



Historical Perspective

Apatite enrichment by rare earth elements: A review of the effects of surface properties



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ABSTRACT

Apatite subspecies depend on their halogen and hydroxyl content; chlorapatite, hydroxylapatite and fluorapatite, with additional substitution of other elements within the lattice such as rare earth elements (REE), sodium, strontium and manganese also possible. Rare earth elements are vital to green and emerging technologies, with demand set to outstrip supply. Apatite provides a possible future source of REE. Processing rare earth deposits is often complex, with surface behaviour having a significant effect on the optimization of a process flow sheet. The effect of enrichment of natural apatite and the doping of synthetic apatite on surface behaviour can be determined by measuring the zeta potential and the isoelectric point of the mineral.

In this paper, we review zeta potential studies of natural and synthetic apatite to determine the effect of elemental enrichment on surface behaviour. Fifty three studies of natural apatite and forty four studies of synthetic apatite were reviewed. The isoelectric point of apatite varied from pH 1 to pH 8.7, with studies of apatite specified to be >90% pure reducing the variation to pH 3 to pH 6.5. Of the four studies of rare earth enriched apatite found, three had IEP values between pH 3 and pH 4. A study of synthetic apatite showing enrichment of between 1 and 10% by the REE europium does not affect surface behaviour. However, no studies were found that investigated the effect of common REE processing reagents on REE enriched apatite zeta potentials.

Therefore, in addition to comparing previous studies we also therefore present new zeta potential measurements of apatite from a REE enriched deposit under water and common flotation collector conditions. The IEP value of this apatite under water conditions was at pH 3.6, shifting to <3.5 under both hydroxamic acid and betacol conditions. When compared to previous studies, the behaviour of REE enriched apatite under collector conditions is similar to non-REE apatite. This result could be important for future processing of apatite enriched with REE, and therefore global apatite and rare earth supply.

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Abbreviations: HREE, Heavy Rare Earth Elements; IEP, IsoElectric Point; LREE, Light Rare Earth Elements; PZC, Point of Zero Charge; REE, Rare Earth Elements.

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1. Introduction

The motivation for this review is to enable researchers who investigate the mineral apatite, to make use of the existing literature which due to inconsistencies in naming practices and methodologies is currently difficult to effectively compare and contrast. The mineral apatite was named after the Greek word for deceit, due to its ability to show in many crystal forms and shapes, some of these effects are due to enrichments of different elements within the structure [1]. Apatite is the main source of phosphate that is mined industrially [2]. As well as being present in mineral form in ore bodies around the world and on both mars and the moon, natural apatite is also present in bones and teeth within mammals [3–5]. Since its discovery within bones, the synthesis of apatite has been identified as important for bone grafts and replacements, with work also investigating its uses as a drug delivery system [6,7]. Synthetic apatite doped with the REE europium has uses in ink jet printing, whereas natural apatite enriched with hydrothermal alteration is of interest due to resource scarcity [8,9].

1.1. Types of apatite

Although the discovery of apatite in mineral form was in 1827 the naming and renaming of the species and sub species, has been ongoing for the last 190 years [10]. According to the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC), currently there are only three minerals of the apatite group, chlorapatite, fluorapatite and hydroxylapatite, named after the substitution of chlorine, fluorine and hydroxyl anion into the crystal lattice respectively [1]. The chemical composition and example geographic locations of apatite are shown in Table 1.

As the IMA-CNMNC was only created in 1959, many more names for apatite are used in earlier literature [14–16]. These include, but are not limited to, collophane and francolite [17–19]. Both these names are still used regularly in published literature even though they do not appear on the IMA-CNMNC master list (July 2017 IMA-CNMNC). Changes within the IMA-CNMNC naming practices, with species of apatite being renamed in both 2008 and 2010, makes a clear historical record of apatite studies challenging to identify [1,16]. Although there is no master list of discredited species, this review has brought together the most

common mineral names for apatite that are now discredited by IMA-CNMNC in Table 2.

Table 2 does not list all synonyms for apatite, these include but are not limited to, naurite, collophanite, ornithite, saamite, and glaubapatite [26]. As these names are not used in common literature relating to zeta potentials we do not explore them further in this review. For future research on apatite to be easily accessible clear naming practices are vital to make sure that studies are not repeated or overlooked in the literature, this paper recommends adhering to the CNMNC nomenclature.

Since the understanding that apatite is a constituent of mammalian teeth and bones, there has been research into synthetic production of apatite as a bone replacement [27]. The first synthetic apatite used as a bone replacement was in 1920 and since then a massive field of interdisciplinary research has developed overlapping dentistry, medicine and materials science [28,29]. Although initially used as a possible bone replacement, synthetic apatite, more commonly hydroxylapatite (HAP), has a lower tensile strength than natural bone and currently is mostly researched as a coating to stronger materials such as titanium for bone replacements [30]. For a review of the full uses of synthetic apatite in medicine, see Ridi et al., [31]. Synthetic apatite is investigated further in a review of literature in section 2.2.

1.2. Apatite as a source of REE

Apatite can substitute up to half the elements within the periodic table into its structure, and as such can become enriched with a number of different elements during either formation or a later hydrothermal alteration [2,32]. Enrichment and alterations can be used to reflect early environments, from geological processes to early sea temperatures and paleo environments [33]. Sometimes the enrichment of a particular element makes the apatite of interest for that enrichment alone, for example in Songwe Hill, Malawi, apatite enriched with REE is under development as a REE mine [34].

The rare earth elements (REE) consist of the lanthanide series of elements plus scandium and yttrium [33]. They are often subdivided into either light REE (LREE) or heavy REE (HREE) depending on their atomic number, with HREE often more valuable than LREE [35,36]. REE have become relevant in the modern economy due to their uses in batteries and catalytic converters as well as wind turbines and mobile phones [37]. REE are contained within over 200 minerals, however

Table 1

Fluorapatite, chlorapatite and hydroxylapatite information and localities, taken from IMA-CNMNC Master List July 2017.

Apatite	Chemical formula	Theoretical chemical composition	Deposits	Reference
Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	Ca 39%, P 18%, O 41%, H 0.02%	Jocao pegmatite, Minas Gerais, Brazil	Baijot et al., [11]
Chlorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$	Ca 38%, P 17%, O 37%, Cl 6.8%	Breves deposit, Carajas, Brazil	Tallarico et al., [12]
Fluorapatite	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	Ca 39%, P 18.4%, O 38%, F 3.7%	Adirondack Mountains, NY, USA	Lupulescu et al., [13]

Table 2
List of discredited and out of use mineral species of apatite. Current status is based upon Commission on New Mineral, Nomenclature and Classification, International Minerals Association (CNMNC).

Name	Named for/by	Current status	Recent references	New Name* according to IMA-CNMNC	References
Francolite	Wheal Franco, Devon	Discredited 2008	Caird et al., [20], Elmandy et al., [18]	Fluorapatite	
Lewistonite	Locality of Lewiston, Utah	Discredited 1978	–	Fluorapatite	Larsen and Shannon [21], Dunn [22]
Dehrnite	Locality of Dehrn, Germany	Discredited 1978	–	Fluorapatite	Larsen and Shannon, [23], Dunn [22]
Collophane	Sandberger [23] “Kollophan”	Discredited 1943		Fluorapatite	Rogers [14], Frondel [24], Sandberger [25]

extracting them is complex, hence the “rare” within their name. Apatite is known to host REE and is a possible source for future expansion in the market [38]. The ability to mine for both phosphate and REE enables a more cost efficient mining practice. There are two processes of REE enrichment within apatite, the first is the substitution of REE^{3+} and Na^+ for Ca^{2+} within the apatite, the second is P^{5+} substituted with REE^{3+} and Si^{4+} [39]. The end member of the second substitution is britholite, a mineral heavily enriched in REE [40]. Table 3 lists a selection of deposits of REE bearing apatite currently identified in literature (as of 2018).

1.3. Surface charge and zeta potential measurements

When a solid surface is submerged in an aqueous solution, the surface of the solid will acquire a charge due to the composition of the atoms at the solids surface [50–56]. The magnitude and sign of this charge is affected by the ions within the liquid and the ions at the surface of the solid. This domain can be described according to the electrical double layer (EDL) [57]. Zeta potential measurements are a common method of interpreting the electrical double layer [58]. For more details into the electrical double layer see Greenwood [59] or Hunter et al., [58]. The electrical double layer is usually defined by the iso electric point (IEP) or the point of zero charge (PZC). The IEP is the measurement of the shear plane [57]. Although often quoted interchangeably, IEP and PZC are different, with IEP being the conditions under which the zeta potential is zero whereas PZC occurs when the surface is uncharged [56]. The aqueous medium in which the zeta potential is measured can affect both the magnitude of the zeta potential and the IEP and PZC. Ions which can affect the surface are called ‘potential determining ions’ [60]. Zeta potentials are measured by a wide range of methods ranging from electro-osmosis to streaming potential [58].

1.4. Use of zeta potential measurements of apatite

There have been many studies investigating processing of apatite, investigations into reagents used in flotation such as oleic acid and

sodium oleate [17,52]. Froth flotation of apatite is one of the main methods of mining the mineral from host ores [61]. Selecting the correct reagents is important in optimizing the process. As each deposit is composed of many different minerals, many studies have been conducted on apatite to identify the optimum conditions for separating from a specific mineral mix. Reagents can be divided into collectors, depressants, pH modifiers and frothers. Collectors attach to the mineral to make it hydrophobic, and depressants, which attach to the gangue (waste) minerals to induce hydrophilicity or prevent interaction with collectors.

In flotation research the adsorption mechanisms of different collectors are important as they may vary across different pH values [60]. The collector mechanism eg. Chemisorption or physisorption can be inferred by zeta potential measurements and directly measured using FTIR and UV spectroscopy. If the collector attaches using physisorption then opposite charges attract, if the collector adsorbs chemically the zeta potential will exhibit a change. The mechanism for hydroxamic adsorption on apatite has previously been investigated by Yu et al., [62]. Alkyl hydroxamic acid was found to chemisorb onto apatite by ionic bonding of the oxygen atoms to the calcium at the surface. Fatty acids are one of the most common collectors for apatite as they are cheap [61]. Fatty acids chemically adsorb onto the surface of fluorapatite by bonding to the Ca site, with hydrogen bonding between the O at the surface and the H of the fatty acid [63]. Pan et al., [64] investigated the adsorption of fatty acids onto hydroxylapatite, with the positive ends of the amino acids attaching to the Ca sites and the negative ends fitting to the P or OH sites.

Although the Khibiny nepheline syenite complex, Kola peninsula, Russia is one of the largest igneous apatite deposits, with apatite enriched with REE, this review could find very little published research relating to flotation of Khibiny ore ([65] Table 3.) Houot [65] showed Khibiny was floated with tall oil collectors and sodium silicate as a depressant. Published research may be limited due to non-disclosure agreements, or not have been published in English [66]. Processing of REE enriched apatite deposits has previously been explored by Soltani et al., [49] and Harbi et al., [67]. The processing of britholite, the end member of the REE^{3+} and Si^{4+} substitution in apatite, has previously

Table 3
Adapted from Broom-Fendley et al., [32]. A sample of REE enriched apatite deposits. This list includes a selection of REE enriched apatite deposits and is not representative of the entire list of deposits. *%REE denotes investigations into the mineralogy of deposits and does not represent the enrichment of all apatite within the deposit or its economic viability.

Deposit name	Geological setting	Country	Type of apatite	REE (% or ppm)	Reference
Phalaborwa	Carbonatite	South Africa		La 1245 ppm	Dawson and Hinton [41]
Songwe Hill	Carbonatite	Malawi	Fluorapatite	6200 ppm Ce, 3400 ppm Nd	Broom-Fendley et al., [32]
Juquia		Brazil	–	1035 ppm	Walter et al., [42]
Kovdor	Carbonatite	Kola,-Russia	–	1740 ppm Nd, 3770 ppm Ce	Kempe and Gotze [43]
Ermakorka (Transbaikalia)	Carbonatite	Russia	–	6610 ppm Ce, 5130 ppm La	Kempe and Gotze [43]
Hillside deposit	Iron-oxide-copper-gold	Australia	Fluorapatite	1100 ppm- >2%	Ismail et al., [44]
Oka, Quebec	Carbonatite	Canada	Fluorapatite- hydroxyl-fluorapatite	6000-34,000 ppm REE	Hornig-Kjarsgaard et al., [45]
Hoidas Lake, Saskatchewan	Monzogranitic and tonalitic gneiss.	Canada	Fluorapatite	1.5–5% REE enrichment	Halpin et al., [46] Pandur et al., [47]
Minami-Torishima Area, Southeastern Japan	Deep sea mud	Japan	–	9300–32,000 ppm REE	Kon et al., [48]
Esfordi		Yazd Province, Iran	Fluorapatite, Britholite		Soltani et al., [49]

been investigated by Yang et al., [68]. Britholite was only a secondary ore mineral to elphidite in the deposit with other ore minerals being the REE fluorocarbonate minerals, parisite, synchysite and bastnäsite. The ore was processed using flotation with recovery of britholite at 85% to the 96–100% of the fluorocarbonate REE minerals (parisite, synchysite and bastnäsite). The flotation used a selection of collectors in the flotation including fatty acids and hydroxamic acids. Sodium Silicate and starch were selected as depressants.

However, there are other studies investigating processing of apatite via bacteria such as using Cellulose enzyme (*Aspergillus Niger*) as a depressant [17]. Some research in mineral processing include the use of oily bubbles to collect apatite instead of conventional gas/water bubbles [69]. Other papers have investigated the theoretical surface charge of apatite with a theoretical IEP value at pH 7.2 conditioned in water in the presence of CO₂ [69].

As there is such a wide range of research in which zeta potentials are used, this study aims to review and consolidate previous zeta potential data for apatite to create a comprehensive review. In particular comparing synthetic apatite doped with REE, Chen et al., [8] studied hydroxyl-apatite doped with Eu, to natural apatite enriched with REE. This review will link to new zeta potential measurements of apatite from a REE enriched deposit in Section 3. This comparison will highlight any differences in zeta potential and consequently collector adsorption, which will affect subsequent separation by froth flotation. These results will be applicable to a wide range of deposits containing REE enriched apatite such as Songwe Hill, Malawi and Kovdor Russia [32,43]. This is also an interdisciplinary approach of applying biomedical research to mineral processing applications.

2. Review of previous studies of apatite

This review aims to consolidate and analyze previous studies of apatite surface behaviour to produce a reference for future use, with a particular focus on natural forms of apatite. One of the findings of the review is that the methodology used to measure zeta potentials changes between disciplines, this partly is driven by the circumstances of the minerals use. For example for studies on calcium phosphate ceramics used in bone, the zeta potential is a measure of the bone structure formation and so this is conducted over 400 h [71]. In contrast, research into mineral processing as it is less time dependent and studies do not often reference over how long the value has been taken over [72]. As this review primarily investigates studies which research the natural mineral forms of apatite, the selection criteria aims to distinguish studies of particular interest in this review. A full review of synthetic apatite is out of the scope of this review, as it is likely to exceed the length at least twice of this one although studies of specific interest will be highlighted that relate to REE enrichment and ion substitution. However the IEP and PZC of synthetic apatite is reviewed along with surface behaviour of different types of synthetic apatite and REE enriched synthetic apatite.

In selecting papers within the review certain areas were omitted.

Not included

- Octo-calcium phosphate.
- Studies where only one pH value was tested.
- Lack of clear description with sample identification or origin.
- When electrolyte solutions were not comparable to other studies. For example oleic acid [17], phosphonates [73], phosphor-citrate [74], sodium oleate [75]. Comparing these studies is beyond the scope of this review.
- When apatite is used as a coating for another material, for example coating apatite titanium and silica [30].
- Measurement must be at low wt% not at high wt% so no measurements conducted in slurry [76].

The review is divided into two main subsections, natural apatite (2.1) and synthetic apatite (2.2).

2.1. Natural apatite

Natural apatite studies mainly focus on the area of mineral processing for optimizing phosphate mining. Of the 53 studies of natural apatite reviewed, ten specified point of zero charge, forty seven specified IEP values. Due to the large number of studies we have subdivided the tables into IEP values and PZC studies, with the IEP values being subdivided into fluorapatite and other types of apatite. The majority of the studies in the last decade originate from China, as over 50% of the world's phosphate rock mined in 2016 was from China [77].

Table 4 overviews the fundamental studies of zeta potentials of apatite not listed explicitly as fluorapatite. There was thirty three studies that this review could identify, of those thirty three, four were listed as colophonite with another four listed as francolite, both of these names are now discredited under the IMCNC [24]. It is not unexpected that some studies would use historical names for apatite due to textbooks not being updated with the many changes to naming nomenclature. Another cause of the use of discredited names could be due to translation errors.

Comparing the studies is problematic due the lack of information in some categories and different methods for reporting the information, previous work by Jordens et al., [101] has shown methodology has a significant effect. Future work comparing identical apatite samples under different methodologies would be of interest. The grind size varies significantly between <2 µm and <74 µm, which has also previously been shown to effect zeta potentials in certain measurement techniques.

Of the 13 papers on fluorapatite reviewed in Table 5, the IEP values ranged between 1 [78] to 8.7 [77]. As fluorapatite is the most common mineral species of apatite, it is expected that fluorapatite would have the largest number of studies specified.

Table 6 reviews the point of zero charge studies of apatite. The point of zero charge is between pH 4.5 and pH >12.

The IEP in Fig. 1 varies from pH_{IEP} of 1 to 8.7, the PZC in comparison only ranges from 4.5 to 8.4. This variation has previously been attributed to a number of various factors, ranging from sample purity to methodology, which are further illuminated below.

2.1.1. Effect of type of apatite

As apatite is divided into three species, fluorapatite, chlorapatite and hydroxylapatite, of the 30 values of IEP denoted in Fig. 1, 17 specify fluorapatite, 2 chlorapatite, and 3 hydroxylapatite. The remaining 8 studies do not specify what type of apatite/colophonite/francolite. Of these sub studies it is expected that a large percentage of them are fluorapatite as its most common mineral subspecies of apatite.

Mishra [99] and Simukanga and Lombe [95] investigate the surface behaviour of chlorapatite from Broken Hill, Australia and Chilembwe, Zambia respectively. The IEP values they obtain are pH 6 and pH 6.7 showing close similarity between the IEP of chlorapatite samples. Hydroxylapatite surface behaviour is analyzed in three papers Vulcinic et al., [90], Kou et al., [88] and Hu et al., [92], only Hu et al., [92] and Kou et al., [88] specify an IEP at pH 3 and pH 4 respectively. This shows a similar range of IEP to chlorapatite compared to fluorapatite which has a range of over 7.7. The location of the sample from Kou et al., [88] is not specified however the sample from Hu et al., [92] was from Wangji Mine, China. From this analysis the IEP value of chlorapatite (6, 6.7) is greater than the IEP of hydroxyapatite (3, 4). The zeta potentials of chlorapatite, hydroxylapatite, and fluorapatite are shown in Fig. 2.

From Fig. 2, chlorapatite has a more positive zeta potential than hydroxylapatite from the four studies compared [88,92,95,99]. The three studies of fluorapatite plotted showed a large variation within zeta potentials [92,102,105].

There are no studies of PZC of chlorapatite and hydroxylapatite however there are seven studies of fluorapatite PZC [19,106,110,112–114]. This may not be due to specific selection of fluorapatite but rather that fluorapatite is the most common natural form of apatite. The PZC of

Table 4
Fundamental Studies of zeta potential of natural apatite not listed as fluorapatite. Mineral name taken from paper description, may be out of date for IMA-CNMNC. Deposit type denotes the most information the source material provides, if no location is provided the acquisition company is listed. DI water is Deionized water DS water is distilled water.

Mineral	Deposit/Type of Deposit*Ac1	Country	Purity	Size μm	PZC	IEP	Electrolyte	Method	Reference
Apatite	–	–	P ₂ O ₅ 41.95 wt%	5	–	2.8	1 M/L KCl	–	Jong et al., [52]
Apatite	Wards natural science establishment	Canada	P ₂ O ₅ 46.06 wt%	<20	–	4.2	10 ⁻³ M KCl	Electrophoresis	Zhou et al., [69]
Collophane	Shanxi Province	China	92.5% pure	–20	–	6.4	10 ⁻³ M KCl	–	Yu et al., [78]
Collophane	Guizhou Province	China	94.51% pure	5	–	3	10 ⁻³ M/L KNO ₃	–	Li et al., [79]
Collophane	Dayukou phosphate mine, Hubei	China	92.05% pure	–2	–	6.5	10 ⁻³ M KCl	–	Yu et al., [80]
Collophane	Zhongxiang, Hubei Province	China	Handpicked (P ₂ O ₅ 38.66 wt%)	–2	–	<2	10 ⁻³ M/dm ³ NaCl	–	Yu et al., [62]
Apatite	Wards natural science establishment	–	P ₂ O ₅ 46.06 wt%	<20	–	4.2	10 ⁻³ M KCl	Electrophoresis	Zhou et al., [81]
Apatite	Obtained from Gregory, Bottley and Lloyd	United Kingdom	–	<5	–	3.8	10 ⁻² M NaCl	–	Karlkvist, Patra [82]
Francolite	Tulear Province, Fort Dauphin	Madagascar	CaO 49.1 wt% (Ce,La 2402 1102 ppm)	<20	–	<3	10 ⁻¹ M KCl	Electrophoresis	Filippova et al., [83]
Apatite	From Centre for Mineral Technology Brazil	–	–	<20	–	<2.5	10 ⁻³ M NaCl	Micro-electrophoresis	Merma et al., [84]
Apatite	Obtained through Geological Museum of Chin	China	0.99	<30	–	3	10 ⁻³ M NaCl	–	Yang et al., [85]
Apatite	Tulear Province, Fort Dauphin	Madagascar	P ₂ O ₅ 33.68 wt%, CaO 49.08%	<20	–	1.5	10 ⁻¹ M NaNO ₃	–	Fillipov et al., [86]
Francolite	From Wards Natural Science establishment	–	P ₂ O ₅ 31.85 wt%	<74	–	<1.5	10 ⁻² M KCl	–	Elmahdy et al. [87], Elmahdy et al., [87]
Hydroxylapatite	Acquired through Ward Natural Sciences	–	No impurities	25 < 89	–	4	1 M KCl	–	Kou et al., [88]
Apatite	Carbonatitico Alcalino Complex	Brazil	92% pure	–	–	<8	–	–	Oliveira et al., [89]
Hydroxapatite	Lisinia deposit, Bosilegrad	Serbia	98.45% pure	5	–	<5	–	Electrophoretic	Vucinic et al., [90]
Apatite	Salitre Phoscorite (Si O2)	Brazil	–	–	–	7.1	–	Electrophoresis	Barros et al., [91]
Apatite	Salitre Weathered Phoscorite (High SiO2)	Brazil	–	–	–	<6.5	–	Electrophoresis	Barros et al., [91]
Apatite	Salitre Pyroxenite (high SiO2 apatite)	Brazil	–	–	–	6.6	–	Electrophoresis	Barros et al., [91]
Apatite	Salitre Phoscorite (high iron/mg apatite)	Brazil	–	–	–	7.2	–	Electrophoresis	Barros et al., [91]
Apatite	Salitre Pyroxenite (high iron.mg apatite)	Brazil	–	–	–	8.1	–	Electrophoresis	Barros et al., [91]
Hydroxylapatite	Wangji Mine	China	Handpicked	<5	–	3.2	10 ⁻³ M KNO ₃	Electrophoretic	Hu et al., [92]
Apatite	Chinese Mine	China	Handpicked	<10	–	3	10 ⁻³ M KNO ₃	Electrophoretic	Hu and Xu [93]
Francolite	Oulad Abdoun trace REE 363.3 ppm	Morocco	P ₂ O ₅ 31.78 wt%	34	8.4	4.8	–	Electro kinetic and titration	Perrone et al., [19]
Apatite	Chilembwe deposit	Zambia	Handpicked	>2	–	6	DS water	Micro electrophoresis	Zheng et al., [94]
Chlorapatite and Hydro-fluro-apatite	Kaluwe deposit	Zambia	Handpicked	>2	–	3.8	DS water	Micro electrophoresis	Simukanga and Lombe [95]
Fluor-hydroxyl-apatite	–	–	–	–	–	7	–	Streaming potential	Simukanga and Lombe [95]
Francolite	–	–	–	–	–	–	–	–	Cases et al., [96]
Apatite	–	–	–	–	–	–	–	–	Moudgil [97]
Apatite	–	–	–	–	–	–	–	–	LeBell and Lundstrom [98]
Chlorapatite	Broken Hill Lead-zinc	Australia	–	<2	–	6.7	2 × 10 ⁻³ M NaClO ₄	Micro electrophoresis	Mishra [99]
Apatite	–	–	–	–	–	–	–	–	Smany et al., [100]

fluorapatite ranged from pH 4.5 [112] to pH 8.15 [113]. Attention should be paid in the future to the exact species of apatite used in the study as additional work on hydroxylapatite and chlorapatite is of particularly interest.

2.1.2. The effect of sample purity

Purity of the sample is not always specified within research so can be difficult to quantify in a review. The methodology for investigating purity also varies, with some studies quoting in percentage terms the purity whereas other use wt% of P₂O₅. Studies were selected which had

specified in percentage the purity of the sample above 90%. There are eleven studies which specify purity over 90% in Table 4 and that state a value of IEP for apatite; these are Cheng et al., [103], Yu et al., [78], Li et al., [79], Yu et al., [62], Cao et al., [112], Yang et al., [85], Vucinic et al., [90], Olivier et al., [89], Raju et al., [107], Wu et al., [113] and Rao et al., [108]. The range of IEP from these studies is reduced from pH 3 [81,90] to pH 6.5 [61]. This however is not an accurate analysis of these results as other samples may have been equally as pure but the format of demonstrating this did not report in percentages. A selection of these high purity studies are plotted in Fig. 3.

Table 5

Fundamental Studies of zeta potential of natural fluorapatite. Mineral name taken from paper description, may be out of date for IMA-CNMNC. Deposit type denotes the most information the source material provides, if no location is provided the acquisition company is listed. DI water is Deionized water DS water is distilled water.

Mineral	Deposit/Type of deposit	Country	Purity	Size μm	PZC	IEP	Electrolyte	Methods	References
Fluorapatite	Van Waters and Rogers	–	–			8.7	Water	Streaming potential	Nduwa-Mushidi [102]
Fluorine- carbonate apatite	Qingping Phosphate company	China	>95% pure	<37		4.3	DI water		Cheng et al., [103]
Fluorapatite	Itataia deposit	Brazil	P ₂ O ₅ 29.9 wt%	37	–	<5	10 ⁻³ M/L KNO ₃	Electrophoretic mobility	Santos et al., [104]
Fluorapatite	Ipira/Pedras Altas, Bahia State	Brazil	–	38		4	Water		Nunes et al., [105]
Fluorapatite	Paraibab	Brazil	Very pure analyzed via microprobe	<10	7.7	1	0.01–0.05 M NaCl	Microelectrophoresis	Chairat et al., [106].
Fluorapatite	Synthetic			30	6.4	6.3		Electrokinetic and titration	Perrone et al., [19]
Fluorapatite	Gregory, Bottley and Lloyd Londno		97% pure			5.6	0.1 M NaCl		Raju eta l., [107]
Fluor-hydroxyl-apatite	Kahwe deposit	Zambia	Handpicked	>2		3.8	DS water	Micro-electrophoresis	Simukanga and Lombe [95]
Fluorapatite	Gregory, Bottley, and Lloyd London	Canada	97% pure	5		4	KNO ₃ (I = 0.002)	Electrophoresis	Rao, Antti, Forssberg [108]
Fluorapatite	Labasco Laboratories, Gothenburg, Sweden		P ₂ O ₅ 39.3 wt%, CaO 52.1 wt%, F 2.7%	<5		3	Water	Micro- electrophoresis	Pugh and Stenius [109]
Fluorapatite	Christmas Island	Indian Ocean		<2		3.5	2 × 10 ⁻³ M NaClO ₄	Micro electrophoresis	Mishra [99]
Fluorapatite	Durango	Mexico		<2		5.5	2 × 10 ⁻³ M NaClO ₄	Micro electrophoresis	Mishra [99])
Fluorapatite					7	6	10–3 M KNO ₂		Somasundaran [110]

Fig. 3 plots four of the high purity studies identified from Tables 4, 5, and 6, in comparison to Fig. 2, there is a noticeable reduction in variation in zeta potential values. From these results highly pure apatite of has an IEP of between pH 3 and pH 6.5. However as half the studies were fluorapatite and half where unknown as Yang et al., [85] and Yu et al., [62] did not specify the mineral enrichment, it is unknown if they are a different type of apatite than fluorapatite. If they are this could affect the results and therefore this topic needs further attention.

2.1.3. Effect of electrolyte

The electrolytes used in the papers reviewed in Table 4–6 varied. Six studies specified the electrolyte the used was water, either pure or distilled [102,103,105,108,109,112]. Nine studies specified KCl as the electrolyte however the concentration varied between 10⁻¹ M to 10⁻³ M [52,69,78,80,81,83,87,88,111]. Seven specified NaCl [80,82,84,85, 99,106,107] and five specified KNO₃ [79,92,93,104,108], however the

concentration used of the electrolytes varied, therefore it is difficult to determine what effect the electrolyte choice had on the IEP or PZC.

The potential determining ions of apatite have been studied in many deposits with H⁺ and OH⁻ ions commonly accepted as potential determining [110]. Somasundaran [110] investigated F, Ca and P ions and determined that P was definitely potential determining and Ca and F have a major effect of the zeta potential. Mishra [99] also investigated potential determining ions also concluding Ca and P had major effects, in particular the type of electrolyte used to determine IEP could affect the IEP. Fillipova et al., [83] conducted zeta potential measurements under both NaNO₃ and KCl concentrations, using the NaNO₃ electrolyte reduced the zeta potential and IEP value. Fillipova et al., [83] suggested this was due to NO₃⁻ and Na⁺ ions blocking the diffuse layer due to their larger size compared to Cl⁻ and K⁺ ions [116–118]. As there are many dissolved ions in flotation, the analysis of the supernatant in a flotation system is important in identifying the ions present. Bell et al., [111] found that

Table 6

Fundamental Studies of zeta potential of natural apatite, with studies specifying PZC. Mineral name taken from paper description, may be out of date for IMA-CNMNC. Deposit type denotes the most information the source material provides, if no location is provided the acquisition company is listed. DI water is Deionized water DS water is distilled water.

Mineral	Deposit/Type of Deposit*Ac1	Country	Purity	Size μm	PZC	IEP	Electrolyte	Method	Reference
Collophane	Yichang, Hubei Province	China	–	–	4.7		10 ⁻³ M/L KCl	–	Sun et al., [111]
Fluorapatite	Wenfu Phosphate company Guizhou Province, chin	China	98% pure	45	4.5		DI water		Cao et al., [112]
Fluorapatite	Paraibab	Brazil	very pure- analyzed via microprobe	<10	7.7	1	0.01–0.05 M NaCl	Micro-electrophoresis	Chairat et al., [106]
Fluorapatite	synthetic			30	6.4	6.3		Electro kinetic and titration	Perrone et al., [19]
Francolite	Oulad Abdoun trace REE 363.3 ppm	Morocco	P ₂ O ₅ 31.78 wt%	34	8.4	4.8		Electro kinetic and titration	Perrone et al., [19]
Fluorapatite	Gregory, Bottley and Lloyd London		97/98% pure	<5	7			Potentiometric titrations	Wu et al., [113]
Fluorapatite	Gregory, Bottley and Lloyd London			<5	8.15			Potentiometric titrations	Wu et al., [113]
Fluorapatite					6.7			Potentiometric	Bell, Posner and Quirk [114]
Fluorapatite					7	6	10 ⁻³ M KNO ₂		Somasundaran [110]
Fluorapatite					>12			Streaming potentials	Borisov et al., [115]

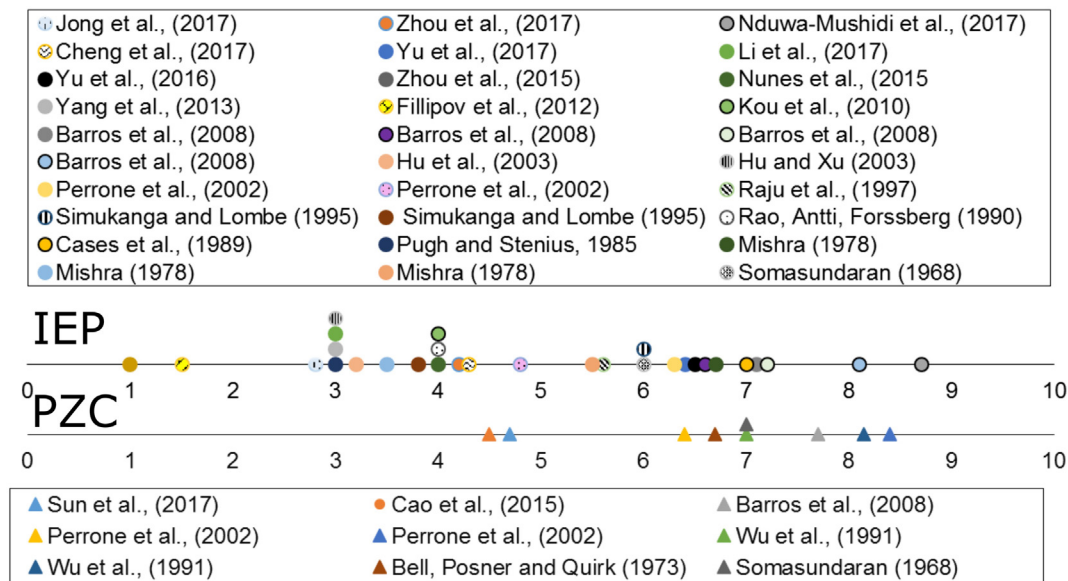


Fig. 1. Plot of IEP and PZC for natural apatite.

KNO_3 , KCl , KClO_4 , $(\text{CH}_3)_4\text{NCl}$ are indifferent electrolytes [114]. From these studies Ca, F, P, NaNO_3 ions/electrolytes are potential determining and KNO_3 , KCl , KClO_4 , CH_3NCl are indifferent ions.

2.1.4. The effect of location

Deposit location has previously been investigated by Mishra [99] and Simukanga and Lombe [108]. Both of these studies could find no link between apatite types/deposit location and surface behaviour. This is not in line with new research from Owens et al., [119] into the mineral bastnäsité, which showed there was a possible link between locality and zeta potential measurements. Due to the limited number of papers that reference the source of the apatite, this study is unable to complete any statistical analysis. However, there exist a few papers that investigate either the same location of sample or multiple samples from the same location.

Santos et al., [104] discusses previous studies investigating apatite from the Itaia deposit in Brazil, these investigations find no IEP value of apatite with all values at negative potentials at the pH values investigated. This implies that multiple samples of Itaia apatite may have the same surface behaviour. Apatite samples from Tulear Province, Fort

Dauphin, Madagascar were also investigated by both Phillipov et al., [86] and Phillipova et al., [83]. Both studies did not specify what type of apatite was acquired but showed IEP values of 1.5 and < 3 . Investigation of the literature suggests that fluorapatite is the apatite group mineral from Tulear Province [120].

Barros et al. [91], in contrast investigated five samples of apatite from different areas of the Salitre deposit in Brazil due to problems with processing of the apatite. They found IEP values ranged from 6.5 to 8.1, however these could be attributed to contamination within the crystal lattice with concentrations of silicon, iron and magnesium altering the IEP to in one case closer to magnetite. In the case of apatite from the Itaia deposit, Brazil and Fort Dauphin, Madagascar there does seem to a correlation between locality of source and surface behaviour agreeing with findings from Owens et al., [119].

2.1.5. Other effects

Most measurements contained within this review are at room temperature (21°C – 26°C) however Cheng et al., [103] conducted zeta potential measurements at 10°C . This can be assumed to be due to matching seasonal fluctuation at the mine site.

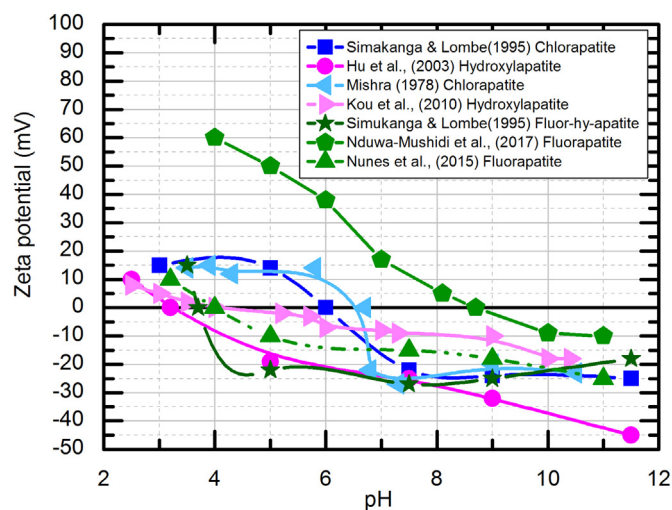


Fig. 2. Plot of zeta potentials of chlorapatite, fluorapatite, hydroxylapatite. Lines are plotted to guide the eye only.

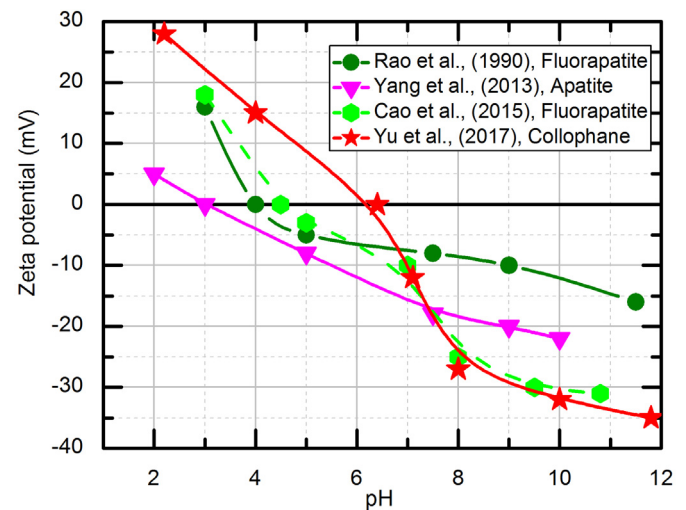


Fig. 3. Plot of zeta potential values of four papers with purity of apatite specified above 90%.

The majority of studies within Table 4–6 conducted the measurements either by electrophoresis or streaming potential. As a large number of studies do not clearly specify a technique for measuring zeta potential this study is unable to determine if the technique affects the value of zeta potential. Previous studies have noted a significant effect of difference in methodologies on samples of bastnäsite as investigated by Jordens et al., [101]. Here, the work suggested that there could be a difference between electroacoustic and electrophoresis measurements [101].

2.2. Synthetic apatite

Synthetic apatite can suggest what highly pure non enriched apatite would behave like, due to the composition being set at fabrication. Since first being synthesized in the early 20th century, synthetic apatite can now be produced by a number of different methods, ranging from sol gel to hydrothermal methods [121,122]. For more details on sol gel see Jilavenkatesca and Contrate [123]. The methodology of producing synthetic apatite affects a wide range of parameters, ranging from surface roughness to crystal size [124]. Previous investigations by Skwarek et al., [51] and Skwarek et al., [125] have shown that the synthesis of the apatite also effect the zeta potential values.

As up to half the elements in the periodic table can be substituted into apatite without it losing its form, there are many avenues in which materials science can investigate in the process of finding a perfect biomaterial replacement for bone [2]. Substitutions within synthetic apatite for medical purposes are often desired to increase the materials bioactivity and osteoconductivity [126]. Doping of particular interest to this review include, Fe, Sr, REE due to them being common trace elements within natural apatite [32]. Table 7 lists the PZC values of synthetic apatite when studied using zeta potential methodology.

From the 19 studies reviewed in Table 7 the PZC ranged from pH 4.3 to pH 8.7 [54,72].

From the 26 papers reviewed the IEP ranged from pH 3 to 8.1 [125,139]. There was a wide range of ions used as electrolytes with KCl, NaCl being the most common (Table 7–8). As many of the apatite samples were synthesized using different methodologies, and previous studies [51,125] have shown that this affects the IEP, direct comparison between studies is difficult. The solid to solution ratio also varied and this has also been found to effect the zeta potential significantly [143]. However, this is the most comprehensive list of apatite zeta potentials created thus far in the literature. The effect of apatite type (chlorapatite, hydroxylapatite and fluorapatite) and the effect of doping in synthetic apatite is compared in Fig. 4 and Fig. 5 respectively (REE, Cl, F, Si).

2.2.1. The type of synthetic apatite

Fig. 4 shows that hydroxyapatite behaves very differently between studies, which is expected due to different synthesis methods, of the four hydroxyapatite zeta potential shown none had close correlation although all started at low surface charge at higher pH and increased. Fahami et al., [138] shows lower zeta potential values than natural studies, which may be due to the production method of synthetic apatite. These values are all lower than natural samples, which can be attributed to them not being enriched with any other elements and having a greater purity. The limited comparison between studies can be attributed to the small range in pH values for three of the plot lines [138]. The zeta potential of hydroxylapatite at pH 8 varies from -50 mV [140] to -5 mV [141], this could be due to a large range of reasons from production method to electrolyte used (Table 8).

The study by Fahami et al., [138] into different types of synthetic apatite showed the close relationship between fluorapatite and hydroxylapatite, whereas chlorapatite had a slightly lower surface charge between pH 5 and 9, although the zeta potential decreased at pH 9 compared to increasing surface charge at pH 9 for fluorapatite. As no study investigated the zeta potential of fluorapatite and chlorapatite under

Table 7
Review of previous studies into synthetic apatite PZC.

Mineral	Synthesis method	Ca/P ratio	Purity	Size (microm)	PZC	IEP	Background electrolyte	Method	Study
Hydroxylapatite (HAP1)	Liu et al., 2003	1.66			6.64	4	0.001–0.1 mol/dm ³ NaCl		Skwarek, Janusz, Sternik [51]
Hydroxylapatite (HAP2)	Suzuki et al., 1998	1.65			6.22	4	0.001–0.1 mol/dm ³ NaCl		Skwarek, Janusz, Sternik [51]
Hydroxylapatite (HAP3)	Dean-Mo et al., 1995	1.64			6.43	4	0.001–0.1 mol/dm ³ NaCl		Skwarek, Janusz, Sternik [51]
Hydroxylapatite				59 microm	6.5	pH 6.2, -14 mV	0.001 mol/dm ³		Skwarek and Janusz [127]
Carbonate hydroxylapatite				36 microm	8	pH 7.1 -12 mV	0.001 mol/dm ³		Skwarek and Janusz [127]
Hydroxylapatite	Liu et al., 2003				7.5	3			Skwarek et al., [125]
Hydroxylapatite	Suzuki et al., 1998				7.05	3			Skwarek et al., [125]
Hydroxyapatite	Dean-Mo et al., 1995				6.7	3			Skwarek et al., [125]
Hydroxylapatite	Wet method'				6.5	<5	0.01 M NaCl		Skwarek et al., [128]
Hydroxylapatite				8.3	6.4	6.2	0.01 M KNO ₃	Micro electrophoresis/titrations	Skarsilla [129]
calcium deficient Hydroxylapatite					6 (3 mins), 7 (168 h)		0.01 N HNO ₃ - KOH	Electrokinetic	Ducheyne et al., [71]
Hydroxylapatite	Synthetic				8.7			Calculation	Mishra [72]
Fluorapatite	Synthetic	1.66			6.7		KCl	Titrations	Bell, Posner and Quirk [114]
Hydroxylapatite	Synthetic	1.66/1.67*		0.5–10	8.5		no ions	Titrations	Bell, Posner and Quirk [114]
Hydroxylapatite	Synthetic	1.65			7.6		NaCl	Potentiometric titration	Nicol and Clarke [130]
Dental enamel		–			<7.4		KCl	Membrane potentials	Waters [131]
Hydroxylapatite	Synthetic	1.66			<7.4		KCl 0.165 ionic strength	Electrophoresis	Leach [132]
Calcium phosphate		1.73			7.6		NaCl	Electrophoresis	Mattson et al., 1951 [133]
Dental enamel		–			4.35		NaOAc	Membrane potentials	Klein [54]

Table 8
Studies that give IEP values of synthetic apatite.

Mineral	Synthesis method	Ca/P ratio	Purity	Size (micro m)	PZC	IEP	Background electrolyte	Method	Study
Hydroxylapatite (HAP1)	Liu et al., 2003	1.66			6.64	4	0.001–0.1 mol/dm ³ NaCl		Skwarek, Janusz, Sternik [51]
Hydroxylapatite (HAP2)	Suzuki et al., 1998	1.65			6.22	4	0.001–0.1 mol/dm ³ NaCl		Skwarek, Janusz, Sternik [51]
Hydroxylapatite (HAP3)	Dean-Mo et al., 1995	1.64			6.43	4	0.001–0.1 mol/dm ³ NaCl		Skwarek, Janusz, Sternik [51]
Hydroxylapatite			doped with Sc/S			pH 7.4, –27 mV			Latifi et al., [134]
Hydroxylapatite		1.68		42		pH 6, –6 mV	0.001 M KCl		Scudeller et al., [135]
Hydroxylapatite Zn		1.74	3.2 wt% Zn	32		pH 6, –1 mV	0.001 M KCl		Scudeller et al., [135]
Hydroxylapatite Sr Fluorapatite		1.68	1.7 wt% Sr	41 484 nm		pH 7, –4.2 mV pH 7, –33 mV	0.001 M KCl purified water	electrophoretic	Scudeller et al., [135] Wojnarowska-Nowak et al., [136]
Hydroxylapatite				581 nm		pH 7, –25 mV	purified water	electrophoretic	Wojnarowska-Nowak et al., [136]
Fluorapatite (Ag doped)			13 wt% Ag	832 nm		pH 7, 6.5 mV	purified water	electrophoretic	Wojnarowska-Nowak et al., [136]
Hydroxylapatite (Ag doped)			9.5% Ag	622 nm		pH 7, –28.2 mV	purified water	electrophoretic	Wojnarowska-Nowak et al., [136]
Hydroxylapatite (Eu doped)			5% Eu doped			pH 6, –21 mV	purified water		Chen et al., [70]
Hydroxylapatite (HAP)			x = 0			pH 7.4, –36 mV	0.154MNaCl		Fahami et al., [137]
Hydroxylapatite with 0.125 sub F, Cl ions			x = 0.125			pH 7.4, –28 mV	0.154MNaCl		Fahami et al., [137]
Hydroxylapatite with 0.25 sub F, Cl ions			x0.25			pH 7.4, –21 mV	0.154MNaCl		Fahami et al., [137]
Hydroxylapatite with 0.375 sub F, Cl ions			x = 0.375			pH 7.4, –20 mV	0.154MNaCl		Fahami et al., [137]
Fluorapatite			x = 0			pH 7.4, –37 mV	0.154MNaCl		Fahami et al., [137]
Chlorapatite			x = 1			pH 7.4, –27.5 mV	0.154MNaCl		Fahami et al., [137]
12 wt% ZnO Carbonate Chlorapatite	Mechanochemical reaction	1.9	milled			pH 7.4, –22.52 mV	0.154MNaCl		Fahami and Beall [138]
13 wt% ZnO Carbonate chlorapatite	Mechanochemical reaction	1.9	appealed			pH 7.4, –20.85 mV	0.154MNaCl		Fahami and Beall [138]
Hydroxylapatite	Liu et al., 2003				7.5	3			Skwarek et al., [125]
Hydroxylapatite	Suzuki et al., 1998				7.05	3			Skwarek et al., [125]
Hydroxyapatite	Dean- Mo et al., 1995				6.7	3			Skwarek et al., [125]
Hydroxylapatite	Wet method'				6.5	<5	0.01 M NaCl		Skwarek et al., [128]
Hydroxylapatite	Hayek and Stadlmann 1955	1.6				8.1	0.1 M NaCl	electrophoretic	Bengtsson and Sjoberg [139]
Fluorapatite	Penel et al., 1997	1.7				5.7	0.1 M NaCl	electrophoretic	Bengtsson and Sjoberg [139]
Hydroxylapatite	Hayek and Stadlmann 1955	1.6				8.1	0.1 M NaCl	electrophoretic	Bengtsson and Sjoberg [139]
Fluorapatite	Penel et al., 1997	1.7				5.7	0.1 M NaCl	electrophoretic	Bengtsson and Sjoberg [139]
Hydroxylapatite				8.3	6.4	6.2	0.01 M KNO ₃	micro electrophoresis/titrations	Skarsiila [129]
Hydroxylapatite with 0.8 wt% Si			0.8 wt% silicon	20–53 micro meters		3.8	10–4 M/L KNO ₃		Botelho, Lopes, Gibson [140]
Hydroxylapatite			Ca/P = 1.44	20–53 micro meters		5.5	10–4 M/L KNO ₃		Botelho, Lopes, Gibson [140]
Hydroxylapatite			specified in Rodriguez thesis 1999			7.3	10–3 M/L KCl		Rodriguez-Lorenzo, Vallet- Regi [141]
Fluorapatite	Dental hygiene	–		600		3.7	fluorapatite supernatant	Streaming potential	Rao et al., [142]
Hydroxylapatite	Dental hygiene	–		>5		8	triply distilled water	electrokinetic	Rao et al., [142]
calcium deficient Hydroxylapatite					6 (3 mins), 7 (168 h)		0.01 N HNO ₃ -KOH	electrokinetic	Ducheyne et al., [71]

pH 5 the IEP value for these synthetic minerals is unable to be determined.

2.2.2. The effect of doping

The effect of adding certain ions to synthetic apatite has been investigated in great detail in regards to the osteoconductive properties but the surface behaviour in relation to zeta potential is not always investigated [144]. Fig. 5 shows studies of hydroxyapatite doped with F, Cl, Ca, and Si in different concentrations and the effect of zeta potential in

comparison to stoichiometrically pure hydroxyapatite. The addition of Si to hydroxyapatite decreases the zeta potential of the surface as shown by Botelho et al., [140] the surface charge at pH 8 is decreased from –52 mV to –70 mV, the IEP value is also shifted to a lower pH with the addition of Si, from pH 5.5 to pH 3.8. In comparison the addition of F and Cl to the hydroxylapatite lattice increases the zeta potential of hydroxylapatite, with greater concentrations of these ions increasing the zeta potential to a larger degree [138]. This behaviour is extended to the addition of Ca ions with Skwarek and Janusz [129] showing an

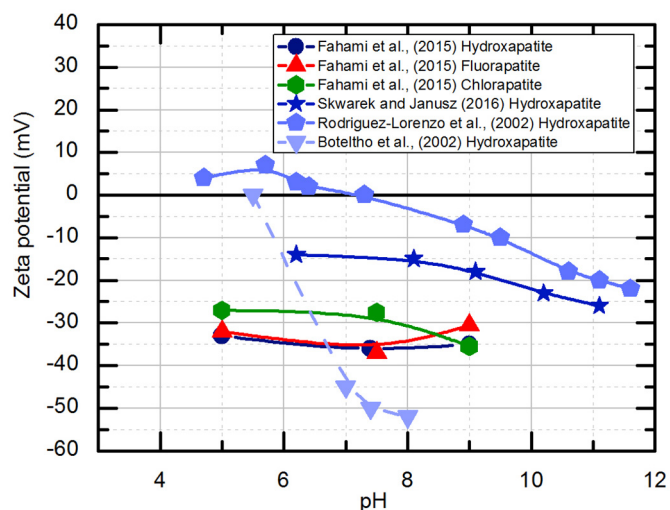


Fig. 4. Zeta potential values from different types of synthetic apatite, hydroxyapatite, fluorapatite and chlorapatite.

increase in the zeta potential with the addition of Ca to the lattice. Hydroxylapatite from the studies by Skwarek and Janusz [127] and Fahami et al., [138] did not demonstrate IEP in any of their values.

The IEP range of natural apatite is from pH 1 to pH 8.7, with synthetic apatite ranging from pH 3 to pH 8.1 (Tables 3, 4). The IEP in natural apatite was affected by the species present with chlorapatite being found to have a greater IEP on average than hydroxylapatite. The IEP of natural fluorapatite ranged so widely it was not possible to determine if it may be different from either chlorapatite or hydroxylapatite. The synthetic chlorapatite also had a less negative zeta potential than hydroxylapatite, showing this behaviour extends from synthetic apatite to natural apatite and vice versa [138]. As the majority of the focus of synthetic apatite research is on hydroxylapatite the range of values in the IEP of this type is large however the range can be attributed to factors including synthesis method and measurement technique.

Natural apatite has element substitutions within its crystal lattice, due to enrichment either during formation or later in hydrothermal alteration [145,146]. If only zeta potential studies which specified high purity were selected, then range of IEP values is reduced to pH 3 to pH 6.3, which is more in line with the IEP values range of synthetic apatite. Impurities such as additional F and Cl ions have been shown to alter the zeta potential significantly in studies of synthetic apatite [138]. As many natural apatite have substitutions of these ions and

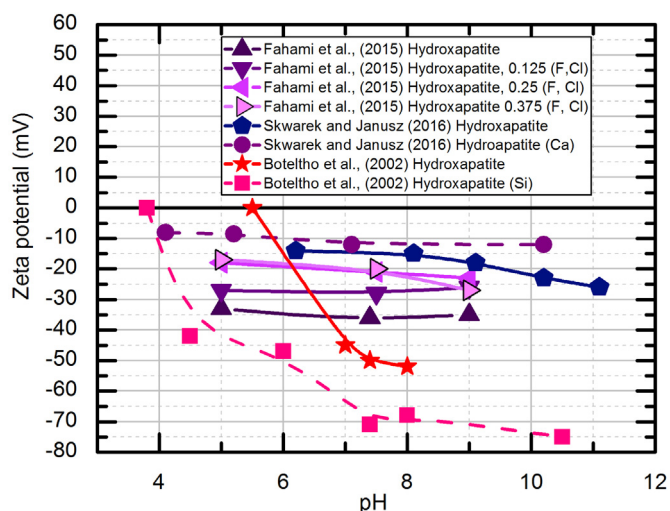


Fig. 5. Zeta potential plots of different doping in synthetic hydroxylapatite.

others within their lattice it is reasonable that the IEP should be different with different enrichments and deposits. The specific enrichment of apatite in deposits could link to similarities in zeta potentials such of those identified in Tular Province, Madagascar and Itaia, Brazil in this review [82,86].

One of the aims of this study is therefore, to review the surface behaviour of both natural and synthetic apatite to provide a resource for future research. A secondary goal is to determine the effect of enrichment of apatite has on surface behaviour. The effect of enrichment on surface behaviour is particular important in the flotation of apatite deposits, which often contain significant enrichment with additional elements. As many studies have been conducted on processing unenriched apatite it is useful for research to determine if these flow sheets can be applied to enriched apatite. REE enriched apatite surface behaviour has been researched by a number of studies [83,86]. However, currently there are no studies of the zeta potentials of REE enriched apatite under collectors. For this reason in this paper we present work on REE enriched apatite under two types of collector, hydroxamic acid and fatty acid. This research should be applicable to a large number of REE enriched apatite deposits such as Hoidas Lake, Canada and Jacquia, Brazil.

3. Materials and methods

3.1. Mineral sample

Apatite from Jacupiranga, Brazil was used for zeta potential measurements (Acquired from Dr. Broom-Fendley, Camborne School of Mines, University of Exeter, UK). Samples from the same location have previously been used in Broom-Fendley et al., [147]. Jacupiranga is a well-studied alkaline carbonatite complex in Sao Paulo State, Brazil first formed 131 Ma in the Cretaceous [45,148–150]. Apatite samples from the Jacupiranga deposit have previously shown high enrichment with REE, with fluid inclusions within the minerals being of interest to research into the formation of carbonatite deposits [150]. The apatite within Jacupiranga has previously been shown to be fluorapatite with F content between 2.21 and 0.62% and a REE enrichment of between 1000 and 3000 ppm [45,150,151]. Chemical and composition analysis of the sample was conducted using X-Ray fluorescence (ARL PERFORM'X Sequential X-Ray Fluorescence Spectrometer, Thermo Fisher) at Colorado School of Mines. Elemental compositional is given in Table 9.

Two types of collectors were supplied by Axis House (hydroxamic acid) and Betachem (fatty acid). These collectors were selected due to previous research into the effect of fatty acid and hydroxamates on both apatite and REE bearing minerals, which enables comparison of these results to previous studies [61,152,153].

3.2. Zeta potential measurements

The apatite minerals were ground to 100% passing 80 μm using steel ring mill (Angstrom Model TE250 Ring Pulverizer). Samples were suspended in water at 0.02 g per 40 mL after which they were agitated on a shaking table for 20 min before each measurement. The same methodology as Owens et al., [119] was used for zeta potential measurements. Zeta potential measurements were conducted using the Microtrac Stabino Particle Charge Mapping surface chemistry device at Colorado School of Mines, U.S.A. Measurements were conducted from

Table 9
Chemical analysis of apatite sample from Jacupiranga, Brazil. For chemical composition under 10% see supplementary composition.

Compound	Wt%
P ₂ O ₅	38
CaO	35.5

pH 3.5 to pH 11, with NaOH and HCl were used to adjust pH. Previous studies have shown that Na ions reduce the value of zeta potential and IEP of apatite therefore the results may be lower than other studies [86].

4. Results

Measurements were conducted from pH 3.5 to pH 11, and showed an IEP of apatite at pH 3.8. Fig. 7 shows the results of zeta potential measurements of apatite in water, hydroxamic acid (5×10^{-4} M) and fatty acids (5×10^{-4} M). Under both hydroxamic and fatty acid conditions the zeta potential is shifted to a lower charge over the entire pH range investigated with the IEP shifted <3.5. The shift of IEP to a lower value under hydroxamic acid conditions and fatty acid conditions is consistent with early work by Yu et al., [62] and Cao et al., [112] respectively.

5. Discussion

The zeta potential results from Fig. 6 can be compared to results within the literature reviewed in Table 4. The IEP of apatite agrees with the range of IEP values extracted from the literature with an IEP of 3.8, near the lower end of the range of pH 1 to pH 8.7. It must be noted that the majority of the studies had an IEP value of between pH 3 and pH 7 in which the IEP from this study fits well, particularly as the IEP is usually lowered under Na ions [83].

Five other studies were selected to compare to the zeta potential measurements conducted in Section 3. Four were selected due to their high purity [62,78,80,92] and Nduwa-Mushidi et al., [102] was selected due to use of the same methodology and equipment. These five studies plus the results from this review were plotted in Fig. 7. Fig. 7 shows that there was a wide range of zeta potential values from apatite studies, although there are common characteristics of the zeta potential curves in which as higher pH values the zeta potential was negative and at lower pH values the zeta potential was positive. The IEP of studies plotted in Fig. 7 ranging from >2 to 8.7.

This review has identified that studies into apatite enriched with REE have already been conducted in particular, into the synthetic doping of apatite with Eu [8]. However there has been no comparison that this study could find that compared the enrichment of natural REE apatite and synthetic REE enriched apatite. The four studies identified as investigating the zeta potential of apatite with REE enrichment are plotted in Fig. 8 [8,81,83,86]. Of the four studies, one was synthetically produced hydroxyapatite [8] and the other three were natural apatite. The exact type of apatite (fluorapatite, chlorapatite, hydroxyapatite) is not

identified within the papers. The enrichment within each apatite is slightly different with Chen et al., [8] hydroxyapatite doped with 5% europium. Chen et al., [8] also investigated the doping of hydroxyapatite with between 1 and 10% of europium at pH 9, which showed little variation. This indicates that doping of between 1 and 10% of europium in apatite does not affect surface behaviour. The apatite studied in Zhou et al., [81] was enriched with 0.77% cerium. Filippova et al., [83] and Fillipov et al., [86] both investigated apatite with enrichment of 2402 ppm of cerium and 1102 ppm of lanthanum. All the natural apatites in Fig. 9 were enriched with LREE. As LREE are the predominant REE in apatite deposits this is not unexpected.

Russia is unusual in containing apatite that is enriched with HREE [30]. In comparison to the zeta potential measurements of other apatite samples plotted in Fig. 7, apatite enriched by REE does not appear to have significantly different surface behaviour.

From studies into doping by synthetic apatite it can be demonstrated that small % (1–5%) of ions such as F, Cl, Ca and Si can significantly affect the zeta potential measurements of a mineral [127,138,140]. From reviewing the purity of the natural apatite used in many of the mineral processing studies it becomes apparent that a large % contain contamination, with ions or increased concentrations of certain elements or do not specify the exact purity [91]. Although REE enrichment (up to 10%) does not appear from the studies reviewed here to have a significant effect on zeta potential values of apatite other ions do and this may be why there is such a large range in both IEP values and zeta potential curves. Recent work by Filippova et al., [154] on calcite and fluorapatite has shown that impurities may be linked to the calcium dissolution and collector adsorption.

Although the zeta potential of apatite under aqueous conditions is important for minerals processing and in particular flotation it is essential to also determine the effect of reagents. As the reagents are the chemicals which make the surface of a mineral hydrophobic or hydrophilic. In this study we investigated the effect of hydroxamic acid and fatty acid on the surface of apatite from a REE enriched deposit. To compare to these values, the results of zeta potential investigations from Nduwa-Mushidi et al., [102] were also extracted. Nduwa-Mushidi et al., [102] was selected due to the use of the same methodology and equipment, these results are plotted on Fig. 9.

In Fig. 9 all zeta potentials showed a negative zeta potential at a pH above 9, with the addition of hydroxamic acid in both this study and Nduwa-Mushidi et al., [102] causing the zeta potential to reduce to a lower charge. Nduwa-Mushidi et al., [102] showed a shift of IEP from pH 8.7 to around pH 4.8 with the addition of hydroxamic acid. In this study the IEP was shifted from 3.8 to <2. The magnitude of the shift

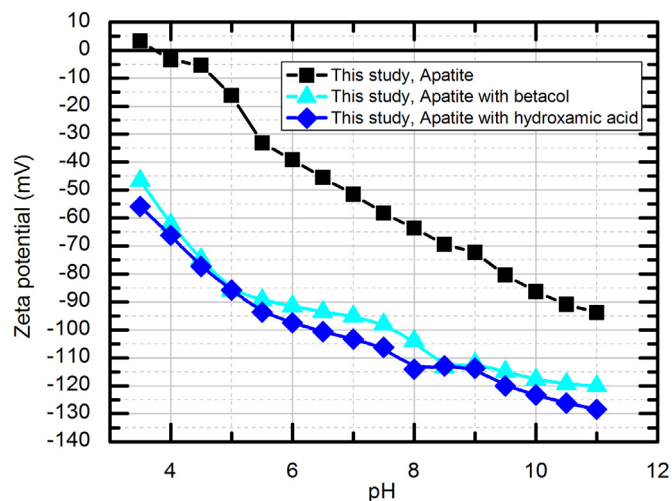


Fig. 6. Plots of REE enriched apatite zeta potential measurements under water conditions, hydroxamic acid, fatty acids.

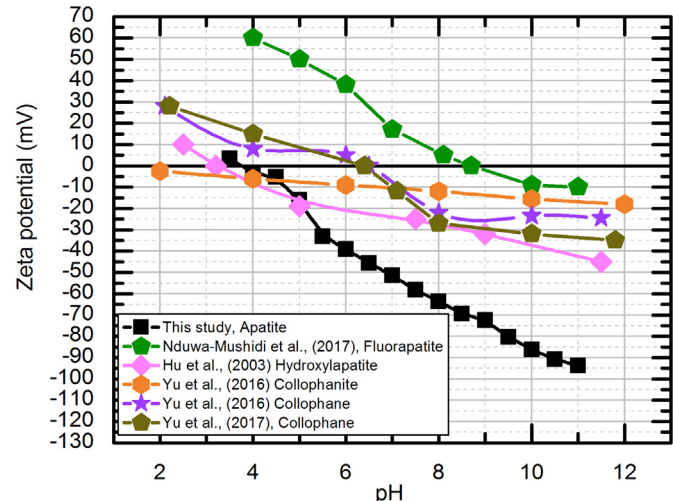


Fig. 7. Comparison of zeta potential measured in this study with other studies. Curves are fitted for ease of eye and are meant not to demonstrate data.

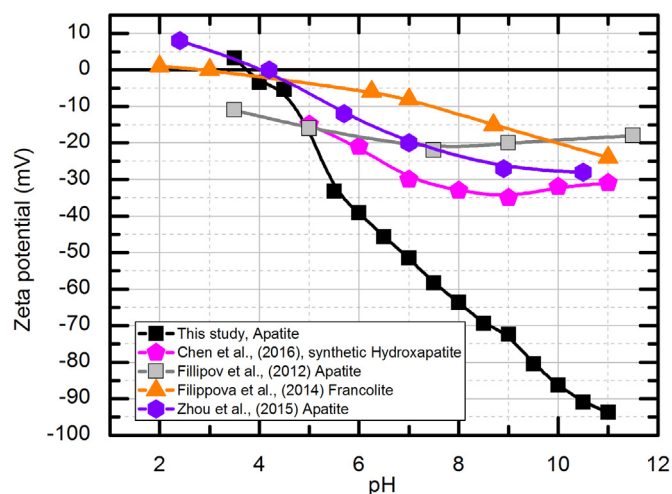


Fig. 8. Comparison of zeta potential measurements of apatite identified within the literature as containing REE.

between studies was of the order of magnitude expected as in previous studies some hydroxamic acids have a larger effect on flotation than others [155]. The mole per liter used was also different with this study using 5×10^{-4} M and Nduwa-Mushidi et al., [102] using 10^{-3} M. The behaviour of apatite containing REE under hydroxamic collector is similar to apatite not containing REE, this may allow apatite containing REE to be processed the same way as its non-enriched counterparts.

As apatite is one of the most bountiful minerals on the planet and a wide range of deposits exist which contain REE bearing apatite, this is of future interest to REE sourcing [2,38]. The results from this review show that REE enriched apatite behaves similarly to non-enriched apatite, and is effected by hydroxamic acid and fatty acid in a similar way. Previous work by Fillipov et al., [83] of a REE enriched apatite under micro flotation showed a high recovery with sodium oleate, similar to non REE enriched apatite. As many deposits such as Hoidas Lake, Canada and Jaquia, Brazil contain REE enriched apatite [42,47] the use of reagent regimes already well researched on apatite is very useful for mineral processing. Although apatite is most commonly enriched with LREE, which are less valuable than HREE some deposits, such as Songwe Hill, Malawi are enriched with HREE making mining more economically viable. These REE deposits could supply the future green technology.

From reviewing the previous studies of apatite there are many studies investigating the surface behaviour of apatite however few give full details of the source location, type and purity of the apatite. Of the thirty

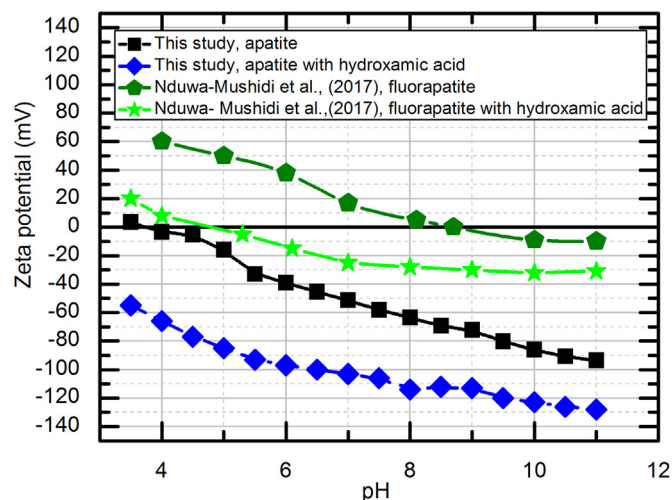


Fig. 9. Plots of apatite zeta potentials from this review and from Nduwa et al., (2017).

studies of natural apatite reviewed in this paper, eight did not give the species of apatite making it challenging to determine the effect of specific parameters. To be able to better compare future studies, greater detail is this area as well as more detail in the background electrolytes used is needed. More recent work goes into more detail with the methodology enabling easier comparison. The future of the field of mineral processing of enriched apatites is bright due to the increased economic viability of deposits which drives industrial research. The increased use of REE in technology such as wind turbines propels the increase in exploration of deposits such as those in Hoidas Lake.

Future research into apatite surface behaviour should focus on creating synthetic samples that are more representative of minerals within mineral processing. Although many studies of synthetic apatites have been conducted, their properties do not always match the properties of natural apatite. This should be improved as manufacturing of synthetic minerals is refined. More studies of hydroxylapatite and chlorapatite is also important due to possible differences in their surface behaviour. Also recent work using attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy to indicate the bonding between mineral and reagents is particularly pertinent in improving the understanding of flotation chemistry and could be applied to enriched apatite studies [155,156].

6. Conclusion

In this review, previous research into the surface behaviour of apatite with different elemental enrichments was analyzed, bringing together a resource for future researchers in this area. The inconsistent naming of the species of apatite is also highlighted, with studies of the discredited mineral names colophonite and francolite still common in the literature. 53 studies of natural apatite and 44 studies of synthetic apatite were reviewed. The iso electric points of the natural apatite studies reviewed ranged from pH 1 to pH 8.7, with the IEP of synthetic apatite IEP ranging from pH 3 to pH 8.1. When the purity of natural apatite studied was >90% the IEP value ranged from pH 3 and pH 6. These results indicate that there is a wide range of surface behaviour of apatite, which has previously been attributed to different methodologies and enrichments within the natural apatite. Comparing studies showed chlorapatite had a higher zeta potential than hydroxyapatite in natural apatite, which agrees results from synthetic chlorapatite and hydroxylapatite. This shows in flotation that chlorapatite and hydroxyapatite may behave differently.

There were four studies that compared the surface behaviour of REE element enriched apatite. Rare earth elements are important for a wide range of technologies from mobile phones to wind turbines and have been listed as critical by the European Union due to the instability in their supply chain. Apatite provides a possible source of rare earth elements for the future. The four studies of REE enriched apatites showed that the IEP value ranged between pH 3 to pH 4.2, where IEP was recorded. When synthetic apatite was doped with between 1 and 10% of europium, a rare earth element, there was little change in surface behaviour, indicating that surface behaviour does not change with enrichment or doping. However, no studies were found that investigated REE enriched apatite surface behaviour under collectors such as hydroxamates and fatty acids, which are commonly used in rare earth element flotation.

Due to the lack of zeta potential studies of REE enriched apatite under collector regimes, additional measurements were therefore conducted to investigate them. The IEP of REE enriched apatite from Brazil was measured at pH 3.6 in water conditions. The surface charge of the REE enriched apatite under hydroxamic and fatty acid conditions was highly reduced, giving a IEP of <3.5. This behaviour is similar to non-REE enriched apatite surface behaviour. Thereby indicating that REE enrichment does not affect the surface behaviour of apatite under common rare earth collectors. This implies that flotation research into

apatite could be applied to future mineral processing of REE enriched apatite.

In summary, the main conclusions of this study are (1) naming practices within the literature are inconsistent, (2) methodologies and enrichment effect the surface properties of apatite, and (3) any variations in the surface properties are not evident in the processing of the minerals using standard flotation collectors.

Conflicts of interest

None.

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Original data presented here relating to REE enriched apatite is publicly accessible at the British Geological Surveys National Geoscience Data Centre [157].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cis.2019.01.004>.

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