Magnetic properties of REE fluorocarbonate 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 fluorocarbonates 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 fluorocarbonate 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 fluorocarbonates other than bastnäsite-(Ce). The magnetic susceptibility of REE fluorocarbonates 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 fluorocarbonate series minerals. Given the wide range of magnetic susceptibility of REE fluorocarbonates, it is important that the mineralogy is determined carefully before setting up a mineral processing flow sheet.

1. Introduction

The rare earth element (REE) fluorocarbonates are the most common REE minerals in REE ore deposits and include the mineral species bastnäsite-(Ce) Ce(CO3)F, parisite-(Ce) CaCe2(CO3)3F2, röntgenite-(Ce) Ca₂Ce₃(CO₃)₅F₃, and synchysite-(Ce) CaCe(CO₃)₂F (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 fluorocarbonate mineral, other members of the series are often also present. They frequently form synticial 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 fluorocarbonates except for bastnäsite-(Ce).

This work measures the magnetic properties of the REE fluorocarbonate 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.

<table>
<thead>
<tr>
<th>REE fluorcarbonate mineral</th>
<th>Chemical formula</th>
<th>Quantity mg</th>
<th>Locality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bastnäsite-(Ce)</td>
<td>Ce(CO3)F</td>
<td>89</td>
<td>Zagi Mountain, Pakistan</td>
</tr>
<tr>
<td>Parisite-(Ce)</td>
<td>CaCe2(CO3)3F2</td>
<td>47</td>
<td>Snowbird Mine, Mineral County, Montana, USA</td>
</tr>
<tr>
<td>Röntgenite-(Ce) A</td>
<td>Ca2Ce(CO3)2F3</td>
<td>55</td>
<td>Narssârussuk, nepheline syenite pegmatite in Greenland</td>
</tr>
<tr>
<td>Röntgenite-(Ce) B</td>
<td></td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Synchysite-(Ce)</td>
<td>CaCe(CO3)2F</td>
<td>5</td>
<td>Mt. Cervadone, Verbano-Cusio-Ossola Province, Piedmont, Italy</td>
</tr>
</tbody>
</table>

2. Materials and methods

2.1. Pure single minerals

Small matrix-free natural crystals (5–89 mg) of bastnäsite-(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 bastnäsite-(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

Bastnäsite-(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 $-\text{(Ce)}$ species (Bayliss and Levinson, 1988) (Table 2; full details are given 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, Ba, Tb, Yb, Lu, 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: bastnäsite-(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). Bastnäsite-(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 TREO: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 bastnäsite and one portion of synchysite with a TREO:Ca ratio of 2:1, while röntgenite-(Ce) is trigonal and formed by
The slope of magnetisation plotted against applied magnetic 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 $3 \times 10^{-4}$ within the REE fluorcarbonate group (Table 3). The value is close to the previously reported value of $2.12 \times 10^{-4}$ (Jordens et al., 2014). Parisite-(Ce) possesses a higher magnetic susceptibility of $0.6 \times 10^{-4}$ compared to röntgenite-(Ce) A and B. Interestingly, röntgenite-(Ce) A and B crystals exhibit positive and negative magnetic susceptibilities of $0.02 \times 10^{-4}$ and $-0.1 \times 10^{-4}$, respectively, with an average value of $-0.08 \times 10^{-4}$.

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 for bastnäsite-(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.
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

![Graph](image1)

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: bastnäsíte-(Ce), parisite-(Ce), röntgenite-(Ce) A, and röntgenite-(Ce) B as measured by VSM.

![Graph](image2)

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.

Table 3

<table>
<thead>
<tr>
<th>REE fluorcarbonate mineral</th>
<th>Magnetic properties</th>
<th>Volume magnetic susceptibility</th>
<th>Published data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bastnäsíte-(Ce)</td>
<td>Strongly paramagnetic</td>
<td>$3.0 \times 10^{-4}$</td>
<td>$2.12 \times 10^{-4b}$</td>
</tr>
<tr>
<td>Parisite-(Ce)</td>
<td>Moderately paramagnetic</td>
<td>$0.6 \times 10^{-4}$</td>
<td>N/A</td>
</tr>
<tr>
<td>Röntgenite-(Ce) A</td>
<td>Weakly paramagnetic</td>
<td>$0.02 \times 10^{-4}$</td>
<td>N/A</td>
</tr>
<tr>
<td>Röntgenite-(Ce) B</td>
<td>Diamagnetic</td>
<td>$-0.1 \times 10^{-4}$</td>
<td>N/A</td>
</tr>
<tr>
<td>Röntgenite-(Ce) A &amp; B</td>
<td>Diamagnetic</td>
<td>$-0.08 \times 10^{-4}$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A = not available.

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

b Jordens et al. (2014).
Ca/Nd
Best fit trend
Ce/Nd
the REE.
Pr which exhibit high molar magnetic susceptibility of bastnäsite-(Ce) through synchysite-(Ce) decreases. 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, synchysite-(Y) would have a lower magnetic susceptibility than synchysite-(Ce) and behave as a diamagnetic mineral, while synchysite-(Nd) might be paramagnetic. Bastnäsite-(Ce) has the highest magnetic susceptibility measured so far in a REE fluorcarbonate but bastnäsite-(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 $3.0 \times 10^{-4}$ for bastnäsite-(Ce) to diamagnetic for röntgenite-(Ce) and synchysite-(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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