend was observed during organic acid leaching; however, there was a shift in the highest recovery during oxidative leaching to heavier REE (Eu to Dy). Of the three bauxites tested, the greatest differences between the bioleaching mechanisms were seen in the clay-rich bauxite. The highest REE recovery was observed with oxidative leaching, followed by organic acid leaching. Minimal REE recovery was observed during reductive leaching (Figure 7).
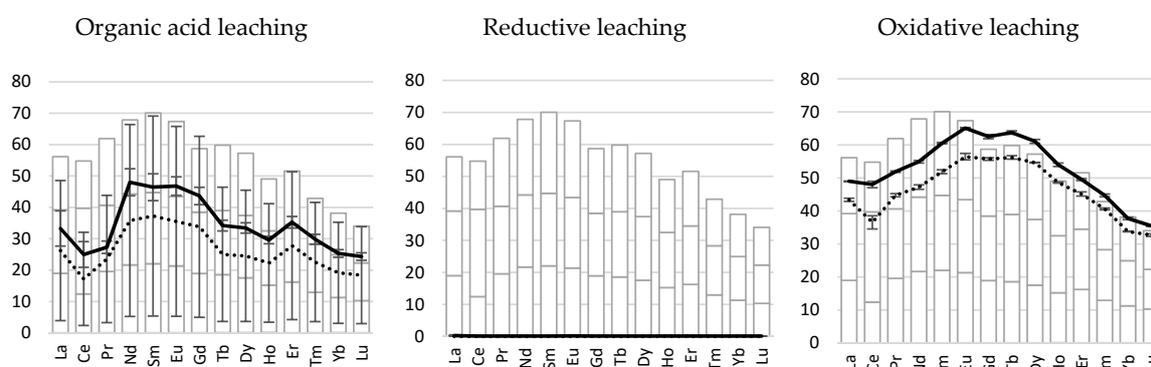

Figure 7. Recovery (%) of individual REE from clay-rich bauxite for each of the leaching techniques tested. Solid lines represent inoculated tests and dotted lines are uninoculated controls. Error bars are plus or minus one standard deviation of triplicate experiments. Bar charts shows sequential extraction data, as in Figure 4.

Leaching with *Aspergillus* sp. enhanced REE recovery over uninoculated controls (50.2% Nd compared to 35.8% Nd). The uninoculated controls were more variable than *Aspergillus* sp. Only one of the uninoculated controls had low REE recovery (0.67% Nd) and the two other triplicates (50.5% and 56.3% Nd) had similar REE recovery rates to *Aspergillus* sp. During 7-day leaching, the pH of the uninoculated controls decreased to a mean of 5.69 (Table 8). The inoculated replicate with the lowest leaching had a higher pH (6.52) than the other two uninoculated replicates (5.15 and 5.39), and all three pH values were higher than the final pH in the presence of *Aspergillus* sp. (3.00).

Table 8. Changes in pH, iron, aluminium and TREE concentrations and percentage of reduced iron in final solutions for clay-rich bauxite during organic acid, reductive and oxidative leaching and uninoculated controls, recorded after 1 h and then at the end of 7 days of leaching. The initial pH for reductive and oxidative leaching was measured after the addition of H_2SO_4. This was required in order to reduce the pH to within the growth range for *A. ferrooxidans*, following pH increase caused by carbonate dissolution. Characterisation of starting fluid conditions is shown in Table 3. Errors are one standard deviation of triplicate experiments.

Bioleaching Technique	Microorganism	pH		Change in Total Fe (mg·L^{-1})	Reduced Fe as % of Total Fe	Change in Al (mg·L^{-1})	Change in Total REE (µg·L^{-1})
		Initial	Final				
Organic acid leaching	*Aspergillus* sp.	7.26 ± 0.10	3.00 ± 0.08	24.5 ± 1.1	n.d.	32.4 ± 11.7	4939 ± 621
	Uninoculated	8.01 ± 0.01	5.69 ± 0.73	12.5 ± 9.7	n.d.	9.26 ± 7.87	3731 ± 3187
Reductive leaching	*A. ferrooxidans*	1.98 ± 0.06	6.92 ± 0.45	−77.0 ± 16.3	94.0 ± 0.5	<d.l.	12.5 ± 15.5
	Uninoculated	2.08 ± 0.20	7.38 ± 0.18	−47.5 ± 16.2	71.1 ± 16.2	<d.l.	0.503 ± 0.338
Oxidative leaching	*A. ferrooxidans*	1.75 ± 0.05	2.07 ± 0.02	26.3 ± 2.1	4.57 ± 0.72	44.8 ± 0.9	7850 ± 101
	Uninoculated	1.80 ± 0.03	2.91 ± 0.30	12.6 ± 5.6	93.9 ± 5.0	39.6 ± 3.3	6499 ± 119

n.d. not determined; d.l. detection limit.

During inoculated reductive leaching, the pH increased from 1.98 to 6.92, which coincides with a large decrease in iron in the solution (Table 8). Aluminium was not present in the final solution, as expected given the neutral pH. A similar trend is also shown by the uninoculated experiment. The observed rise in pH in the final solution could cause minimal leaching of, sorption to or precipitation of mineral phases that are pH sensitive. Unfortunately, any evidence for new REE mineral phases in the final solid material was obscured by the high prevalence of calcium sulphates and amorphous elemental sulphur when observed under SEM. The final concentration of total phosphorous in solution was below the detection limit (<0.04 mg·L^{-1}) in both inoculated and uninoculated controls compared to a range of 0.8 to 7.46 mg·L^{-1} for the other bauxite samples (Table S1), indicating that the precipitation of phosphates (present in the original growth medium) had occurred, which could incorporate REE during precipitation [48], along with iron mineral phases.

Unlike the previous samples, oxidative leaching, in the presence of *A. ferrooxidans*, resulted in a clear increase in REE leaching by 2.8% to 11.4% over the uninoculated control. More Fe was released in the presence of *A. ferrooxidans* (Table 8), which is reflected in the increase in REE recovery, providing a potential indication of REE associated with iron minerals in this bauxite.

4. Discussion

A sequential chemical extraction of three karst bauxite samples indicated that each bauxite contained REE that could be released sequentially by acidification, reduction and oxidation. For the low-Ca and high-Ca bauxite, the sequential extraction data indicated that the highest REE recovery is likely to occur under reducing conditions (with smaller amounts released by the acetic acid and oxidising agent), but for the clay-rich bauxite, roughly equal recovery occurred under all three conditions. Bioleaching experiments were then set up to create or enhance oxidising, reducing and acidic conditions. Due to the differences in the contact time, strength and types of leaching agents and the non-sequential nature of the bioleaching, the sequential extraction and bioleaching would not be expected to give the same REE recovery. Therefore, individual steps of the sequential extraction should not be compared to or used to predict bioleaching results. However, the total REE recovered from all sequential extraction steps was a reasonable predictor of the amount and trend of REE recovered by the most effective bioleaching technique for all bauxites (Figures 2, 6 and 7). Using single-step chemical extractions, or altering the time and strength of chemical leaching conditions, may make this approach more directly relevant to predicting bioleaching potential. Similar to the sequential extraction results, in the bioleaching tests, the REE recovery was found to vary across the three bauxite samples of this study. In addition, differences were found in each bauxite among the leaching methods and between inoculated and control samples within each method. Considering the low-Ca bauxite, the reductive and oxidative tests recovered similar amounts of REE, with the organic leaching performing almost as well.

For this sample, a lower recovery of cerium was also seen in the oxidative leaching compared to the other two conditions and the sequential chemical extraction. The presence and acid-producing activity of *Aspergillus* sp. resulted in a large increase in REE recovery compared to the uninoculated control, but the presence of *A. ferrooxidans* made very little difference. For the high-Ca bauxite, the amount of REE recovered by oxidative leaching was a little higher than by reductive dissolution. Similar to the low-Ca bauxite, the presence of the *A. ferrooxidans* made little difference to the REE recovery. Organic leaching was much less effective than the autotrophic leaching methods for the high-Ca bauxite, which is likely to be due to the higher pH-buffering capacity of this sample. Finally, for the clay-rich bauxite, reductive dissolution was ineffective, but oxidative leaching recovered a similar amount of REE as the sequential extraction, with greater leaching achieved for several heavy REE, including valuable elements such as Dy. Organic leaching did not recover as much REE as the oxidative leaching. Although the presence of *Aspergillus* sp. resulted in more REE recovered, this sample was unusual in that a similar amount of REE was recovered in the uninoculated control. Furthermore, this sample was the only one where the presence of *A. ferrooxidans* increased the recovery of REE (by up to 11.4%).

The organic acid bioleaching was most effective when applied to the low-Ca bauxite, almost completely leaching all the REE associated with non-detrital material, as defined by the sum of the steps during sequential extraction. It was considerably less effective in the high-Ca and clay-rich samples. The near neutral initial pH in the high-Ca and clay-rich bauxites indicated that the organic acid lixiviant was neutralised at contact with these bauxite samples, most likely by dissolution of calcium carbonate. Although the final pH was lower than the initial pH, due to continual production of organic acids, the evolution of pH is unknown, and it was reasonable to assume that contact time at the lower pH was less than the 7-day incubation. This higher initial pH is likely to be responsible for the lower REE recovery from these bauxite types. It was also observed that some of the bauxite became attached to the side of the flask, and there was microbial growth throughout the leaching experiments, which resulted in the powdered bauxite forming small clumps (Figure S1), creating potential micro-environments within each experiment. If fungal growth occurred before pH decreased sufficiently, the bauxite at the core of these clumps could be isolated from the low pH of the bulk media, reducing the proportion of the bauxite available for leaching. In other parts of these micro-environments, there is direct contact between fungi and bauxite. Leaching may be enhanced here, as seen with increased REE recovery by the heterotroph *Enterobacter aerogenes* in contact with monazite-bearing ore [27]. If this is the case in the high-Ca and clay-rich experiments, then the bioleaching setup would need to be modified to avoid this isolation of some of the samples from the bulk fluid. If there was any locally enhanced REE release, this was not seen in an increase in bulk REE recovery. The creation of these micro-environments could contribute to the variability among the replicates (large error bars in Figure 6; Figure 7, as small initial changes in the size and shape of the encapsulated sample could lead to differences in contact time between bulk fluid and bauxite. As at least one of the uninoculated controls leached REE at similar concentrations, or higher than the experiments inoculated with *Aspergillus* sp., a natural community capable of heterotrophic leaching was present in the sample at the start of the experiment and could be exploited for REE recovery. Relying on a natural community alone would need careful control as REE recovery by stimulating the natural community is more variable and may take longer to establish [16].

Leaching by acidophilic autotrophs such as *A. ferrooxidans* in an aerobic environment is typically described as bioleaching by oxidative dissolution, and in this paper, it is referred to as "oxidative leaching". The involvement of exogenous sulphur, as described in the Introduction, indicates that the microbially enhanced dissolution of non-iron sulphide minerals is not necessarily a direct result of an oxidation process (as in the case of bioleaching from sulphidic ores), but rather, it is driven by the presence of the sulphuric acid generated by microbial oxidation of the sulphur [49]. Although the term oxidative bioleaching is used here, in keeping with the wider literature, this is not meant to imply that the dissolution of REE from the bauxite is by oxidation of mineral phases.

Bauxites are oxidised ores, and the sequential extraction showed that considerable amounts of REE could be recovered using a reducing agent: this reducible fraction was the largest for the low-Ca and high-Ca bauxite samples. It might therefore be expected that microbially-induced reducing conditions would be the most effective at leaching. However, reductive and oxidative leaching gave similar REE recovery trends and abundances in these two bauxites, both in the presence of *A. ferrooxidans* and in the uninoculated controls. There were small differences among these four leaching experiments. These small differences are discussed further to help understand the potential for bioleaching of REE from bauxite, including the leachability of the REE associated minerals. Significant increase in REE recovery in the presence of *A. ferrooxidans* was only observed during oxidative leaching for the clay-rich bauxite.

To better understand the leaching mechanisms that were involved, studying leaching trends of major elements can be a useful guide. As aluminium is not redox sensitive, it is used to represent leaching due to acidolysis, while iron represents the combined effect of acidity and redox. Differences in leaching trends between aluminium and iron can therefore be used to indicate potential redoxolysis. In addition, comparing the leaching trends of these elements with differences in REE recovery provides guidance on the REE-associated minerals. Considering low-Ca bauxite first, more iron is leached in the presence of *A. ferrooxidans* during reductive and oxidative leaching than the respective uninoculated controls. This could be due to the lower pH in these samples. However, a similar trend is not seen in the leaching of aluminium, suggesting the involvement of redox processes. *A. ferrooxidans* can enhance the leaching of iron from FeOOH or similar material in reducing and oxidising conditions (Equations (4) and (6)). A minor increase in REE recovery was only observed during reductive leaching in the presence of *A. ferrooxidans*. This indicates that REE could be hosted in iron oxide phases, e.g. goethite [8,50]. As the differences were small and only observed under reductive leaching, further investigations would be required to confirm this. There was also a clear difference between the reductive and oxidative bioleaching in the speciation of iron in solution, indicating ongoing microbial activity in the inoculated samples compared to the uninoculated controls. This was mostly Fe^{3+} in the oxidative bioleaching and mostly Fe^{2+} in the reductive leaching. This is expected and reflects the *A. ferrooxidans* mediated reactions shown in Equation (2) and Equations (5) and (6), respectively.

Consideration of the different behaviours of iron and aluminium can help us to understand the differences seen between the three sample types. The high-Ca bauxite sample was collected from the margin of the deposit and shows different leaching behaviour to the low-Ca bauxite in terms of the REE and their relationship to the major elements. Leaching of the REE is higher when the final pH is lower; however, this trend is not seen in the iron leaching results (Table 7), indicating that the REE are likely to be associated with pH sensitive minerals other than iron. REE fluorcarbonates were observed in thin section and are a possible source of recoverable REE in these samples and in other karst bauxites [51]. The behaviour of the REE was distinctly different in the clay-rich bauxite. The pH increased drastically during reductive leaching, resulting in low REE recovery. This pH increase was observed in both inoculated and uninoculated conditions, indicating that the material itself exerts the most control in raising the pH, under reducing conditions. The explanation for this is unclear without further investigation: one possibility might be the presence of organic carbon in the sample, the decomposition of which, in anaerobic conditions, can increase the pH. In contrast to the reductive leaching, REE recovery from the clay-rich bauxite under oxidising conditions was more successful, especially in the presence of *A. ferrooxidans*. This was the only instance where the presence of *A. ferrooxidans* showed a clear improvement in REE leaching compared to the controls (e.g., 50.2% recovery Nd compared to 35.7%). Higher REE recovery is associated with lower pH and higher release of iron and aluminium, indicating the potential for leaching from acid and/or redox sensitive minerals.

Although not the focus of this study, the combined extraction of REE and bio-beneficiation of low-grade bauxite ore could provide opportunities in bauxite bioprocessing by simultaneously increasing the value of both the waste stream and raw material for downstream processing. Previous research into the bio-beneficiation of bauxites focused on removal of silica, iron and

calcium [36–41]. *Bacillus polymyxa* has been shown to remove up to 42% iron from bauxite (containing 31.4 g·kg^{-1} iron) in a similar microbial media to that used with *Aspergillus* sp. [39]. In the same study, up to 100% of Ca was also removed under similar conditions. In this study, bioleaching techniques only removed up to 1.2% iron (Tables 4 and 6, Tables 7 and 8, details of mass and volumes in Table S1). However, further research could be focused on the combined goals of beneficiation and REE extraction of bauxites.

5. Implications for Industry

As low-Ca bauxite is the most representative of the feed material for alumina processing, it is encouraging to note that it can be processed by each of the bioleaching methods tested, and, with optimisation, greater REE recovery could be achieved. When considering the relevance of these results to industry, other factors, such as material costs, infrastructure and expertise required, need to be considered, which differ for each of the bioleaching methods tested here.

Although the subject of many studies, heterotrophic leaching has made little if any impact upon commercial biomining. Unlike autotrophic leaching, organic acid leaching requires a continual supply of organic material and increasing input costs, and much work is required to reduce these costs before this process becomes industrially relevant. This research could involve the reduction of organic compositions and/or the use of organic waste sources. Although REE can be leached by organic acids, it is unlikely to be the preferred "early" choice for bioleaching due to the cost and the fact that better results were achieved by autotrophic leaching for each bauxite. Furthermore, as there are no commercial scale heterotrophic leaching operations, considerably more scaled-up work would be needed in order to encourage pilot scale projects to be considered.

The benefit to commercial operations of using autotrophic bioleaching for sulphidic ores over heterotrophic leaching is that it is self-sustaining, i.e., it can use CO_2 from the atmosphere as the sole carbon source. It is also self-sustaining in the sense that in oxidative dissolution, once acidic conditions suitable for the growth of acidophiles have been achieved, the low pH is maintained through the regeneration of acid by the microbial population. Here, we have presented some evidence that *A. ferrooxidans* could play this role in bauxite leaching and contribute to REE recovery in this way, although sulphur may need to be added. The commercial operation of bioreactors maintaining anoxic conditions will be more expensive than bioreactors operating in oxic conditions, due the costs of maintaining an anoxic (typically nitrogen) atmosphere within the system. Oxidative bioleaching was marginally better than reductive bioleaching, so oxidative leaching will be the more likely method to use for bioleaching of REE from bauxite. Further investigation into reductive bioleaching should be explored using other microorganisms, as leaching of La was enhanced in the presence of *A. thiooxidans* but not *A. ferrooxidans* [30].

Although material such as clay-rich bauxite is unlikely to be of commercial interest for aluminium extraction, oxidative leaching of the clay-rich bauxite shows the most potential for an autotrophic bioleaching approach. In contrast to the other samples, for the clay-rich bauxite, the presence of *A. ferrooxidans* considerably increased the overall REE recovery and also showed greater recovery of the more valuable element dysprosium (compared to total sequential extraction). Further work would need to be carried out, e.g., testing without the addition of sulphur and comparing to a sulphuric acid leach for the same duration to confirm whether larger scale bioleaching might be possible and the reduced input cost outweighs the technical requirements.

The large volume of karst bauxites processed annually and their wide geographical distribution mean that they are a promising resource of REE. This work demonstrates the potential for simple, low energy chemical and biological extraction methodologies; however, significant development, including integration into alumina processing, is required.

6. Conclusions

Bioleaching relies on microbial activity to maintain appropriate conditions. Due to the variety of REE-bearing minerals present in bauxite material, and therefore the variety of targets for bioprocessing, enhanced REE recovery might be expected in all bioleaching processes tested here. This is true for organic acid bioleaching, as REE recovery in the presence of *Aspergillus* sp. is considerably higher than in the uninoculated controls for all three bauxite samples. However, the differences in REE recovery were generally limited when leaching with *A. ferrooxidans* compared to the controls. The data show that *A. ferrooxidans* has a role in acid formation, or regenerating Fe^{3+} but that, in most cases, there was little improvement in the amount of REE recovered. The exception to this was for the clay-rich bauxite, in which the amount of REE was noticeably higher under oxidative conditions when inoculated with *A. ferrooxidans*. Despite only small increases in REE recovery, improvements in REE recovery could be made through modifications to leaching conditions, including the microorganisms used.

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