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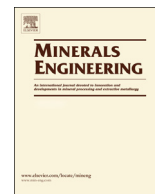
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Magnetic properties of REE fluorcarbonate minerals and their implications for minerals processing



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ABSTRACT

Rare earth elements (REE) are considered as critical metals for electronics and green technology. The REE fluorcarbonates are one of the main REE ore minerals, common in many different types of REE deposit and yet some of their fundamental properties have still not been determined. This study measured the magnetic properties of pure REE fluorcarbonate single crystal minerals using a vibrating sample magnetometer (VSM) and determined their elemental compositions using electron probe microanalysis (EPMA). The results provide the first measurements of the magnetic behaviour and susceptibility of REE fluorcarbonates other than bastnäsite-(Ce). The magnetic susceptibility of REE fluorcarbonates varies systematically from one mineral to another and is highly dependent on the mineral chemistry. It is positive (paramagnetic) for bastnäsite-(Ce) and gradually decreases as the amount of Ca increases in parisite-(Ce), becoming negative (diamagnetic) for the Ca-rich member of the series, röntgenite. Synchysite-(Ce) is difficult to measure, generate good signal and acquire accurate readings because it practically always occurs as < 5 mg crystals. Its magnetic susceptibility in samples from a REE ore deposit was experimentally determined by magnetic separation and checked by an associated study using a SQUID magnetometer, synchysite-(Ce) behaved as a diamagnetic mineral. This can be explained by the increase of Ca content and decrease of REE content, in addition to the variations in the layered structure common to the REE fluorcarbonate series minerals. Given the wide range of magnetic susceptibility of REE fluorcarbonates, it is important that the mineralogy is determined carefully before setting up a mineral processing flow sheet.

1. Introduction

The rare earth element (REE) fluorcarbonates are the most common REE minerals in REE ore deposits and include the mineral species bastnäsite-(Ce) $\text{Ce}(\text{CO}_3)\text{F}$, parisite-(Ce) $\text{CaCe}_2(\text{CO}_3)_3\text{F}_2$, röntgenite-(Ce) $\text{Ca}_2\text{Ce}_3(\text{CO}_3)_5\text{F}_3$, and synchysite-(Ce) $\text{CaCe}(\text{CO}_3)_2\text{F}$ (Wall, 2014). In practice, all contain a mixture of La, Ce, Pr, and Nd in addition to Ca, and also smaller amounts of the other heavier REE. Bastnäsite is the best known of these and one of three most important REE ore minerals (together with monazite-(Ce) and xenotime-(Y) (Krishnamurthy and Gupta, 2016). Synchysite-(Ce) is also an important ore mineral in several REE deposits now under development. Moreover, in practice, even when bastnäsite is named as the major REE fluorcarbonate mineral, other members of the series are often also present. They frequently form syntaxial intergrowths with each other.

One of the main challenges in developing new deposits of the REE

needed for permanent magnets, batteries, catalysts, phosphors, wind turbines, hybrid cars, polishing powders, glass additives, ceramics and more (Bauer et al., 2010; British Geological Survey, 2011; Krishnamurthy and Gupta, 2016) is the lack of knowledge about the REE minerals themselves. Many of the fundamental properties relevant to minerals processing are lacking for all of the REE fluorcarbonates except for bastnäsite-(Ce).

This work measures the magnetic properties of the REE fluorcarbonate minerals, and links their magnetic behaviour with their elemental compositions and crystallographic structure. The results will enable mineral processors to determine if magnetic separation might be applicable in a particular REE deposit and help choice of equipment and conditions.

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Table 1

The REE fluorcarbonate mineral samples together with their chemical formulae, quantities and localities that were used for measurement their magnetic properties.

REE fluorcarbonate mineral	Chemical formula	Quantity mg	Locality
Bastnäsité-(Ce)	Ce(CO ₃)F	89	Zagi Mountain, Pakistan
Parisite-(Ce)	CaCe ₂ (CO ₃) ₃ F ₂	47	Snowbird Mine, Mineral County, Montana, USA
Röntgenite-(Ce) A	Ca ₂ Ce ₃ (CO ₃) ₅ F ₃	55	Narssárssuk, nepheline syenite pegmatite in Greenland
Röntgenite-(Ce) B		29	
Synchysite-(Ce)	CaCe(CO ₃) ₂ F	5	Mt. Cervandone, Verbano-Cusio-Ossola Province, Piedmont, Italy

2. Materials and methods

2.1. Pure single minerals

Small matrix-free natural crystals (5–89 mg) of bastnäsité-(Ce), parisite-(Ce), röntgenite-(Ce) and synchysite-(Ce) from several localities were purchased and used for measurement of their magnetic properties (Table 1).

Small crystal pieces of bastnäsité-(Ce) and parisite-(Ce), and whole small crystals of röntgenite-(Ce) and synchysite-(Ce), were used to check the mineral identities using scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM-EDS) (see below) before magnetic measurement was made using a vibrating sample magnetometer (VSM). After measurement, these crystals were picked out from the VSM sample holder, made into polished mounts, and a precise chemical composition was determined by electron probe microanalysis (EPMA).

2.2. Analysis of the REE fluorcarbonates

SEM-EDS is the most useful technique to determine the mineral identities (especially when the crystals are too small to be analysed by X-ray diffraction) and to establish if they are monomineralic or contain any syntaxial ingrowths or inclusions of other minerals. The SEM-EDS analyses were carried out with a JEOL JSM-5400LV Low Vacuum SEM equipped with Oxford Instruments EDS system at Camborne School of Mines, University of Exeter, UK, operated at 25 kV accelerating voltage.

Quantitative mineral compositional data of the single crystal minerals were obtained using an electron probe microanalysis JEOL JXA-8200 instrument with wavelength dispersion spectrometry (WDS) at Camborne School of Mines, University of Exeter, UK.

The analyses were carried out using operating conditions of 20 kV accelerating voltage, 20 nA beam current, and 7 µm beam diameter. The peak counting times were 20 s for Mg, Si, Al, Sr, F, Tb, Er, Yb, and Lu; 30 s for Mn, Fe, La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy; and 40 s for Ca, Ba, Y, Th, and U, with an equal time off-peak for each element. Backscattered electron imaging was used to check for homogeneity of the crystals and to locate suitable areas for analysis. 10 spot points for each single mineral were analysed.

The REE were calibrated against synthetic silicate glasses from the Edinburgh Ion Probe Facility, while the other elements were calibrated against a combination of natural and synthetic minerals and metals. Empirical interference corrections were applied for La and Ce on the heavier REE, Sm, and Gd (Pyle et al., 2002). Furthermore, chondrite-normalised distributions for the REE values of each measured mineral were calculated and plotted relative to the primitive mantle values of McDonough and Sun (1995), as a means of quality control.

2.3. Vibrating sample magnetometer

A vibrating sample magnetometer, LakeShore 7300 series system connected to a computer interface for system operation, data acquisition and analysis at the School of Metallurgy and Materials, University of Birmingham, UK was used to measure the magnetic properties of REE fluorcarbonate minerals.

A 29–89 mg sample of each mineral was prepared and placed in the

VSM sample holder and vibrated sinusoidally perpendicular to the applied field. This causes an induced voltage in the pickup coils that is proportional to the magnetic moment of the sample, along with a signal received by the hall probe measuring the applied field. These signals are transferred to produce a magnetic hysteresis loop between +2 Tesla and –2 Tesla. The same procedure was applied to an empty sample holder prior to measuring the mineral samples, so that any magnetic effects from the sample holder could be taken into account. The magnetic moment values were converted into magnetisation using the volume of each sample, while the magnetic induction data were converted into magnetic field strengths using the constant permeability of free space $12.566 \times 10^{-7} \text{ N A}^{-2}$ (Jordens et al., 2014; Sheridan, 2014).

2.4. Additional study by SQUID of synchysite

Along with VSM, superconducting quantum interference device (SQUID) was used specifically to measure the magnetic behaviour of synchysite-(Ce). SQUID has higher sensitivity than VSM and it is capable of measuring the magnetic moment of materials too small to measure by VSM (Belley et al., 2009; Coey, 2010), such as the synchysite in this study (see Supplementary Appendix A).

3. Results and discussion

3.1. Mineral chemistry and crystallographic structure of the REE fluorcarbonates

Bastnäsité-(Ce), parisite-(Ce), röntgenite-(Ce) A, and röntgenite-(Ce) B single crystals, along with synchysite crystals from Songwe Hill carbonatite, are all enriched in LREE, with Ce predominant, i.e. each is the –(Ce) species (Bayliss and Levinson, 1988) (Table 2; full details are in Supplementary Appendix B Tables B.1–B.5).

The FeO content is below the detection limit of 0.07 wt% in all the measured minerals (Supplementary Appendix B Table B.6). This rules out the most common ferromagnetic element that could have affected the magnetisation of the measured minerals. The concentrations of other elements including Mg, Al, Fe, Ba, Tb, Er, Yb, Lu, U, and in many cases Dy and Si are below detection limit of the electron microprobe.

There is a simple negative correlation between the average content of CaO and total rare earth oxides (TREO) within the minerals. As the CaO content increases, the TREO content decreases through the series: bastnäsité-(Ce), parisite-(Ce), röntgenite-(Ce) and synchysite-(Ce).

REE fluorcarbonates have a layered structure with ordered stacking of at least two of three layers of (CeF), (CO₃), and (Ca) along the c-axis (Oftedal, 1931; Donnay and Donnay, 1953; Donnay, 1953; Van Landuyt and Amelinckx, 1975; Ni et al., 1993; Wang et al., 1994; Ni et al., 2000). Bastnäsité-(Ce) is an end member of this series with the simplest hexagonal crystal structure, the highest REE content, and no or just a trace of Ca. It is composed of CeF and CO₃ layers (Donnay and Donnay, 1953). Synchysite-(Ce), is also an end member of this series and the most Ca-enriched, it is monoclinic and consists of stacking layers of Ca and CeF separated by layers of CO₃ with a TREE:Ca ratio of 1:1 (Ni et al., 1993). Parisite-(Ce) and röntgenite-(Ce) are in the middle of the REE fluorcarbonate group. Parisite-(Ce) is monoclinic and formed by stacking one portion of bastnäsité and one portion of synchysite with a TREE:Ca ratio of 2:1, while röntgenite-(Ce) is trigonal and formed by

Table 2

Average composition and standard deviation for bastnäsite-(Ce), parisite-(Ce), röntgenite-(Ce) A, and röntgenite-(Ce) B single crystals along with synchysite-(Ce) in a multi-mineral sample from the Songwe Hill carbonatite, Malawi determined by electron probe microanalysis.

Oxides (wt%)	Bastnäsite-(Ce) Ce(CO ₃)F		Parisite-(Ce) CaCe ₂ (CO ₃) ₃ F ₂		Röntgenite-(Ce) A Ca ₂ Ce ₃ (CO ₃) ₅ F ₃		Röntgenite-(Ce) B		Synchysite-(Ce) ^a CaCe(CO ₃) ₂ F	
	10 points	σ	10 points	σ	10 points	σ	10 points	σ	10 points	σ
SiO ₂	0.09	0.09	b.d.	–	0.08	0.24	b.d.	–	b.d.	–
CaO	0.04	0.02	11.34	0.17	12.92	0.58	13.82	0.36	16.59	0.66
MnO	0.07	0.03	0.05	0.02	0.05	0.05	0.06	0.02	0.04	0.05
FeO	b.d.	–	b.d.	–	b.d.	–	b.d.	–	0.30	0.29
SrO	0.15	0.06	0.10	0.06	0.36	0.07	0.35	0.08	0.30	0.23
BaO	b.d.	–	b.d.	–	b.d.	–	b.d.	–	0.04	0.05
Y ₂ O ₃	0.48	0.05	1.74	0.21	0.64	0.26	0.65	0.13	0.57	0.46
La ₂ O ₃	16.18	0.38	13.83	0.21	17.20	0.48	16.76	0.59	13.91	2.81
Ce ₂ O ₃	34.15	0.61	26.92	0.28	27.23	1.29	26.61	0.98	24.51	1.12
Pr ₂ O ₃	4.00	0.12	3.08	0.09	2.82	0.07	2.71	0.12	2.45	0.30
Nd ₂ O ₃	15.75	0.16	11.41	0.12	9.84	0.21	9.72	0.40	8.13	1.79
Sm ₂ O ₃	2.13	0.07	1.86	0.07	1.32	0.19	1.39	0.06	0.86	0.44
Eu ₂ O ₃	0.25	0.03	0.21	0.04	0.15	0.06	0.21	0.03	0.11	0.11
Gd ₂ O ₃	1.62	0.14	1.76	0.15	1.11	0.31	1.17	0.10	0.21	0.24
Dy ₂ O ₃	b.d.	b.d.	0.33	0.04	0.03	0.10	b.d.	b.d.	0.12	0.12
ThO ₂	0.11	0.08	2.00	0.11	0.36	0.44	0.38	0.22	0.74	0.56
F calc ^b	9.08	0.21	7.41	0.04	6.01	0.08	6.03	0.14	5.89	0.07
CO ₂ ^b	21.03	0.48	21.83	0.17	22.62	0.42	23.15	0.30	27.28	0.30
–O=F	3.82	0.09	3.12	0.02	2.53	0.03	2.54	0.06	2.48	0.03
Total	101.31	0.64	100.75	0.54	100.22	0.76	100.48	2.05	99.57	1.13

Atoms per formula unit (apfu) on the basis of 4, 11, 17, and 7 anions for bastnäsite, parisite, röntgenite, and synchysite, respectively

Si	0.003	–	0.011	–	–
Ca	0.002	1.114	1.956	2.064	1.028
Mn	0.002	0.004	0.006	0.007	0.002
Fe	–	–	–	–	0.015
Sr	0.003	0.005	0.029	0.028	0.010
Ba	–	–	–	–	0.001
Total	0.010	1.123	2.003	2.098	1.055
Y	0.009	0.085	0.048	0.048	0.018
La	0.207	0.467	0.897	0.862	0.297
Ce	0.434	0.903	1.409	1.358	0.519
Pr	0.051	0.103	0.145	0.138	0.052
Nd	0.195	0.373	0.497	0.484	0.168
Sm	0.025	0.059	0.064	0.067	0.017
Eu	0.003	0.006	0.007	0.010	0.002
Gd	0.019	0.054	0.052	0.054	0.004
Dy	–	0.010	0.002	–	0.002
Th	0.001	0.042	0.012	0.012	0.010
Total	0.944	2.101	3.133	3.032	1.088
TREE:Ca	1:0	2:1	3:2	3:2	1:1

Full data are given in Supplementary Appendix B Tables B.1–B.5.

^a Elemental composition data of synchysite-(Ce) in the Songwe Hill carbonatite deposit in Malawi.

^b Calculated by stoichiometry, b.d. is below detection limit, TREE is total rare earth elements, and other analysed elements including Mg, Al, Tb, Er, Yb, Lu and U are also below detection limit.

stacking one portion of bastnäsite and two portions of synchysite with a TREE:Ca ratio of 3:2 (Van Landuyt and Amelinckx, 1975; Ni et al., 2000).

Syntaxial intergrowth is common feature among the REE fluorcarbonate minerals owing to the similarity of their layered structures, with an identical surface amenable to grow any of the phases as the fluid composition changes (Donnay and Donnay, 1953; Ni et al., 1993). It is reported that syntaxial intergrowths are recognised between all pairs of minerals in the series bastnäsite, parisite, röntgenite, and synchysite except for bastnäsite-synchysite (Donnay and Donnay, 1953).

3.2. Magnetic properties of the REE fluorcarbonate minerals

The slope of magnetisation plotted against applied magnetic field strength, which represents the magnetic susceptibility of the minerals shows that bastnäsite-(Ce), parisite-(Ce), and röntgenite-(Ce) A behave as paramagnetic minerals with a positive linear slope that becomes less steep through the series bastnäsite-(Ce) to parisite-(Ce) and röntgenite-

(Ce) A (Fig. 1). Röntgenite-(Ce) B behaves as a diamagnetic mineral with a negative linear slope. Combined measurement of röntgenite-(Ce) A and B crystals produces a diamagnetic graph (Fig. 2).

Bastnäsite-(Ce) possesses the highest magnetic susceptibility of 3×10^{-4} within the REE fluorcarbonate group (Table 3). The value is close to the previously reported value of 2.12×10^{-4} (Jordens et al., 2014). Parisite-(Ce) possesses a higher magnetic susceptibility of 0.6×10^{-4} compared to röntgenite-(Ce) A and B. Interestingly, röntgenite-(Ce) A and B crystals exhibit positive and negative magnetic susceptibilities of 0.02×10^{-4} and -0.1×10^{-4} , respectively, with an average value of -0.08×10^{-4} .

3.3. Magnetic properties of synchysite-(Ce)

It was not possible to acquire a large enough pure crystal of synchysite-(Ce) to measure the magnetic properties directly by VSM. However, it should now be possible to estimate the magnetic properties of synchysite by comparing its composition with the trend established

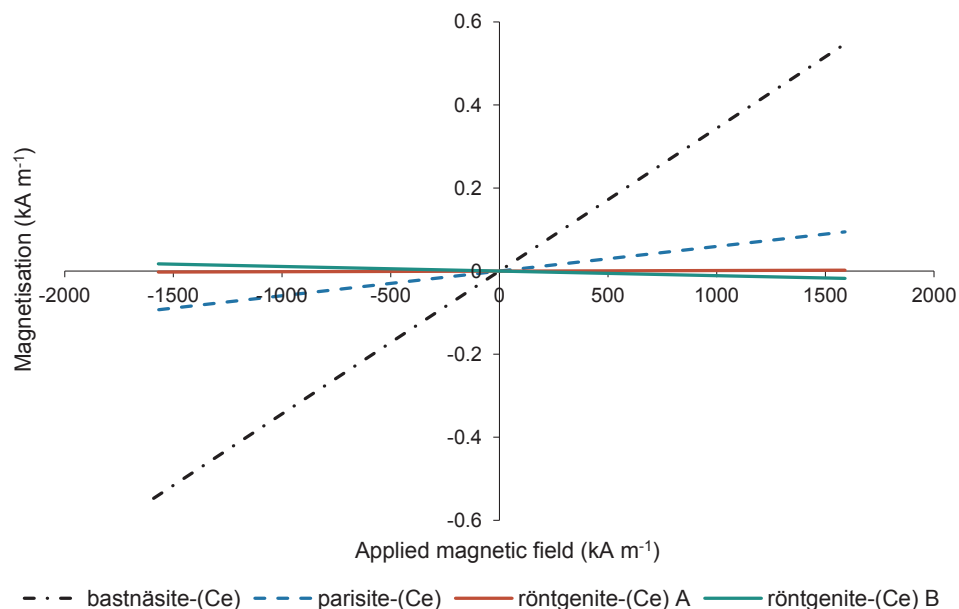


Fig. 1. Magnetisation as a function of applied magnetic field strength showing the variations in the magnetic behaviour of pure single crystals of the REE fluorcarbonate minerals: bastnäsite-(Ce), parisite-(Ce), röntgenite-(Ce) A, and röntgenite-(Ce) B as measured by VSM.

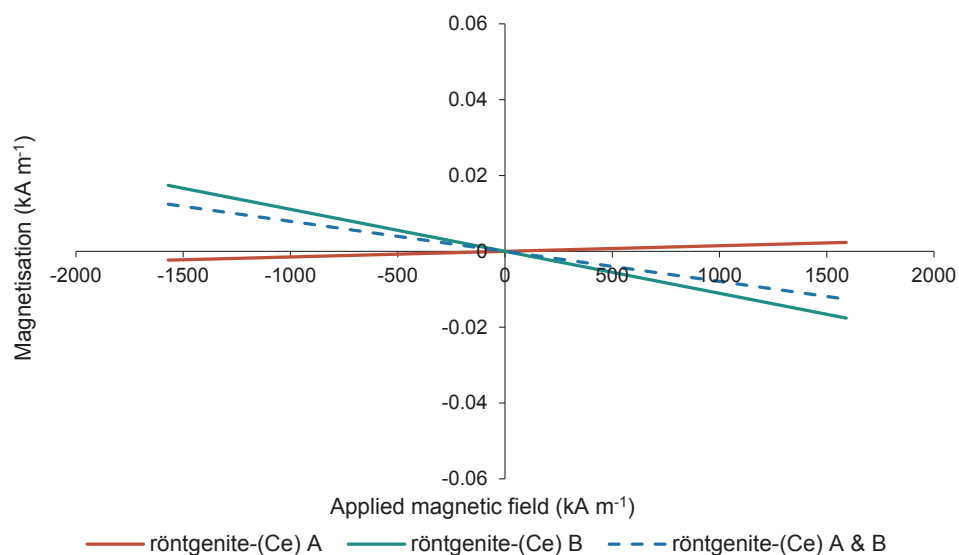


Fig. 2. Magnetisation as a function of applied magnetic field strength showing the variations in the magnetic behaviour of röntgenite-(Ce) A and röntgenite-(Ce) B single crystals in addition to the combined crystals of röntgenite-(Ce) A & B as measured by VSM.

from the measured pure REE fluorcarbonate minerals. This was done and the prediction checked in two ways. First, the magnetic properties were measured by a using a SQUID instrument that can make determinations on 5 mg samples (Supplementary Appendix A) and second,

the properties were checked experimentally on a synchysite-bearing carbonatite from Songwe Hill, Malawi (Broom-Fendley et al., 2017) by conducting a number of magnetic separation experiments using a wet high intensity magnetic separator (WHIMS) as described in Al-Ali

Table 3

Summary of the VSM results showing the relative magnetic properties and volume magnetic susceptibility of the REE fluorcarbonate single crystal minerals.

REE fluorcarbonate mineral	Magnetic properties ^a	Volume magnetic susceptibility	Published data
Bastnäsite-(Ce)	Strongly paramagnetic	3.0×10^{-4}	2.12×10^{-4b}
Parisite-(Ce)	Moderately paramagnetic	0.6×10^{-4}	N/A
Röntgenite-(Ce) A	Weakly paramagnetic	0.02×10^{-4}	N/A
Röntgenite-(Ce) B	Diamagnetic	-0.1×10^{-4}	N/A
Röntgenite-(Ce) A & B	Diamagnetic	-0.08×10^{-4}	N/A

N/A = not available.

^a The minerals are classified based on their relative magnetic susceptibilities to each other.

^b Jordens et al. (2014).

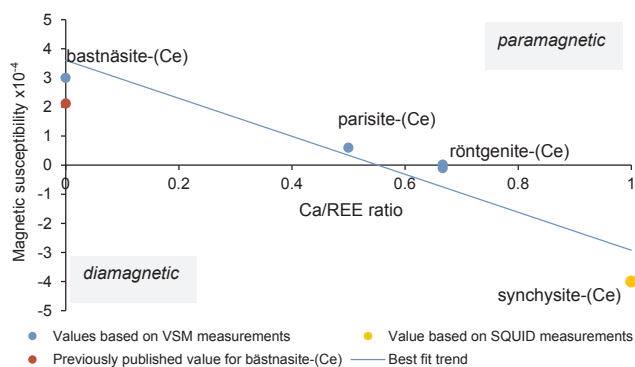


Fig. 3. Variations in magnetisation of the REE fluorcarbonate minerals as a function of Ca/REE ratio.

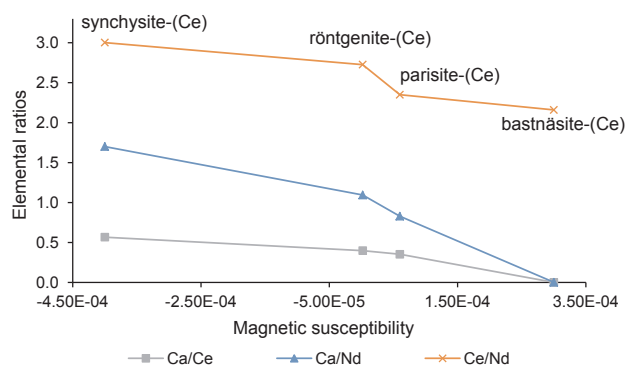


Fig. 4. Correlation between some elemental ratios and the volume magnetic susceptibility of the REE fluorcarbonate minerals.

(2016) and Supplementary Appendix C. It is evident from the magnetic separation experiments and confirmed by the automated mineralogy, that the liberated synchysite-(Ce) crystals in the Songwe Hill carbonatite deposit behaved as diamagnetic minerals as they recovered to the non-magnetic product.

3.4. Relationship between REE fluorcarbonates mineral chemistry and magnetic properties

The REE fluorcarbonate minerals show a successive increase in the Ca content and decrease in total REE from bastnäsité-(Ce) through synchysité-(Ce). Bastnäsité-(Ce) and parisité-(Ce) are paramagnetic but parisité-(Ce) has lower magnetic susceptibility. Röntgenité-(Ce) is weakly paramagnetic to diamagnetic and synchysité-(Ce) is diamagnetic. This systematic decrease in the magnetisation and magnetic susceptibility of these minerals may be due to the increase in the Ca content, because Ca possesses a low molar magnetic susceptibility of $0.503 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ compared to all the REE, particularly Nd and Pr which exhibit high molar magnetic susceptibility of $74.5 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ and $69.5 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$, respectively (Lide, 2000). The electronic bonding environment is similar in each of the REE fluorcarbonates because of the stacked later structure and the dilution of the REE layers with Ca layers appears to control the magnetism.

The correlation between Ca/REE ratio and the volume magnetic susceptibility is plotted in Fig. 3. It illustrates a gradual decrease in the magnetic susceptibility as the Ca/REE ratio increases between the end members of the REE fluorcarbonate minerals.

Also, other elemental ratios including Ca/Ce, Ca/Nd and Ce/Nd show similar relationship with the volume magnetic susceptibility (Fig. 4). As these ratios increase the magnetic susceptibility from bastnäsité-(Ce) through synchysité-(Ce) decreases. The magnetic

susceptibility being negative as the ratio of Ca/Ce, Ca/Nd and Ce/Nd increases from 0.40 to 0.57, from 1.09 to 1.70 and from 2.73 to 3.00 respectively.

The effect of varying proportions of the individual REE is more difficult to determine because all natural minerals contain mixtures of REE. Species in which Ce is the REE in highest concentration, as used in this study, are by far the most common and make up practically all of the REE fluorcarbonates that are being considered as ores. It is possible that the more subtle variations in La, Ce, Nd and Pr proportions in the – (Ce) species may have some effect on magnetic susceptibility. The magnetic susceptibility depends on the bonding environment in the mineral but taking into account individual element magnetic properties, the molar magnetic susceptibility of Nd at $74.5 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ is higher than that of Ce which is $31.4 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ (Lide, 2000). A first hypothesis to follow up is that REE fluorcarbonates with higher Nd/Ce ratios would be more magnetic. In contrast, the molar magnetic susceptibility of Y is much lower than either Nd or Ce at $2.359 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ (Lide, 2000). The, much rarer, Y species of REE fluorcarbonate may be diamagnetic. So, for example, synchysité-(Y) would have a lower magnetic susceptibility than synchysité-(Ce) and behave as a diamagnetic mineral, while synchysité-(Nd) might be paramagnetic. Bastnäsité-(Ce) has the highest magnetic susceptibility measured so far in a REE fluorcarbonate but bastnäsité-(Y) may have a much lower value, or even be diamagnetic. This discussion emphasises the importance of determining the process mineralogy before designing processing flowsheets.

4. Conclusions

The magnetic susceptibilities of the REE fluorcarbonates vary widely, from paramagnetic at 3.0×10^{-4} for bastnäsité-(Ce) to diamagnetic for röntgenité-(Ce) and synchysité-(Ce). It is essential to make accurate compositional determinations before carrying out magnetic separations involving REE fluorcarbonates.

The variation in magnetic properties can be accounted for by a simple hypothesis in which paramagnetic REE fluorcarbonate layers are progressively diluted by Ca rich layers in the REE fluorcarbonate mineral structures.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2018.11.042>.

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