Controls on critical metals in magmatic and hydrothermal systems

Michael Anenburg

February 2019

A thesis submitted for the degree of Doctor of Philosophy of The Australian National University

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Declaration

I declare that the work in this thesis is that of the candidate alone, except where indicated below. The work was undertaken between February 2015 and February 2019 at the Australian National University, Canberra. It has not been submitted in whole or in part for any other degree or award at ANU or elsewhere.

The work in this thesis consists of three published papers, and three papers undergoing peer review.

Published papers:


Papers in peer review:

6. Anenburg, M. Molybdenum and rhenium disulfide synthesis via high-pressure carbonate melt. Submitted to *CrystEngComm*.

The majority of the technical and intellectual work on each paper was conducted by me (Michael Anenburg). I prepared and performed the experiments, analysed the samples using optical microscopy, electron microscopy, and laser ablation. I did the
literature reviews, wrote the papers, prepared the figures and supplementary material, submitted the papers and was the corresponding author with the journals. The role of John Mavrogenes was the initial realisation of the potential importance of studies (particularly for the first paper). He provided supervisory support throughout my PhD, guiding me on the right track and diverting me from the wrong track (albeit not with my full cooperation at times). He assisted editing and polishing the manuscripts, posters, and oral presentations. Antony Burnham provided the calculations relating to Ce⁴+/Ce³+ and oxygen fugacity considerations in paper 3. Charles Le Losq assisted with Raman and FTIR analyses, calculation of H₂O contents and CO₂ contents in papers 4 and 5.

This declaration is signed by:

John Mavrogenes, the Chair of the supervisory panel, and a co-author on the published papers.

Michael Anenburg, the student.
Acknowledgements

This work could not have been possible without the support of many people. First and foremost, my wife Adi. These four years have been challenging with the birth of our two children, Tal and Lia, but highly rewarding and fun.

Special thanks to my supervisor, John Mavrogenes, for taking me on as a student, and to Hugh O’Neill for providing immense amount of support. I would like to thank the members of the experimental petrology lab, and the wider petrology community of RSES. This includes academics, students, administrative staff, and technical staff.

I am indebted to Kelvin Hussey at Arafura Resources for financial support.

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Abstract

Metals with high demand and a supply risk are called critical metals. One solution to the criticality problem is source diversification. We do not fully understand critical metal enrichment in ore deposits. I focus on two groups: the rare earth elements (REE) and the platinum group elements (PGE).

At Nolans, NT, REE are hosted in fluorapatite veins up to several metres thick. I show experiments testing two formation hypotheses. First, I tested whether REE are hydrothermally mobile. I ran layers of rock-like compositions, REE-free apatite, REE, and a saline solution in piston cylinder experiments at 2–5 kbar and 550–700 °C. The results show that the REE layer bonded with the more soluble elements (Si, Al, Mg, Fe) to produce insoluble REE minerals such as allanite or britholite. Formation of REE-bearing apatite was limited to a thin zone between the REE and apatite. In a P–F dominated fluid, the solubility of REE is negligible. Second, I tested the reaction between a REE–P–F-bearing carbonatite layer and a silicate layer, at 6 kbar and 650–900 °C. The experiments resulted in a reaction zone consisting of diopside and REE-rich apatite. This indicates that carbonatites can carry P and REE, and form REE-rich apatite in reaction with silicate rocks. These textures closely reproduce the Nolans ore.

The Nolans REE are now hosted in alteration products consisting of carbonates, phosphates and silicates. This study documents the alteration mineralogy. I show a decoupling between Ce and La, caused by oxidation of Ce(III) to Ce(IV), leading to its incorporation in Th-bearing minerals. La, Nd and Pr are concentrated in Ce-free phases. This has implications for mineral processing. Thorium is an unwanted by-product of REE production, and Ce is a lower-value product. The concentration of Ce and Th in a single mineral may allow its separation before processing, increasing the monetary value and reducing the environmental hazard. Analysis methods for fluorapatite compositions typical for carbonatite (LREE-enriched, carbonate bearing) are discussed.

Rhenium is another critical metal that commonly occurs in molybdenite. Carbonatite-hosted molybdenites commonly host 100s ppm of Re. Carbonatites are usually considered as deposits for REE or Nb, and the occurrence of Re-rich molybdenite is perplexing. I performed experiments which tested whether (1)
carbonatites can recrystallise molybdenite powder, and (2) whether rheniite can crystallise in carbonatites. The powder was recrystallised to coarse crystals, and similarly sized rheniite crystals formed by reaction of perrhenate and sulfate. Thus, carbonatites flux molybdenite and rheniite growth. It is a first step in understanding the reason for the occurrence of molybdenite in carbonatites.

These experiments also tested the behaviour of other PGE in peralkaline melts. It is uncertain whether PGE must be concentrated from silicate melts by sulfide saturation, or can they be transported as nanonuggets in silicate melts independently of any presence of a sulfide phase. Nanonuggets are well known from PGE solubility experiments in which they are treated as experimental artefacts. I exploited the tendency of these metals to form nanonuggets to further explore their behaviour. These experiments were conducted in Ag–Pd, Au, or Pt capsules at 5 kbar and 1050–1100 °C. Textural evidence indicates that the nanonuggets formed by reduction of an initially oxidised melt. They preferentially stick to magnetite and coarsen by consumption of existing nanonuggets. PGE can be transported as nanonuggets in silicate melts regardless of the presence of sulfide, and their concentration can be greater than that allowed by equilibrium solubility. Re-bearing sodalite that formed in those experiments was in equilibrium with Re metal, suggesting the role of the peralkaline melt for stabilising the higher oxidation state. This has implications for nuclear waste management, since Re-sodalite is commonly used as an analogue for Te-sodalite. This study shows that Re-sodalite is thermodynamically stable and can crystallise for sodic silicate melts.
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Introduction

The past decade has seen metal price changes due to global political and economic reasons. For example, the platinum group elements (PGE: Rh, Ru, Pd, Os, Ir and Pt) experienced a steep price hike followed by a sharp drop around the global financial crisis of 2008–2009. The price of the rare earth elements (REE: Y and La to Lu) increased by several hundred percent due to Chinese export restrictions during 2011. This price volatility of some metals and metal groups led to the widespread recognition of the concept of the metal “criticality”.

The criticality of metals is governed primarily by two factors: the importance of the metal for modern technological applications (i.e. “how much we need the metal”), and the supply risk for the metal (i.e. “who controls production”). The two metal groups mentioned above (PGE and REE) are indeed critical: The world’s supply of PGE is dominated by South Africa and Russia. Both countries have seen unstable political environments in the past decades. Recently, PGE supply from South Africa has been threatened by worker’s strikes. Additionally, recent political tensions between Russia and the Western world has also increased the risk of Russian PGE supply disruption. Rhenium is another metal that is often grouped together with the PGE. It is never extracted on its own, but it is produced as a by-product of molybdenum and copper extraction. Therefore, Re supply and prices may vary due to effects which do not concern Re, such as the closure of a Cu mine. Likewise, global REE production is dominated by China, with the light REE produced primarily from the Bayan Obo in Inner Mongolia, and heavy REE produced as a by-product of the former or from ion-adsorption clays in southern China. There are periods of increased tensions between China and the Western world, which put a question mark over the long-term supply stability of the REE.

One of the solutions to the supply risk problem is diversification of sources. The better we know how to explore for and understand critical metal deposits, the lower the supply risk becomes. Thus, studying the underlying geological processes that lead to enrichment of critical metals in geological systems will allow us to improve exploration models. These new discoveries would ideally be in Australia or its allies, diversifying the supply chain and mitigating some of the supply risk.
This study employs a combined analytical and experimental approach. The first is a description of natural rocks of initially unknown genesis (e.g., chapter 2) and the second is a progress in the analytical technique required to analyse these rocks (e.g., chapter 3). The observation from these natural rocks lead to hypotheses which can then be tested experimentally (e.g., chapters 1 and 5). Additionally, chapters 4 and 6 experimentally investigate the geochemistry of a critical element (rhenium) on a more fundamental level.

This thesis is by compilation and as such each chapter (i.e., paper) contains its own set of references. Therefore, references are not repeated in this introduction, the final conclusions, or elsewhere in this thesis.
This study focuses on Nolans Bore, a REE ore deposit in the Northern Territory, Australia. The REE are hosted in fluorapatite veins several centimetres to metres thick, with the grade reaching 5% TREO (total REE oxide). The fluorapatite is surrounded by a diopside selvage. The formation process of Nolans Bore is currently unknown. Hydrothermal fluids have been invoked to explain this unique deposit, but do not fully explain Nolans Bore as the solubility of REE in P+F rich fluids is extremely low. I hypothesised that an alternative model involving a carbonatite may have been operating. Carbonatites are the traditional source for REE. For instance, Bayan Obo formed by carbonatite-derived fluids, and two of the other historically operating REE mines (Mount Weld, Australia, and Mountain Pass, USA) are similarly carbonatite-hosted. However, Nolans Bore is not a carbonatite per se. Instead, I suggest that Nolans Bore formed by a metasomatic reaction between a REE-bearing carbonatite and a silicate host rock.

I show experiments testing the two hypotheses. In the first series of experiments, I tested whether REE are mobile in hydrothermal conditions. This was conducted using a noble metal capsule filled with layers of chemicals (e.g., MgO, SiO2), a layer of REE-free apatite, a layer of REE (either Nd or Pr), and a saline solution. The experiments were run in a piston cylinder apparatus at elevated pressure (2–5 kbar) and temperature (550–700 °C). The results showed that the REE layer remained intact and bonded with the more soluble elements (Si, Al, Mg, Fe) to produce insoluble REE minerals such as allanite or britholite in situ. Formation of REE-bearing apatite was either not observed, or limited to a few tens of micrometres thick reaction zone between the REE and apatite layers. This demonstrates that in a P–F dominated fluid, the solubility of REE is low and it is not expected to be mobilised on the scale required to form a deposit such as Nolans Bore. The second set of experiments tested the reaction between a REE–P–F-bearing carbonatite layer and a silicate layer. These experiments were run at 6 kbar and 650–900 °C, simulating a mid-crustal, granulite facies, setting. The experiments resulted in a reaction rim consisting primarily of diopside and REE-rich apatite. The silicate layer has been mostly unchanged, and the REE were leached out of the carbonatite layer. This
indicates that carbonatites are an excellent carrier for P and REE, and able to form REE-rich apatite in reaction with silicate rocks. In an open system, the leftover carbonatite—now poorer in REE—will migrate elsewhere. These textures closely reproduce textures observed in Nolans Bore. Additionally, these results have important implications of general REE mobility in the crust, which is likely to be facilitated by carbonatite metasomatism.
CARBONATITIC VERSUS HYDROTHERMAL ORIGIN FOR FLUORAPATITE REE-Th DEPOSITS: EXPERIMENTAL STUDY OF REE TRANSPORT AND CRUSTAL “ANTISKARN” METASOMATISM

MICHAEL ANENBURG*† and JOHN A. MAVROGENES*§

ABSTRACT. Nolans-type ore deposits contain REE and Th mineralization hosted in fluorapatite veins. These veins intrude granulite facies rocks and are surrounded by a diopside selvage. Nolans-type deposits are thought to form by REE, F and P-rich hydrothermal fluids derived from alkali or carbonatitic intrusions. However, REE are not effectively transported in F and P-rich systems. REE ore deposits are commonly hydrothermally overprinted, possibly obscuring the igneous nature of the primary mineralization. We conducted a series of piston cylinder “sandwich” experiments, testing the hydrothermal fluid hypothesis, and a newly suggested process of carbonatite metasomatism. Our results confirm theoretical predictions that REE are hydrothermally immobile in these systems and the experimental phase assemblage is not compatible with the natural rocks. Our results show that fluorapatite can only host several weight percent levels of REE at temperatures higher than ~600 °C. Below that temperature, a miscibility gap exists between REE-poor fluorapatite and REE-rich silicates such as britholite or cerite. In contrast, experiments reacting P and REE-rich carbonatite with silicate rock above 700 °C closely resemble natural rocks from Nolans-type deposits. Selvage mineralogy is sensitive to the MgO content of the carbonatite. A diopside selvage formed at carbonatite MgO/(CaO+MgO) ~ 0.2 while wollastonite and forsterite formed at lower and higher ratios, respectively. Phosphate solubility in carbonatites decreases with decreasing MgO contents. As diopside formed, REE-rich fluorapatite preferentially crystallized from the selvage inwards. Thus, carbonatites are effective at simultaneously mobilizing REE, F and P to the site of deposition. Nolans-type deposits are the cumulate residue of this reaction, with the carbonatite liquid migrating elsewhere. At temperatures below 700 °C the carbonatite–silicate reaction additionally formed monticellite, cuspidine and magnesioferrite, resembling a skarn assemblage. Whereas skarns form by infiltration of silicate magmas or related fluids to carbonate rocks, our experiments are the opposite: intrusion of carbonatite into silicate rock. These mid-crustal skarn-like rocks may host elevated ore elements of carbonatitic affinity, such as F, P, Y, REE, Th, Ba, Sr, and Nb. We propose the term “antiskarn” to describe such systems, and suggest they trace the migration of carbonatite liquids through the crust. Hydrothermal reworking, retrogression, or metamorphism of antiskarns may obscure the carbonatitic genesis of the rocks. These metasomatic zones are the crustal equivalent of wehrlites that form by peridotite–carbonatite reaction at mantle depths.

Key words: Carbonatite, metasomatism, decarbonation, rare earth element, skarn, fluorapatite

GLOSSARY OF SYMBOLS

List of mineral and other abbreviations used in the figures and tables of this work. We followed the recommendations of Whitney and Evans (2010) where possible.

ab: albite
act: actinolite
aln: allanite
bc: barytocalcite
bm: bari-an-mica
The rare earth elements are a group of metals increasingly used in modern technological applications (Hoatson and others, 2011; Atwood, 2012; Chakhmouradian and Zaitsev, 2012; Linnen and others, 2014; Wall, 2014). Historically, production came from a small set of deposits, and research and exploration for new deposit types has been limited (Chakhmouradian and Zaitsev, 2012; Verplanck and others, 2016). The classification of REE as “critical metals” (Chakhmouradian and Zaitsev, 2012; Vidal and others, 2013; Nassar and others, 2015) and the need to secure new sources for these elements has spawned numerous exploration and research projects (Wall, 2014; Weng and others, 2015). New types of REE deposits are being discovered and incomplete understanding of these new types may cause confusion regarding their mode of genesis, tectonic setting and classification, resulting in impaired exploration targeting.

A recently identified REE ore deposit type is the Nolans-type, named after the type locality at Nolans Bore, Northern Territory, Australia (Schoneveld and others, 2015; Huston and others, 2016). This deposit type is characterized by centimeter to meter wide veins or dikes dominated by fluorapatite, hosting up to 5 percent by weight of REE contents via the charge balanced substitution
known as the “britholite” component in apatite (Pan and Fleet, 2002). Other notable examples of the Nolans-type deposits are Hoidas Lake, Saskatchewan, Canada (Hogarth, 1957; Pandur and others, 2014; Pandur and others, 2016) and Kasipatnam, Andhra Pradesh, India (Narasayya and Sriramadas, 1974; Choudhuri and Banerji, 1976; Rao, 1976; Panda and others, 2015). Deposit type hosts LREE with significant Th contents. The relative proportion of Nd and Pr is high, unlike other LREE deposits dominated by La and Ce, strengthening the economic attractiveness of this type. The fluorapatite veins are hosted in high metamorphic grade terranes of amphibolite or granulite facies with spatially associated felsic plutonic activity. The contact between the veins and host rocks consists of diopside selvages, centimeter to meters thick, with hyalophane-bearing zones (for example, Hogarth, 1957; Narasayya and Sriramadas, 1974; Choudhuri and Banerji, 1976; Rao, 1976).

The REE-rich fluorapatite is almost completely altered to REE-poor apatite and a plethora of secondary REE silicates, phosphates and carbonates (Panda and others, 2015; Schoneveld and others, 2015; Anenburg and others, 2018). Secondary silicates commonly host considerable Th in addition to the REE. Allanite occurs between the fluorapatite veins and diopside selvages, and as patches or veins cross-cutting the fluorapatite zones. The diopside selvages are commonly altered to a secondary assemblage of amphibole, epidote and grandite garnet (Schoneveld and others, 2015; Huston and others, 2016).

The formation of Nolans-type deposits is not currently well understood. Nolans Bore has been classified as hydrothermal, alkali, carbonatitic, metasomatic and combinations thereof (Orris and Grauch, 2002; Hoatson and others, 2011; Weng and others, 2013; Jaireth and others, 2014; Linnen and others, 2014; Wall, 2014; Schoneveld and others, 2015; Weng and others, 2015; Huston and others, 2016), or simply as an “unknown” type (Simandl, 2014). The most detailed study to date (Huston and others, 2016) suggested that Nolans Bore formed by P-bearing hydrothermal fluids derived from alkali magmas. Similarly, Hoidas Lake has been classified into a non-genetic “monazite±apatite vein” group (Simandl, 2014). Narasayya and Sriramadas (1974) initially suggested a carbonatitic origin for Kasipatnam, but that idea was later challenged (Choudhuri and Banerji, 1976; Rao, 1976). Nolans-type deposits are dominated by P, which is known to be an ineffective ligand for the transport of REE in aqueous fluids (Pourtier and others, 2010; Louvel and others, 2015; Zhou and others, 2016), and the solubility of apatite is rather low except in highly saline brines (Antignano and Manning, 2008). Sodium can facilitate the uptake of REE by fluorapatite via the following reaction:

$$2Ca^{2+} + P^{5+} = REE^{3+} + Si^{4+}$$  \( (1) \)

but Na is found only in trace amounts in Nolans-type apatite (Pandur and others, 2016), contrary to the ubiquity of this substitution vector in alkali rocks (Larsen, 1979). The total absence of sodic or potassic alteration (fenitization), so conspicuously common around alkali intrusions (silicate and carbonatite alike) and their hydrothermal offshoots (Pirajno, 2013), leads one to question the role of alkali magmas or fluids in the formation of Nolans-type deposits. Both Nolans Bore and Hoidas Lake have been suggested to form by distal carbonatite-derived hydrothermal fluids (Huston and others, 2016; Pandur and others, 2016). However, similar systems elsewhere are rich in the HREE such as the Bear Lodge complex (Andersen and others, 2016), Lofdal (Bodeving and others, 2017), Malawi (Broom-Fendley and others, 2016; Broom-Fendley and others, 2017), whereas Nolans Bore and Hoidas Lake are nearly devoid of HREE. The apatite–diopside association is known from phosphorites, but phosphorites...
also contain abundant magnetite, which is absent from Nolans-type deposits (Krasnova and others, 2004). Phoscorites are also part of larger scale alkaline–carbonatite intrusive complexes, unlike the isolated Nolans-type deposits. Finally, apatite from phoscorites contains low REE contents compared to Nolans-type apatite (Krasnova and others, 2004; Zaitsev and others, 2014).

**REE Transport in Hydrothermal Fluids**

REE were not traditionally considered hydrothermally mobile, but recent studies indicate aqueous fluid transport is possible, given proper complexing ligands (Williams-Jones and others, 2012; Migdisov and Williams-Jones, 2014; Migdisov and others, 2016). Indeed, REE were hitherto mined from magmatic sources such as carbonatites and pegmatites, or derivative sedimentary placer deposits (Linnen and others, 2014). However, hydrothermal origins are increasingly implicated for many ore deposits (Giere, 1996). Hydrothermal REE deposit formation is often the working hypothesis for recent discoveries, not least because the distinction between hydrothermal and magmatic is not straightforward and hydrothermal overprinting is common in carbonatite-magmatic systems (Wall and Mariano, 1996; Weng and others, 2015).

An understanding of REE-bearing hydrothermal systems is still lacking. Although there has been progress in recent years, experimental studies have yet to cover all relevant \( P-T-X_{\text{fluid}} \) conditions that prevail in these systems (Migdisov and others, 2016). Therefore, erroneous conclusions may be drawn, as deposits not easily interpreted as magmatic are considered hydrothermal by default. Even in the case where hydrothermal processes played an important role, their role may be overestimated because REE may only have been “... mobilised on the scale of metres and perhaps tens of metres...” (Williams-Jones and others, 2012). This is common in many carbonatites and alkali intrusions, where magmatic processes were responsible for the initial concentration of the REE, and hydrothermal activity merely upgraded the deposit to economic grades (Wall and Mariano, 1996; Andrade and others, 1999; Walters and others, 2013; Wall, 2014; Feng and others, 2016; Trofantenko and others, 2016; Prokopyev and others, 2017). Hydrothermal activity in Nolans Bore redistributed the REE among various minerals on the centimeter scale (Schoneveld and others, 2015; Anenburg and others, 2018).

In this study, we experimentally evaluate the hydrothermal formation model by testing whether LREE are mobile in hydrothermal fluids saturated with fluorapatite, and whether decreasing pressure and temperature can deposit REE-rich fluorapatite (down to 400 °C, for example, Huston and others, 2016). We then test an alternative model in which Nolans Bore formed by reacting P, REE and Mg-rich carbonatite with silicate wall rocks, producing REE-fluorapatite as cumulate residue of carbonatite melt. Following the study of Biggar (1969), the magmatic experiments cover a temperature range of 650 to 900 °C. We then generalize our results to identify a process forming skarn-like assemblages due to the carbonatite-melt–silicate-rock reaction, which we term “antiskarn”.

**Experimental Strategy, Materials and Methods**

Field relations show that Nolans-type deposits form by reaction between a mineralizing fluid or melt with silicate wall rock (fig. 1, Pandur and others, 2014; Schoneveld and others, 2015; Huston and others, 2016; Pandur and others, 2016). Therefore, two sets of experiments were conducted: one hydrothermal and a second, magmatic. A homogenous equilibrium assemblage was not sought in our experiments. Instead, layers of starting materials were placed in experimental capsules in order to observe reactions between the materials, in what are often referred to as “sandwich” experiments (see for example, Wallace and Green, 1988; Dasgupta and Hirschmann, 2007; Pistone and others, 2016; Gervasoni and others, 2017). Nolans-type deposits are LREE
deposits, therefore we used a single REE in each experiment: either Pr or Nd. Praseodymium has the advantage of imparting a characteristic green color to minerals, allowing a quick and easy visual estimate of Pr transport in the capsule.

Hydrothermal Experiments

Hydrothermal experiments were run in a piston-cylinder apparatus using standard Teflon–talc–graphite–MgO assemblies in 19 mm pressure vessels (fig. 2). Temperature and pressure were controlled and monitored by a Eurotherm controller and in-house software. Although experiments in talc assemblies usually require pressure correction owing to high friction, we did not apply any pressure correction because (1) run durations were on the order of several days, allowing friction to dissipate, (2) the automated pressure control immediately compensated for any pressure loss due to friction dissipation, (3) the large Ag capsule (see below) expands with temperature, exerting pressure independently of the piston, and (4) pressures were often varied during the experimental runs and were arbitrarily chosen as a first approximation, therefore the improved accuracy given by friction correction was not deemed necessary.

The capsule materials used were cold-seal type Ag capsules as described by Hack and Mavrogenes (2006) (fig. 2). These capsules provide several advantages: (1) no hot welding is required, thus the volatile content of the starting materials (H2O and CO2)
is precisely known, (2) the large internal capsule volume allows simulation of a more complex hydrothermal system, and (3) the thick capsule walls minimize the internal thermal gradient.

Several silicate mix compositions were prepared by mixing dried oxides (SiO$_2$, TiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$) and carbonates (CaCO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$) in an agate mortar and pestle with acetone and then firing at 1000 °C to a dehydrated and decarbonated sintered material that was then ground to powder (table 1). This powder is composed of quartz, feldspars, hematite and other aluminosilicates and closely represents an oxidized and anhydrous variant of the most common granulites hosting the Nolans Bore veins. The silicate-granulite (“Gran1”) mix compositions were placed in each capsule along with MgO or MgCO$_3$, “fluorapatite” (stoichiometric mix of Ca$_3$(PO$_4$)$_2$ and CaF$_2$), Pr$_6$O$_{11}$ or Nd$_2$O$_3$, ThO$_2$, CaCO$_3$ and SrCO$_3$ as detailed in figure 3A. Oxygen fugacity ($f$O$_2$) was buffered by adding Re metal powder to each capsule. As the starting materials are oxidized, some of the Re was oxidized during each run to ReO$_2$, buffering $f$O$_2$ to the Re–ReO$_2$ buffer. This buffer was chosen because Nolans Bore contains sulfates, which require $f$O$_2$/H$_2$O $\approx$ Ni–NiO, and iron is present as both Fe$^{2+}$/H$_2$O and Fe$^{3+}$/H$_2$O in allanite, suggesting $f$O$_2$ $<$ Fe$_2$O$_3$–Fe$_3$O$_4$. The Re–ReO$_2$ buffer is conveniently located between these two buffers and is inert with respect to the capsule and starting materials. Two kinds of fluids were used in the runs. An acidic fluid consisting of 1 M HCl and 20 weight percent NaCl, and a basic fluid prepared by neutralizing and saturating the acidic fluid with CaCO$_3$. Details of all hydrothermal experiments are given in table 2 and figure 3.

Temperature control was accurate to within 2 °C, except several transient excursions lasting several seconds in which the accuracy was within 10 to 15 °C. Pressure was accurate to within $\sim$0.05 kbar. After each experiment, the capsule was pierced with a 1 mm drill, to see if fluid bubbled from the capsule indicating fluid had remained for the duration of the run. The open capsule was rinsed with deionized water, filled with epoxy, and cut in half. Both halves were then mounted in epoxy and prepared as described below.

### Table 1

Synthetic compositions used for the piston cylinder runs. Units are weight percent

<table>
<thead>
<tr>
<th></th>
<th>Gran1</th>
<th>Gran2</th>
<th>Gran3</th>
<th>NBC3</th>
<th>NBC4</th>
<th>NBC5</th>
<th>NBC6</th>
<th>NBC7</th>
<th>NBC8</th>
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<td>68.5</td>
<td>66.64</td>
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<td>Al$_2$O$_3$</td>
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<td>16.8</td>
<td>15.97</td>
<td></td>
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<td>Fe$_2$O$_3$</td>
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<tr>
<td>FeO</td>
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<td>CaO</td>
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<td>34.65</td>
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<td>50.27</td>
<td>41.24</td>
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<td>SrO</td>
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<td>1.31</td>
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<tr>
<td>MgO</td>
<td>18.36</td>
<td>11.65</td>
<td>7.34</td>
<td>3.96</td>
<td>10.39</td>
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<td>2.95</td>
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<tr>
<td>K$_2$O</td>
<td>3.38</td>
<td>3.38</td>
<td></td>
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<tr>
<td>Pr$<em>6$O$</em>{11}$</td>
<td>2.50</td>
<td>3.00</td>
<td>3.00</td>
<td>3.50</td>
<td>5.50</td>
<td>5.50</td>
<td>5.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td>0.50</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>4.48</td>
<td>4.79</td>
<td>4.92</td>
<td>4.79</td>
<td>4.04</td>
<td>9.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>4.79</td>
<td>4.92</td>
<td>4.79</td>
<td>4.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>29.79</td>
<td>28.74</td>
<td>28.01</td>
<td>27.02</td>
<td>29.98</td>
<td>21.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>3.23</td>
<td>3.07</td>
<td>2.09</td>
<td>2.06</td>
<td>1.80</td>
<td>2.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>7.00</td>
<td>6.14</td>
<td>6.11</td>
<td>6.05</td>
<td>4.74</td>
<td>5.70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Magmatic Experiments

Magmatic experiments were run in a similar fashion as the hydrothermal runs described above, with several differences. Some experiments were run in noble metal tubes, crimped and arc-welded. Capsules were filled with two layers: carbonatite on the bottom followed by silicate on top. Oxygen fugacity in the oxidized “Gran1” composition runs was buffered by placing Re metal in the bottom of the capsule. Runs
employing the reduced “Gran2” and “Gran3” compositions were not buffered. These compositions contain Fe$^{2+}$/H$_{1001}$ added in the form of fayalite, synthesized by reducing a mixture of silica and hematite in a 1 atm furnace. Carbonatite starting mixes contained varying Mg contents in order to constrain carbonatite composition that would result in diopside, and to explore the expected phase assemblage outside of this range. All experiments were run at constant pressure and temperature, and quenched at the end. The magmatic experiment did not suffer from the transient temperature spikes experienced during the hydrothermal runs, thus temperature was known to within 2 °C throughout each run. Details of magmatic experiments are given in table 3.

**TABLE 2**

Run conditions and summary of resulting phases for each hydrothermal experiment

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°C)</th>
<th>P (kbar)</th>
<th>Fluid</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2145</td>
<td>60 hr at 650</td>
<td>60 hr at 4</td>
<td>Acidic</td>
<td><em>actinolite</em>, <em>allanite</em>, <em>biotite</em>, <em>britholite</em>, <em>fluorapatite</em>, <em>monazite</em>, <em>talc</em></td>
</tr>
<tr>
<td>D2172</td>
<td>24 hr at 700, 144 hr to 400</td>
<td>48 hr at 5, 120 hr to 2.5</td>
<td>Acidic</td>
<td><em>actinolite</em>, <em>allanite</em>, <em>biotite</em>, <em>britholite</em>, <em>clinopyroxene</em>, <em>fluorapatite</em>, <em>fluorite</em>, <em>norbergite</em></td>
</tr>
<tr>
<td>D2182</td>
<td>24 hr at 650, 96 hr to 500</td>
<td>48 hr at 5, 72 hr to 3</td>
<td>Basic</td>
<td><em>allanite</em>, <em>biotite</em>, <em>britholite</em>, <em>calcite</em>, <em>cerite</em>, <em>fluorapatite</em>, <em>norbergite</em></td>
</tr>
<tr>
<td>C5214</td>
<td>48 hr at 660, 80 hr to 500</td>
<td>48 hr at 5, 80 hr to 4</td>
<td>Basic</td>
<td><em>actinolite</em>, <em>allanite</em>, <em>biotite</em>, <em>britholite</em>, <em>cerite</em>, <em>clinopyroxene</em>, <em>fluorapatite</em>, <em>monazite</em></td>
</tr>
<tr>
<td>D2216</td>
<td>24 hr at 500, 96 hr to 400, 20 hr at 400</td>
<td>24 hr at 4, 96 hr to 3, 20 hr at 3</td>
<td>Basic</td>
<td><em>allanite</em>, <em>biotite</em>, <em>calcite</em>, <em>cerite</em>, <em>fluorapatite</em>, <em>monazite</em>, <em>Pr-carbonate</em>, <em>talc</em></td>
</tr>
<tr>
<td>D2249</td>
<td>96 hr at 700, 48 hr to 600</td>
<td>96 hr at 5, 48 hr to 4</td>
<td>Acidic</td>
<td><em>allanite</em>, <em>britholite/cerite</em>, <em>calcite</em>, <em>chondrodite</em>, <em>clinopyroxene</em>, <em>fenghuangite</em>, <em>fluorapatite</em>, <em>fluorite</em>, <em>huttonite</em>, <em>monazite</em>, <em>thorianite</em></td>
</tr>
<tr>
<td>D2329</td>
<td>160 hr at 650</td>
<td>160 hr at 5</td>
<td>Acidic</td>
<td><em>actinolite</em>, <em>allanite</em>, <em>biotite</em>, <em>britholite/cerite</em>, <em>clinopyroxene</em>, <em>huttonite</em>, <em>Mg-hydroxyfluoride</em>, <em>fluorapatite</em>, <em>fluorite</em>, <em>norbergite</em>, <em>Pr-oxychloride</em>, <em>Pr-(hydro)oxyfluoride</em>, <em>thorianite</em></td>
</tr>
</tbody>
</table>

Phases in italics occur only in trace amounts.

**ANALYTICAL METHODS**

Experimental charges were embedded in epoxy and polished with diamond paste to $\frac{1}{4}$ μm grit. Samples were then studied using a Hitachi S-4300 SE/N field emission scanning electron microscope (FE-SEM). Chemical analyses were performed using an Oxford Instruments INCA X-MAX energy dispersive spectroscopy (EDS) system, employing an 80 mm$^2$ silicon drift detector (SDD) and calibrated using various synthetic and natural reference materials. Beam conditions were 15 kV accelerating voltage and 0.6 nA beam current measured on a Faraday cup. As each experiment contained only a single REE (either Pr or Nd), there were no interferences in the EDS spectra and the method is considered sufficient (see for example, Reed and Ware, 1975; Ware, 1991; Robinson and others, 1998). Most analyses should be considered as semi-quantitative, due to the small size of the resulting phases—commonly smaller than 5 μm across. Therefore, the data are of poor quality and are not reported here, apart from specific chemical compositions relevant to the discussion.
In this work, the terms “diopside” and “hedenbergite” are loosely applied to any clinopyroxene richer in Mg or Fe, respectively. We use “britholite” to refer to end-member britholite or close compositions, “REE-fluorapatite” to refer to fluorapatite with appreciable Pr or Nd contents (>1 wt%, but far from end-member britholite), and “fluorapatite” to refer to REE-poor fluorapatite, in which Pr or Nd contents are at or below detection by EDS (<0.5 wt%).

## Hydrothermal Experiments

In all runs, the silicate starting material recrystallized to an assemblage of quartz, amphibole, epidote, feldspars, magnetite, and other minerals too small to analyze. Occasional halite and sylvite cubes were found on the polished surface of the samples, which most likely formed by opening trapped fluid cavities during polishing and subsequent evaporation during carbon coating. The results described below only address the interfaces between layers. Although Pr used in the starting materials was oxidized (Pr$_6$O$_{11}$, a mixed oxide: 4Pr$^{4+}$O$_2$Pr$^{3+}_2$O$_3$), it completely reduced to Pr$^{3+}$ during the runs, as evident by the bright green color of the resulting Pr-bearing phases (in contrast to dark brown to black Pr$^{4+}$-bearing phases) and by the lack of any Pr in the Th$^{4+}$-bearing phases: huttonite and thorianite. A summary of resulting phases in each run is given in table 4.

**Run D2145.**—The interface between silicate and MgO consists of actinolite on the silicate side, and biotite on the MgO side. Small allanite prisms (up to 20 µm wide) and actinolite needles (up to 50 µm long) occur in the biotite matrix. The Pr$_6$O$_{11}$ layer recrystallized to monazite crystals up to 10 µm wide, with talc filling the space between
crystals. The contact between the Pr$_6$O$_{11}$ and fluorapatite layers is mostly sharp, with monazite crystals in direct contact with fluorapatite grains just several μm wide. Locally, allanite crystals grew from the monazite layer into the fluorapatite layer,

### Table 4

**Description of resulting phases in the hydrothermal runs and their characteristics**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Approximate formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinolite</td>
<td>(Ca)$_2$(Mg,Fe)$_5$Si$<em>8$O$</em>{22}$(OH)$_2$</td>
<td>May contain up to 1% Na$_2$O and K$_2$O, and up to 5% Al$_2$O$_3$.</td>
</tr>
<tr>
<td>Allanite</td>
<td>(Pr,Ca)$_2$(Al,Fe)$_3$(SiO$_4$)$_3$(OH) *†</td>
<td>Occurs as elongated prisms, occasionally several crystals splay from a single point. Commonly zoned.</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg,Fe)$_3$AlSi$<em>5$O$</em>{10}$(OH,F)$_2$</td>
<td>Commonly F-rich. Occurs as anhedral masses that transform into well-formed sheeted crystals in open cavities.</td>
</tr>
<tr>
<td>Britholite</td>
<td>(Pr, Ca)$_5$([Si,P]O$_4$)$_3$(F,OH,Cl) *†</td>
<td>Occur as individual sub-hexagonal crystals, commonly zoned, or as overgrowths around fluorapatite. May be non-stoichiometric, having more Pr and less Ca than end-member britholite: Pr$_3$Ca$_2$(SiO$_4$)$_3$(F,OH,Cl). See comment for cerite for additional details.</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$ †</td>
<td>May contain minor Mg. Mostly occurs as euhedral crystals.</td>
</tr>
<tr>
<td>Cerite</td>
<td>(Pr, Ca)$_9$(Mg,Fe)(SiO$_4$)$_3$(HSiO$_4$)$_4$(OH,F,Cl)$_2$</td>
<td>Forms sub-cubic prisms when well formed. In some cases, cerite is P-bearing and Fe- and Ca-poor, making it compositionally very similar to Ca-poor and Pr-rich britholite. Our resulting phases were not available for X-ray diffraction analysis, and identification by Raman is not possible as the two reference spectra for cerite and britholite from the RRUFF database (Downs, 2006)–IDs R060708 and R070412, respectively–are almost identical. Therefore, distinction between the two is possible only when the composition is unequivocal or the crystal habit is unambiguous. These difficulties are also known from natural cerite, britholite and “unnamed mineral E” found in Bastnäs, Sweden (Holtstam and Andersson, 2007).</td>
</tr>
<tr>
<td>Chondrodite</td>
<td>(Mg,Fe)$_3$(SiO$_4$)$_3$(F,OH)$_2$</td>
<td>A humite-group mineral. Occurs as anhedral porous masses.</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>Ca(Mg,Fe)Si$_2$O$_6$ †</td>
<td>Occurs as anhedral masses, octagonal prisms or elongated needle-like crystals. Occasionally zoned. Contains up to 1% Na$_2$O and 5% Al$_2$O$_3$. Some Fe is present as Fe$^{3+}$, evident by low analytical totals. The most likely substitution mechanism is Fe$^{2+} +$ Si$^{4+} = $ Fe$^{3+} + $ Al$^{3+}$.</td>
</tr>
</tbody>
</table>
enclosing pre-existing fluorapatites in a poikilitic manner. Uncommon aggregates of REE-fluorapatite needles 5 to 10 μm long occur at the monazite–fluorapatite interface, and some fluorapatite grains—immediately adjacent to monazite—have thin (< 1

### Table 4 (continued)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Approximate formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenghuangite</td>
<td>(Th, Ca, Sr, Pr)₅[[Si,P]O₄]₃(F,OH)</td>
<td>A Th-rich analogue of britholite. May or may not contain Pr. Forms coarse anhedral crystals.</td>
</tr>
<tr>
<td>Fluorapatite</td>
<td>Ca₅(PO₄)₃(F,OH,Cl) †</td>
<td>Occurs as fine µm-scale anhedral crystals. May contain small amounts of Si and Na, even when no Pr is detected.</td>
</tr>
<tr>
<td>Fluorite</td>
<td>CaF₂</td>
<td>Occurs as coarse subhedral crystals.</td>
</tr>
<tr>
<td>Huttonite</td>
<td>ThSiO₄</td>
<td>Occurs as anhedral overgrowths around thorianite. May contain up to 1.5% CaO.</td>
</tr>
<tr>
<td>Mg-hydroxyfluoride</td>
<td>Mg(OH)F</td>
<td>Occurs as coarse subhedral crystals.</td>
</tr>
<tr>
<td>Monazite</td>
<td>PrPO₄</td>
<td>Occurs as porous anhedral crystals. May contain 1% to 3% of CaO and SiO₂.</td>
</tr>
<tr>
<td>Norbergite</td>
<td>Mg₃(SiO₄)₃(F,OH)₂</td>
<td>Humite-group mineral. Occurs as irregular crystals or overgrowths around biotite.</td>
</tr>
<tr>
<td>Pr-(hydro)oxyfluoride</td>
<td>Pr-O-F-(H?)</td>
<td>Contains excess O and F over Pr, and together with low totals suggesting presence of H⁺. However, compositions are not consistent and we were unable to derive a formula. Occurs as subhedral crystals, commonly with inclusions of a similar phase with different ratios of Pr, O and F.</td>
</tr>
<tr>
<td>Pr-carbonate</td>
<td>Pr₂(CO₃)₃</td>
<td>Occurs as a porous aggregate of small tabular crystals. Composition inferred based on low totals that match Pr₂(CO₃)₃.</td>
</tr>
<tr>
<td>Pr-oxycarbonate</td>
<td>PrOCl</td>
<td>Occurs as elongated prims with two excellent cleavage planes at right angles.</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH,F)₂</td>
<td>Contains up to 1% F. Occurs as irregular sheets, possibly a polishing artifact.</td>
</tr>
<tr>
<td>Thorianite</td>
<td>ThO₂</td>
<td>Occurs in the cores of other Th-bearing minerals, anhedral. May contain up to 3% SiO₂ and 0.5% CaO.</td>
</tr>
</tbody>
</table>

* Allanite and britholite in run D2172 consist of Nd instead of Pr.  
† Has SrO substituting for CaO in run D2249.
μm) britholite overgrowths. The overwhelming majority of fluorapatite in the experimental charge is unremarkable and contains no Pr.

*Run D2172.*—The interface between silicate and MgO consists of a 20 μm wide layer of clinopyroxene followed by a wide zone of norbergite. The Nd₂O₃ layer recrystallized to hexagonal prisms of britholite up to 30 μm across, set in a matrix of biotite. Spectacular elongated allanite crystals (often longer than 100 μm) commonly nucleate on top of the Nd layer and grew towards the silicate layer, trapping inclusions of britholite, fluorite, actinolite, rare clinopyroxene, and fluorapatite that occur in the Nd₂O₃–CaF₂–silicate transition zone (fig. 4A). The fluorapatite layer is unremarkable and contains no Nd-enriched zones.

**Fig. 4.** Back-scattered images of hydrothermal runs. (A) Run D2172, (B) Run D2182, (C) Run C5214, (D) Run D2216, (E) Run D2249, (F) Run D2329. Scale bars are divided to 1/10 sections of the annotated length.
Run D2182.—The mineral sequence from the silicate to the MgCO₃ and the CaF₂ layers is clinopyroxene, small tabular allanite crystals embedded in massive biotite, euhedral calcite, and anhedral norbergite. The Pr₆O₁₁ layer recrystallized to euhedral cerite up to 50 μm wide. At the Pr₆O₁₁–fluorapatite interface, cerite grains are much finer (< 10 μm), with some of the smallest grains surrounded by britholite overgrowths, both of which are mostly trapped as inclusions in coarse allanite (> 50 μm) nucleated on cerite and grown into the fluorapatite layer (fig. 4B). The fluorapatite is fine grained and contains no Pr, even when next to cerite–britholite or when included in allanite.

Run C5214 (fig. 5A).—The silicate–MgCO₃ interface consists of clinopyroxene followed by actinolite hosted in biotite matrix. All carbonate dissolved during the run, resulting in a large cavity filled with loosely dispersed biotite crystals. Fluorapatite remained unchanged while the interlayered Pr₆O₁₁ layers recrystallized to subhedral cerite, with occasional britholite overgrowths near the fluorapatite layers. Monazite at interfaces with allanite (up to 100 μm long) grown from the interface towards fluorapatite, trapping both monazite and fluorapatite as inclusions (fig. 4C). The CaCO₃ in the top of the capsule was completely dissolved during the run, and large (~200 μm) elongated crystals of clinopyroxene grew in the resulting cavity. No other carbonate phases were observed elsewhere in the capsule, suggesting complete dissolution into the fluid.

Run D2216.—Both MgCO₃ layers recrystallized to massive biotite, irregular talc, and euhedral calcite. Figure 4D shows a Pr₆O₁₁ layer recrystallized to porous blocky cerite (several 10s of μm wide) with zones of Pr-carbonate aggregates. The interface between Pr₆O₁₁ and fluorapatite consists of fine-grained cerite on the Pr₆O₁₁ side and monazite on the fluorapatite side. Both phases host abundant fluorapatite inclusions. Allanite splays (up to 50 μm long) occasionally occur next to monazite, trapping abundant fluorapatite as inclusions. No fluorapatite in this run contains detectable Pr.
Fluorapatite throughout the capsule contains at least 3.5 percent SrO. Most fluorapatite grains are homogenous but others are zoned with the rims containing > 10 percent SrO. Most of the CaF\textsubscript{2} dissolved, leaving a cavity with several remnant fluorite crystals up to 20 μm wide. Rare Sr-bearing calcite occurs with fluorite, which is surprising since the fluid in this run was acidic. The silicate–MgO interface consists of Sr-free clinopyroxene and chondrodite. The SrCO\textsubscript{3} layer dissolved completely, leaving a large cavity in which euhedral crystals of Sr-bearing (1–2% SrO), Fe-rich clinopyroxene crystals formed. The ThO\textsubscript{2} layer recrystallized to huttonite with embayed thorianite cores. Fenghuangite appears at the contact of this layer and the fluorapatite layer. Some rare Pr is observed in fenghuangite. The Pr\textsubscript{6}O\textsubscript{11} recrystallized to elongated hexagonal britholite up to 50 μm long. While most crystals are close to end-member britholite, many of them have rims with a higher Ca/Pr ratio (that is, containing some REE-fluorapatite component). The Pr\textsubscript{6}O\textsubscript{11}–fluorapatite interface is poorly defined. Figure 4E shows fluorapatite crystals adjacent to the original Pr\textsubscript{6}O\textsubscript{11} layer partially recrystallized to REE-fluorapatite, commonly with euhedral Pr-rich (approaching britholite) overgrowths, forming some of the largest fluorapatite crystals seen in our experiments (15–20 μm). The grain size and Pr-content of the crystals decreases with distance from the Pr\textsubscript{6}O\textsubscript{11} layer, until no Pr is detectable in fluorapatite 200 to 250 μm away (yellow “pr-fap” in fig. 5B). Rare allanite crystals occur in this zone.

Run D2329 (fig. 5C).—Fluorapatite in this run contains no detectable Pr, regardless of location in the capsule. The MgO layer recrystallized to large (100 μm) crystals of Mg-hydroxyfluoride, surrounded by norbergite, biotite, and clinopyroxene, respectively. Occasional actinolite crystals nucleated on the biotite layer and grew outward. The CaF\textsubscript{2} layer consists of fluorite and euhedral clinopyroxene, commonly up to 50 μm long. Clinopyroxene is also abundant at the CaF\textsubscript{2}–silicate interface and its abundance decreases through the silicate layer. Fine-grained britholite occurs in the silicate–Pr\textsubscript{6}O\textsubscript{11} interface, with abundant allanite-cored epidote in the silicate side of the interface, and cerite in the Pr\textsubscript{6}O\textsubscript{11} side. The interior of the Pr\textsubscript{6}O\textsubscript{11} layer is composed of large euhedral crystals of Pr-(hydro)oxyfluoride and Pr-oxycloreide 50 to 100 μm long (fig. 4F). The Pr\textsubscript{6}O\textsubscript{11}–ThO\textsubscript{2} interface mirrors that of Pr\textsubscript{6}O\textsubscript{11}–silicate, and consists of coarse cerite and fine-grained britholite. The ThO\textsubscript{2} layer consists of 10 to 20 μm large subhedral huttonite with thorianite cores.

The main REE recrystallization features observed in these runs are shown in figure 6. The REE oxide recrystallized to phosphates (monazite and P-bearing britholite) when in direct contact with a P-bearing layer—fluorapatite in our case. Phosphorus is
rarely found outside of this zone. Given an acidic fluid, high temperatures (650–700 °C), and time (several days at least), REE migrates to the fluorapatite layer in a contact-metasomatic reaction. Allanite grows out from the REE-oxide layer, regardless of what it is growing into. This suggests high mobility of Ca, Al, Fe and Si. Most of the REE layer will recrystallize to cerite or P-free britholite, with the heart of the layer recrystallizing to REE fluorides or chlorides, suggesting these compounds are extremely insoluble and grew metastably even though Ca and Si (the main components of cerite or britholite) are present in the fluid.

**Magmatic Experiments**

All magmatic experiments except for run D2178 had carbonate and silicate layers on the bottom and top of the capsule, respectively. In general, the silicate starting mix melted or recrystallized to an assemblage of glass (in high \( T \) runs), quartz (in low \( T \) runs), plagioclase, clinopyroxene, and magnetite. Fayalite, occasionally mantled by magnetite or hedenbergite, was observed in Fe\(^{2+}\)-bearing runs. The carbonatite layers show features consistent with melting, but as carbonate liquids do not quench to glass it is not straightforward interpreting the resultant textures. Chemical equilibrium was not attained. Many crystals are zoned or vary compositionally with capsule position. For example, clinopyroxenes are Mg-rich (diopside) in contact with Mg-bearing carbonatite and Fe-rich (hedenbergite) in the Fe-bearing silicate layer. In contrast to the abundance of REE phases in the hydrothermal runs (cerite, britholite, monazite, allanite, \textit{et cetera}), magmatic runs of \( \geq 700 \) °C contain only fluorapatite with varying amounts of REE, and REE-bearing vesuvianite. End-member britholite does not occur in these runs. Fluorapatite REE contents vary between runs and within a single run, and REE contents will be described qualitatively as REE-poor or REE-rich.

**Run D2161.**—This experiment resulted in three parts: bottom, middle and upper. The bottom is composed of calcite crystals (up to 40 \( \mu \)m wide) with interstitial fine-grained fluorapatite (bottom of fig. 7A). Fluorapatite contains no Nd in the bottom of the capsule, but gradually becomes Nd-bearing towards the contact with the middle part, evident by the gradient of back-scattered electron brightness. The middle part is composed of a calcite layer with sub-spherical calcite blebs that appear to rise into the silicate layer (middle of fig. 7B). The top part is composed of silicate glass, quartz, plagioclase, hedenbergite, magnetite and a fine-grained phase suspected to be amphibole. The contact between the calcite blebs and the silicates is dominated by diopside with a thin rim of hedenbergite on the silicate side (fig. 7B). The calcite blebs contain abundant zoned fluorapatite with Nd-rich rims, and occasional clintonite occurring next to it. The calcite blebs also contain vugs (fig. 7A).

**Run D2178.**—In this run, the carbonate layer was placed on top of the silicate layer. The resulting texture is similar to Run D2161, in reverse. That is, the silicate is on the bottom, and the coarse-grained calcite with interstitial fluorapatite is on the top. The reaction zone consists of diopside on the silicate side, occasionally with hedenbergitic cores (particularly next to the silicate layer), and Nd-rich fluorapatite, rounded calcite, spinel and occasional clintonite plates on the carbonatite side (fig. 7C). The fine-grained interstitial fluorapatite does not show variable Nd contents across the capsule, in contrast to run D2161.

**Run D2194.**—This run is similar to run D2161. The bottom consists of calcite and fine-grained interstitial fluorapatite with increasing Nd contents upwards. The silicate on the top consists of glass, magnetite and silicates. The contact zone consists of a thick layer of calcite, Nd-rich fluorapatite and chondrodite (bottom of fig. 7D). The top of this layer protrudes into the silicate above it. The contact consists of hedenbergite on the silicate side and diopside on the carbonatite side (top left of fig. 7D). Spinel,
coarser Nd-rich fluorapatite and clintonite occur between the clinopyroxenes and the carbonatite (center of fig. 7D).

Run D2222.—As above, the bottom consists of calcite and fine-grained fluorapatite with increasing Pr contents upwards. The contact zone consists of blebs protruding into the silicate with calcite, Pr-rich fluorapatite and chondrodite (bottom of fig. 7E). The interface between the blebs and the silicate consists of clintonite, diopside,
hedenbergite and vesuvianite (middle to top of fig. 7E). The vesuvianite is commonly zoned, with Pr-rich zones closer to the carbonatite.

Run D2250 (fig. 8A).—The bottom of this capsule is similar to previous runs except that calcite cores are Sr-free and rims are Sr-bearing, and fluorapatite contains Th. However, the contact zone is fundamentally different to previous runs (fig. 7F). The bulk of the blebs are composed of calcite with dispersed chondrodite, and the carbonatite–silicate interface composed of clintonite, vesuvianite, cuspidine and minor diopside. Large wollastonite crystals grew from the interface into the silicate.

Run D2277.—This run is similar to run D2250, with the main difference being the presence of small amounts of fluorapatite at the base of the carbonatite blebs (fig. 7G).

Run D2294.—The bottom contains the usual calcite and fine grained fluorapatite. The contact zone consists of sub-vertical arrays of Pr-rich fluorapatite in a matrix of...
calcite and chondrodite (fig. 7H). The carbonatite–silicate interface is composed of diopside and hedenbergite (on the carbonatite and silicate sides, respectively), vesuvianite and a fine-grained Ca–Mg–Al–Si phase, most likely clintonite (top of fig. 7H). There are abundant gas cavities throughout the contact zone.

**Run C5290 (fig. 8B).** —The textures obtained in this run are essentially identical to run D2294, apart from vesuvianite, that is not present here, and higher Pr contents of fluorapatite.

**Run C5296 (fig. 8C).** —Again, calcite and fine grained fluorapatite at the capsule bottom, with monazite, thorianite and MgOHF. Praseodymium contents of fluorapatite increase upwards towards the contact zone. The contact zone consists of calcite blebs with vertical arrays of fluorapatite–britholite, similar to runs D2294 and C5290. The calcite blebs contain minor MgOHF, magnesioferrite and spinel (fig. 7I). The carbonatite–silicate interface consists of a thin layer of diopside (< 10 μm), with plagioclase growing from the interface towards the silicate (top of fig. 7I).

**Run D2319.** —The bottom contains a mixture of fine-grained calcite, monazite, fluorapatite, thorianite and cerite. The modal cerite/monazite ratio increases upwards. Fluorapatite does not contain REE detectable by EDS. The reaction zone is thin (50–70 μm) and contains calcite, thorianite, cerite, diopside, plagioclase, norbergite and epidote occasionally zoned to allanite (fig. 7J).

**Run D2332 (fig. 8D).** —Unlike the previous runs which have three distinct zones (bottom carbonatite, contact carbonatite and silicate), this run has several zones (see fig. 7K). The bottom zone contains calcite, magnesite, fluorapatite and monazite. The lower green zone consists of calcite and Pr-rich fluorapatite. The yellow zone consists of calcite, clintonite, monticellite, cuspidine, magnesioferrite, fluorite and rare Pr-rich...
fluorapatite. Fluorite and cuspidine dominate towards the top of this zone. The upper green zone consists of potassic ferririchterite. No clinopyroxenes were observed in this run.

Run D2346.—The bottom zone consists of calcite with abundant fluorapatite needles, becoming Pr-rich upwards with occasional Pr-poor cores. This zone also contains large forsterite crystals up to 200 µm long and zoned spinel–magnesioferrite crystals, some of which are included in forsterite (fig. 7L). The contact zone contains cavity-bearing blebs that appear to have risen up through the sides of the capsule around the silicate (fig. 7M). These blebs are composed of calcite, diopside and Pr-rich fluorapatite. The carbonatite–silicate interface consists of diopside on the carbonatite side and hedenbergite on the silicate side.

Run D2594.—The overall texture is similar to run D2294. The blebs in the top of the contact zone contain barytocalcite, calcite, platy aggregates of barian F-biotite, Pr-rich fluorapatite needles, celsian, and rare grandite (fig. 7N). The carbonatite–silicate interface consists of diopside–hedenbergite as above, and hyalophane zoned to Ba-free K-feldspar (fig. 7O). No phases containing Ba as a major or minor element occur in the bottom, below the reaction zone.

Run C5571.—The blebs consist of calcite, chondrodite, Pr-rich fluorapatite (occasionally zoned to britholite), and irregular holes suggesting sodium carbonates that were lost during sample preparation. The carbonatite–silicate interface is a fine intergrowth of abundant Pr-rich fluorapatite, F-biotite, diopside, and rare albite (fig. 7P). The interface is rimmed by hedenbergite on the silicate side. Na₂O contents of diopside are 0.5 to 1.5 percent.

DISCUSSION OF EXPERIMENTS

Ruling Out Hydrothermal Origin

Our hydrothermal experiments demonstrate that REE and Th are exceptionally immobile in the chemical system hypothesized for the hydrothermal Nolans Bore
model. As the host rocks for the Nolans Bore deposit do not contain significant amounts of REE, P or F (the essential components for the britholite–fluorapatite series), these elements had to be transported together. Britholite was observed in all runs except D2216, the lowest temperature run (500 °C), suggesting britholite is a high-temperature phase and a hypothetical fluorapatite–britholite solvus occurs around 600 °C. This suggests a higher temperature of formation than estimated by Huston and others (2016) for Nolans Bore (400–450 °C) and by Pandur and others (2014) for Hoidas Lake (< 350 °C), based on fluid inclusion analyses. This provides evidence that the fluid inclusions in these deposits record the later hydrothermal alteration stage (see for example, Schoneveld and others, 2015; Anenburg and others, 2018). Although britholite is stable at higher temperatures, it must be demonstrated that REE, Th, P and F are mobile. Unfortunately, this is not the case and it appears that the REE and Th are the least mobile elements in our runs. A common feature is that Pr$_6$O$_{11}$, Nd$_2$O$_3$ and ThO$_2$ react with the components in immediately adjacent layers (figs. 4B and 4C). This stands in stark contrast to the mobility of other elements in the experiment (Ca, Sr, Si, Al, Mg, Fe, F, Cl, K and Na). Phases containing these elements as major components formed near where they were placed in the capsule (for example, humites at the Mg–F interface, or biotite and amphibole at the MgO layer). These elements also occur in phases elsewhere in the capsule where they were not immediately available. For example, cerite contains Mg and Fe, allanite contains Si, and F, Cl, Al, and Sr occur in phases throughout the capsule. In contrast and importantly, monazite occurs only at the Pr–P interface. End-member britholite occurs within the Pr$_6$O$_{11}$ layer and becomes P-bearing (that is, containing some fluorapatite component) only when it is in direct contact with pre-existing fluorapatite (fig. 4E). Allanite mostly nucleates on the REE layers and grows outward. Perhaps most surprisingly, run D2329 contains Pr-oxychloride and Pr-(hydro)oxyfluoride at the Pr$_6$O$_{11}$–ThO$_2$ interface (fig. 4F), where it had neither adjacent Si nor P to react with, suggesting that Pr$_6$O$_{11}$ formed insoluble Pr-oxyhalides with the same ligands thought to make it mobile.

The observed REE phase assemblage is most likely metastable. Monazite can react with SiO$_2$ and CaF$_2$ to form britholite, or Pr-oxychloride and fluoride can react with monazite and SiO$_2$ to form britholite as well. Pr-free fluorapatite, P-free britholite and intermediate compositions should not co-exist at constant pressure–temperature–fluid-composition conditions. This is similar to the results obtained by Krenn and others (2012) at similar temperatures (≥ 650 °C) showing that REE-bearing apatite is stable, whereas other phases (monazite and end-member fluorapatite) are not. Indeed, two runs (D2145 and D2249) showed a reaction in which fluorapatite is progressively enriched in the britholite component towards the Pr$_6$O$_{11}$ layer. These reaction zones only occurred at the Pr–P interface. The reaction zone in run D2145 was only several micrometers wide, while in run D2249 it was wider (fig. 4E), but this run was held at 700 °C for 4 days. Both were run with acidic fluid at high temperature (> 650 °C). All other runs, including high temperature runs with basic fluid did not produce Pr-rich overgrowths on fluorapatite. Run D2329, with acidic fluid, was held for almost a week at 650 °C, but Pr$_6$O$_{11}$ was placed in contact with silicate, not phosphate. In this case, no reaction zone is seen, suggesting that the enrichment of Pr in fluorapatite is a contact dissolution-precipitation reaction assisted by acidic fluids. It may be argued that fluorapatite is unreactive and reaction kinetics are sluggish, but the presence of Sr-bearing fluorapatite in run D2249 requires addition of Sr from an external source. This indicates fluorapatite reacted with elements in the fluid. It was expected that lowering pressure and temperature during the runs would cause the formation of Pr-rich overgrowths around fluorapatite, but none were observed in any of the runs. Several experimental studies examined the effect of varied fluid compositions.
on apatite, monazite, allanite, and related phases (Harlov and others, 2002; Harlov and Förster, 2003; Harlov and others, 2003; Harlov and others, 2005; Harlov and others, 2007; Hetherington and others, 2010; Budzyň and others, 2011; Harlov and others, 2011; Mair and others, 2017). These studies reacted large natural crystals with fluids of varying compositions, a method useful to investigate reactions with preexisting crystals. However, it is commonly unclear whether a phase was unstable and partially dissolved due to incomplete reaction, or was stable and partially dissolved as an adjustment to new equilibrium conditions. Regardless of these complications, most studies show that reactions in these systems are extremely sluggish and new phases nucleate on previously existing phases in a dissolution-precipitation process. In most cases, REE-rich phases such as monazite will nucleate on apatite, suggesting that the britholite substitution in apatite is not preferred at hydrothermal conditions. Significant mobilization of the REE to form REE-richapatite was observed only with peralkaline fluids employing Na$_2$Si$_2$O$_5$ (Budzyň and others, 2011; Krenn and others, 2012).

REE solubility is enhanced in low pH fluids (Migdisov and Williams-Jones, 2014; Migdisov and others, 2016), and neutralization of this acidic fluid was suggested by Huston and others (2016) as the depositional mechanism at Nolans Bore. However, neutralization of acidic fluids by reaction with wall rock would cause formation of hydrous phases such as biotite and amphibole, as seen in our experiments. However, no such phases are observed in Nolans Bore and the reaction zone consists of an anhydrous assemblage dominated by clinopyroxene.

Our experimental results agree with the recent results of Migdisov and Williams-Jones (2014) and Migdisov and others (2016) showing that F and P act to deposit REE rather than transport them. The presence of Cl in the fluid does not matter as the solubility is determined by the least soluble components (fluorides and phosphates). The low solubility of REE phosphates was also experimentally demonstrated by Zhou and others (2016). The observation of calcite and CO$_2$ inclusions in apatite raises the possibility that CO$_3^{2-}$/H$_2$CO$_3$ might be the complexing ligand for REE transport, but its effectiveness has yet to be demonstrated. Taken together with the presence of F but absence of REE fluorocarbonates, transport by carbonate-bearing hydrous fluids process seems unlikely. Furthermore, Ayers and Watson (1991) showed that CO$_2$ in aqueous fluids reduces the solubility of fluorapatite, thereby immobilizing REE, making transport by carbonic species less likely.

Following the above arguments, we conclude that Nolans Bore could not have formed by hydrothermal transport of REE in aqueous or aqueous-dominated fluids. The combination of REE, P, and F is insoluble and it is not possible to transport them together from any source to the deposition site under geologically plausible conditions relevant to Nolans-type deposits. It is only possible by the action of extremely acidic or peralkaline fluids, both of which would react significantly with the Nolans Bore wall rocks to form features that are not observed, such as hydrous alteration zones or fenites, respectively.

**Experimental Evidence for Magmatic-Carbonatitic Origin**

Any textural interpretation of the magmatic experiments reported here must be made with caution, as carbonate melts do not quench to glass. There are several features common to most runs. First, in the lower parts of each capsule, rounded calcite is surrounded by fine-grained fluorapatite (for example fig. 7G). While resembling two immiscible liquids, this is most probably unlikely (also see discussion of carbonatite quench textures by Martin and others, 2013). For these to be the result of immiscibility, one of the phases must be pure liquid calcium carbonate that melts at temperatures well above our run conditions (> 1300 °C, Biggar, 1969). The second liquid would be close to fluorapatite composition, with a strong chemical gradient of
increasing REE contents upwards. This too would have a melting point higher than achieved in our runs as indicated by single phase studies (\(> 1600\ °C\), Bhatnagar, 1969) and ternary calcite–apatite–\(\text{H}_2\text{O}\) mixtures which consist of calcite, apatite, melt and vapor at our experimental conditions (Biggar, 1969). Additionally, liquid carbonates and phosphates quench to intergrown dendritic and skeletal crystals, none of which are observed here. Instead of liquid immiscibility, we interpret the calcite+fluorapatite zone in the bottom of our capsule as crystal settling from the carbonatitic liquid. As our starting compositions did not correspond to pure liquids at experimental pressure and temperature, calcite and fluorapatite were both on the cotectic (see Biggar, 1969). Initially, the fluorapatite could not accommodate REE, but as the experiment progressed, two processes occurred. Firstly, loss of \(\text{H}_2\text{O}\) from the liquid carbonatite to the melting silicate led to crystallization of the carbonatite along the fluorapatite–calcite cotectic. Secondly, carbonatite melt assimilated SiO\(_2\) from the silicate layer, which facilitated REE uptake by newly-crystallized fluorapatite via britholite-type substitution (see for example, Hammouda and others, 2010). Crystal settling of fluorapatite is particularly evident in run D2346, where crystals accumulated on top of large forsterite crystals (fig. 7L). Rounded calcite crystals in contact with carbonatite melts were observed in previous studies as well (Cooper and others, 1975; Weidendorfer and others, 2017). Wyllie and others (1962) and Biggar (1966) reported that apatite in equilibrium with liquid is usually equant whereas quench apatite is usually needle-like. Fluorapatite in our experiments is commonly elongated and rarely equant, indicative of quenching. However, we interpret the elongated crystal habit to result from chemical quenching rather than temperature drop, as suggested by Pistone and others (2016) for other experiments where two compositions with contrasting \(\text{H}_2\text{O}\) contents reacted.

The second common feature is the existence of calcite-rich blebs protruding upwards into the silicate layer (figs. 7A, 7F, and 7M). These blebs are readily interpreted as diapirs: liquid carbonatite that rose into denser silicate magma (fig. 8A). Quench textures are absent from these blebs because of \(\text{H}_2\text{O}\) loss and subsequent crystallization of the liquid. There are two main areas in the blebs: the silicate–carbonatite reaction selvages and the carbonate interiors. The composition of the reaction selvage is mostly controlled by the \(\text{CaO}/\text{MgO}\) ratio of the carbonatite. All runs conducted at \(\geq 700\ °C\) contain minerals that correlate with this ratio (fig. 9), regardless of the carbonatite/silicate ratio of the starting mix or temperature. The selvage contains wollastonite, vesuvianite, diopside and forsterite in order of increasing MgO contents of the carbonatite. All runs contain an aluminous phase (either clintonite or spinel), most likely because of the \(\text{Al}_2\text{O}_3\)-rich composition of the silicate starting mix. Surprisingly, allanite is only observed in the low-temperature run (650 °C, D2319), even though it is known to be stable to higher temperatures (Hermann, 2002). Allanite is ubiquitous in all Nolans-type deposits, and it may seem to be part of the primary magmatic mineral assemblage. However, our failure to synthesize allanite at magmatic temperatures taken together with the abundance of allanite in our hydrothermal runs suggests it to be a later hydrothermal overprint.

The resulting textures show striking similarities to Nolans-type deposits. The selvages in these rocks are essentially monomineralic diopside, a feature easily reproduced in our experiments, which constrains the MgO/(CaO + MgO) ratio of the carbonatite to about 0.2 (fig. 9). It is not clear whether an aluminous phase existed in the natural selvages as they are universally altered, but it is possible that allanite—commonly occurring at the diopside–fluorapatite interface of the natural rocks—replaced any aluminous phases that may have formed during the carbonatite–silicate reaction.
Our runs contain volumetrically significant calcite in the blebs whereas igneous calcite is rare in Nolans-type deposits. This is likely because our experiments are closed systems, where the liquid carbonatite cannot exit the capsule. Calcite sequesters Ca and CO$_3^{2-}$/H$_2$CO$_3$, whereas forsterite or humite-group minerals sequester Mg, F and H$_2$O, with a contribution of SiO$_2$ assimilated from the silicate (as suggested for the Barra do Itapirapuá carbonatite by Andrade and others, 1999). In a natural open system, the carbonatite flows through and reacts with the silicate wall rock according to the reaction:

$$\text{CaMg(CO}_3\text{)}_2 + 2\text{SiO}_2 = \text{CaMgSi}_2\text{O}_6 + 2\text{CO}_2.$$  \hspace{1cm} (3)

in carbonatite in wall rock in selvage volatile gas

Magnesium solubility in carbonatites increases with pressure (Dasgupta and Hirschmann, 2007; Hammouda and Keshav, 2015). Apart from the conventional decarbonation process illustrated by equation (3) and widely known from skarns and marbles, this process could be further promoted by rising carbonatitic liquids undergoing decompression. Carbonatites in general are effective in dissolving P$_2$O$_5$ (Biggar, 1969; Wallace and Green, 1988; Baker and Wyllie, 1992; Ryabchikov and others, 1993; Klemme and Dalpé, 2003; Gorbachev and others, 2017). Calcic carbonatites can dissolve less fluorapatite than magnesian carbonatites (Hammouda and others, 2010), such that decreasing Mg contents decrease fluorapatite solubility promoting equation (3) wherever a continuous stream of carbonatite liquid occurs. The carbonatite also assimilates silica from the wall rock, allowing REE to enter the fluorapatite lattice via the britholite substitution. Rare monomineralic igneous calcite patches observed in Nolans-type deposits are probably not melt pockets: Lee and others (2000) show that even Mg-rich carbonatitic liquid precipitate calcite instead of dolomite. Therefore, the observed calcite in Nolans Bore crystallized along the carbonatite cotectic. The residual Mg-bearing carbonatitic liquid flowed away from the fluorapatite mineralization zone, to form a crystalline carbonatite elsewhere. Linnen and others (2014) write that carbonatites rich in P and F will crystallize abundant apatite, sequestering the REE.
early. Fractionated carbonatites will then have little REE left (Bühn and others, 2001; Xu and others, 2010; Zaitsev and others, 2014; Xu and others, 2015). Nolans-type deposits can be seen as the extreme case of that process, trapping REE in the cumulate fluorapatite and depleting the residual carbonatite of any economic contents of REE. Fractionation of apatite (together with calcite and clinopyroxene) is invoked in a recent model for Na-carbonatite genesis (Weidendorfer and others, 2017).

The BaCO$_3$-bearing experiment (D2594) demonstrated the efficiency in which carbonatites mobilize Ba. The initial carbonatite mix contained 20 times more CaCO$_3$ than BaCO$_3$ on a molar basis, and additional Ca in the phosphate, fluoride, and hydroxide components. Yet, at the conclusion of the run, the cumulate assemblage at the bottom of the capsule contained no Ba-bearing phases, concentrating it into the residual liquid immediately below the contact zone. The liquid lost abundant Ba by reaction with the silicate, evident by the presence of celsian, hyalophane and Ba-micas. Nonetheless, the residual liquid crystallized to barytocalcite, suggesting the final CaCO$_3$/BaCO$_3$ ratio in the melt was close to unity (consistent with the large solubility of Ba in carbonatites reported by Jones and Wyllie, 1983). In natural systems unconstrained by our closed capsule, the Ba contents of the carbonatite will likely be buffered by continuous reaction with silicate rocks to form hyalophane and will never reach such extreme concentrations. Furthermore, carbonatites also contain sulfur that will exsolve along with Ba in aqueous fluids following solidification, depositing insoluble barite rather than barytocalcite. Nonetheless, the abundance of Ba-rich silicates that exclusively formed at the reaction zone was unexpected.

An additional run was conducted with 5 percent Na$_2$CO$_3$ in the carbonatite to test the effect of alkalis on the silicate–carbonatite reaction (C5571). The Na remained largely dissolved in the carbonatite and did not react extensively with the silicate. The clinopyroxenes remained Na-poor (that is, negligible aegirine component), and only limited formation of albite was observed. The silicate glass contained only ~1.5 percent Na$_2$O adjacent to the reaction zone, suggesting it contributed very little to flux-melting the silicate as it partitions heavily into the carbonatite liquid. Run C5571 was conducted at a relatively low temperature (730 °C) and we suspect that at higher temperatures the albite would not be stable, thus eliminating any modal evidence for the presence of Na in the carbonatite. Essentially, Na remains in the carbonatite and does not participate in the metasomatic reaction until it reaches shallower levels (see discussion about fenitization below).

Rao (1976) and Choudhuri and Banerji (1976) both considered the possibility that the veins at Kasipatnam are carbonatites, but settled on either hydrothermal skarn or pegmatite, respectively. Both noted the lack of abundant carbonates as one of the reasons to reject a carbonatitic origin. Our model does not require abundant carbonates as the deposit represents cumulate fluorapatites and the carbonatite liquid was transported elsewhere. The Kasipatnam veins are hosted in Fe-rich charnockites and clinopyroxene that occurs in these rocks are Fe-rich. However, the clinopyroxenes in the selvages grade to diopside the closer they are to the fluorapatite (Choudhuri and Banerji, 1976), in agreement with our model of introduced Mg-rich carbonatite and with strikingly similar textures observed in figures 7B–7E, 7H, and 7M. Rao (1976) also notes elevated Sr and Ba contents in the diopside relative to the Fe-rich clinopyroxenes, which we suggest is further evidence for equilibration with carbonatitic melt.

**Carbonatite Metasomatism**

Formation of diopside by reaction with carbonatite melt is known to occur in the mantle. It was observed in mantle xenoliths of wehrlite and shown experimentally to form by the same mechanism of equation (3) (Wallace and Green, 1988; Dalton and Wood, 1993; Hammouda and Keshav, 2015; Gervasoni and others, 2017). These
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Wehrlites are enriched in REE relative to their surrounding mantle rocks and commonly contain apatite (Green and Wallace, 1988; Yaxley and others, 1991; Hauri and others, 1993; Rudnick and others, 1993; Yaxley and others, 1998; Neumann and others, 2002; Su and others, 2010; Woodard and others, 2014). The wehrlitization process is commonly used to explain how magnesian carbonatites (and carbonatites in general) rise from mantle depths to escape the “carbonate ledge”, which causes reaction of the carbonatite liquid with mantle rocks to release of CO₂ (Dalton and Presnall, 1998; Hammouda and Keshav, 2015).

The fate of the carbonatites as they escape mantle depths has not been fully explored. An experimental study by Hammouda and others (2014) recreated decompression of a partially molten enstatite–dolomite mixture at high temperatures, avoiding the “carbonate ledge”. The mixture melts to forsterite, diopside and carbonatitic liquid (essentially forming a wehrlite), and as pressure decreases to lower crustal depth equivalents, the liquid back-reacts with diopside to form forsterite, increasing the Ca proportion of the carbonatite. The study of Hammouda and others (2014) is isochemical, limiting its applicability to natural systems: crustal rocks are not wehrlites, but rather felsic granitoids. Formation of forsterite cannot happen in these rocks because the activity of SiO₂ is too high. In contrast, our experiments show that a process similar to wehrlitization also occurs when a magnesian carbonatite reacts with typical crustal rocks: formation of diopside. In terms of phase relations, this reaction zone might not be different from skarns. Whereas some skarns form when silicate magma or derived fluids intrude a carbonate rock (see for example, Carter and Dasgupta, 2016), our experiments show the reaction of carbonatite magma with silicate rock: an “antiskarn”. The mineral assemblage of our “antiskarns” (diopside, calcite, vesuvianite, wollastonite, also cuspidine, monticellite and magnesioferrite in run D2332) highly resembles the assemblage of hydrothermal skarns, raising the possibility that some skarns or mineralogically similar rocks may in fact be paleo-conduits of carbonatite magma as it traversed the crust. For example, the Nolans-type deposit at Kasipatnam, which Rao (1976) suggested to be a skarn is more likely an “antiskarn”.

**Comparison with fenites and endoskarns**

There are two other well-known processes that involve carbonate metasomatism of silicate rocks: fenitization and formation of endoskarns.

Fenitization is a well-recognized process in which aqueous alkali fluids exsolving from a carbonatite metasomatize the wall rocks, altering them to an assemblage of alkali feldspars, aegirine, and alkali amphiboles such as arfvedsonite and riebeckite (Pirajno, 2013; Elliott and others, 2018). Fenites, which commonly host REE and Nb mineralization, form when carbonatites are emplaced in the upper crust at depths of 10 km up to near-surface environments. Fluid temperatures range from 400 to 700 °C, which corresponds to temperatures at which carbonatite melts solidify and decompress, releasing a separate fluid phase into which alkalis and some ore elements partition. This is commonly accompanied by hydrofracturing and brecciation (Elliott and others, 2018). Depending on the hydraulic properties of the wall rocks, fenitization can occur several hundreds of meters away from the carbonatite intrusion. Antiskarns, in contrast, are the result of the direct reaction between carbonatite liquid and silicate wall rocks, and the skarn-like assemblage is only centimeters to several meters wide. They form while alkalis and H₂O are still dissolved in the carbonatite, and they are not required for antiskarnification as the process primarily exchanges Ca, Mg, Al, Si, and Fe, rather than Na and K. Antiskarns form at higher temperatures (> 700 °C) and pressures (> 5 kbar or ~15 km deep) than fenites. There is no brecciation, and the minerals formed at the reaction zone are calcic diopsides instead of alkali–ferric aegirines. Grandite garnets and calcic amphiboles, not alkali amphiboles, form
during later hydrothermal alteration. The alkali feldspar that primarily forms at the reaction zone is hyalophane, which forms by addition of Ba to pre-existing alkali feldspars in the wall rock. Minor albite may form if the temperature is low enough. Finally, the mineralization is confined to the interior of the vein and the reaction zone itself is barren (although later remobilization can transport REE to the diopside zones, for example, Schoneveld and others, 2015; Pandur and others, 2016).

The term “skarn” by itself has no genetic meaning and merely describes metasomatic rocks comprising a calc-silicate mineral assemblage, commonly containing significant Mg, Fe, and Al (Einaudi and Burt, 1982; Misra, 2000). Nevertheless, skarns are commonly discussed in the context of aqueous hydrothermal fluids exsolved from crystallizing intermediate to felsic plutons (Meinert, 1993; Misra, 2000; Pirajno, 2013). Endoskarns, in particular, are metasomatic domains that form inside the intruding plutons themselves, commonly in the contact with carbonate rocks (Einaudi and Burt, 1982; Misra, 2000). Our “antiskarn” remains faithful to the non-genetic term “skarn”, as it contains the same mineral assemblage. However, the genetic term “endoskarn” implies the presence of a silicate intrusion and an aqueous fluid – neither of which are present in antiskarns. Alternatively, endoskarns may form by direct assimilation of carbonates by the silicate magmas at high temperatures (Di Rocco and others, 2012; Carter and Dasgupta, 2016). Like fenitic fluids, the skarn-forming metasomatic aqueous fluid exsolves due to decompression and crystallization of a pluton at shallow depths (< 5 kbar, Meinert, 1993), whereas the metasomatism of antiskarns results from direct reaction of a carbonatite with silicate wall rocks at mid-crustal depths (> 5 kbar). This process resembles carbonatite metasomatism in the mantle more than formation of skarns and around silicate intrusions in the upper crust. The presence of H2O is not required for antiskarn formation, although it helps flux the carbonatite to a liquid. Mineralization in most skarns consists of chalcophile elements: Cu, Mo, Zn, Pb, Ag, Au, et cetera, in association with sulfides. Non-sulfide Fe, W, and Sn mineralization also occurs in some skarns (Einaudi and Burt, 1982; Misra, 2000; Pirajno, 2013). This mineralization style is different than that of antiskarns, which consist of carbonatite-mobile elements such as REE, Th, Ba, Sr, F, P, and possibly Nb and Zr (although not tested in our study). Although some carbonatites contain sulfide or sulfate, sulfur is not essential for the mineralization.

A schematic diagram (fig. 10) clarifies the difference between fenites, conventional hydrothermal skarns, and antiskarns.

CONCLUSIONS AND IMPLICATIONS

Large-scale transport of LREE by aqueous fluids in a phosphate–fluoride-rich system is ineffective and unlikely to form Nolans-type mineral systems. The composition and distribution of REE-phases observed in the hydrothermal experiments followed initial layer placement inside the capsule. REE migration within the capsules was negligible compared to all other elements in the experiments. REE-phases were commonly metastable and unreactive, demonstrating their low solubility. In contrast, magmatic experiments employing carbonatite as a REE carrier closely reproduced key features of the Nolans-type deposits. Firstly, fluorapatite contains a significant britholite component and formed without immiscibility. The carbonatite–silicate reaction produced selvages that mimic the diopsidic selvages observed in nature [given a ratio of MgO/(CaO + MgO) ≈ 0.2 in the carbonatite], with fluorapatites most abundant near the selvage.

Primary features of REE mineralization occurrences are commonly obscured by hydrothermal alteration, resulting in a pseudo-hydrothermal appearance. This alteration may lead workers to mistakenly conclude that REE were mobilized from source to the deposition site by aqueous fluids. The source may be the mantle or a hidden igneous intrusion. We show that the mode of REE transport must be carefully
considered, as REE are potentially insoluble in fluids containing the elements with which they precipitated at Nolans Bore. “Exotic” melts should be the principal mechanism considered: a carbonatite-derived residual cumulate in the case of Nolans-type deposits. Carbonatite liquids have low viscosity and strong wetting capabilities (McKenzie, 1985; Hunter and McKenzie, 1989; Hammouda and Laporte, 2000; Kono and others, 2014)—resembling aqueous fluids rather than silicate magmas—forming hydrothermal-like textures in otherwise magmatic systems. Furthermore, the solubility of H₂O in carbonatites is known to be high, so a vapor phase only exsolves at a very late stage of carbonatite evolution (for example, Wyllie and others, 1996), at shallower levels than we suggest for Nolans-type deposit formation. Thus, the process of hydrothermal fluid exsolution from an unexposed magmatic source (as suggested by Huston and others, 2016, and Pandur and others, 2016) does not apply here because such a source does not exist, and Nolans-type veins represent an early (as opposed to late) stage in carbonatite evolution.

This fluid-like behavior of carbonatite melts and their reactivity with crustal rocks to form skarn-like assemblages in our experiments suggests this process may be overlooked in nature. Recognizing this process in natural rocks can shed light on mass transfer of carbonatite-mobile elements such as P, REE, Th, and Ba as in the case of Nolans-type deposits. More studies are required to understand this process of “antiskarnification”, including experimental studies and re-evaluation of high-temperature skarn assemblages where the silicate fluid source is not immediately obvious.

ACKNOWLEDGMENTS

This research is supported by an Australian Government Research Training Program (RTP) Scholarship. Michael Anenburg acknowledges a Ringwood Scholarship from the Research School of Earth Sciences, Australian National University. Access to the facilities of the Centre for Advanced Microscopy (CAM), with funding through the Australian Microscopy and Microanalysis Research Facility (AMMRF), is gratefully acknowledged. We thank Kelvin Hussey and others at Arafura Resources for financial support and access to the Nolans Bore drill core collection, which inspired this experimental study. Jindřich Kynický and four other reviewers are acknowledged for critique that greatly improved this work.
REFERENCES


REE-Th deposits: Experimental study of REE transport and crystal “antiskarn” metasomatism 363


Chapter 2: Anenburg, Burnham & Mavrogenes (2018)—CanMin

The previous chapter demonstrated that the hydrothermal mobility of REE is limited in fluorapatite dominated environments. However, hydrothermal alteration is ubiquitous in Nolans Bore. This study was motivated by a previous study on Hoidas Lake, a similar ore deposit in Saskatchewan, Canada. They describe a texture that they consider as magmatic, but we observe a similar texture in the alteration facies of Nolans Bore. To further understand the texture, we studied it in the context of the full range of alteration textures in Nolans Bore. We used EPMA mapping and 3D X-ray imaging to show that this texture is indeed secondary alteration, and does not represent a primary igneous feature. Other than determining the nature of the texture, our study led to two important insights:

All REE were initially accommodated in fluorapatite. I show a strong decoupling between Ce and La. This results from the oxidation of Ce$^{3+}$ to Ce$^{4+}$, leading to its incorporation in solid solution together with Ce–Th-bearing minerals such as stetindite or thorite. On the other hand, La is commonly concentrated together with Pr and Nd in Ce-free phases. This is important as Ce has a lower economic value than most of the REE, and Th is likewise undesirable due to its radioactivity. Therefore, the concentration of both of these elements in a single mineral may allow its separation before feeding the ore into processing, increasing the monetary value and reducing the environmental hazard of radioactivity.

In chapter 1, we performed hydrothermal experiments that demonstrated the limited mobility of the REE. Nolans Bore is an excellent natural laboratory to test this hypothesis. Indeed, the REE were not mobilised any more than the millimetre to centimetre scale. There is no REE halo around the deposit, an observation that has strong exploration consequences.

This chapter is preceded by a description of the data acquisition methods, which has been uploaded together with the database to figshare at https://doi.org/10.6084/m9.figshare.5602720.

Geochemistry data of Nolans Bore obtained by LA-ICP-MS

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I. Introduction and acknowledgements

This document accompanies the dataset freely available for download at doi:10.6084/m9.figshare.5602720 and describes acquisition and data reduction methods. This dataset contains elemental analysis of samples from Nolans Bore, Northern Territory, Australia obtained by LA-ICP-MS (laser ablation – inductively coupled plasma – mass spectrometry).

This dataset consists of the following:

1. This file.
2. A table of all analytical results, including unknowns and BCR-2G: database.csv and bcr2g.csv
3. Comparison of BCR-2G values with reference values: bcr2g.pdf
4. Files required for correction: apepi_corr.xls and ree-for-hon.xlsx
5. Image files annotated with the laser spots.
6. Raw laser data as output from the mass spectrometer software.
7. Iolite–Igor “experiment” files for all samples.

We thank Kelvin Hussey of Arafura Resources for assistance with funding. We thank James Tolley, Patrick Goodarzi and Laura Crisp for their help during the analytical sessions. John Mavrogenes and Hugh O’Neill are thanked for their supervisory guidance.
II. Data acquisition

Laser ablation was conducted using a 193 nm ArF excimer (Coherent CompexPro 110) laser ablation system, feeding into an Agilent 7700 series quadrupole ICP-MS with dual-mode discrete dynode electron multiplier detector. Our protocols were similar to those of Eggins et al. (1997), Eggins et al. (1998) and Jenner and O'Neill (2012). Ablation was conducted in a custom-built ‘HelEx’ two-volume vortex sampling cell in an atmosphere of He and Ar. Ablated material was transported to the ICP-MS in this gas mixture, with a small amount of H₂ added during sample introduction for interference minimisation. The laser was run at a frequency of 5 Hz, an energy of 80 mJ, and an operating fluence at the sample surface of ~9.25 J/cm². Laser spots were round with diameters of 28, 37, or 47 µm depending on material suitability. For each spot, we measured 20 seconds of backgrounds (“laser off”) followed by 40–45 seconds of ablation signal (“laser on”). Masses analysed were ²³Na, ²⁵Mg, ²⁸Si, ⁴³Ca, ⁴⁵Sc, ⁴⁷Ti, ⁵⁵Mn, ⁵⁷Fe, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁷Ba, ¹⁴⁶Ce, ¹⁴⁷Nd, ¹⁴⁷Sm, ¹⁵³Gd, ¹⁵⁷Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th, and ²³⁸U. Not all elements were analysed in all minerals.

Each 8–12 analyses were bracketed by an analysis of NIST-610 followed by BCR-2G reference materials, using the same conditions as the unknowns.

III. Data reduction

Data reduction was conducted using Iolite 2.5 running on Igor Pro 6.37 (Woodhead et al. 2007, Paton et al. 2011). Primary reference material was NIST-610 using GeoReM recommended values from Jochum et al. (2011). We used a value of 5.0457 for ⁴³Ca as an internal standard. Integration times usually consisted of the entire “laser on” duration, but shortened in some cases to avoid mineral inclusions. Spots with less than 20 continuous seconds of usable analysis time were discarded.

We used BCR-2G as a secondary reference material. We compared our results with the BCR-2G values given in GeoReM (2009 recommended values) and in Jenner and O’Neill (2012). The comparison is given in the attached bcr2g.pdf file. One element is displayed per page, spread over three analytical sessions. Our analyses of BCR-2G are given as the dot symbols with error bars (1 SD). Mean values for GeoReM
and Jenner and O'Neill (2012) are displayed as green and red lines, respectively, with the shaded areas representing 1 SD.

Our values tend to agree with Jenner and O'Neill (2012) better than they agree with the GeoReM values. Major elements (Mg, Ti, Si, etc.) in BCR-2G were significantly different to their accepted values. Trace elements were mostly in agreement, with the exception of HFSE (Zr, Nb, Ta), Y and HREE (Tm, Yb, Lu) consistently below both reference values. Time-dependent difference is observed in Sc and Fe in each analytical session. This is likely the result of atmospheric interference of $^{29}$Si+$^{16}$O=$^{45}$Sc and possibly $^{40}$Ar+$^{17}$O=$^{57}$Fe. Therefore, Sc and Fe values from this database should not be used, unless a correction is applied.

Internal standard values were obtained using EDS analyses (see Anenburg et al. 2018 for details). Some apatite analyses were categorised as “unaltered”, “altered”, or “symplectite” according to texture. Likewise, some calcite were categorised as “unaltered” or “unaltered”.

IV. Error correction

Several spurious “anomalies” are present in the analyses with the highest LREE/HREE ratios. For example, a chondrite-normalised plot of allanite from sample 080-13A is given in figure 1.
Other than the expected negative Eu anomaly, there are two additional positive anomalies: An obvious Er anomaly, and a subtler Gd anomaly (slightly obscured by the neighbouring Eu anomaly). These anomalies are the rest of oxide interferences. For example, $^{150}\text{Nd}^{16}\text{O}$ interferes with $^{166}\text{Er}$. This is clearly seen in figure 2:

Figure 2 shows a positive correlation between the Er anomaly calculated using $\text{Er}/\sqrt{(\text{Ho} \times \text{Tm})}$, similar to how Eu anomalies are calculated. The higher the Nd to Er ratio in the spot analysis, the higher the anomaly. This confirms that the anomaly is caused by the oxide interference. Unfortunately, it is not possible to use the same method to determine the Gd anomaly as the neighbouring Eu is anomalous as well.

It is possible to identify and correct the anomalies using the spreadsheet given by O’Neill (2016). The spreadsheet allows fitting of an REE pattern to orthogonal polynomials in order to represent the shape with $\lambda$ coefficients. The spreadsheet also outputs the ratio of a single element to the expected value from the fit, the average of the ratios, and the standard deviation of the ratios. Positively anomalous values have ratios $>1$, and greater compared to non-anomalous values. The standard deviation is also likely to be greater.
To do that, we considered only epidote–allanite analyses, as this mineral has the highest LREE/HREE ratio. We removed most epidote analyses as they often have low REE contents and the analytical error is larger. We created a spreadsheet (ree-for-hon.xlsx) where correction factors were entered. The resulting REE contents were then copied to the O’Neill (2016) spreadsheet (the final iteration is given in apepi_corr.xls).

The results of this exercise are given in table 1. The first row of each section shows the data with no corrections. As expected, Gd and Er show the highest ratios and standard deviations. Later on, Tb and Yb were also found to be slightly anomalous and require correction factors. Corrections were made by applying a correction factor to four elements:

1. $\text{Er}_{\text{corr}} = \text{Er}_{\text{uncorr}} - a\text{Nd}$ (for $^{150}\text{Nd}+^{16}\text{O}=^{166}\text{Er}$)
2. $\text{Gd}_{\text{corr}} = \text{Gd}_{\text{uncorr}} - b\text{Pr}$ (for $^{141}\text{Pr}+^{16}\text{O}=^{157}\text{Gd}$)
3. $\text{Tb}_{\text{corr}} = \text{Tb}_{\text{uncorr}} - c\text{Nd}$ (for $^{143}\text{Nd}+^{16}\text{O}=^{159}\text{Tb}$)
4. $\text{Yb}_{\text{corr}} = \text{Yb}_{\text{uncorr}} - d\text{Gd}_{\text{corr}}$ (for $^{156}\text{Gd}+^{16}\text{O}=^{172}\text{Yb}$)

Where $a$, $b$, $c$, and $d$ are the correction factors for Er, Gd, Tb, and Yb, respectively, given in table 1. Several iterations of applying correction factors and recalculating the spreadsheet output were done until the standard deviations plateaued and the ratios of the anomalous elements were not significantly higher than non-anomalous elements. It is interesting that by correcting these four elements, ratios below unity of non-anomalous elements were corrected as well. This results from the fitted polynomial not being artificially “above” them, giving them spurious negative anomalies. This is observed for all elements, but particularly for Sm and Dy.

The final correction factors are therefore:

1. $\text{Er}; a = 0.000105$
2. $\text{Gd}; b = 0.0186$
3. $\text{Tb}; c = 0.00012$
4. $\text{Yb}; d = 0.001$
This dataset was acquired over three days, each with its own calibration. It is probable that oxide production rates differed, and it is possible to apply the correction separately for each day in order to achieve ratios closer to unity and smaller standard deviations. However, the corrected results obtained so far are sufficiently satisfactory and such an endeavour was not pursued.

Figure 3 shows the corrected REE pattern for the allanite analyses given in figure 1:

The conspicuous Er anomaly is now absent, and the transition from Sm past the Eu anomaly is smoother. Also note how the Eu anomaly appears less strong than in the uncorrected pattern.

Note that the attached file “database.csv” is not corrected and corrections should be applied before working with the data!
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V. References


REE REDISTRIBUTION TEXTURES IN ALTERED FLUORAPATITE: SYMPLECTITES, VEINS, AND PHOSPHATE-SILICATE-CARBONATE ASSEMBLAGES FROM THE NOLANS BORE P-REE-Th DEPOSIT, NORTHERN TERRITORY, AUSTRALIA

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Research School of Earth Sciences, Australian National University, Canberra ACT 2601, Australia

ABSTRACT

The geochemical behavior and genesis of rare earth element (REE) ores remains poorly understood. In addition, the processes responsible for many features observed in REE ore deposits are not easily determined. Importantly, the distinction between igneous versus post-magmatic genesis, or the nature of the mineralizing and modifying fluids or melts, remains in dispute. Nolans Bore is a P-REE-Th deposit in the Northern Territory, Australia, hosting REE mineralization in fluorapatite and its alteration products. These mineralization textures are imaged in 3D by X-ray computed tomography and in 2D by electron microscopy, cathodoluminescence, and X-ray mapping. Primary igneous REE-rich fluorapatite was replaced in two stages. The first, at high temperature, was to endmember fluorapatite-britholite symplectite. The second, at lower temperatures, was to hydrothermal veins and patches comprised of REE-Th phosphate, silicate, and carbonate minerals. Quadrivalent Ce occurs together with Th, suggesting oxidized, low-temperature conditions. Strikingly similar textures are observed at Hoidas Lake, Saskatchewan, Canada, where igneous immiscibility or a pegmatitic boundary layer have been implicated in their formation. Our textural and chemical investigations establish that these symplectites and other similar textures are not primary igneous textures, but formed by subsequent cooling and alteration. Understanding the processes that formed these symplectic and vein textures is key to their theoretical and experimental modeling and should lead to a better understanding of “hydrothermal” REE deposits globally. The decoupling of Ce from the rest of the REE and the mineralogical preferences of the light REE versus the heavy REE should be considered when evaluating similar ore deposits for their economic value and mineral processing.

Keywords: fluorapatite, carbonatite, cerium anomaly, phosphate, REE-carbonates, critical metals, thorite, stetindite, rhabdophane.

INTRODUCTION

Rare earth elements (REE: La to Lu), a group of technologically critical metals (Hoatson et al. 2011, Atwood 2012, Chakhmouradian & Wall 2012, Linnen et al. 2014, Wall 2014), are mostly obtained from carbonatites or carbonatite-related ore deposits (Chakhmouradian & Zaitsev 2012, Verplanck et al. 2016). REE-rich carbonatites are commonly hydrothermally altered and overprinted, such that some degree of REE mobility is observed. REE can be redistributed in situ into different minerals (commonly LREE; Andrade et al. 1999, Ruberti et al. 2008, Doroshkevich et al. 2009, Cooper et al. 2015, Moore et al. 2015, Trofancenko et al. 2016, Andersen et al. 2017), or transported externally from the carbonatite to a secondary distal deposit (commonly HREE; Bühn 2008, Andersen et al. 2016, Bodeving et al. 2017, Broom-Fendley et al. 2017a, b). The REE are also considered hydrothermally mobile based on theoretical and experimental studies (e.g., Williams-Jones et al. 2012, Migdisov & Williams-Jones 2014, Migdisov et al. 2016). However, these theoretical and experimental studies represent simplified model systems that might miss geochemical complexities of natural systems. Fluorapatite is a typical mineral in carbonatites and commonly hosts significant amounts of REE (Chakhmouradian et al. 2017). Alteration of apatite releases crystal-bound REE into hydrothermal systems, making them available for transport by aqueous fluids. It is thus crucial to document the secondary alteration textures and qualitative geochemical signa-

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tures of igneous REE-rich fluorapatite to better understand the fate of REE in such hydrothermal systems. The mineral assemblage and composition of the secondary alteration can reveal whether the REE were redistributed or recrystallized in situ, leached and possibly deposited elsewhere, enriched or depleted by supergene processes, etc. Also, studies of secondary alteration chemistry can reveal differential mobilities of REE (e.g., LREE versus HREE). It is thus important to distinguish and recognize secondary alteration from primary mineralization, which may not be obvious.

Nolans Bore is a Mesoproterozoic P-REE-Th-U ore deposit in the Northern Territory, Australia, which is composed of centimeter- to meter-wide veins and dikes of fluorapatite. The Nolans project is being developed by Arafura Resources for production of REE and P. It was thought to have formed from phosphate-rich hydrothermal fluids or from evolved carbonatitic or alkali associated melts, but no cognate source has been identified (Huston et al. 2016). Instead, it has recently been reconsidered as an igneous cumulate that crystallized directly from carbonatitic melt (Anenburg & Mavrogenes 2018). In this scenario, Nolans Bore was initially composed of REE-rich fluorapatite (via britholite substitution: $\text{Ca}^{2+} + \text{P}^{5+} \rightarrow \text{REE}^{3+} + \text{Si}^{4+}$), which experienced several episodes of hydrothermal alteration (Schoneveld et al. 2015, Huston et al. 2016). This alteration transformed the fluorapatite to REE-poor fluorapatite with abundant inclusions and veins of REE and Th phosphate, silicate, and carbonate minerals. The alteration mostly redistributed REE and Th between minerals within Nolans Bore itself, and did not transport any of these elements into the wall rocks (Schoneveld et al. 2015).

Here we document the textures that resulted from alteration of an initially REE-rich fluorapatite at Nolans Bore. We also compare it to Hoidas Lake, a similar ore deposit in Saskatchewan, Canada, which contains nearly identical textures (Pandur et al. 2015, 2016).

Methods

Scanning electron imaging was conducted using a Hitachi S-4300 SE/N field emission-scanning electron microscope (FE-SEM) at the Centre for Advanced Microscopy, Australian National University (ANU). A Gatan MonoCL4 Elite cathodoluminescence (CL) system installed on an FEI Verios FE-SEM was used to generate color-CL images from three composite images acquired using red (620–750 nm), green (525–555 nm), and blue (390–485 nm) Edmund Optics filters.

X-ray element mapping was conducted using WDS (wavelength dispersive spectroscopy) via a Cameca SX100 electron probe microanalyzer (EPMA) at the Research School of Earth Sciences (RSES), ANU. Beam conditions for the EPMA were 15 kV accelerating voltage, 100 nA beam current, and a spot size of 1 μm. Mapping resolution was 256 by 192 pixels, with a pixel dwell time of 150 ms and 1 μm step size. A list of analyzed elements and their X-ray lines are given in Table 1. The raw count data were then plotted as matrices and phase maps using hexagonal binning, with hexagon greyscale intensities corresponding to the log-transform of the counts for that bin. Coordinates of raw data for each map were corrected for beam drift between subsequent passes, as only four elements could be analyzed simultaneously. Therefore, scatter plots of elements measured in different passes have more noise relative to those measured in a single pass. Ratios and absolute values of La and Ce counts (see La-Ce cell in the matrix) were used to construct the phase map. For details of the procedure and source code written in R, see the supplementary information (available from the Depository of Unpublished Data on the MAC website, document REE Redistribution Textures CM56_10.3749/canmin.1700038).

Three-dimensional X-ray micro computed tomography (XRCT) was conducted using a HeliScan MicroCT system at the X-ray Micro Computed Tomography lab (CTLab) at ANU to yield images at a resolution of approximately 2 μm (Latham et al. 2008, Myers et al. 2011, Varslot et al. 2011). A polychromatic X-ray beam with an energy of 120 kV and tube current of 50 μA was used. XRCT data for the sample was rendered using Drishti v2.3.2 (Limaye 2012). X-ray absorption scales with density and atomic number, and therefore a backscattered electron image (Fig. 1) is approximately equivalent to an XRCT image, such as Figure 2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Kα₁</td>
<td>TAP</td>
</tr>
<tr>
<td>P</td>
<td>Kα₁</td>
<td>PET</td>
</tr>
<tr>
<td>Ca</td>
<td>Kα₁</td>
<td>PET</td>
</tr>
<tr>
<td>Fe</td>
<td>Kα₁</td>
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</tr>
<tr>
<td>Y</td>
<td>Lα₂</td>
<td>TAP</td>
</tr>
<tr>
<td>La</td>
<td>Lα₂</td>
<td>LIF</td>
</tr>
<tr>
<td>Ce</td>
<td>Lα₂</td>
<td>LIF</td>
</tr>
<tr>
<td>Pr</td>
<td>Lβ₁</td>
<td>LIF</td>
</tr>
<tr>
<td>Nd</td>
<td>Lβ₁</td>
<td>LIF</td>
</tr>
<tr>
<td>Sm</td>
<td>Lβ₁</td>
<td>LIF</td>
</tr>
<tr>
<td>Th</td>
<td>Mβ₁</td>
<td>PET</td>
</tr>
</tbody>
</table>

TABLE 1. X-RAY EMISSION LINES AND WDS CRYSTALS USED FOR MAPPING, FOLLOWING THE GUIDELINES OF PYLE ET AL. (2002)
Fig. 1. Scanning electron images showing secondary alteration textures in fluorapatite from Nolans Bore. (A) Sample 153-35B: Coarse primary REE-rich fluorapatite with a horizontal fine oscillatory zoning pattern (medium grey) altered to REE-poor fluorapatite (dark grey) and REE-rich phases (white). Arrows denote symplectic alteration zones. (B) Sample 153-35B: Close-up of a symplectic alteration zone. (C) Sample 291-10A: Fluorapatite-hosted pore with REE-rich phases coating the interior walls. (D) Sample 157-4C: Close up of a boytroidal aggregate composed of nanometer-scale REE- and Th-rich minerals. (E) Sample 157-4C: An unknown bladed REE-carbonate mineral and an aggregate of REE-Th silicate and phosphate minerals. (F) Sample 157-4C: Fibrous carbonate, most likely calcioancylite-(Nd), in fluorapatite. Note growth at the vein–pore interface.
Trace elements were acquired using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) via an Agilent 7700 quadrupole mass spectrometer coupled to a Coherent CompexPro 193 nm ArF excimer laser using methods outlined by Eggins et al. (1998). NIST-610 was used as a primary calibration standard and BCR-2G as a secondary standard. Ablation time was 20 s on background (laser off) and 40–45 s of sample measurement (laser on). Data were reduced using Iolite 2.5 running on Igor Pro 6.37 (Woodhead et al. 2007, Paton et al. 2011). Full analytical details and results are freely available on Figshare at https://doi.org/10.6084/m9.figshare.5602720 or by request from the corresponding author.

**GEOLOGICAL SETTING**

The geological history of Nolans Bore has been described by Schoneveld et al. (2015) and Huston et al. (2016) and of the Aileron province, more...
generally, by Scrimgeour (2013). Therefore, only a
summary relevant to this work is given here. The
Nolans Bore fluorapatite-diopside-hyalophane veins
formed at ca. 1525 Ma in shear zones within
granulite-facies gneisses and schists (Huston et al.
2016) during the late stages of the Chewings Orogeny
2008, Anderson et al. 2013). Peak conditions were
estimated to have been ca. 850 °C and 7 kbar
(Morrissey et al. 2014). The Nolans Bore mineral
assemblage is consistent with formation by reaction
of a moderately magnesian carbonatite with the
silicate wall rocks at 750–850 °C (Anenburg &
Mavrogenes 2018). Nolans Bore was subsequently
affected by two metamorphic events: (1) the Redbank
Thrust Zone event at 1500–1400 Ma (Shaw & Black
1991) and (2) the Alice Springs Orogeny at 450–300
Ma (Haines et al. 2001, Buick et al. 2008). These
events resulted in regional shearing, hydrothermal
activity, and metasomatism (Shaw & Black 1991,
Hand & Sandiford 1999, Raimondo et al. 2011). Peak
conditions for the Alice Springs Orogeny are
estimated to have been ca. 550 °C and 5 kbar
(Raimondo et al. 2012). These regional metamorphic
events also affected Nolans Bore, resulting in the
REE redistribution textures discussed in this article.

Fig. 2. (continued)
An additional thermal event at ca. 1140 Ma may also have overprinted the primary igneous features at Nolans Bore (the Teapot event; Shaw & Black 1991, Biermeier et al. 2003).

**Petrography**

Nolans Bore is composed primarily of fluorapatite and its alteration products. We highly recommend that the reader view Supplementary Video 1 alongside this section for a better understanding of the three-dimensional textures discussed. Idealized compositions of the mineral phases are given in Table 2. Four different types of fluorapatite are present, distinguished by their compositions and textures:

**Primary igneous fluorapatite.** This type of fluorapatite is characterized by millimeter- to centimeter-scale euhedral to subhedral crystals with common oscillatory growth zones (Figs. 1A, 2B). This fluorapatite appears dull-green in SEM-CL (Fig. 3A) and is composed of strong narrow peaks at about 600 and 630 nm and a weaker, wider peak at 450 nm (Fig. 3C). Although primary fluorapatite should be yellow or bright green in the images (given the strong 600 nm peak), it is not (in this case) because the RGB filters used in the CL system do not transmit yellow light. Patches of finer-grained rounded fluorapatite aggregates (termed pill texture by Chakhmouradian et al. 2017) are also observed (Fig. 2B, H). The igneous fluorapatite contains ca. 5% total rare earth element oxides with a smooth LREE-enriched pattern (Schoneveld et al. 2015). Its REE-rich nature is evident by its brightness observed in BSE and XRCT images. The morphology of this fluorapatite is consistent with types 1 and 2 of Chakhmouradian et al. (2017), interpreted by them to crystallize from the carbonatic magma (also observed by Decrée et al. 2016).

**Primary hydrothermal fluorapatite.** This is commonly found between grains of igneous fluorapatite (as mesostasis), protruding into cavities, or as rare veins (Fig. 2A, D, E, G, H). It is commonly associated with allanite and rare ekanite. It is poorer in LREE than igneous fluorapatite due to its co-crystallization with allanite. Therefore, it appears darker in BSE and XRCT images.

**Symplectic fluorapatite.** Symplectic fluorapatite consists of a micrometer-scale vermicular britholite-group mineral hosted by fluorapatite (Figs. 1A, B, 2B, C, E). It appears as euhedral to subhedral alteration domains within igneous fluorapatite, with the BSE and XRCT brightness of the fluorapatite matrix matching that of the REE-rich adjacent unaltered primary fluorapatite. Supplementary video 2 and Figure 4 show the three-dimensional shape of one symplectite region.

**Secondary altered fluorapatite.** This type of fluorapatite is characterized by alteration of primary fluorapatite into REE-poor fluorapatite with abundant inclusions of REE and Th-rich phases, connected by a mesh texture of thin (0.5 to 2 μm) veins composed of the same phases (Figs. 1A, C–F, 2). The altered fluorapatite is REE-poor, appears dark in BSE and XRCT images, and appears bright blue to violet in SEM-CL (Fig. 2B). In contrast to igneous fluorapatite, altered fluorapatite has weaker peaks at 600 and 630 nm and the lower wavelength peak is shifted slightly towards 400 nm. The morphology of this fluorapatite is consistent with the hydrothermally altered type 3 fluorapatite discussed by Chakhmouradian et al. (2017). Our secondary fluorapatite is also texturally similar to altered fluorapatites from carbonatites (e.g., Narasayya & Sriramadas 1974, Nadeau et al. 2015, Feng et al. 2016, Prokopiev et al. 2017) and elsewhere (Pan et al. 1993, Li & Zhou 2015, Uher et al. 2015, Jonsson et al. 2016, Ondrējka et al. 2016, Zeng et al. 2016, Lupulescu et al. 2017). The two most common fluorapatite alteration products are REE-carbonates and Ce-Th-silicates. The REE-carbonates consist of parsite, galgenbergite, and calcioancylite (Schoneveld et al. 2015, Huston et al. 2016), with the dominant REE in each of these being La, Ce, or Nd, varying

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicates</td>
<td>Thorite, Stetindite, Allanite, Britholite, Calciotrorite, Thorogummite, Coffinite, Soddyite, Ekanite</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Apatite, Monazite, Rhabdophane</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Bastnásíte, Parisite, Synchysite, Ancylite, Calcioancylite, Galgenbergite</td>
</tr>
<tr>
<td>Oxides</td>
<td>Thorianite</td>
</tr>
</tbody>
</table>

**TABLE 2. MINERAL NAMES AND ENDMEMBER FORMULAE**

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**SUPPLEMENTARY MATERIAL**

- Supplementary Video 1
- Figure 1A
- Figure 1B
- Figure 1C
- Figure 1D
- Figure 1E
- Figure 1F
- Figure 1G
- Figure 1H
- Figure 2A
- Figure 2B
- Figure 2C
- Figure 2D
- Figure 2E
- Figure 2F
- Figure 2G
- Figure 2H

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**ACKNOWLEDGMENTS**

The authors would like to thank...

**REFERENCES**

Chakhmouradian et al. 2017. Our secondary fluorapatite is also texturally similar to altered fluorapatites from carbonatites (e.g., Narasayya & Sriramadas 1974, Nadeau et al. 2015, Feng et al. 2016, Prokopiev et al. 2017) and elsewhere (Pan et al. 1993, Li & Zhou 2015, Uher et al. 2015, Jonsson et al. 2016, Ondrējka et al. 2016, Zeng et al. 2016, Lupulescu et al. 2017). The two most common fluorapatite alteration products are REE-carbonates and Ce-Th-silicates. The REE-carbonates consist of parsite, galgenbergite, and calcioancylite (Schoneveld et al. 2015, Huston et al. 2016), with the dominant REE in each of these being La, Ce, or Nd, varying

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**APPENDIX A**

- Table 2: Mineral names and endmember formulae

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**APPENDIX B**

- Supplementary Figure 1
- Supplementary Figure 2
- Supplementary Figure 3
- Supplementary Figure 4

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**APPENDIX C**

- Supplementary Table 1
- Supplementary Table 2

---

**APPENDIX D**

- Supplementary Methods
- Supplementary Results
- Supplementary Discussion

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**APPENDIX E**

- Supplementary References
- Supplementary Acknowledgments
- Supplementary Funding Information
across growth zones in the same crystal (e.g., Schoneveld et al. 2015). The REE-carbonates are commonly boytroidal coatings on the walls of pores, exhibiting an irregular ring-shaped morphology in polished section (Fig. 1C, D). In other cases, they are euhedral, and often bladed (Fig. 1E). Calcioancylite-(Nd) occasionally appears as curved fibers or plates (Fig. 1F). The Th-Ce silicates include thorite, stetindite, and intermediate solid solutions, with several compositions present in the same vein or pore (Fig. 1E). Other less-common alteration phases include monazite, allanite, and thorianite (Schoneveld et al. 2015, Huston et al. 2016). The multiphase, hydrated, porous, and metamict nature of these phases commonly results in mixed analyses and low analytical totals when analyzed by EDS, suggesting the phases may in fact be—at least partially—rhabdophane (hydrated REE phosphate) instead of monazite, calciothorite, thorogummite (metamict and hydrated Th silicates), and hydrated REE carbonates such as hydroxylparisite. Some of the larger veins, occasionally up to several millimeters thick, are composed mostly of calcite, with minor REE-carbonates (occasionally present along calcite cleavage planes, Fig. 2D), hydrous Mg-silicates (talc or humite-group minerals), and quartz.

Nolans Bore is dominated by secondary altered fluorapatite. The distribution of the relict igneous fluorapatite seems random and does not correlate with depth or location within the deposit, other than being completely absent in the shallow supergene zones (Schoneveld et al. 2015). The degree of alteration seems to correlate with the initial REE content of the
fluorapatite, resulting in less-intense alteration of the hydrothermal primary fluorapatite. Likewise, igneous pill-textured fluorapatites are preferentially preserved due to lower REE contents relative to the coarser fluorapatites. Symplectic fluorapatite is extremely rare. The focus of this work is the transformation of primary igneous to symplectic and secondary fluorapatite. The formation of Nolans Bore and the primary fluorapatite will be discussed in a future publication.

**MINERAL CHEMISTRY**

Due to the small size of the alteration products, it was not possible to obtain meaningful compositions of each individual phase, and semi-quantitative compositions obtained by EDS are given in Table 3. Instead, we used two methods: qualitative major and minor element mapping by EPMA and trace element characterization of alteration regions by LA-ICP-MS.

**EPMA mapping**

Element correlation plots, derived from element maps, are shown in Figure 5. Additionally, a phase map using La-Ce abundance ratios was drawn to emphasize the textural association of each phase. The maps were measured with 1 μm steps, but the analyzed volume is larger due to electron scattering and secondary fluorescence (Reed 2006). Because the REE-rich phases are on the scale of sub-μm to a few μm, the arrays in the matrix show mixing lines between the most volumetrically dominant fluorapatite and the other less-abundant endmembers present in each field of view. Yttrium is used as a proxy for the HREE, which are below detection by EPMA. Figure 5A shows a symplectite-dominated field of view from sample 153-35B. Using the La-Ce plot, at least four distinct phases can be clearly distinguished and can also be seen in most of the other matrix cells. The most common phase is REE-poor fluorapatite (light green), clearly seen on the WDS maps, phase map, and matrix as the P-rich phase poor in all other elements. A second phase (dark green) appears to contain both LREE and HREE. This phase forms the REE-rich part of the symplectite. We suggest that this phase is britholite or fluorcalciobritholite (see Pekov et al. 2007 for the distinction between the two). A third phase (pink) contains Th and Ce, is Si-rich, and shows a preference for HREE, with some Nd and virtually no La. We interpret this phase to be a thorite–stetindite solid solution. The last phase (purple) is an LREE phase with exceptionally high La contents, some P and Si, but no Th and Ce. We are not aware of any mineral that qualitatively fits this composition and suspect it is a new, unknown mineral. Possibly, it is the britholite-cerite-like mineral reported by Holtstam & Andersson (2007) and synthesized in the hydrothermal experiments of Anenburg & Mavrogenes (2018). Even though some phases seem to be part of the symplectite, their composition is different from britholite. Only the thin elongated phases (e.g., top right of the maps) are britholite—thus forming part of the symplectite—whereas the similar looking but slightly larger rounded phases (e.g., bottom center), which lack REE other than Ce, are thorite–stetindite. Figure 5B shows a vein-dominated field of view from sample 157-5A. REE-poor fluorapatite is again the dominant phase (here in light cyan). Relict unaltered primary fluorapatite,

**TABLE 3. AVERAGES OF MINERAL COMPOSITIONS MEASURED BY EDS, GIVEN IN wt.%**

<table>
<thead>
<tr>
<th></th>
<th>Fluorapatite symplectite</th>
<th>Fluorapatite igneous</th>
<th>Fluorapatite altered</th>
<th>Stetindite</th>
<th>Thorite</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>4</td>
<td>8</td>
<td>7</td>
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<td>3</td>
</tr>
<tr>
<td>SiO₂</td>
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<td>2.64</td>
<td>26.33</td>
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</tr>
<tr>
<td>Al₂O₃</td>
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<td>bdl</td>
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<tr>
<td>MgO</td>
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<tr>
<td>CaO</td>
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<tr>
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<tr>
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<td>0.78</td>
<td>0.70</td>
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<td>bdl</td>
</tr>
<tr>
<td>Ce₂O₃⁷</td>
<td>4.50</td>
<td>2.37</td>
<td>2.73</td>
<td>42.19</td>
<td>1.23</td>
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<td>Nd₂O₃</td>
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<td>1.08</td>
<td>1.05</td>
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<tr>
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<td>P₂O₅</td>
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<tr>
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<tr>
<td>F</td>
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<tr>
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<tr>
<td>Total</td>
<td>98.81</td>
<td>99.06</td>
<td>99.44</td>
<td>79.91</td>
<td>81.74</td>
</tr>
</tbody>
</table>

bdl: below detection limit, n: number of analyses.
equally rich in all REE and Th, is light brown. The same color represents rare patches of REE-rich phospho-silicate, most likely britholite. A third phase (dark brown) is similar to the Ce-Th-silicates mentioned above, and here it occurs in veins in addition to the patches observed in sample 153-35B. The dark cyan veins are interpreted as two separate phases, i.e., the unknown LREE-P-Si phase described above and an...
Fig. 5. (continued) (B) Sample 157-5A.
LREE carbonate, with low P and Si in most points. The carbonate interpretation is also supported by the occurrence of REE-carbonates where the veins intersect pores (e.g., Fig. 1F).

**REE patterns and trace element compositions**

The rare earth element patterns presented here are similar to the results obtained by Schoneveld et al. (2015) and Huston et al. (2016), with a steep LREE-enriched slope (La₃/Pr₃ ≈ 500) and flattening in the lightest LREE (Fig. 6A). As observed in Table 3, the symplectites are the REE-richest domains and hydrothermal alteration mostly affects the LREE and the Ce anomaly (Fig. 6A). The addition of Mg and Al hinted at by the EDS analyses (Table 3) is clear in the LA-ICP-MS data, with a clear distinction between unaltered primary fluorapatite and hydrothermally altered fluorapatite (Fig. 6B). Symplectic fluorapatite plots well within the hydrothermally altered field. All fluorapatite analyses show a moderately negative Eu anomaly with a restricted range of 0.74–0.82. Symplectic fluorapatite analyses show a narrower range of 0.79–0.81, but are not significantly different from either the altered or unaltered fluorapatites. There is no Ce anomaly for the primary fluorapatite grains (Fig. 6C). On the other hand, hydrothermally altered fluorapatites show a variety of Ce anomalies (likely determined by the inclusion or lack of thorite or
stetindite inclusions in the analysis), whereas symplectic fluorapatites show a small positive Ce anomaly (Fig. 6A, C). This anomaly may be caused by loss of non-Ce LREE, rather than by addition of Ce (see discussion below).

**Discussion**

**Hydrothermally altered fluorapatite and the oxidation state of cerium**

The REE-bearing phase assemblage that forms during metasomatically induced alteration of fluorapatite (i.e., REE-carbonates and Ce-Th-silicates) is distinct from the symplectites (i.e., britholite). It occurs in veins and pore fillings that form by reduction in molar volume as the fluorapatite loses REE (Oberti et al. 2001). Also, La and Ce are decoupled in most of these phases. As La$^{3+}$ and Ce$^{3+}$ behave almost geochemically identically, the absence of Ce from La-rich phases and vice versa requires Ce to exist in the quadrivalent instead of the more common trivalent state. This is supported by the occurrence of Ce in Th-rich phases (e.g., thorite–stetindite), as Ce$^{4+}$ behaves in a similar way to Th$^{4+}$. Figure 7 shows the ionic radii of all elements in discussion for eightfold coordination. It demonstrates the preference in element uptake of each phase: small cations such as Ce$^{4+}$, Th, Y, and HREE are hosted by silicates in thorite–stetindite solid solutions (as observed by Cooper et al. 2015), and larger cations such as LREE (excluding Ce$^{4+}$) are hosted by carbonates and phosphates with variable silica contents.

The presence of a Ce$^{4+}$-rich silicate mineral suggests either high oxygen fugacities ($f_{O2}$) or low temperatures during the hydrothermal alteration. Although Ce$^{3+}$ stability persists into oxidizing conditions at low pH, this is not the case for Nolans Bore. Acidic conditions would cause breakdown of allanite to hydrous Fe-oxides and aluminosilicates (Meintzer & Mitchell 1988, Berger et al. 2008), but the allanite at Nolans Bore is unaltered. The concentration of Ce in zircon (a member of the same mineral group as thorite and stetindite; Förster 2006) is widely recognized as an oxybarometer (Trail et al. 2011, Burnham & Berry 2012, Smythe & Brenan 2016), but no zircon formed during hydothermal alteration at Nolans Bore. Trace-element data for coexisting thorite and zircon (Pettke et al. 2005) can be used to estimate the composition of a hypothetical zircon that would be in equilibrium with the thorite solid-solution observed at Nolans Bore (see supplementary appendix). Onuma-type parabolic fits (Onuma et al. 1968, Blundy & Wood 2003) to the REE (for $D_{Ce^{3+}}$) and to Hf, U, and Th (for $D_{Ce^{4+}}$) in magmatic zircon and thorite from their sample “Yankee 8.1 E” allow us to predict that $D_{Ce^{4+}}/D_{Ce^{3+}}$ is ca. 190,000 for zircon and

**Fig. 7.** Ionic radii versus valence of elements appearing in mineral phases appropriate to this study, with approximate element preference for each mineral phase. The arrowhead size represents the degree of preference a phase has for cations of that radius.
ca. 1200 for thorite. Hence the Ce anomaly (Ce/Ce*, where Ce* = $\sqrt[3]{\text{La} \times \text{Pr}}$ after normalizing all three elements to chondritic abundances) in zircon would be 150 times larger than Ce/Ce* in coexisting thorite. Although a quantitative analysis of the thorite–stetindite phase was not possible, the X-ray intensity (Fig. 5B) and EDS (Table 3) data suggest it has Ce/Ce* > 10 (and more probably >50), which would correspond to Ce/Ce* > 1500 in zircon. Such exceptional values are seldom encountered in zircon. For example, Ce/Ce* exceeded 1000 in one out of 656 samples in one survey of zircon from a range of rock types (Beloussova et al. 2002) and six out of 188 samples from a series of oxidized porphyry intrusions in which S was thought to occur primarily as sulfate (Ballard et al. 2002). Ce/Ce* for zircon increases with decreasing temperature, with increasing $f_{O_2}$, and with increasing alkali content in the precipitating fluid (Paul & Douglas 1965, Trail et al. 2011, Smythe & Brennan 2016). However, as Ce is predominantly incorporated in fluorapatite as Ce$^{3+}$, mass-balance considerations necessitate a source of oxygen for a Ce$^{4+}$-rich silicate to precipitate, and hence the presence of an oxidizing fluid is envisaged. By comparison to the data from natural samples containing magmatic zircon (Ballard et al. 2002), whose $f_{O_2}$ is poorly known but likely formed above the sulfide–sulfate transition (Klimm et al. 2012, Matjuschkin et al. 2016), the $f_{O_2}$ during thorite–stetindite precipitation was at least two orders of magnitude above FMQ, but likely much higher. Nolans Bore also contains several hundred ppm of U in addition to Th (Huston et al. 2016). It would be expected that U would be enriched to notable levels in the REE and Th minerals, but no U was detected. Instead, U is only observed in late veins in the hydrous minerals clinozoisite and soddyite (Huston et al. 2016), suggesting that the U was transported separately and more effectively than Th. This decoupling is only possible if U is hexavalent (Langmuir 1978), providing further evidence for oxidizing conditions. Moreover, Schoneveld et al. (2015) reported parsite and calcioanacylite with contrasting Ce-bearing and Ce-absent zones, suggesting oxidation-state fluctuation. This was most likely the latest alteration stage, occurring in or near the supergene zone. Similar boytroidal textures, breaking down of REE-rich fluorapatite, and Ce-La decoupling are known elsewhere from supergene zones (Lottermoser 1990, Andersen et al. 2017, Xu et al. 2017).

Several studies have explored the metasomatic alteration of REE-bearing apatite by fluids. Experimental studies over the past two decades demonstrate that alteration of REE-rich fluorapatite results in inclusions of monazite and xenotime. The inclusions commonly nucleate within the REE-rich fluorapatite, whereas fluorapatite in the immediate area surrounding the inclusions is depleted in REE (Wolf & London 1995, Harlov et al. 2002b, Harlov & Förster 2003, Harlov et al. 2005). Our secondary REE-rich phases exhibit identical textures (e.g., Fig. 1A), but they are not monazite or xenotime. This is probably because of the high activities of Si and CO$_2$ relative to P, stabilizing phases other than monazite or xenotime. Harlov et al. (2007b) showed that in metasomatism experiments containing both REE and Th, ThSiO$_4$ forms a separate phase from monazite. Thorite formed at low temperatures (300 °C) as aggregates of submicrometer grains with a striking resemblance to the boytroidal textures observed in our samples (Fig. 1D). Ce$^{4+}$ and Th$^{4+}$ have similar ionic radii and thorite and stetindite are isostructural, permitting solid solution. The low-temperature stability of Ce$^{4+}$ and the nanoscale morphology of this phase support our hypothesis that these features formed at similarly low temperatures. Huston et al. (2016) reported primary fluorapatite-hosted fluid inclusions with homogenization temperatures up to 400 °C. Given the rarity of primary fluorapatite, their lack of distinction between primary and secondary fluorapatite, and the secondary appearance of fluorapatite in their SEM imaging, we attribute their fluid-inclusion data to secondary alteration, which agrees with the temperature estimates suggested above. Hydrous Th-Ce-silicates and REE-carbonates with similar boytroidal, fibrous, or microfracture-filling textures are widely known elsewhere and are always interpreted as having formed via hydrothermal Th and REE redistribution at ca. 400 °C or lower (e.g., Ermolaeva et al. 2007, Seydoux-Guillaume et al. 2012, Saveljeva et al. 2016, Macdonald et al. 2017a, Macdonald et al. 2017b, Saveljeva et al. 2017).

Symplectite formation

Symplectites are vermicular intergrowths of two or more phases considered to form by subsolidus unmixing or replacement processes during cooling, metamorphism, and metasomatism, generally in the presence of limited amounts of fluid (see Gaidies et al. 2017, Spruzeniece et al. 2017, and references therein). Notable examples are myrmekite (metasomatic replacement of K-feldspar by sodic plagioclase and quartz), kelyphite (decompression-induced breakdown of garnet to anorthite, orthopyroxene, and spinel), muscovite-quartz, amphibole/clinoipyroxene-plagioclase, etc., particularly from metamorphic rocks where subsolidus reactions dominate. The formation of pearlite (x-Fe and Fe$_3$C) by slow cooling of carbon steel is another example from the field of metallurgy.
Primary fluorapatite contains REE and Y as well as Th as an intermediate fluorapatite–britholite solid solution. Figure 5A shows perfect mixing lines between REE-poor fluorapatite, REE-rich fluorapatite, and britholite. This suggests that the apatite–britholite symplectites formed during isochemical subsolidus exsolution (with respect to major elements), most likely along a solvus during slow cooling. Both LREE and HREE are present in the fluorapatite and britholite, as expected from the relatively flat partition coefficient pattern for the REE in carbonatitic fluorapatites (Brassinnes et al. 2005, Hammouda et al. 2010, Chakhmouradian et al. 2017).

The symplectites most likely formed at temperatures higher than the hydrothermally altered fluorapatite. Fluorapatite and britholite exhibit complete miscibility at high temperatures (Boyer 1997), but form two phases along a solvus at lower temperatures (Fig. 8; Anenburg & Mavrogenes 2018). This miscibility gap is poorly characterized, but there are plenty of hints as to its existence. For example, Betkowski et al. (2016) reported coexisting fluorapatite and britholite at 500 and 600 °C and 1 kbar. The CaO contents of the britholite increased from ~8.3 to ~13.8% with temperature, indicating a higher fluorapatite component in britholite. Similarly, Budzyń et al. (2017) reported increasing REE contents from ~30 to 40% in fluorapatite with increasing temperature from 450 to 750 °C. Anenburg & Mavrogrenes (2018) showed that an appreciable solid solution between fluorapatite and britholite is only observed at 700 °C and above, and two immiscible phases occur at lower temperatures. Additionally, Budzyń et al. (2011) synthesized coexisting fluorapatite and britholite at 450 and 500 °C. Symplectites in similar systems were reported by Betkowski et al. (2016) to occur at 600 °C, but were absent at 500 °C. Observations from natural rocks confirm the apatite–britholite miscibility gap forming during late stages of igneous activity below ca. 600 °C (Pekov et al. 2007, Macdonald et al. 2013, Uher et al. 2015, Zozulya et al. 2017), whereas the gap is not as clear at higher temperatures (Petrella et al. 2014). We thus suggest that the fluorapatite–britholite symplectites formed at or below 600 °C (Fig. 8). Unlike the clear hydrothermally induced formation of the altered apatite (e.g., veins and porosity), there is little petrographic evidence to support a hydrothermal origin for the symplectites. This is not surprising, as replacement of fluorapatite commonly occurs on the nano-scale, and the fluid pathways are only observed.

Fig. 8. A schematic phase diagram showing secondary processes in Nolans Bore fluorapatite. Igneous REE-rich fluorapatite is stable at high temperatures above a solvus. As the system cools, a solvus is encountered, causing exsolution of britholite from fluorapatite as symplectites. Further cooling reduces the amount of REE soluble in fluorapatite and oxidation of Ce$^{3+}$ to Ce$^{4+}$. The high CO$_2$ and Si activities stabilize carbonate and silicate minerals instead of phosphates as fluorapatite alteration phases.
using transmission electron microscopy (TEM) imaging (e.g., Harlov et al. 2005, Birski et al. 2018). There is, however, significant trace element evidence for symplectite formation by hydrothermal fluids. Magnesium and Al are incompatible during igneous crystallization of fluorapatite, evident by their low contents in primary fluorapatite (Fig. 6B). In contrast, hydrothermally altered fluorapatite grains are richer in Mg and Al. The symplectites are similarly rich in Mg and Al, suggesting introduction of these elements by fluids. These elements are probably not in the fluorapatite or britholite crystal structures, but more likely within unobserved nanoscale mineral phases or porosity. Hydrothermal alteration is also evident by the positive Ce anomalies observed for most symplectites (Fig. 6A, C). Figure 6D shows that Ce and Th contents of symplectic fluorapatite are similar to the Ce-Th-richest igneous fluorapatites. Had Ce been introduced to form the anomaly, one would expect Th to be introduced as well, causing both to be higher than observed. Instead, we suggest that LREE except Ce\(^{4+}\) were removed from the symplectite, explaining the La and Pr dip observed in Figure 6A. These LREE were likely deposited nearby in the non-stoichiometric britholite-cerite-like phase (Fig. 5A), which also has a strong negative Ce anomaly, consistent with the retention of Ce\(^{4+}\) in the symplectites. A similar phase formed in the experiments of Anenburg & Mavrogenes (2018) at temperatures of 550 to 650 °C, within our temperature estimate for symplectite formation.

**Comparison with Hoidas Lake**

The Hoidas Lake REE deposit in Saskatchewan, Canada (Pandur et al. 2014, 2015, 2016) shares many characteristics with Nolans Bore, in that it hosts REE mineralization in veins and dikes of fluorapatite with allanite, diopside, and hyalophane. Both ore deposits are Proterozoic in age and are hosted in granulite-facies metamorphic rocks. In both cases, ore deposition is believed to be from phosphate-rich hydrothermal fluids or evolved melts of carbonatite or alkali association, but no distinct source has been identified. The primary and secondary assemblages in Hoidas Lake are very similar to Nolans Bore and additionally contain hydroxybastnäsite, hydroxylsynchysite, and ancylite (Pandur et al. 2016). Pandur et al. (2016) also document REE-rich inclusions in fluorapatite and Ce-rich thorite, features commonly observed in the secondary assemblage at Nolans Bore.

Pandur et al. (2014, 2015, 2016) describe a previously unobserved texture involving fluorapatite and REE-rich inclusions with a graphic texture. This texture was mentioned briefly by Pandur et al. (2014), elaborated upon by Pandur et al. (2015), and was an essential part of a wider genetic model for Hoidas Lake by Pandur et al. (2016). The two models given by Pandur et al. (2015) involve magmatic processes: (1) crystallization from a boundary layer, similar to equivalent models in granite pegmatites, or (2) entrapment of two immiscible REE-rich melt fractions in the crystallizing fluorapatite. However, we interpret the texture described by Pandur et al. (2015) as two distinct textures: symplectites and hydrothermal alteration, similar to the secondary fluorapatite at Nolans Bore. Pandur et al. (2014) document fluid inclusions indicating aqueous alteration at temperatures up to 310 °C, which is consistent with our estimate of hydrothermal overprint at Nolans Bore. In the following sections, we examine each of the claims raised by Pandur et al. (2015) to support a magmatic origin for this texture, reinterpret it, and supplement this reinterpretation with observations from Nolans Bore.

*Is the texture igneous “graphic” or hydrothermally altered?*

Pandur et al. (2015) stated that the observed texture is reminiscent of the graphic texture of quartz and feldspar common in granitic pegmatites. These textures are explained as simultaneous growth of quartz and feldspar (Fenn 1986, London 2014, Xu et al. 2015). However, the rocks at Hoidas Lake and Nolans Bore are not granitic pegmatites and the minerals comprising this textural association are neither quartz nor feldspar. Furthermore, minerals intergrown in graphic textures commonly have straight or parallel crystal edges and a systematic spatial distribution (Lentz & Fowler 1992).

The interiors of the Hoidas Lake fluorapatite crystals contain fine euhedral intergrowths with a REE-rich phase, texturally identical to our symplectite, whereas the exterior resembles primary igneous fluorapatite overprinted by hydrothermally altered fluorapatite (compare Fig. 2B, C in Pandur et al. 2015 and Fig 11 in Pandur et al. 2016 with Fig. 1 of this study). Chemical evidence for hydrothermal alteration in Hoidas Lake is evident in Figure 4 of Pandur et al. (2015) and Figure 12 of Pandur et al. (2016), which show the same La-Ce decoupling observed at Nolans Bore. This is only possible if most of the Ce is quadrivalent, requiring low temperatures and oxidizing conditions. High Ce\(^{4+}/Ce^{3+}\) is unlikely at magmatic temperatures, as it requires unrealistically high \(O_2\) as described above. Specifically, one of their inclusions is a LREE-carbonate (with LREE, C, F, low Ce), and the other is likely to be a mixed carbonatostetindite (evident by the association of Ce and Si). A third inclusion reported by Pandur et al. (2016) is clearly stetindite. Harlov & Förster (2003) demon-
strated that metasomatic monazite after fluorapatite can form rims on the exterior of the original fluorapatite crystal, similar to Figure 2C in Pandur et al. (2015).

**Shortcomings of the boundary layer model**

One of the models suggested by Pandur et al. (2015) invokes a boundary layer melt between the bulk melt and the growing crystals: diffusion between the boundary layer and the bulk melt was kinetically limited, causing the boundary layer melt to become depleted in the components forming fluorapatite (e.g., Ca, P) and oversaturated in the other components (e.g., Si, REE). These oversaturated components crystallized, trapping the solid Si-REE phases as inclusions in the fluorapatite. This model is basically the same as the granitic pegmatite model summarized by London (2014). We claim that the boundary layer model is not applicable to Hoidas Lake or Nolans Bore. Silicon and REE together are compatible in fluorapatite via the britholite component coupled substitution $\text{Ca}^{2+} + \text{P}^{5+} \rightarrow \text{REE}^{3+} + \text{Si}^{4+}$ (Gorbachev et al. 2017, Anenburg & Mavrogenes 2018) at magmatic temperatures. The primary mineralization observed at Nolans Bore (and likely Hoidas Lake) is hosted by fluorapatite with a significant britholite component. This leads to a paradox: if the inclusions are representative of a boundary-layer melt enriched in elements that are incompatible in apatite (according to Pandur et al. 2015), why do they contain phases in which REE and Si are the major elements? Therefore, the boundary-layer melt model is untenable.

Boundary-layer melts exist in granitic pegmatites because these melts are extremely viscous. The combination of high Si contents and low temperatures result in low diffusion rates, causing the formation of a kinetically controlled graphic texture (London 2014). Furthermore, recent research shows that Li may promote the formation of graphic textures (Maneta & Baker 2014). However, neither Hoidas Lake nor Nolans Bore contain Li-bearing granitic pegmatites. They formed either from a phosphate-bearing carbonatite (Pandur et al. 2015, Anenburg & Mavrogenes 2018) or a hydrothermal fluid (Huston et al. 2016, Pandur et al. 2016). Although an alkali source has been suggested (Huston et al. 2016, Pandur et al. 2016), there is no clear evidence to support such a source, especially since both deposits are devoid of fenitization. Carbonatites are among the least viscous melts on Earth (Jones et al. 2013, Kono et al. 2014). Diffusion is so rapid that it is almost impossible to quench them to glass. Experiments involving carbonatites equilibrate in minutes to hours, as opposed to days to weeks for granitic compositions (e.g., Wyllie & Tuttle 1960, Wyllie et al. 1962, Biggar 1969, Cooper et al. 1975, Irving & Wyllie 1975, Lee & Wyllie 2000, Martin et al. 2013). A diffusion-controlled boundary layer melt can only exist during rapid crystallization of fluorapatite, but such fluorapatite crystals are commonly needle-like (Wyllie et al. 1962) and are not observed at Hoidas Lake or Nolans Bore. Therefore, a diffusion-controlled boundary-layer melt is unlikely to have existed in these melts.

**Are the inclusions immiscible melt droplets?**

Pandur et al. (2015) raised the possibility that the REE-rich solid inclusions are immiscible melt fractions. It is not clear whether their model suggests that the two compositions (Ce-Th-Si-rich and LREE-rich) are conjugate melts or if another melt, not represented in the inclusions, was present. Both cases suffer from the problem of temperature. Pure REE phosphates and silicates have melting points well above 1500 °C (Hikichi & Nomura 1987), and the incorporation of Th or Ce⁴⁺ will only make these phases more refractory. Fluorine does not act as a flux in this case, as it is an essential component of the solid REE-carbonate, and there is no other F-rich phase in the solid inclusions. Fluxing by water is also not possible because the solubility of REE in H₂O is very low, particularly in the presence of P and the absence of F or Cl (Pourtier et al. 2010, Tropper et al. 2011, 2013, Zhou et al. 2016, Mair et al. 2017), and these are hypothesized melt inclusions, not fluid inclusions. Paradoxically, these inclusions melt above the melting point of the host fluorapatite, precluding their origin as liquids trapped in crystallizing fluorapatite. The REE-carbonate observed in the inclusions by Pandur et al. (2015, 2016) is unlikely to represent a melt. In all cases where igneous REE-carbonates are observed in natural carbonatites, they are dissolved in a melt dominated by calcite or dolomite components. Also, REE-carbonates are rarely igneous in natural rocks and usually form in late hydrothermal stages of magmatic evolution. They crystallize at relatively low temperatures with an upper limit of about 800 °C, but commonly much lower than 500 °C (Jones & Wyllie 1986, Williams-Jones & Wood 1992, Doroshkevich & Ripp 2004, Ruberti et al. 2008, Gysi & Williams-Jones 2015, Verplanck et al. 2016, Broom-Fendley et al. 2017b, Liu & Hou 2017). Thus, their temperature range of formation is not compatible with the high temperature range for the REE-Th silicates and phosphates and we doubt the coexistence of immiscible liquids with these compositions (carbonates and phosphate-silicates). These hypothesized REE-carbonate-silicate-phosphate melts are not known elsewhere and their existence is suspect.
Order of fluorapatite crystallization

Pandur et al. (2016) reported four generations of fluorapatite: (1–2) ca. 1.5–2% REE oxides, inclusion-bearing, Ce-dominant; (3) ca. 5.5% REE oxides, inclusion-free, Ce-dominant; and (4) ca. 1% REE oxides, inclusion-bearing, Nd-dominant. Based on this order, Pandur et al. (2016) proposed a model of changing source fluid or melt conditions. We suggest that the order ought to be: REE-rich and inclusion-free first, followed by REE-poor and inclusion-bearing, as seen at Nolans Bore, where primary igneous assemblages are followed by secondary symplectites and hydrothermal alteration. The Nd-dominant fluorapatite crystallized last, indicating that Ce was oxidized and consequently sequestered in thorite and stetindite, forming negative Ce anomalies in this late-stage fluorapatite. Interestingly, the Hoidas Lake REE-rich and inclusion-free fluorapatite exhibits both morphologies observed at Nolans Bore: smaller pill-textured and large oscillatory zoned fluorapatite (e.g., bottom right and top of Fig. 2C in Pandur et al. 2015, respectively). A summary of the textures observed in Nolans Bore and Hoidas Lake and their interpretation is given in Figure 9.

Similar Symplectites from Other Localities

Symplectites after REE-rich fluorapatite are not unknown. Although the specific assemblage of fluorapatite–britholite in natural rocks has not yet been reported in the literature, other closely related textures are abundant. Examples include monazite-fluorite from the Oktiabrski Massif, Ukraine (Dumańska-Słowiak et al. 2012, Dumańska-Słowiak 2016) and monazite-fluorapatite from the Bohemian Massif, Czech Republic (Finger & Krenn 2007). Non-symplectic inclusions of REE minerals in replaced fluorapatite are also widely known (Harlov et al. 2002a, Ziemann et al. 2005, Harlov et al. 2007a, Torab & Lehmann 2007, Harlov 2011, Jonsson et al. 2016, Krneta et al. 2016). Specifically, Ali (2012) reports irregularly shaped REE phosphates in apatite. In all cases these textures were interpreted by the authors as metasomatic replacements of apatite, facilitated by hydrothermal alteration.

Conclusions and Implications

Primary REE-rich fluorapatite at Nolans Bore was altered in two stages. First, a high-\(T\) (~600 °C) exsolution process created a symplectite of REE-poor fluorapatite and britholite. Second, fluid infiltration at lower temperatures (<500 °C) generated a network of patches and veins composed of various Ce-Th-silicates and LREE-carbonates. Cerium was oxidized and consequently decoupled from the rest of the LREE. Almost identical textural and chemical features occur in the Hoidas Lake REE deposit, precluding the magmatic origin suggested by Pandur et al. (2015).

Although Nolans Bore experienced several stages of post-magmatic secondary alteration (described here
and by Schoneveld et al. 2015), the REE remained mostly contained within Nolans Bore itself and did not migrate into the wall rocks. The REE were sequestered in insoluble phases such as carbonates, silicates, and phosphates, regardless of the ligands that promote REE dissolution (e.g., Cl⁻). Thus, under the hydrothermal conditions prevailing at Nolans Bore during post-magmatic alteration, REE mobility was limited to the micrometer to millimeter scale (as was observed elsewhere, e.g., Förster 2000, Williams-Jones et al. 2012). The ore grade of many REE deposits was upgraded by hydrothermal alteration (Andersen et al. 2017). However, hydrothermal alteration did not upgrade the ore grade at Nolans Bore, suggesting it is not a significant mineralization process in Nolans-type apatite vein deposits (although the ore grade can be modified by supergene processes; see Schoneveld et al. 2015).

The observed variety of REE phases has important implications for theoretical studies of REE transport in hydrothermal fluids (e.g., Migdisov et al. 2016). REE transport and phase stability is commonly based on the stability of various ligands over a range of fluid pressure-temperature-compositions, but the solubility of complex REE silicates, phosphates, and fluorides is poorly constrained. Solid phases considered in these studies are usually only either well-known phases (monazite, xenotime, apatite, etc.), or phases that do not generally occur in nature (simple REE-fluorides). They do not take coexisting phosphates, carbonates, and silicates into consideration, and the potential implications of these assemblages on REE solubility. All insoluble phases must be considered when applying theoretical or simplified experimental studies of REE solubility to natural systems.

Carbonatite-hosted REE deposits are commonly rich in Ce and Th, both of which are undesirable to industry. Cerium is usually the most abundant REE, yet its economic value is low relative to other LREE such as Pr or Nd (2 US$/kg for CeO₂ versus 52 US$/kg and 42 US$/kg for Pr₆O₁₁ and Nd₂O₃, respectively). Thorium is radioactive and requires special handling procedures (Chen 2011, Haque et al. 2014, Zhu et al. 2015). Avoiding silicates when designing metal extraction processes could reduce Ce and Th quantities and remove uneconomic trace HREE impurities from an LREE concentrate (e.g., Abdel-Khalek 2000). The case of Nolans Bore demonstrates that primary magmatic mineralization and later redistribution of REE and Th during alteration events must be considered during ore deposit evaluation. Furthermore, fluid flow and chemistry—and consequently the particular phases present—might vary spatially throughout a deposit. The economic value of specific portions of a deposit can depend on this variability, even though the bulk composition is the same.

ACKNOWLEDGMENTS

This research is supported by an Australian Government Research Training Program (RTP) Scholarship and a Ringwood Scholarship from the Research School of Earth Sciences, Australian National University to Michael Anenburg. Financial support by Arafura Resources is gratefully acknowledged. Access to the facilities of the ACT Node of the Australian National Fabrication Facility (ANFF) and Centre for Advanced Microscopy (CAM), with funding through the Australian Microscopy and Microanalysis Research Facility (AMMRF), is gratefully acknowledged. We thank Daniel Harlov and an anonymous reviewer for their comments that allowed us to improve the manuscript.

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Chapter 3: Anenburg & Le Losq (I)—AmMin

The focus of the two previous chapters was apatite. Apatite is a challenging mineral to analyse. It can contain carbonate, which is not easily analysed by EPMA. Additionally, halogens can migrate during EPMA analysis. For example, F counts are known to increase and then decrease again during exposure to the beam. If the combination of analysis conditions (e.g., time on peak, crystal orientation, beam diameter, beam current) are such that F counts are acquired during increasing counts, this will lead to excess F. In some cases, the measured amount of F may exceed the permitted F contents according to stoichiometry. Therefore, recent studies which report excess F commonly cite this problem and disregard the higher F contents. However, sedimentary apatite ("francolite") is known to contain excess F charge balanced by carbonate. This suggests that this “analytical artefact” may indeed be real in carbonate and F rich systems.

As shown in the previous chapters, Nolans Bore was derived from a F-rich carbonatite. Any future study on the Nolans Bore apatite (by EPMA or other methods) will require correct analysis of carbonate and F in order to draw the correct conclusions. Before embarking on a Nolans Bore apatite study, I tested the problem of “excess F”. I contacted two authors of recently published papers, which reported excess F, asking them for their samples. One set of apatites came from a granite, whereas the other came from a REE-enriched carbonatite–alkaline complex. I reanalysed their apatites using an optimised EPMA analytical protocol to obtain reliable F contents, and using FTIR to obtain carbonate contents.

Our study of the granite-hosted apatite show that it is an end-member fluorapatite, and the excess F reported were in fact an analytical artefact. On the other hand, the carbonate-hosted apatite proved to contain real excess F, which was charge balanced by carbonate. The realisation that this can happen is important for any future studies on apatite from F–carbonate-rich settings, such as Nolans Bore.
**Excess fluorine in high-temperature carbonate-apatite**

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**Abstract**

End-member fluorapatite (Ca\(_5\)(PO\(_4\))\(_3\)F) contains 3.77 wt% F. Higher F contents are known from sedimentary fluorapatite, where the excess negative charge is balanced by substitution of phosphate for carbonate (Ca\(_5\)(PO\(_4\))\(_{3-x}\)(CO\(_3\))\(_x\)F\(_{1+x}\), commonly known as “francolite”). However, reports of excess F in high-temperature fluorapatite have often been dismissed as analytical artifacts because F counts have been known to increase on exposure to an electron beam. In other cases, excess F values are reported in studies that do not discuss the reasons or mechanisms for the additional F, the reality of which is therefore equivocal.

In this study we compare two groups of natural fluorapatite which were previously reported to contain excess F. We analyzed the two groups with an electron probe microanalyzer using a protocol that minimizes F migration. Carbonate contents were also measured using infrared spectroscopy by attenuated total reflection (ATR). The first group does not contain excess F nor carbonate, whereas the second group contains both excess F and carbonate in quantities consistent with the charge-balanced substitution (PO\(_4\))\(^{3-}\) = (CO\(_3\))\(^{2-}\) + F\(^-\).

These results indicate that excess F in fluorapatite is not limited to sedimentary settings and can occur in high-temperature environments (magmatic, metamorphic or metasomatic). It should not be dismissed as an analytical artifact, nor should it be reported without justification. As
accommodation of excess F requires high activities of both F and CO₂, this can potentially be used as an indicator for F–CO₂ rich systems which may be ore-bearing, such as carbonatites and related systems. Additionally, the possibility of simultaneous incorporation of \((CO_3)^{2-} + F^-\) and \(OH^-\) may lead to 3.77 wt% F, making it easy to overlook the presence of volatiles in apatite, and hampering thermodynamic modelling of partitioning of volatiles into apatite. High CO₂ activities are not unusual in geological environments, suggesting that significant incorporation of carbonate into apatite might be more common than previously thought.

**Introduction**

The composition of end-member fluorapatite is \(Ca_5(PO_4)_3F\) with Ca, P and F occupying the M, Z and X sites, respectively (Hughes and Rakovan, 2002; Hughes and Rakovan, 2015; Pan and Fleet, 2002). However, natural apatites are rarely of end-composition. This makes their full chemical characterization challenging as they contain an element mix that requires several methods to fully analyze. Heavy cations (≥ Na) are easily and routinely analyzed by microbeam energy-dispersive (EDS) or wavelength-dispersive (WDS) X-ray spectroscopy. Determining the concentrations of lighter elements and anions is less straightforward. The accuracy and precision of halogen analysis depend on crystal orientation and beam parameters, and do not always behave in a predictable way (Goldoff et al., 2012; Stock et al., 2015; Stormer et al., 1993).

Accurate analysis of F by EPMA could also be hampered by interferences from other elements (Potts and Tindle, 1989; Raudsepp, 1995). Hydrogen (as OH⁻) and carbonate \((CO_3)^{2-}\) can be analyzed using FTIR (Antonakos et al., 2007; Beasley et al., 2014; Clark et al., 2016; Fleet and Liu, 2007; Marks et al., 2012; Rehman and Bonfield, 1997; Tacker, 2004; Tacker, 2008; Wang et al., 2011) or SIMS (Barnes et al., 2013; Boyce et al., 2012; Marks et al., 2012; McCubbin et al., 2010a; McCubbin et al., 2010b; Riker et al., 2018), which require well characterized matrix-
matched reference materials and may not be available. Therefore, OH has been inferred from F and Cl contents assuming full X-site occupancy (Gross et al., 2013; Howarth et al., 2016; McCubbin et al., 2011; McCubbin et al., 2010a; Patiño Douce et al., 2011; Piccoli and Candela, 1994; Webster et al., 2009), and carbonate is usually assumed to be absent (Ketcham, 2015; Piccoli and Candela, 2002). This is further complicated by the possibility of carbonate occupying either the Z site (type B) or the X site (type A), and by the possibility of “oxyapatite”, various oxidation states of S, or vacancy components (Kim et al., 2017; McCubbin and Ustunisik, 2018; Pan and Fleet, 2002; Rabone and de Leeuw, 2007; Schettler et al., 2011; Sommerauer and Katz-Lehnert, 1985).

Nevertheless, the light element contents of apatite are commonly used to infer the apatite growth conditions (Harlov, 2015), with applications ranging from determining the volatile contents of extra-terrestrial melts (Barrett et al., 2016; Boyce et al., 2014; McCubbin and Jones, 2015; Robinson and Taylor, 2014) to using apatite as an indicator mineral for provenancing and ore deposit exploration (Teiber et al., 2015; Webster and Piccoli, 2015). Of particular interest are apatites with excess F, i.e. containing greater than 1 apfu F (equivalent to > 3.77 wt% for end-member fluorapatite). This is commonly observed in “francolite”—sedimentary carbonate-bearing fluorapatite—and was suggested to result from the charge-balanced substitution (PO$_4$)$^{3-}$ = (CO$_3$)$^{2-}$ + F$, but the precise crystallographic location of the additional F is still debated (Bacquet et al., 1981; Jahnke, 1984; Knudsen and Gunter, 2002; Leventouri et al., 2000; Mason et al., 2009; McClellan, 1980; McClellan and Lehr, 1969; Nathan, 1996; Rabone and de Leeuw, 2007; Regnier and Berner, 1996; Regnier et al., 1994; Smith and Lehr, 1966; Yi et al., 2013).

Accurate analysis of F is challenging because F counts increase with time on exposure to an electron beam, resulting in spurious excess F. Thus, there might be an ambiguity whether any
measured excess F is real or is merely an analytical artifact. To mitigate this problem, analysis protocols were suggested which recommended defocusing of the electron beam diameter to at least 10 µm, using a beam current of ≤10 nA, orienting the c-axis perpendicular to the beam if possible, and analyzing the F peak first and only for a short time (Goldoff et al., 2012; Stock et al., 2015; Stormer et al., 1993). Even with these protocols, beam exposure prior to analysis can cause F-migration, for example during cathodoluminescence imaging or simply during BSE imaging while programming points for WDS analysis.

In the recent literature, excess F in apatite has been treated according to two schools of thought: either as an analytical artifact, or as a real effect without explaining how apatite accommodates the excess F. Other studies simply reported > 3.77 wt% F, without any mention of the values being suspect. In this study, we analyzed apatites from two recent studies that reported excess F in apatite. The first study described apatites from the Cretaceous Xiuwacu granite pluton, Sanjiang, China (Pan et al., 2016, hereafter referred to as CXWC, Fig. 1a). The second study described apatites from carbonate veins that cross-cut the Ditrău alkaline complex, Romania (Honour et al., 2018, hereafter referred to as DL14, Fig. 1b). The analysis protocols of both studies appear to follow best practices for apatite analysis (Table 1), and our goals were to test (1) whether the high F contents are reproducible and indeed real, and (2) whether the excess F is charge balanced by carbonate.

**Methods**

The CXWC apatites were received as individual separated grains, whereas the DL14 apatites were still embedded in the carbonate veins (Fig. 1). Both samples were mounted in 1-inch epoxy mounts, and polished with SiC paper followed by diamond paste down to a final grade 0.25 µm. The DL14 apatites were first identified using EDS in order to familiarize ourselves with their
shape and location within the sample. This sample was then polished again to remove the beam-exposed layer.

Quantitative WDS analysis was conducted on a JEOL 8530F Plus field emission EPMA at the Centre for Advanced Microscopy, Australian National University. Analysis conditions were an accelerating voltage of 15 kV, beam diameter of 10 µm, and a beam current of 10 nA. Fluorine, Cl and Na were analyzed first for a duration of 15 seconds. Major elements (Ca and P) were analyzed for 20 seconds, and other elements were analyzed for at least 30 seconds. Reference materials were fluorite (F, Kα, LDE), albite (Na, Kα, TAP), periclase (Mg, Kα, TAP), sanidine (Si, Kα, TAP), apatite (P, Kα, PET), tugtupite (Cl, Kα, PET), diopside (Ca, Kα, PET), celestine (Sr, Lα, PET, and S, Kα, PET), rhodonite (Mn, Kα, LIF), and metaphosphates for the REE (Y, La, PET; La & Ce, Lα, LIF; Nd, Lβ, LIF). We used diopside instead of apatite for Ca because Ca-Kα counts are known to slightly increase with time on unoriented apatite (Stormer et al., 1993). All reference materials were sourced from Astimex. The samples were not exposed to an electron beam prior to analysis, and points were programmed solely using the optical image provided by the installed camera, with the Faraday cup blocking the beam path. Using these analytical conditions, F migration is limited, just above the background noise under worst-case-scenario crystal orientation (c-axis parallel to the beam, Goldoff et al., 2012), and negligible in any other orientations. This is confirmed by the lack of any consistent increase in F counts during our analytical sessions (Fig. 2).

The samples were polished again following WDS analysis with 1 and 0.25 µm diamond paste for five minutes each, in order to obtain cathodoluminescence (CL) and backscattered electron (BSE) images showing the WDS spots in relation to the internal structure of the apatite. Imaging was conducted using a Robinson CL detector installed on a Hitachi 4300 SE/N Schottky field
emission scanning electron microscope. Imaging conditions were 15 kV and 3.4 nA. Images were acquired over 200 seconds (Figs. 1a, 1d–1f), or 400 seconds (Figs. 1b, 1c).

To calculate apatite stoichiometry, we modified the method from Ketcham (2015), which assumes all cations are analyzed and recalculation is done using 25 negative charges. In the present case, carbonate could not be analyzed on the EPMA and we assumed only full occupancy of the M site and normalized all monovalent, divalent and trivalent cations to 5. Using this calculation, the DL14 apatites contained an excess of Na+Si over REE of 0.03–0.04 apfu, suggesting the presence of unanalyzed REE. Therefore, they were recalculated with M-site normalization to 4.96 cations.

To measure the infrared absorbance of the samples, we used infrared spectroscopy by attenuated total reflectance (ATR, Bruno, 1999; Fahrenfort, 1961). It allows practical measurements of infrared signals from single-polished samples, with ~30 µm spatial resolution, and is generally considered reliable for apatite (Beasley et al., 2014). It also avoids the problem of fluorescence, common for Raman spectroscopy on apatite and observed for the samples reported in this study. ATR spectra of the apatite crystals were acquired with a Bruker Hyperion IR microscope equipped with a liquid nitrogen-cooled MCT detector and wire-grid polarizer, and coupled to a Bruker Tensor IR spectrometer with a Globar infrared source. A Ge crystal was used in a measurement chamber continuously purged with dry air in order to minimize atmospheric contamination of the infrared signal. Measurements were performed using 128 scans and a spectral resolution of 4 cm\(^{-1}\).

Carbonate content quantification from the ATR spectra was done using the method of Grunenwald et al. (2014). It relies on the linear relationship between wt% CO\(_3\) and the area ratio of the \(\nu_3\) CO\(_3\) and \(\nu_1 + \nu_3\) PO\(_4\) bands. Therefore, it does not require knowledge of the sample
thickness or orientation. We measured the area of the $\nu_3$ CO$_3$ peak between 1330 and 1530 cm$^{-1}$ (a$_{CO3}$), and that of the $\nu_1 + \nu_3$ PO$_4$ peak between 900 and 1230 cm$^{-1}$ (a$_{PO4}$). Then, the carbonate concentration was calculated from the area ratio a$_{CO3}$/a$_{PO4}$ using the equation provided in Grunenwald et al. (2014). The absolute error of this technique is estimated as $\pm$0.5 wt% CO$_3$ (Grunenwald et al., 2014).

All raw data files and data analysis scripts written in R and Python are available in the online supplementary files.

**Results and discussion**

DL14 apatite grain size range from ~150 $\mu$m to over 1 mm (Figs. 1a–1c). They exhibit fine scale oscillatory zoning, most obvious in CL imaging. The apatites have numerous secondary veins and other late stage alteration features, which although visible in BSE, are clearly discerned in CL imaging. The altered zones commonly contain monazite–cheralite solid solution grains of up to 2 $\mu$m across. These features indicate hydrothermal REE mobilization characteristic for REE-rich apatites (Anenburg et al., 2018; Chakhmouradian et al., 2017).

CXWC apatite crystal fragments are 100–150 $\mu$m across and contain rare inclusions of muscovite and zircon (Figs. 1d–1f). Occasional sub-micrometer inclusions could not be identified, but we suspect these to be late-stage REE-minerals (Birski et al., 2018; Harlov, 2015; Harlov et al., 2005). The apatites exhibit zoning patterns free of alteration, consistent with the textures reported by Pan et al. (2016).

Even though the samples were polished again after WDS analysis, it was possible to identify the analyzed spots by the non-luminescing 10 $\mu$m circles observed in the CL image (e.g., Fig. 1a).
All spots are located within the unaltered apatite, demonstrating the usefulness of the optical image when programming points.

Fluorine contents measured in this study are given in Figure 2. All analyses of DL14 but one plot well above the 3.77 wt% line, showing clear evidence for excess F. In contrast, all analyses of CXWC plot below the 3.77 wt% line, or within error of 3.77 wt%. Chlorine was always below or within error of the detection limit for both DL14 and CXWC (~100 ppm).

A plot of F anions versus Z-site cations is given in Figure 3. Analyses of CXWC plot close to the hypothetical endmember fluorapatite, whereas the DL14 analyses plot at higher F anions (as expected, e.g. Fig. 3), and lower Z-site cations. Previous EPMA work on synthetic endmember apatites shows deviations of up to 0.03 apfu from ideal stoichiometry (Goldoff et al., 2012). Therefore, we consider the large spread of up to 0.05 apfu for both F and P+Si in our apatites of natural composition as.

ATR spectra show systematic signals assigned to $\nu_1 + \nu_3$ PO$_4$ vibrations between 900 and 1230 cm$^{-1}$ in all crystals (Fig. 4, Antonakos et al., 2007; Clark et al., 2016 and references therein for assignment details). Overtones of phosphate vibrations are visible in all spectra between 1900 and 2200 cm$^{-1}$. In some crystals, we observe a small signal near 3540 cm$^{-1}$, which can be assigned to stretching of OH groups in the apatite structure (Wang et al., 2011 and references therein). However, a significant difference is observed between the CXWC and DL14 apatite ATR spectra. While the first show noisy peaks in the 1250-1500 cm$^{-1}$ range, the latter display two peaks at ~1429 and ~1456 cm$^{-1}$, with a small shoulder near 1510 cm$^{-1}$. According to Tacker (2008), the two main peaks at ~1429 and ~1456 cm$^{-1}$ can be assigned to $\nu_3$ vibrations of CO$_3$ cations substituting for PO$_4$ (B-type substitution), and the shoulder at ~1510 cm$^{-1}$ to $\nu_3$ vibrations of CO$_3$ cations substituting OH groups (A-type substitution). Slight variations in peak
positions can originate from the existence of two type A and two type B substitutions (Tacker, 2008). From the present data, CO$_3$ primarily substitutes for PO$_4$ (type-B) in the DL14 apatite crystals, with negligible CO$_3$ substitution for OH (type-A). This is consistent with experimental work showing type-B to be preferred when halogens are present, whereas type-A occurs in halogen-free hydroxylapatite (Riker et al., 2018).

Carbonate contents estimated by the area-ratio method of Grunenwald et al. (2014) are given in Table 2. Carbonate values for DL14 (0.15±0.02 apfu) are consistent with the upper range of F contents (right side of Fig. 4), providing strong evidence that carbonate and F are introduced together as part of the exchange reaction PO$_4^{3-}$ = CO$_3^{2-}$ + F. On the other hand, the low values (0.021±0.007 apfu) obtained for CXWC, which are not well resolved from the background noise (Fig. 5), are not sufficient to explain any excess F in the crystal structure by the “francolite” substitution. It is possible to accommodate carbonate in apatite together with Na via the reaction Ca$^{2+}$ + PO$_4^{3-}$ = Na$^+$ + CO$_3^{2-}$, most commonly observed in hydroxylapatite (Fleet and Liu, 2007; Rabone and de Leeuw, 2007). CXWC apatite has negligible Na at 0.008±0.003 apfu, but DL14 contains 0.029±0.010 apfu Na. Sodium can also charge balance REE via 2Ca$^{2+}$ = Na$^+$ + REE$^{3+}$, which might be relevant for the DL14 apatites as they are REE-rich. However, the Ca$^{2+}$ + PO$_4^{3-}$ = Na$^+$ + CO$_3^{2-}$ reaction would shift the data in Figure 3 downwards below the exchange line, but the points plot above the line, indicating it does not occur in the apatite crystals studied here.

From the ATR spectra, OH stretching signals are just above the noise level for CXWC, but are clearly detectable for DL14 (Fig. 4). While this indicates the presence of a small amount of hydroxyl groups in DL14, to the knowledge of the authors, there is no calibration for OH quantification from ATR spectra of apatite. A rough estimate can be provided by comparing the OH signal to that of the carbonate peaks. In DL14, they correspond to ~1.7 wt% CO$_3^{2-}$, such that
the small OH signals may correspond to OH contents of ~1000 ppm, equivalent to about 0.02 apfu. Whilst negligible when calculating the “francolite” component, this shows this exchange reaction is possible even when the X site is not completely filled by F.

A comparison of our analyses versus the previously reported analyses for CXWC and DL14 is given in Figure 5. For sample D14, the present values mostly overlap with those reported by Honour et al. (2018), with our mode being higher by about 0.1 wt%. Taken together with the measurement uncertainty, the present values are indistinguishable from those of Honour et al. (2018). Interestingly, these authors were skeptical of their observed values ("...the excess F is likely due to electron beam induced F migration", Honour et al., 2018) and suggested that low totals resulted from unanalyzed heavy REE. According to the present study, their F data were correct and the low totals resulted primarily from unanalyzed carbonate. On the other hand, values reported for CXWC by Pan et al. (2016) have a wide spread from 3 wt% to as much as 5 wt%, with the mean just below 4 wt%. In contrast, our values for CXWC show a tight cluster at ~3.7 wt%. This probably results from their previous imaging of the apatites by CL, and beam exposure for various durations.

Carbonate-bearing high-temperatures apatites were previously described from experimental studies (Fleet and Liu, 2004; Fleet et al., 2004; Riker et al., 2018), but these studies did not address the issue of excess F. Natural carbonate-apatites from high-temperature environments are rarely reported. Prins (1973) and Santos and Clayton (1995) measured up to 1.0 wt% CO$_2$ in apatites from igneous alkaline complexes, but these were mixed hydroxyfluorapatites without excess F. In contrast, Binder and Troll (1989) measured excess F using wet chemistry methods in apatites from a variety of igneous and metamorphic rocks, but they did not measure any M-site
cations nor Si, which does not allow determination of the exchange mechanism facilitating the excess F.

**Implications**

Our study provides compelling evidence that excess F in high-temperature apatite can be accommodated by a charge-balanced substitution with carbonate: $\text{PO}_4^{3-} = \text{CO}_3^{2-} + \text{F}^-$ This means that any measured excess F cannot be simply dismissed as an analytical artifact, if the appropriate analysis protocols have been used. The corollary is that excess F should not be reported without supporting evidence showing the presence of carbonate. While some studies claim that cathodoluminescence imaging of apatite does not necessarily lead to F migration (e.g. Xu et al., 2010), we would argue that this should not be left to doubt or luck. Apatite compositions should only be determined using microbeam techniques with no previous beam exposure, including simple BSE imaging while programming points, and the optical image should be used for navigation instead. It is possible to image the apatites post-EPMA analysis to determine the textural association of the analyzed spots to avoid beam exposure. For example, combined SE/BSE imaging can locate the beam-damaged carbon coat layer. Additionally, cathodoluminescence imaging will reveal previously-analyzed spots as “dark holes”, which are easily seen in the background of generally strongly luminescent apatite, because prolonged electron beam exposure strongly quenches CL emissions (e.g. Fig. 1a and Wang et al., 2014). Our experience shows that a 5-minute polish with 1 µm diamond paste is not sufficient to remove any beam damaged layer.

We only detected significant amounts of carbonate in DL14, which contains apatite grains in a calcite matrix. The granite-hosted apatite from CXWC did not contain any carbonate. This may lead to the assumption that the presence of carbonate minerals or carbonatitic melt is required,
but this is not the case. While bulk CO$_2$ contents allow for more carbonate to be partitioned into apatite, CO$_2$ activity in the system is the driving force for this substitution. CO$_2$ solubility in silicate melts is pressure dependent and can reach values in the wt% range (Papale et al., 2006).

A rising melt would easily reach CO$_2$ saturation, yielding exsolution of a gas phase with CO$_2$ activity of ~1. As other volatiles (e.g. H$_2$O, SO$_2$) degas at lower pressures than CO$_2$ (Moretti et al., 2003; Witham et al., 2012), there is an interval in which the gas phase in equilibrium with the silicate melt is essentially pure CO$_2$, allowing maximum incorporation of the “francolite” component in apatite, given that the F/OH activity ratio is sufficiently high (although not necessary, cf. Riker et al., 2018). This effect is magnified for alkaline silicate melts which can dissolve greater amounts of CO$_2$, and are also commonly F-rich (such as the Ditrău complex, which the DL14 apatites were obtained from). Additionally, many high-grade metamorphic rocks contain CO$_2$-rich fluid inclusions, indicating high CO$_2$ activities during their formation (Frezzotti and Touret, 2014; Touret and Huizenga, 2011). Therefore, magmatic and metamorphic apatites are likely to contain some amount of carbonate, and possibly excess F.

The possibility of X-site F$^-$ exchanging with OH$^-$—resulting in a non end-member fluorapatite— together with the (CO$_3$)$_2^-$ + F$^-$ component may result in a seemingly end-member fluorapatite, when in fact it has F$^-$, (CO$_3$)$_2^-$, and OH$^-$, all at the same time (e.g. the simultaneous F deficiency and excess described by De Toledo et al., 2004; McArthur, 1990; McClellan, 1980). This complicates thermodynamic models that assume exchange of F$^-$, Cl$^-$ and OH$^-$ on a fully occupied X-site (Boyce et al., 2014; Brenan, 1993; Doherty et al., 2014; Kusebauch et al., 2015; Li and Hermann, 2015; 2017; Mathez and Webster, 2005; Patiño Douce et al., 2011; Piccoli and Candela, 1994; Tacker and Stormer, 1989), and requires caution when using apatite compositions to estimate volatile contents during crystallization.
On a more positive note, the DL14 apatites originated from mineralized veins, and generally carbonate and F-rich environments (such as carbonatites or peralkaline rocks) are prospective for economic mineralization. Apatite is already being used as an indicator for mineral exploration (Bruand et al., 2017; Mao et al., 2016), and the detection of carbonate (ideally coupled with excess F) can be added to the apatite toolbox to assist in the discovery of new ore deposits.

Acknowledgements

MA and CLL acknowledge funding from Australian Research Council grant FL130100066 to Hugh O’Neill. This work was funded by Australian Government Research Training Program (RTP) and a Ringwood Scholarship to MA. We acknowledge the facilities, and the scientific and technical assistance of Hua Chen and Jeff Chen at Microscopy Australia, Centre for Advanced Microscopy, ANU.

We thank Victoria Honour (University of Cambridge), Richard Shaw (British Geological Survey), Li-chuan Pan and Rui-zhong Hu (Institute of Geochemistry, Chinese Academy of Sciences) for so generously sharing their samples for this study. We thank Hugh O’Neill for constructive comments.

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Figure captions

Figure 1. SEM images of apatites from samples (a–c) DL14, and (d–f) CXWC. Each panel contains a CL image (AUX1) and a BSE image (BSE1). Horizontal streaking in (a) and (b) results from the slow CL response of calcite to the electron beam (see Anenburg et al., 2018 for details).

Figure 2. X-ray counts on the F-Kα line peak as a function of time for sample DL14. Several minutes between each analysis were trimmed to improve readability (see the supplementary files for details).

Figure 3. Fluorine contents measured in apatites from DL14 (open circles) and CXWC (filled circles). Error bars indicate instrumental uncertainty.

Figure 4. Z-site cations (Si and P) versus F for apatites from DL14 (open black circles for 4.96 M-site cations, and small grey circles for 5 M-site cations) and CXWC (filled circles). Grey diamond indicates a hypothetical endmember fluorapatite, with the arrow indicating the “francolite” exchange vector.
Figure 5. Representative ATR spectra for the DL14 (top three spectra) and CXWC (bottom three spectra) apatites. There is significant vertical exaggeration, causing the phosphate peaks at ~1000 cm\(^{-1}\) to plot above the scale of the figure. Grey vertical lines indicate OH\(^-\) and CO\(_3^{2-}\) vibrations.

Figure 6. Kernel density plots of F contents, comparing the values obtained in this study with previously reported values. P16–Pan et al. (2016), H18–Honour et al. (2018).

Tables

Table 1. Details of the apatite samples used in this study and their analysis protocols from the original studies.

<table>
<thead>
<tr>
<th>Locality (sample name)</th>
<th>Time on F peak (sec)</th>
<th>Accelerating voltage (kV)</th>
<th>Beam diameter (µm)</th>
<th>Beam current (nA)</th>
<th>Prior beam exposure</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cretaceous Xiuwacu pluton (CXWC13)</td>
<td>Not detailed</td>
<td>25</td>
<td>10</td>
<td>10</td>
<td>Cathodoluminescence</td>
<td>Pan et al. (2016)</td>
</tr>
<tr>
<td>Carbonate veins in Ditrău alkaline complex (VH-DL-</td>
<td>20</td>
<td>20</td>
<td>12</td>
<td>10</td>
<td>Not detailed</td>
<td>Honour et al. (2018)</td>
</tr>
</tbody>
</table>
Table 2. Carbonate contents measured by ATR and the corresponding C cation contents.

<table>
<thead>
<tr>
<th></th>
<th>CXWC (n=6)</th>
<th></th>
<th>DL14 (n=5)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3^{2-}$ (wt%)</td>
<td>C (apfu)</td>
<td>CO$_3^{2-}$ (wt%)</td>
<td>C (apfu)</td>
<td></td>
</tr>
<tr>
<td>0.32</td>
<td>0.028</td>
<td>2.02</td>
<td>0.176</td>
<td></td>
</tr>
<tr>
<td>0.28</td>
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<td>1.58</td>
<td>0.137</td>
<td></td>
</tr>
<tr>
<td>0.19</td>
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<td>1.53</td>
<td>0.133</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>0.013</td>
<td>1.72</td>
<td>0.149</td>
<td></td>
</tr>
<tr>
<td>0.17</td>
<td>0.015</td>
<td>1.78</td>
<td>0.155</td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>0.028</td>
<td></td>
<td></td>
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<tr>
<td>0.24±0.08</td>
<td>0.021±0.007</td>
<td>1.73±0.19</td>
<td>0.15±0.02</td>
<td></td>
</tr>
</tbody>
</table>
fig. 2

Counts

0 50 100 150 250 300 350 400

Time (sec)

fig. 3

F wt%

DL14

CXWC

fig. 4

Si+P (apfu)

Ca\(_5\)(PO\(_4\))\(_3\)F\(^{4-}\) \(\rightarrow\) Ca\(_5\)(PO\(_4\))\(_3\)F\(^{3-}\) + CO\(_3\)\(^{2-}\) + F\(^-\)

fig. 5

H\(_2\)O\(^+\) \(\rightarrow\) OH\(^-\) + CO\(_3\)\(^{2-}\)

fig. 6

DL14

CXWC

this study

H18

P16

Density

F wt%
Chapter 4: Anenburg—CrystEngComm

The ability of carbonatites to crystallise Re compounds (in particular rheniite: rhenium sulfide) has been explored in this study. Rhenium is another critical metal, which is commonly used in high performance jet engine alloys. This strategical metal is never mined on its own. Instead, it is produced as a by-product of copper and molybdenum extraction. As such, its price and availability are influenced by fluctuations in the copper and molybdenum markets. Rhenium commonly occurs in molybdenite, and it has been empirically observed that carbonatite-hosted molybdenite commonly host significant Re contents, up to several hundreds of ppm. Carbonatites are usually considered as deposits for REE or Nb, therefore the occurrence of molybdenite and its enrichment in Re is perplexing. I performed experiments which tested whether (1) carbonatites can recrystallise molybdenite powder, and (2) whether rheniite can crystallise in carbonatites, when Re and S are introduced as oxidised species (perrhenate and sulfate). The results of these experiments show that carbonatites can act as an effective flux for molybdenite and rheniite growth. The molybdenite powder was recrystallised to coarse crystals tens of micrometres wide, and similarly sized rheniite crystals formed by reaction of perrhenate and sulfate. Although solubility data could not be obtained from these experiments, the discovery that carbonate melts have excellent fluxing capabilities for Mo and Re sulfides is a first step in understanding the reason for the occurrence of Re-rich molybdenite in carbonatites. This may also have implications for better understanding Re–Os isotope systematics during carbonatite metasomatism.

This paper has been written for a materials science audience because of the method’s usefulness for TMDs (transition metal dichalcogenides) crystallisation for industrial applications. However, the link between critical metals (i.e., Re) and carbonatites and the relation to the main topic of this thesis should be readily apparent, and is further discussed in the Conclusions section below.
Introduction

Transition metal dichalcogenides (TMDs or TMDCs) are layered materials with applications in fields such as sensors, nano- or opto-electronics, and energy storage.1-3 Two-dimensional TMDs, which are a single layer or few layers thick, can be produced by a variety of methods.1,2,4 A popular method is exfoliation: disaggregation of larger precursors in bulk form by chemical or mechanical methods. Exfoliation commonly results in higher quality products than competing methods such as chemical vapour deposition (CVD).1,5 MoS2, an important TMD, is widely available in nature as the mineral molybdenite;5 and it is commonly used in 2D MoS2 production by exfoliation.1-3,6-10 ReS2 is an additional TMD sharing some crystallographic and chemical properties with MoS2, but it has other unique properties which make it a promising material for additional applications in solid state electronics, catalysis, and energy applications.11-13 However, it is not as common as MoS2 due to its high price. Additionally, rheniite (natural ReS2) is extremely rare14 and not available as single crystals for exfoliation precursor material, requiring alternative sources.11,15-19 Growth of large area ReS2 by CVD may be a promising avenue for large single crystal or exfoliation-precursor production, but problems have included low yields due to the high melting point of Re, unwanted by-products when using Re(vi) compounds, low quality crystals resulting from the halogen vapour transport method, and long reaction times (multiple weeks).11,20 Although recent advances have mitigated many of these problems, enabling both nano- and micro-scale MoS2 and ReS2 to be grown in sufficient quality for emerging applications,21-24 producing bulk single crystals of ReS2 is time consuming (up to several weeks), and often only one crystal can be grown at a time.25-27

Therefore, an alternative method for growing TMD crystals (particularly ReS2) may ease some of the challenges of synthesising and working with these promising materials. Here we report the results of experiments inspired by occurrences of molybdenite (natural MoS2) in magmatic carbonate deposits (i.e. carbonatites),28-40 and the similar geochemical behaviour of Mo and Re. The aim of these experiments was to explore whether the natural processes that lead to large molybdenite crystals in geological environments can be reproduced in a controlled laboratory setting.

Experimental

Two experiments were conducted in sealed noble metal capsules using a high-pressure piston-cylinder apparatus.41 The first was designed to recrystallise powdered MoS2 in liquid carbonate (run D2554). The second reacted oxidised species of molybdenite (natural MoS2) in magmatic carbonate deposits (i.e. carbonatites),28-40 and the similar geochemical behaviour of Mo and Re. The aim of these experiments was to explore whether the natural processes that lead to large molybdenite crystals in geological environments can be reproduced in a controlled laboratory setting.

Various applications of transition metal dichalcogenides (TMDs) require preparation by exfoliation of precursor bulk materials. However, bulk TMDs are not always available in suitable forms and current synthesis methods may not result in appropriate crystals. This study reports synthesis of large crystals (50-100 μm) of MoS2 and ReS2, by recrystallisation of MoS2 powder or reaction of sulfate with perrhenic acid, respectively. The reactions have been performed at high pressure and temperature (≥1 GPa; ≥800 °C) in a liquid Ca-carbonate flux. The resulting crystals were characterised by electron microscopy imaging, EDS and WDS chemical analyses, and Raman spectroscopy. The carbonate matrix can be easily dissolved to recover the product TMDs. This method allows synthesis of large well-crystalline TMD compositions that are otherwise challenging to obtain.
For the MoS$_2$ experiment, about 20 mg of starting powder was loaded into a 2.3 mm wide Au tube. About 2 mg of MoS$_2$ powder was added in the centre of the tube, and about 2 mg of SiO$_2$ and a small graphite fragment were added to the bottom of the tube. This allows coexistence of CO$_2$ gas and graphite, buffering oxygen fugacity conditions in which sulfide is stable. Both ends were triple-crimped and arc-welded.

For the Re$_2$S$_6$ experiment, we used a cold-weld 6.4 mm Ag capsule, to which we added 143.6 mg of the starting mix listed in Table S1,† 9.3 mg of Na$_2$SO$_4$, and 58.2 mg of Re (in three different layers, bottom, centre, and top). 20.8 mg of a 1 M CaBr$_2$ solution and 22.3 mg of concentrated perrhenic acid were added using a syringe. Minor effervescence was observed because perrhenic acid reacted with the CaCO$_3$-dominated powder already present in the capsule.

The two experiments were conducted in 200 ton end-loaded piston cylinder apparatus.‡ We used a 1 inch (15.875 mm) assembly (Fig. S1) inside a steel pressure vessel with a WC core. The assembly consisted of a noble metal capsule (D2626: Ag; D2554: Au) surrounded by MgO, with NaCl as the pressure medium, separated by a graphite cylinder used as the heater.‡ The assembly was wrapped in Teflon foil before loading into the pressure vessel and capped with a hardened steel plug and a pyrophyllite mitre. Pressure was monitored by a Heise gauge. Temperature was monitored by a type-B thermocouple (70% Pt/30% Rh–94% Pt/6% Rh) sheathed in mullite. The thermocouple in run D2554 was further protected by a 5 mm alumina to minimise contamination at high temperature (>1000 °C). Pressure and temperature were automatically controlled by in-house software running on the LabVIEW platform.

The MoS$_2$ experiment (D2554) was initially compressed to 1 GPa. Then, temperature was increased to 1050 °C at a rate of 100 °C per minute, while simultaneously increasing pressure to 2 GPa in 8 minutes. The experiment was left running for 46 hours at high pressure and temperature. The Re$_2$S$_6$ experiment (D2626) was compressed to 1 GPa, and then temperature was increased to 800 °C at a rate of 100 °C per minute. The experiment was run for 147 hours. Both experiments were terminated by quenching, reaching room temperature in about 20 seconds.

### Analytical

After each experiment, the samples were mounted in round 1 inch epoxy mounts. The experimental charges were exposed with sand paper, and then polished with diamond paste in successive grades of 6, 3, 1, and 0.25 μm. An overview of the entire experimental charges is given in Fig. S2.†

Both samples were carbon coated and investigated using a Hitachi 4300 SE/N Schottky field emission SEM. The various solid phases were identified based on morphology and chemical composition obtained using an Oxford Instruments INCA X-MAX EDXA with a silicon drift detector (SDD). Spectra of resulting sulfides is available in Fig. S3.† Standardless semi-quantitative chemical compositions of the disulfides were calculated from a WDS scan conducted on a JEOL 8530F plus electron probe microanalyser (EPMA). Scans were conducted simultaneously using TAP, PET, and LIF crystals on separate spectrometers over 15 minutes. Beam conditions were 15 kV accelerating voltage, 100 nA beam current, and a 5 μm defocused beam to minimise beam damage at the point of analysis.

Raman spectra were acquired using a Renishaw InVia spectrometer, equipped with a Peltier-cooled detector, a 2400 1 mm$^{-1}$ grating and a confocal system. Samples were excited using a 532 nm laser line focused on sample surface using a ×50 Leica objective. The laser power on the sample was ∼1.2 mW. The spatial resolution was ∼1 μm, and the spectral resolution ∼1.2 cm$^{-1}$. The full widths at half maximum amplitude (FWHM) of peaks were calculated using Fityk 1.3.1 and a pseudo-Voigt function.‡

### Results

The MoS$_2$ experiment resulted in a dendritic intergrowth of CaMg(CO$_3$)$_2$ (dolomite) and a micaceous silicate phase (Fig. 1a) with a composition roughly consistent with "aspidolite" (NaMg$_3$[Al$_2$Si$_3$O$_9$](OH)$_2$, the Na analogue of phlogopite end-member of the common K–Mg biotite micas). This texture is a clear indicator of the former presence of liquid carbonate at high temperature. Several crystals of CaMg$_2$Si$_6$O$_{16}$ (diopside clinopyroxene) were found mostly along the capsule edges. These formed by the reaction CaMg(CO$_3$)$_2$ + SiO$_2$ = CaMgSi$_3$O$_6$ + CO$_2$, a well-known reaction between silicate and carbonate dominant materials from a variety of natural settings.‡ This reaction releases CO$_2$ and indeed vapour bubbles were observed, mostly at the top of the capsule. The rising CO$_2$ bubbles caused flotation of some MoS$_2$ which was originally placed in the middle of the capsule.‡ Most MoS$_2$ powder recrystallised to coarser hexagonal MoS$_2$, up to 100 μm wide and 20 μm thick (Fig. 1b and c), representing coarsening by two orders of magnitude. It is not possible to accurately calculate the yield as the MoS$_2$ product differs from the reactant only by grain size, but it may be visually estimated (e.g., Fig. S2†) that at least 70% of the starting powder recrystallised. Elongated crystals of MoS$_2$ present in the quenched material (Fig. 1a) indicate solubility of this component in the carbonate melt, but the amount could not be quantified due to the heterogeneous distribution of the quench crystals.

The Re$_2$S$_6$ experiment resulted in relatively coarse Re$_2$S$_6$ crystals 10s of micrometres long (Fig. 1d–f). Most Re$_2$S$_6$ was trapped in coarse-grained CaCO$_3$ (calcite) matrix, but some Re$_2$S$_6$ occurs in a mixed carbonate–phosphate–silicate matrix of CaCO$_3$, Ca$_5$(PO$_4$)$_3$F (fluorapatite), and Mg$_6$(SiO$_4$)(F,OH) (norbergite). As the Re$_2$S$_6$ experiment was run at 800 °C (in contrast to 1050 °C for the MoS$_2$ experiment), no dendritic quench textures are observed, indicating that melting of the carbonate was not widespread. However, a small melt fraction did exist, evident by characteristic rounded CaCO$_3$ crystals. The perrhenic acid solution is completely soluble in the
high-pressure carbonate liquid, but was entirely consumed to form ReS$_2$, with no other solid Re-bearing impurities detected. Hence the yield of ReS$_2$ is essentially quantitative.

Compositions of the resulting disulfides obtained by WDS scans are shown in Fig. 2. Full details including matrix contamination are given in Table S2.† From these analyses, the composition of molybdenum disulfide was calculated as Mo$_{0.94}$S$_2$, and rhenium disulfide as either Re$_{0.96}$S$_2$ or Re$_{1.09}$S$_2$, depending on whether the Re-M$\alpha$ line used for quantification was obtained by the TAP or PET crystal, respectively. Considering the uncertainty of standardless quantification and the minor inclusion of matrix material, the results suggest that the produced TMDs are stoichiometric or nearly so.

Raman spectra of TMDs in this study are given in Fig. 3, and show excellent agreement with previously described spectra for bulk ReS$_2$ and MoS$_2$. A common measure of crystallinity is FWHM, where smaller values mean better crystallinity. FWHM obtained for MoS$_2$ are 4.5 and 4.7 for E$_{1g}$ and A$_{1g}$, respectively (Fig. 3b), which are within the range commonly obtained by other methods.$^{21}$ Likewise, the two strong E$_{2g}$-like peaks of ReS$_2$ have FWHM of 4.9, demonstrating good crystallinity.

Discussion

The above results show that liquid carbonate is highly effective in crystallising large crystals of ReS$_2$ and MoS$_2$. In the case of MoS$_2$, the experiment resulted in coarsening of the starting MoS$_2$ powder due to Ostwald ripening in the carbonate liquid. These liquids have exceptional low viscosity$^{19}$ and wetting capabilities.$^{50-53}$ Carbonate liquids are not polymerised, retarding crystal nucleation. Taken together with their ability to dissolve significant sulfur as both sulfide and sulfate,$^{54}$ and their higher density relative to gas or supercritical fluids, they serve as an excellent recrystallisation flux.

Unlike the MoS$_2$ experiment, the ReS$_2$ experiment did not include powdered ReS$_2$ in the starting materials. Instead, the ReS$_2$ crystals grew from sulfate and Re(VII) dissolved in the liquid carbonate. In terms of thermodynamic components, the reaction can be written as:

$$8\text{SO}_3 + 2\text{Re}_2\text{O}_7 = 4\text{ReS}_2 + 19\text{O}_2. \quad (1)$$

However, the excess oxygen is not stable in equilibrium with Re metal$^{55}$ and will react via:

$$\text{Re} + \text{O}_2 = \text{ReO}_2. \quad (2)$$

but no ReO$_2$ was observed in the experimental products. Therefore, a different oxygen sink is required. The interior of the capsule contains Ag blebs, which requires oxidation of Ag in order to mobilise Ag from the capsule. As the experiment contained a separate aqueous vapour phase at run conditions, the redox reaction can be thought to occur as the acid–base reaction:

$$2\text{SO}_3^- + \text{ReO}_4^- + 24\text{H}^+ + 19\text{Ag} = \text{ReS}_2 + 19\text{Ag}^+ + 12\text{H}_2\text{O}. \quad (3)$$

The quenched experimental products do not contain any Ag salts and it is unclear what served as the final oxygen sink.
during the experiment. Interestingly, the ReS_2 crystals appear to have often nucleated on the powdered Re layer. Reactions (1) and (3) do not contain Re(0) in the reactants, and the lack of ReO_2 suggests that the Re metal did not react by itself but simply acted as a catalyst for the redox reaction. ReS_2 was mostly concentrated around the Re layers, but was also found elsewhere in the experimental charge. This indicates that having a redox catalyst may promote ReS_2 formation, but is not necessary.

The high pressure is a potential difficulty for widescale application of the method. The experiments described here were conducted at 1 and 2 GPa, requiring specialised equipment that can commonly accommodate sample materials of only up to several grams. Scaling the process to grow larger amounts of TMDs cheaply and easily requires equipment that operating at lower pressures. This can be solved by using Na–Ca-rich carbonates which remain liquid to low pressures (e.g. 0.1 GPa).^{56–60}

Our growing method mitigates some of the problems with large single crystal growth by CVD outlined earlier. The reactions described herein were rather rapid, requiring less than one week. Additionally, as liquid carbonates are strong fluxes, any metastable or unwanted by-products are dissolved in the carbonate during the experiment, and are then easily dissolved and separated by the use of weak acids (or water, in the case of Na-rich carbonates).

A promising application of this method is growth of mixed-metal TMDs. Layered disulfides such as MoS_2, ReS_2, and WS_2 are known to exhibit solid solutions and mutual solubilities at high temperature.^{3,61–64} However, accurately doping one metal into another TMD by CVD is extremely challenging due to the varying transport rates and non-equilibrium thermodynamics and kinetic effects governing the deposition process.^{65,66} As liquid carbonate fluxes at high pressure and temperature are thermodynamically equilibrated, it is possible to obtain stable TMDs solid solutions. A possible future research avenue is calibration of liquid–solid metal partitioning for known binary systems (such as MoS_2–ReS_2).^{63} Eventually, by controlling the metal proportions added to the carbonate, it is possible to obtain large crystals of binary or ternary TMDs, improving current CVD-based methods that may only result in nanoscale crystals.^{13,67,68}

Finally, carbonate-assisted TMDs crystallisation requires simple starting materials. The MoS_2 product presented here formed by recrystallisation of commercially available MoS_2 powder. The ReS_2 formed by reaction of perrhenic acid and sulfate (introduced by adding Na_2SO_4). There is no requirement for pre-treating reagents, or use of organic or potentially toxic starting materials.

The exact recipe for the carbonate flux can be tuned according to experimental requirements. Ideally, a composition leading to low eutectic melting point for the flux is

![Fig. 2 WDS scans of the resulting phases. (a) Combined three-spectrometer spectra of MoS_2 and ReS_2. (b) A close-up of the quantified X-ray emission lines for Mo and S. (c) A close-up of the quantified X-ray emission lines for Re and S. Unlabelled peaks are the second order signal of already-identified peaks.](image-url)
preferable. However, such melting conditions require a larger proportion of alkali metals such as Na and K, which then allow more sulfide to be dissolved in the liquid, potentially lowering yields. Slow cooling rather than quenching would solve the problem of sulfide solubility in the carbonate, but may negatively influence fine-tuned doping (e.g., mixed Re–Mo sulfides, etc.) as these are thermodynamically constrained by temperature. On the other hand, higher solubility might facilitate increased crystal size by heat-cycling assisted Ostwald ripening. These considerations have to be taken into account when choosing the carbonate flux composition, and should be determined according to desired sulfide composition, size, and availability of experimental equipment.

Conclusions

The method shown in this contribution demonstrates that MoS$_2$ and ReS$_2$ can be recrystallised from powder or grown from reagents into large, well-crystallised, products. Although large crystals of MoS$_2$ are widely available, they may contain impurities or inclusions of other minerals. Growing them by carbonate liquid allows for easy separation from the flux matrix, potentially leading to purer MoS$_2$ crystals. As for ReS$_2$, this method allows for large scale production of multiple single crystals allowing abundant feedstock for exfoliation or any other potential applications. Future research should explore the possibility of crystallising equilibrium solid solutions of mixed TMDs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is supported by an Australian Government Research Training Program Scholarship and a Ringwood Scholarship. The author acknowledges the facilities and technical assistance of Microscopy Australia at the Centre for Advanced Microscopy, The Australian National University. This work was supported by Australian Research Council grant FL130100066 to Hugh O’Neill who provided constructive comments on the manuscript. Charles Le Losq generously assisted with Raman spectroscopy.

Notes and references


Chapter 5: Anenburg & Mavrogenes (2016)—GCA

This next work expands the topic of Re to all other PGE, while focusing on alkaline magmas.

The use of experimental petrology methods to the study of PGE is hampered by several challenges. Particularly, PGE solubility experiments are challenging due to the formation of sub-micrometre wide PGE metallic alloys, commonly known as “micronuggets” or “nanonuggets”. The presence of nanonuggets in the analysed material obscures its true PGE content. For example, the solubility of PGE in silicate glass is commonly in the ppm range or below, and only a handful of nanonuggets included in the analysis volume can skew the analysed concentration upwards. Researchers in the field have successfully developed methods to minimise or eliminate the formation of nanonuggets over the past decade or so, and analytical methods have become good enough to separate the nanonugget contribution from the signal of interest. The ubiquitous formation of nanonuggets in experiments raises the question of relevance to natural systems. The laws of thermodynamics are the same whether in the deep earth or an experimental capsule. Several studies have showed the presence of such nanonuggets in natural minerals and glasses, but their significance is not fully understood yet.

In a pilot study of trace element partitioning in alkaline melts, we noticed a large abundance of nanonuggets forming in our experiments. We melted an ijolitic composition consisting of equal amounts of nepheline (NaAlSiO₄) and aegirine (NaFe³⁺Si₂O₆) inside silver–palladium (AgPd) capsules. Surprisingly, alkali-bearing minerals did not form. Instead, we witnessed the formation of magnetite with countless nanonuggets in the surrounding glass and larger PGE minerals sticking to the magnetite itself. Having realised that by using alkaline melts and AgPd capsules we can produce orders of magnitude more nanonuggets than previously seen in experiments, we decided to explore it further. Instead of attempting to eliminate the formation of nanonuggets, we used their abundance to study their formation mechanism in a way not possible before.

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¹ An ijolite is a nepheline–clinopyroxene rock found in alkaline magmatic provinces, occasionally in association with carbonatites. Ijolites may represent the cumulate crystallisation products of parental melts that lead to carbonatite formation by liquid–liquid immiscibility.
The results of this study and their significance is as follows:

1. We demonstrate that it is possible to visually inspect glasses for nanonugget presence. In some cases, the observed colour can provide information on the nanonugget size.
2. We now have a better understanding of nanonugget formation mechanisms, and their relation to oxide mineral crystallisation.
3. We show a pathway for nanonugget coarsening into PGE minerals larger than ~1 µm.
4. We propose a method for the elimination of nanonuggets in experiments once they form.
5. We suggest that PGE enrichments in sulfur-poor natural settings could result from transport as nanonuggets, beyond the PGE equilibrium solubility in silicate melts.
Experimental observations on noble metal nanonuggets and Fe-Ti oxides, and the transport of platinum group elements in silicate melts

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Received 10 February 2016; accepted in revised form 5 August 2016; Available online 13 August 2016

Abstract

Platinum group element (PGE) nanonuggets are a nuisance in experimental studies designed to measure solubility or partitioning of noble metals in silicate melts. Instead of treating nanonuggets as experimental artifacts, we studied their behaviour motivated by recent discoveries of PGE nanonuggets in a variety of natural settings. We used an experimental setup consisting of AgPd, Pt or AuPd capsules and Fe(-Ti) oxide-saturated hydrous peralkaline silicate melts to maximise nanonugget production. TABS (Te, As, Bi, Sb, Sn) commonly occur in PGM (platinum group minerals), prompting addition of Bi to our experiments to investigate its properties as well. Three-dimensional optical examination by 100× objective and immersion oil reveals variable colour which correlates with nanonugget size and shape due to plasmon resonance effects. We observe two textural types: (1) intermediate-sized nanonuggets dispersed in the glass and adhering to oxides, and (2) abundant fine nanonuggets dispersed in the glass with coarse euhedral crystals in contact with oxides. Slow cooling removes dispersed nanonuggets and greatly coarsens existing oxide-associated metal crystals. Nanonugget-free halos are commonly observed around oxide grains. All metal phases are composed of major (Ag, Pd) and trace (Pt, Ir, Au) capsule material.

Our results show reduction processes, imposed by growing oxides, causing local metal saturation in the oxide rich zones with preferential nucleation on smaller oxide grains. The redox gradient then blocks additional metals from diffusing into oxide rich zones, forming halos. As the entire experimental charge is reduced throughout the run, nanonuggets form in the distal glass. Bismuth contents of metal phases do not depend on Bi2O3 amounts dissolved in the melt. Further PGM crystallisation consumes nanonuggets as feedstock. We conclude that the appearance of metallic PGE phases happens in two stages: first as nanonuggets and then as larger PGM. Once formed, nanonuggets cannot be removed by oxidation or dissolution, but only by PGM coarsening.

Sulfur-poor PGE ore deposits commonly contain more PGE than permitted by existing estimates of equilibrium solubility in silicate melts. This is commonly explained by initial scavenging of PGE by sulfide liquids followed by S-loss, but evidence for S-loss is not conclusive. We suggest that nanonuggets may be a means to transport PGE from source regions to form ore deposits, followed by direct PGM crystallisation from silicate melt without intermediate concentration by sulfide liquids. © 2016 Elsevier Ltd. All rights reserved.

Keywords: PGE; Nanonuggets; Magnetite; Sulfide; HSE; Silver

1. INTRODUCTION

The behaviour of noble metals (Ag, HSE—highly siderophile elements: Re, Au and the PGE—platinum group elements Ru, Rh, Pd, Os, Ir and Pt) in silicate melts is...
critical for understanding how noble metal deposits form, as increasing uses for noble metals accelerates our need to identify new resources (Brenan, 2008). In the Earth’s mantle and crust, the noble metals are characterised by their highly chalcophile character. They are overwhelmingly associated with sulfides, whether in mantle rocks or in crustal ore deposits (Mungall and Naldrett, 2008).

The accepted model for PGE ore deposit formation is based nearly exclusively on their high sulfide/silicate partition coefficients. Immiscible sulfide droplets in silicate magmas scavenge PGE and concentrate them where the dense droplets eventually accumulate (Naldrett, 2004; Latypov et al., 2013; Godel, 2015; Barnes and Ripley, 2016). Thus all PGE are expected to be associated with sulfide, either as trace elements in base metal sulfides or as PGM (PGE metal alloy or sulfide minerals) crystallised from an initially PGE-enriched sulfide phase (Godel, 2015). PGM—often associated with group 15 and 16 elements such as Te, As, Bi, Sb, and Se (TABS)—are commonly observed in contact or as inclusions within silicate (commonly olivine) or oxide minerals (chromite, magnetite or ilmenite in discrete oxide horizons such as chromitites or magnetitites). They are often very small: their size ranges from tens of nanometres to just a few micrometres across, earning them the name ‘micronuggets’ or ‘nanonuggets’. Examples are given in Table 1. These relations are not limited to Earth and also occur in meteorites (Geiger and Bischoff, 1995; Schwander et al., 2015b). In all of these cases the PGM are not always in contact or in proximity to sulfides. These occurrences are commonly explained via sulfur-loss: a sulfide liquid phase concentrated the PGE, but was subsequently lost (Von Gruenewaldt et al., 1986; Merkle, 1992; Andersen et al., 1998; Barnes and Maier, 2002; Maier et al., 2003; Peregoedova et al., 2004; Cuthlorn, 2005a, b; Andersen, 2006; Maier and Barnes, 2008; Barnes et al., 2009; Locmelis et al., 2009; Naldrett et al., 2012; Bowles et al., 2013; Coggon et al., 2015). However, the degree to which sulfur-loss actually occurs is debatable (Barnes, 1993; Prichard et al., 2004; Maier, 2005; Godel et al., 2007; Godel, 2015; Barnes et al., 2016; Barnes and Ripley, 2016). In other cases, PGM are observed in between sulfides and other phases (oxides and silicates), and it is unclear whether or not these PGM crystallised from the sulfides.

Table 1
A list of localities with documented occurrences of PGE ± TABS minerals that did not necessarily form by liquid sulfide concentration.

<table>
<thead>
<tr>
<th>Locality</th>
<th>References</th>
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<tbody>
<tr>
<td>Jinbaoshan, China</td>
<td>Wang et al. (2008)</td>
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<tr>
<td>Keivitsa-Satovaara, Finland</td>
<td>Mutanen (1997) and Gervilla and Kojonen (2002)</td>
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<td>Skaergaard, Greenland</td>
<td>Nielsen et al. (2015)</td>
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<td>Owendale, Australia</td>
<td>Johan et al. (1989)</td>
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<tr>
<td>Thetford Mines, Canada</td>
<td>Pagé et al. (2012)</td>
</tr>
<tr>
<td>Bird River Sill, Canada</td>
<td>Talkington et al. (1983)</td>
</tr>
<tr>
<td>Monts de Cristal, Gabon</td>
<td>Maier et al. (2015)</td>
</tr>
<tr>
<td>Josephine, USA</td>
<td>Stockman and Hlava (1984)</td>
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<tr>
<td>Dobromirtsi, Bulgaria</td>
<td>González-Jiménez et al. (2010)</td>
</tr>
<tr>
<td>Vourinos, Greece</td>
<td>Augé (1985)</td>
</tr>
<tr>
<td>Rio Jacare, Brazil</td>
<td>Sai et al. (2005)</td>
</tr>
<tr>
<td>Freetown, Sierra Leone</td>
<td>Bowles et al. (2013)</td>
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<tr>
<td>Penikat, Finland</td>
<td>Halkoaho et al. (1990a, b)</td>
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<td>Moncheorgi, Russia</td>
<td>Grokhovskaya et al. (2012)</td>
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<td>Troodos, Cyprus</td>
<td>McElduff and Stumpfl (1990)</td>
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<tr>
<td>Pindos, Greece</td>
<td>Kapsiotis et al. (2011)</td>
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<tr>
<td>Isle of Rum, Scotland</td>
<td>Parry (1984), Butler et al. (1999) and O’Driscoll et al. (2014)</td>
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<tr>
<td>The Eastern Goldfields superterrane of the Yilgarn Craton, Australia</td>
<td>Locmelis et al. (2009, 2011)</td>
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<tr>
<td>Kapitanov, Ukraine</td>
<td>Gornostayev et al. (2001)</td>
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<tr>
<td>Stihlwater, USA</td>
<td>Parry (1984), Talkington and Lipin (1986) and Pagé et al. (2012)</td>
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<tr>
<td>Kap Edvard Holm, Greenland</td>
<td>Arnason and Bird (2000)</td>
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<tr>
<td>Across the entire Ural range, Russia</td>
<td>Melcher et al. (1997), Garuti et al. (1999, 2002, 2003), Augé et al. (2005), Badanina et al. (2015) and Kamenetsky et al. (2015)</td>
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<td>Campo Formoso, Brazil</td>
<td>Garuti et al. (2007)</td>
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<td>Guli, Russia</td>
<td>Malitch et al. (2011) and Ryabchikov and Kogarko (2012)</td>
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<td>Berit, Turkey</td>
<td>Kozlu et al. (2014)</td>
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<td>Tulameen, Canada</td>
<td>Nixon et al. (1990)</td>
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<td>Kondapalli, India</td>
<td>Meshram et al. (2015)</td>
</tr>
<tr>
<td>Stella, South Africa</td>
<td>Maier et al. (2003)</td>
</tr>
<tr>
<td>Ujaragssuit nunat, Greenland</td>
<td>Coggon et al. (2015)</td>
</tr>
<tr>
<td>Ambae, Vanuatu</td>
<td>Park et al. (2012) and Kamenetsky et al. (2015)</td>
</tr>
</tbody>
</table>
either as subsolidus exsolutions or from the sulfide liquid (Power et al., 2000; Prendergast, 2000; Godel et al., 2010; Rose et al., 2011; Grokhovskaya et al., 2012; Kozhu et al., 2014). In some sulfide-poor or sulfide-absent PGE deposits, tenors too high for reconciliation by traditional models of silicate-sulfide partitioning require special pleading to explain their existence (Barnes, 1993; Maier and Barnes, 1999; Barnes and Maier, 2002; Naldrett, 2004; Augé et al., 2005; Godel et al., 2007; Barnes et al., 2015; Godel, 2015; Maier et al., 2015). Even in sulfide-rich ore deposits, the total amount of PGE is higher than could be dissolved in an entire magma chamber, according to equilibrium solubility determinations (e.g. the Merensky Reef, Bushveld, Naldrett et al., 2008, 2009).

Several experimental studies documented PGM and nanonugget formation in sulfur free or sulfide undersaturated systems (Sattari et al., 2002; Bockrath et al., 2004b; Finnigan et al., 2008; Wijbrans et al., 2015; Schwander et al., 2015a; Malavergne et al., 2016), suggesting that solution of PGE in sulfides may not be the sole cause of PGE enrichment. In this study we further explore the association of PGM and nanonuggets with oxides. PGE are thought to exist in silicate melts as cationic species, with the valence state determined by oxygen fugacity ($O_2$). Higher valence species exist at higher $O_2$, whereas lower valence (and possibly zero-valence) exist at low $O_2$. Similarly, solubility depends on $O_2$ with higher $O_2$ allowing more PGE to dissolve in the silicate melt (O’Neill et al., 1995; Ertel et al., 1999, 2006, 2008; Laurens et al., 2013; Bennett et al., 2014; Médard et al., 2015; Brenan et al., 2016). In addition, it has been suggested that PGE in melts may exist as metallic species, from ‘nanoclusters’ of several atoms (Tredoux et al., 1995) to nuggets visible by optical or microbeam analytical techniques without any coarser thermodynamically stable PGE phase (Ballhaus and Sylvester, 2000; Fiorentini et al., 2004; Helmy et al., 2013). Attempts to quantify noble metal solubility in silicate melts have been plagued by the presence of nanonuggets that ‘pollute’ the quenched glass (Borisov and Palme, 1995, 1997; O’Neill et al., 1995; Ertel et al., 1999, 2006, 2008; Blaine et al., 2005; Forfenfant et al., 2006). The ubiquitous presence of these nanonuggets poses a challenge in determining the actual solubility of the noble metals in the silicate melt using both bulk methods (e.g. INAA) and in-situ methods (e.g. laser ablation inductively coupled plasma—LA-ICP-MS). Some methods used to circumvent this problem include analysing ‘between the nanonuggets’ by integrating only uncontaminated sections of the LA-ICP-MS signal (Ertel et al., 2006, 2008; Laurens et al., 2013), preventing nanonugget formation in the first place (Borisov and Walker, 2000; Brenan and McDonough, 2009; Bennett and Brenan, 2013; Bennett et al., 2014), or mechanically removing existing nanonuggets by stirring or centrifuging (Ertel et al., 1999, 2008; Forfenfant et al., 2006; Médard et al., 2015). However, these methods do not elucidate the properties of the nanonuggets themselves.

Studies of nanonuggets are made difficult by their rarity, small size, and seemingly haphazard spatial distribution (Brenan et al., 2016). To circumvent this, we explore the formation of nanonuggets using techniques that exacerbate the nanonugget ‘problem’: using a highly peralkaline melt capable of initially dissolving a relatively large amount of PGE, and by using Ag, a more soluble semi-noble analogue for the PGE. By purposely creating an environment favourable for nanonugget formation, we are able to observe previously unrecognised relations.

Although Ag is not a PGE, it has several properties that make it a good analogue:

1. Silver is a moderately siderophile element that shows depletion in the mantle similar to the PGE (Righter, 2003). Silver is also a highly chalcophile element, and among the transition metals surpassed only by Ni and Cu (Barnes and Ripley, 2016).
2. In contrast to Ni and Cu, Ag is the only moderately siderophile metal that does not form silicate or oxide minerals. Instead, it occurs in its native form, or readily forms sulfides or minerals with PGE and TABS (see http://www.mindat.org/chemsearch.php?nc=Ag for a comprehensive list).
3. Redox reactions are crucial for PGE geochemistry, and their redox characteristics are one of the defining properties of the PGE. The electric potential of silver is well within the range of the PGE (Table 2), resulting in similar redox behaviour for Ag and the PGE.
4. Silver nanoparticles are commonly used in nanotechnology. Their preparation methods are similar to other common nanoparticle metals (Au, Pt and Pd), they exhibit similar chemical and physical properties, and are used in related applications.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Experimental strategy

The melt composition used in the experiments is Fe-rich, hydrous and peralkaline. This melt has several characteristics helpful for this study: (1) At the high-T experimental conditions used in this study (1050–1100°C), the only stable non-metallic mineral phases are Fe-Ti oxides, (2) noble metal solubilities are higher than in other melt compositions commonly used in similar studies (e.g. Ca-Mg silicate melts) owing to higher Fe contents (Laurens et al., 2016).

<table>
<thead>
<tr>
<th>Element</th>
<th>Reaction</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>Au$^+ + e^- → Au$</td>
<td>1.692</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt$^{2+} + 2e^- → Pt$</td>
<td>1.18</td>
</tr>
<tr>
<td>Iridium</td>
<td>Ir$^{3+} + 3e^- → Ir$</td>
<td>1.156</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd$^{2+} + 2e^- → Pd$</td>
<td>0.951</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag$^+ + e^- → Ag$</td>
<td>0.7996</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Rh$^+ + e^- → Rh$</td>
<td>0.600</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Ru$^{3+} + 2e^- → Ru$</td>
<td>0.455</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu$^{2+} + 2e^- → Cu$</td>
<td>0.3419</td>
</tr>
<tr>
<td>Rhenium</td>
<td>Re$^{3+} + 3e^- → Re$</td>
<td>0.300</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni$^{2+} + 2e^- → Ni$</td>
<td>−0.257</td>
</tr>
</tbody>
</table>

Table 2: Electron potential of redox reactions for selected metals (CRC Handbook of Chemistry and Physics, 2014).
2.2. Materials

The melt composition is based on an ijolitic 50:50 mixture of end member nepheline (NaAlSiO₄) and aegirine (NaFe³⁺Si₂O₆), producing a normalised composition of 47.1 wt% SiO₂, 17.6 wt% Na₂O, 17.9 wt% Al₂O₃ and 17.3 wt% Fe₂O₃. This composition was doped with Bi₂O₃ ranging from the ppm level up to 1 wt%, and TiO₂ from 0 to 5 wt% (Table 3). Approximately 5 wt% H₂O was added as hydrated forms of the other solid reagents. Starting materials included various combinations of powdered SiO₂, Fe₂O₃, Fe(OH)₃, TiO₂, Bi₂O₃, Al₂O₃, Al₄(OH)₆, Na₂CO₃, Na₅Si₃O₁₀ and Na₂Si₅O₁₈. Highly sodic silicate glasses and crystalline starting materials readily absorb H₂O and CO₂, so several different preparation methods were attempted: melting to glass in air, solid sintering and plain mixing. No method seemed to be more advantageous. Other than the amount of observed vapour bubbles (most likely CO₂, known not to affect noble metals in silicate melts, Borisov and Palme, 2000), the different methods did not seem to have any effect on any run products which are the focus of this work. Noble metals derived either from the capsule material (Ag–Pd, Pt and Au–Pd) or from metal strips and wires placed inside the capsule (Re, Ir, Pt–Rh). This ensured that PGE solubility is not limited by availability of the starting materials. This also has an advantage over using noble metal powders or noble metals in the silicate starting materials (either in glass or in silicate minerals) by ensuring that noble metal phases observed in the experiments are the products of crystallisation from the silicate melt rather than unreacted remnants of the starting materials. All capsule materials contain trace amounts of all noble metals. Therefore, Pd, Ag, Ir, Pt and Au were present in all experiments, and likely Ru, Rh and Os, which were not analysed in this study.

2.3. Experimental methods

Experiments were run in 200-ton piston cylinder apparatus. About 15 mg of the starting mix were loaded into noble metal capsules (2.3 mm outer diameter), which were welded shut using an argon arc welder. The capsule was placed inside an MgO rod, surrounded by Pyrex glass and NaCl (Fig. 1a). The assembly was wrapped in Teflon foil and placed inside a ¾” pressure vessel. A type-B thermocouple (Pt/30% Rh – Pt/6% Rh) was used to monitor temperature. An automated Eurotherm controller programmable by the Eurotherm iTools software was used to control both pressure and temperature. After an initial pressure increase to 1–2 kbar, the temperature and pressure were gradually increased over 10–15 min to run conditions (P = 5 kbar, T according to Table 3). Experiments were quenched by cutting power to the graphite heater. A typical T drop during quench as recorded by the thermocouple is given in Fig. 1b.

3. ANALYTICAL METHODS

Compositionally analysing nanonuggets can be difficult (Brenan et al., 2016). Their small size makes finding nanonuggets of rare composition difficult if not impossible, does not allow accurate composition determination using energy-dispersive X-ray spectroscopy (EDS), and even then only allows analysis of exposed nanonuggets. Thus, nanonuggets of particular compositions might be missed entirely by chance, as occurred during this study (for example, Ir and Au nanonuggets were inferred from LA-ICP-MS, but were not detected by EDS). This problem also exists for transmission electron microscopy (TEM) studies owing to the small volume analysed. In order to study representative nanonugget compositions from a wider area we used a combination of two methods: reflected optical microscopy and LA-ICP-MS. Using optical microscopy has two advantages: one is the ability to observe nanonuggets (and other objects) deep in the glass and record their three-dimensional distribution. The second is the ability to observe a distinct nanonugget colour because of plasmonic effects (Atwater, 2007; Dionne and Atwater, 2012). The colour can then be used to infer the relative size distribution of multiple nanonuggets, as discussed below. Using LA-ICP-MS traverses allows the determination of nanonugget compositions over a region.

After each successful experiment, the entire assembly was embedded in epoxy. The experimental charge was...
exposed using a coarse diamond lap and then polished using SiC paper and diamond paste down to a grit size of 1/4

m. Optical examination was conducted using a Nikon Eclipse LV100POL microscope. Nanonuggets were clearly visible using a Plan Apo 100/C2 objective (NA = 1.4, 1/0) and Type A immersion oil (n = 1.515). Selected experiments were carbon coated and compositions of metallic alloys and oxide minerals were studied using a Hitachi S-4300 SE/N field emission scanning electron microscope (FE-SEM) or a JEOL JSM-6610A SEM. Beam conditions for the Hitachi were 15 kV accelerating voltage and 0.6 nA beam current. Standards for Al, Ti and Fe were albite, rutile and pyrite, respectively. Beam conditions for the JEOL were 15 kV and 1 nA beam current. No standards were used, but several samples were cross-checked with data obtained by the Hitachi and were found to be within analytical error. The small size of the nanonuggets permitted only qualitative composition determinations. Laser ablation traverses were conducted using a 193 nm ArF excimer (Coherent CompuPro 110) laser ablation system, feeding into an Agilent 7700 series quadrupole ICP-MS with dual-mode discrete dynode electron multiplier detector. Ablation was conducted in a custom-built ‘HelEx’ two-volume vortex sampling cell in an atmosphere of He and Ar. Ablated material was transported to the ICP-MS in this gas mixture, with a small amount of H2 added during sample introduction. The laser was run at a frequency of 5 Hz, with an operating fluence at the sample surface of 5–6 J/cm2. Traverses were usually 400 l

m long and 16 l

m wide. The sample stage was moved at 1 l

m/sec. The following element masses were measured: 49Ti, 57Fe, 106Pd, 109Ag, 187Re, 193Ir, 193Pt, 197Au and 209Bi. No attempt was made to measure 103Rh because of strong interference with 56Fe and 47Ti, even though it was used in the starting materials. Oxide identification was conducted using a Renishaw inVia Raman spectrometer. Laser wavelength was 532 nm, 50 mW power, 2400 lines/mm diffraction grating. Each spectrum was acquired for 30 s using a 100/C2 objective. Experimental glasses from selected runs were broken to expose nanonuggets for high resolution examination. Imaging was conducted on uncoated samples using a Zeiss Table 3

A list of experimental conditions, starting materials, result summary, oxide compositions for all runs in this study.

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>Capsule</th>
<th>Bi (wt%)</th>
<th>Ti (wt%)</th>
<th>Results</th>
<th>mt-us-he</th>
<th>hm-il-co</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1891</td>
<td>1100</td>
<td>19</td>
<td>Ag0.5Pd0.5</td>
<td>40 ppm</td>
<td>40 ppm</td>
<td>Textural type 1</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1892</td>
<td>960</td>
<td>19</td>
<td>Ag0.5Pd0.5</td>
<td>40 ppm</td>
<td>40 ppm</td>
<td>Textural type 1</td>
<td>97.5-0.0-2.5</td>
<td></td>
</tr>
<tr>
<td>D1900</td>
<td>1100</td>
<td>19</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>0</td>
<td>Textural type 1</td>
<td>95.0-0.0-4.8</td>
<td></td>
</tr>
<tr>
<td>D1901</td>
<td>1100 → 900</td>
<td>13 + 13</td>
<td>Pt</td>
<td>0.1</td>
<td>0</td>
<td>No nanonuggets; PGM on oxides</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1906</td>
<td>1100</td>
<td>19</td>
<td>Pt</td>
<td>0.1</td>
<td>0</td>
<td>Nanonuggets, rare PGM on oxides</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1911</td>
<td>1100</td>
<td>7</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>0</td>
<td>Textural type 1</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1912</td>
<td>1100</td>
<td>4</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>0</td>
<td>Textural type 2</td>
<td>97.4-0.0-2.6</td>
<td></td>
</tr>
<tr>
<td>D1920</td>
<td>1100</td>
<td>12</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>0</td>
<td>Textural type 2</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1921</td>
<td>1100</td>
<td>2</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>0</td>
<td>Textural type 1</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1933</td>
<td>1050</td>
<td>12</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 2</td>
<td>89.9-6.7-3.4</td>
<td></td>
</tr>
<tr>
<td>D1943</td>
<td>1050</td>
<td>3</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 2</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1945</td>
<td>1050</td>
<td>6</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 2</td>
<td>95.5-2.0-2.5</td>
<td>81.6-17.3-1.1</td>
</tr>
<tr>
<td>D1946</td>
<td>1050</td>
<td>24</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 2</td>
<td>85.4-13.6-1.0</td>
<td></td>
</tr>
<tr>
<td>D1953</td>
<td>1050</td>
<td>8</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 1</td>
<td>89.2-8.1-2.7</td>
<td></td>
</tr>
<tr>
<td>D1954</td>
<td>1050</td>
<td>2</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 1</td>
<td>90.1-6.9-3.0</td>
<td>66.5-32.1-1.4</td>
</tr>
<tr>
<td>D1955</td>
<td>1050</td>
<td>10 min</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>3</td>
<td>Textural type 1</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1976</td>
<td>1050</td>
<td>12</td>
<td>Ag0.5Pd0.5</td>
<td>1</td>
<td>1</td>
<td>Textural type 2, quench</td>
<td>98.5-0.4-1.0</td>
<td></td>
</tr>
<tr>
<td>D1986</td>
<td>1050</td>
<td>24</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>0</td>
<td>Textural type 2, quench</td>
<td>98.8-0.3-1.0</td>
<td></td>
</tr>
<tr>
<td>C5057</td>
<td>1050</td>
<td>14</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>0</td>
<td>Textural type 1</td>
<td>97.4-0.2-2.4</td>
<td></td>
</tr>
<tr>
<td>C5064</td>
<td>1050</td>
<td>14</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>0</td>
<td>Textural type 2</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D1996</td>
<td>1050 → 650</td>
<td>16 + 24</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>0</td>
<td>No nanonuggets, large PGM on oxides</td>
<td>98.3-0.0-1.7</td>
<td></td>
</tr>
<tr>
<td>D2001</td>
<td>1050</td>
<td>16</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>5</td>
<td>Textural type 1, quench</td>
<td>71.1-27.9-1.0</td>
<td></td>
</tr>
<tr>
<td>C5068</td>
<td>1050</td>
<td>16</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>5</td>
<td>Textural type 2, quench</td>
<td>78.5-20.3-1.1</td>
<td></td>
</tr>
<tr>
<td>D2002</td>
<td>1050</td>
<td>19</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>0</td>
<td>Rare nanonuggets</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D2007</td>
<td>1050</td>
<td>19</td>
<td>Ag0.5Pd0.5</td>
<td>0.5</td>
<td>0</td>
<td>Textural type 2, minor quench</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>D2188</td>
<td>1050</td>
<td>0.5</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>2</td>
<td>Textural type 1</td>
<td>79.1-19.6-1.1</td>
<td></td>
</tr>
<tr>
<td>D2200</td>
<td>1050</td>
<td>48</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>2</td>
<td>Textural type 2</td>
<td>75.2-23.7-1.2</td>
<td></td>
</tr>
<tr>
<td>D2203</td>
<td>1050 → 650 → 1050</td>
<td>10 + 24 + 4</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>2</td>
<td>No nanonuggets, large PGM on oxides, quench</td>
<td>88.9-10.2-0.9</td>
<td></td>
</tr>
<tr>
<td>C5220</td>
<td>1050</td>
<td>2</td>
<td>Ag0.5Pd0.5</td>
<td>0.1</td>
<td>2</td>
<td>Pd–PdO–O2, quench</td>
<td>n.a.</td>
<td></td>
</tr>
</tbody>
</table>

1 Molar proportions of magnetite (mt: Fe2+Fe3+O4), ulvöspinel (us: TiFe2+O4) and hercynite (he: Fe2+Al2O4).
2 Molar proportions of hematite (hm: Fe3+O2), ilmenite (il: Fe3+TiO3) and corundum (co: Al2O3).
3 n.a.: detected by Raman, but not analysed by EDS.
UltraPlus FE-SEM using 1–3 kV accelerating voltages and short working distances (<4 mm), facilitating use of in-lens secondary electron (SE) and backscattered electron (BSE) detectors. Images were acquired in pixel average (BSE) or frame integration (SE) modes.

4. RESULTS

Details of each experiment, including run conditions and results are given in Table 3. All experiments formed a dark brown glass that macroscopically appears black because of abundant oxide crystals. Nepheline occurs in the lower $T$ runs (D1892, D1901, D1996) and a rhenate-sodalite (ideally Na$_8$(AlSiO$_4$)$_6$ReO$_4$) occurs in the Re-bearing runs (D1900, D1901, D1906). Occasionally nepheline crystals occur in high $T$ runs and nucleate on gas bubbles, suggesting that (1) gas was a stable phase, and (2) nepheline can crystallise on quench given an appropriate nucleation site. Metallic phases other than the starting materials appear in all runs. Rhenium was highly soluble in the melt, and did not occur in nanonuggets or metallic phases other than the starting materials. Therefore, Re will not be considered further.

The variety of observed textures and analysed materials is too great for inclusion in this report. For details, please see full results in the online Supplementary content.

4.1. Fe-Ti oxides

Oxide minerals were characterised by EDS for composition and by Raman spectroscopy for phase identification, results of which are summarised in Fig. 2. TiO$_2$-free runs consisted of either pure hematite or magnetite, corresponding to final $f_O_2$ conditions higher or lower relative to the HM buffer, respectively. Magnetite–ulvöspinel and hematite-ilmenite spectra were acquired from runs D1996 and D1976, respectively. (b) Analysed compositions of oxides, plotted in the magnetite–ulvöspinel–hercynite and the hematite–ilmenite–corundum triangles. Coexisting oxides are connected with a line.

Fig. 2. (a) Raman spectra obtained for two oxides. Magnetite–ulvöspinel spectra do not vary between runs. The relative intensities of the peaks of hematite–ilmenite vary between runs and between individual crystals in a single run but their positions do not. Magnetite–ulvöspinel and hematite-ilmenite spectra were acquired from runs D1996 and D1976, respectively. (b) Analysed compositions of oxides, plotted in the magnetite–ulvöspinel–hercynite and the hematite–ilmenite–corundum triangles. Coexisting oxides are connected with a line.

4.2. Metallic phases

Metallic phases appear in two distinct morphologies. The first are spherical particles up to ~1 $\mu$m in diameter that we refer to as ‘nanonuggets’. The second are euhedral to subhedral alloys larger than ~0.5 $\mu$m that we refer to as ‘PGM’. Although the nanonuggets may strictly be PGM as well, their spatial distribution and relation to larger faceted crystals warrants this distinction.

Nanonugget size can only be inferred by optical methods: By using the 100× objective and the camera in our setup, 1 pixel of a full resolution image equals roughly 50 nm. However, the diffraction limit of light is ~150 nm
and only larger objects will be theoretically fully resolvable, whereas anything smaller will be a point of light. Plasmon resonance occurs when light hits a conducting nanoparticle (e.g. noble metal nanonugget) embedded in a non-conducting medium (e.g. silicate glass). As a result, the scattered light has distinct light intensity and colour, as a function of composition, size and shape (Mock et al., 2002). The scattered light spectrum can be easily calculated for spherical monoatomic particles using Mie theory. Fig. 3 shows the expected intensity and colour of a spherical nanonugget for several compositions and particle sizes. At a diameter of 150 nm, Au is red, Ag is green, and both Pd and Pt are white. At decreasing sizes, Ag is orange at 100 nm, and at 50 nm Ag is vivid blue, Au is low intensity lime–green, and Pt and Pd are dull violet. In general, only Ag and Au exhibit clearly discernible colour changes with size. As nanonuggets deviate from ideal spherical shape and become angular, their scattering spectrum shifts to longer wavelengths (Jin et al., 2001; Mock et al., 2002). Nanonugget alloys display different colours that may or may not be a linear mixing function. These confounding factors may complicate the optical observation interpretations, but the experimental charges are overwhelmingly dominated by spherical Ag nanonuggets (see below), making interpretation straightforward. In theory, the lower detection limit of nanonugget size using this method is roughly 15 nm (Dionne and Atwater, 2012), but in our runs the nanonuggets are embedded in dark silicate glass so it is possible that the smallest observable nanonuggets will be somewhat larger.

Compositions of metallic phases were determined using two methods: EDS and LA-ICP-MS. The two methods are complementary: EDS is capable of determining major element composition of a single PGM or a large-enough nanonugget (normally at least 500 nm), whereas LA-ICP-MS can determine major and trace element composition of numerous metallic phases regardless of size, but cannot necessarily distinguish between phases (i.e. two adjacent phases often register as one), and the size of each phase can only be estimated.

4.2.1. Ag–Pd capsule runs

High-T runs in Ag–Pd capsules contain abundant nanonuggets mostly homogenously dispersed throughout the glass. The abundance of nanonuggets is variable from one experiment to another (Fig. 4).

Because Ag-nanonuggets are the most abundant (see below), the dominant colour observed in a certain area corresponds to Ag-nanonugget size and can be used as a proxy for the relative sizes of the other nanonuggets. For example, Fig. 4a and b show a transition of nanonugget colour from white (coloured yellow-orange by the glass, around 150 nm and larger) to vivid blue (~50 nm). Representative examples of LA-ICP-MS traverses crossing nanonugget size gradients are D1892-2, D1981-3 and D2002, available in the Supplementary files. High resolution imaging reveals that most nanonuggets are sub-spherical, with weakly defined crystal faces (Fig. 5a).

Metallic phases are particularly abundant on Fe-Ti oxide crystal faces, surrounded by apparently nanonugget-free halos (Fig. 4). We can observe two textural types involving metallic phases and oxides:

Type 1: Nanonuggets roughly 200 nm wide. Always larger than ~50 nm and smaller than 1 µm. The size does not depend on location, whether on oxides or in surrounding glass (Figs. 4c, 5a, 5c, video 1).

Type 2: coarse PGM larger than 0.5 µm on oxides associated with fine nanonuggets in the surrounding glass, up to ~150 nm (Figs. 5d, 5b, 5d, 5e, video 2).

Commonly type 2 runs had more abundant nanonuggets dispersed in the glass (e.g. Figs. 4b, 5b). Also, although most oxide-associated nanonuggets adhere externally to the oxides, they are occasionally partly included in them, suggesting coeval growth of both phases (Fig. 5c, f). No nanonugget inclusions were observed by SEM in nepheline. Unfortunately, it was not possible to image the transparent nepheline using the 100× objective, and nanonuggets are just barely visible using a 50× objective. However, it was sufficient to observe some nanonuggets included inside

Fig. 3. Scattering efficiency versus optical wavelength for various nanoparticle compositions and sizes. Calculated using MiePlot 4.5.03 (http://philiplaven.com/mieplot.htm) using the n–k data of Hagemann et al. (1975) and Rakić et al. (1998) from Polyanskiy (2015).
nepheline whereas none were found on nepheline exteriors (a relatively clear example is given in Fig. 6). This occurred in runs where nepheline was an equilibrium phase and in runs where it formed on quench.

Most nanonuggets analysed by EDS were composed of pure Ag, although rare Ag–Pd and Ag–Pd–Bi alloy nanonuggets were observed. In the PGM bearing runs, a variety of Ag–Pd, Ag–Pd–Bi and Ag–Pd–Pt alloys of varying
compositions are seen (examples in Fig. 7). PGM compositions vary in a single experiment and also between experiments. We could not find any correlation between composition, size, location, or any other factor.

Several runs exhibit quench textures such as nanorods (Fig. 4e), dendrites (Fig. 4f), and whiskers (Fig. 4g, video 3), that all nucleate on pre-existing nanonuggets or coarser PGM. These commonly show green, red or blue colours owing to their nanoscale width. Where nucleation spots do not exist, quench textures include various blobby features (Fig. 4h, video 3) that may appear similar to nanonuggets, but are distinguished by the inability to optically focus on them, and by their distinct morphology in electron imaging. Whilst equilibrium nanonuggets are spherical to sub-spherical with occasional crystal faces and sharp contacts with the glass, quench phases are commonly zoned and elongated with irregular shapes (Fig. 5h). Quench phases large enough to be analysed by EDS were always composed of pure silver, with no PGE detected.

Three low-T runs were conducted in Ag–Pd capsules. The first is D1982 at 960°C, in which nanonuggets were identical to those seen at 1050°C or 1100°C runs. The second is D1996 which was gradually cooled to 650°C over 24 h after dwelling at 1050°C for 16 h. This experiment shows two marked differences from the high-T runs. Firstly, nanonuggets are extremely scarce, and in oxide-free regions all Au, Pt, Pd and Ir barely detectable. Secondly, PGM are larger than in any other run, reaching up to 10 μm (Fig. 5g). Run D2203 was similar, except that it was heated back up to 1050°C over 4 h. Similarly, it contains coarse PGM and no nanonuggets, but it contains abundant quench whiskers (Fig. 4g).

We buffered fO2 in run C5220 by placing powdered Pd and PdO inside the capsule. Instead of nanonugget free halos prevalent in other experiments, nanonuggets were especially concentrated near hematite (Fig. 4h). The distal glass contained filamentous regions of nanonuggets dispersed between nanonugget-free, quench-rich zones. Overall, the density and colour of the nanonuggets resembles type 2 runs, but no PGM are present. Vapour bubbles appear next to PdO which we interpret as pure or almost pure O2 (Fig. 4i). Hematite crystals were slightly more abundant in these regions, but the overall textural nanonugget relations were not affected by the presence of O2.

Two experiments were run with 5 wt% TiO2: D2001 (Fig. 4e) and C5068 (Fig. 4f). In run D2001 aggregates of Ag nanonuggets and quench nanorods occur dispersed in the glass, commonly with nanonugget-free halos. Nanonuggets also occur on oxide faces, similar to the other experimental runs. In run C5068 similar quench aggregates occur, but are associated with Fe-Ti oxides and are much larger, up to 20 μm wide, occasionally exhibiting a dendritic
form. The surrounding nanonuggets are identical texturally and chemically to those in type 2 runs.

A representative LA-ICP-MS time resolved spectrum is given in Fig. 8, in which most of the features discussed below are represented. However, we highly recommend the reader review the spectra attached in the Supplementary files. Fig. 4l shows a typical laser traverse and demonstrates the poor spatial resolution of this method, even when using a small spot size. Still, it provides valuable data: LA-ICP-MS analyses confirm that Ag nanonuggets are the most common. However, we found that Ag nanonuggets contain trace amounts of all PGE. In addition, discrete PGE nanonuggets were observed as well. Pd and Pt were usually hosted in the same nanonuggets, although rare pure Pd and Pt were observed as well. Au was commonly associated with the Pd–Pt nanonuggets, but occasionally formed its own nanonuggets. Ir is generally found in nanonuggets without the other metals. Due to high Bi$_2$O$_3$ contents of the glasses, the nanonugget Bi signal was obscured by high backgrounds. Thus, Bi peaks were only observed in the larger PGM encountered by the laser. An exception is run D1891 where Bi$_2$O$_3$ was used only in trace amounts and Bi containing nanonuggets are clearly visible.

PGE counts were particularly high around oxides, as expected from the textural observations. Furthermore, the two types of metal–oxide associations are clearly observable. In runs where similar-sized nanonuggets appear both on oxide faces and in glass, nanonuggets of all kinds were also abundant in the glass not associated with any oxide. Conversely, in type 2 runs, where PGM occurred on oxides and nanonuggets were finer in the glass, PGE contents were much lower in the glass (with Au and Ir almost undetected in some regions).

4.2. Pt and Au–Pd capsule runs

Two experiments were run in Pt capsules. Run D1906 was a high-$T$ run at 1100 °C, which resembles the type 2 PGM-bearing experiments run in the Ag–Pd capsules, except for fewer nanonuggets and PGM on oxide crystal faces. This is expected as Ag is a trace element, but otherwise, nanonugget compositions are similar to the Ag–Pd experiments: Pt, Pd, Au, Ag and Bi are commonly associated whereas Ir often forms a separate phase. Run D1901 was gradually cooled to 900 °C over 13 h after dwelling at 1100 °C for 13 h. Similar to the low-$T$ experiment in Ag–Pd capsule (D1996), the glass is completely devoid of nanonuggets and several coarse PGM are found in contact with oxides, but not nesphelinitite.

One experiment was run in a Au–Pd capsule (D2007). The resulting nanonugget and PGM distribution was similar to the high-$T$ Pt experiment (D1906).

4.3. PGE in oxides

As laser ablation traverses encounter oxides, Fe and PGE counts increase. Because the oxides commonly occur in aggregates of crystals smaller than the laser spot size, it is not possible to define a glass-free area in the laser signal (e.g. Fig. 4l). Multiple nanonuggets are ablated simultaneously, occasionally appearing as a gradual increase in PGE counts associated with elevated Fe counts, with individual spikes representing the larger nanonuggets or PGM. Iridium, however, behaves differently than the other PGE: its gradual increase is usually smoother and closely mirrors the Fe signal. Even in cases where no nanonuggets are detected, Ir contents follow Fe. We interpret this as incorporation of Ir into oxides by solid solution (in agreement with Brenan et al., 2012 and Page` and Barnes, 2016), in addition to any Ir nanonuggets that are observed on the oxide faces. This was observed regardless of the oxide: it occurred in both mt-us and hm-il.

5. DISCUSSION

5.1. Equilibrium or quench?

It could be argued that the observed nanonuggets formed during quench (e.g. Cottrell and Walker, 2006; Barnes et al., 2015) rather than during the experiments. The nanonuggets are finely dispersed throughout the glass, and appear to adhere to mineral grains. Whilst we did observe features consistent with quench origin, these were limited to a handful of experiments that were either oxidised (runs D1976, D1986, D2002, D2203, C5220, Fig. 2b) or rich in TiO$_2$ (runs D2001, C5068, see discussion below). However, there are several lines of evidence to suggest that the nanonuggets were in fact part of an equilibrium assemblage. Firstly, the nanonuggets appear only in
contact with (or partially included in) newly formed oxide minerals. No nanonuggets or halos were found around unreacted Fe$_2$O$_3$ or Al$_2$O$_3$ that appeared in the shorter experiments (e.g. run D1955). Secondly, no halos were found around nepheline that formed in the lower $T$ runs (D1892, D1901 and D1996). Nanonuggets were included in equilibrium nepheline, establishing their presence at run conditions (Fig. 6). Thirdly, had nanonuggets formed during quench, this would be reflected in their size with finer and coarser nanonuggets occurring closer to the capsule walls and in the centres of experimental charges, respectively. However, as clearly evident by the colour of the nanonuggets (e.g. run D2002: Fig. 9), this is not the case and the size distribution does not support formation during quench. Our interpretation agrees with Ertel et al. (2006), Yokoyama et al. (2009), Méard et al. (2015), and Malavergne et al. (2016) to show that nanonuggets do not form on quench.

5.2. Textural interpretation

Interpreting the observed textures is not straightforward since the difference between initial and final $f$O$_2$ ($\Delta f$O$_2$) is unknown. Whereas the final $f$O$_2$ can be inferred from the Fe-Ti oxide assemblage or compositions, all that is known about the initial $f$O$_2$ is that it is higher than the HM buffer. Large $\Delta f$O$_2$ would allow more noble metals to precipitate as metallic phases, whereas small $\Delta f$O$_2$ would cause a larger proportion of noble metals to remain dissolved in the melt. There is no correlation between the final $f$O$_2$ and the textural type. We suggest that type 1 runs correspond to small $\Delta f$O$_2$, evident by the lower abundance of nanonuggets overall and the lack of PGM. Similarly, type 2 runs, with coarse PGM and abundant nanonuggets are consistent with large $\Delta f$O$_2$. As large $\Delta f$O$_2$ must be preceded by smaller $\Delta f$O$_2$, we...
suggest that all type 2 runs started as type 1 runs, and given enough reductant, type 1 runs progressed to type 2.

5.2.1. Initial nanonugget formation

Glass-hosted nanonuggets in type 1 runs are rarely blue (~50 nm), and are thus coarser than type 2 nanonuggets. There are two cases where blue nanonuggets appear in the distal glass in type 1 runs: in run D1955 which ran for only 10 min beyond the initial T ramp (Fig. 4j). In this run, the colour distribution of nanonuggets in the glass is seemingly random, and there is no association between blue or white (>100 nm) nanonuggets and oxide rich zones. The second case is run D1986 (24 h), which has blue nanonuggets trapped in a magnetite-hosted melt inclusion in an otherwise yellow–white nanonugget bearing glass (Fig. 4k). This suggests that the initial nanonugget formation is a gradual process of coarsening, which is still progressing after 10 min, but is complete after 2 h evident by shorter runs (D1921, D1954 and D2188).

Preferential nucleation of nanonuggets on chromite and spinel-group minerals (e.g. magnetite) has been previously observed experimentally (Capobianco et al., 1994; Bockrath et al., 2004b; Finnigan et al., 2008; Wijbrans et al., 2015; Schwander et al., 2015a). Two explanations have been proposed for the association of nanonuggets and spinels: (1) precipitation by local reduction in the spinel-melt interface (Finnigan et al., 2008), and (2) preferential nucleating and wetting on spinel surfaces (Ballhaus et al., 2006; Wijbrans et al., 2015).

We suggest that both processes are occurring in our experiments. In type 1 runs, there is no positive correlation between the oxide crystal size and the amount of adhered nanonuggets. For example, Fig. 4d shows small magnetite crystals that are covered with nanonuggets, even in preference to larger crystals (similar phenomena were observed by Wijbrans et al., 2015). This does not fit with the model of Finnigan et al. (2008), which predicts more nanonuggets on larger crystals because of increased depletion of Fe^{3+} from the neighbouring silicate melt. On the contrary, our observation suggests that nanonuggets preferentially stick to small crystals. However, there are not enough nanonuggets adhering to oxides to explain the nanonugget-absent halos (see the type 1 runs D1955, D1989 and C5057 in the Supplementary files). In order to explain this, we need to understand the time progression of the stages. When ramping up temperature, oxide phases are already growing in silicate melt, as implied by the phase assemblage in the 650 °C run (D1996). However, noble metal solubilities are still low. Therefore, at this stage, a redox gradient already exists in the silicate melt, before any significant amount of noble metals are dissolved in from the capsule material. Small amounts of noble metals were nonetheless dissolved by this stage and then reduced to form nanonuggets due to redox gradients imposed by growing oxides. These nanonuggets preferentially stick to the smaller oxide crystals. The redox gradient then blocks any additional dissolved metals from diffusing though the silicate melt to the oxide-rich regions, and they remain only in the distal glass. As the experiment progresses the gradient is relaxed, but the overall O_2 inside the capsule is lowered due to H_2 diffusion from the assembly and as a result nanonuggets form in the distal glass.

Further insight can be gained from the PdO-bearing run. In this case the high fO_2 imposed by the oxygen buffer allowed noble metals to diffuse throughout the capsule, but they were precipitated as nanonuggets only next to hematite (Fig. 4h and i). Elsewhere in the experimental chamber, noble metals remained dissolved in the melt as a result of the extremely high O_2. Interestingly, once nanonuggets formed they could not be redissolved by oxidation. Even nanonuggets in proximity to O_2 bubbles did not redissolve in the silicate melt. This exceptional stability of noble metal nanoparticles is also known from nanotechnology studies where Ag nanoparticles could only redissolve when treated with substances that would decrease their electron potential, thereby making them less ‘noble’ (Pal et al., 1997). Exceptional stability of nanoscale phases is also known from other geological materials and is currently a subject of intense research (e.g. Goldberg et al., 2016). In our experiments, nanonuggets could only be removed by formation of PGM, as described below.

5.2.2. PGM formation

Type 2 runs had higher ΔO_2, and therefore more nanonuggets. However, this also caused growth of PGM, which did not occur in type 1 runs. Interestingly, the PGM occur almost exclusively on oxide minerals and rarely in the open glass (Fig. 4), irrespective of the fact that similar nanonuggets initially appeared in both places. We attribute this to the redox gradient imposed by the growing oxides—thus more PGM were precipitated from the melt as noble metal solubility was especially reduced in the redox gradients surrounding oxide grains compared to the distal glass.

During PGM growth, PGE from the adjacent melt diffused to the growing PGM crystal. As this depletes the more distal areas of PGE, coarser nanonuggets redissolve in the silicate melt causing them to become finer or disappear altogether (particularly next to the oxides), as is clearly evident in all type 2 runs. Curiously, this process occurred only as solubility decreased rather than increased by relaxation of redox gradients, especially evident in run C5220. However, this process can only progress so far because the piston cylinder apparatus has a limited reducing capability. Noble metal solubility also depends on temperature (Borisov and Palme, 2000; Forfenfant et al., 2003; Brenan et al., 2016), therefore additional PGM formation was achieved by slow cooling. Run D1996, which dwelled at 1050 °C for 16 h, sufficient for the formation of either type 1 or type 2 textures within, and then cooled to 650 °C over 24 h. The trend observed in the type 2 runs proceeded to completion: the PGM coarsened at the expense of nanonuggets until none were left. Surprisingly, noble metals were removed from nanonuggets, transported through the silicate melt and attached to growing PGM—all this occurring in a regime of decreasing temperature, far below the melting point of the metals (except Ag), and in an environment where noble metal solubility is decreasing over time. Similar textures were observed in equivalent runs in Pt capsules (runs D1901 and D1906). We suggest that the ‘PGM growth by redox gradient’ model of Finnigan et al. (2008)
should be extended to a more comprehensive solubility gradient, of which redox is one factor. \( T \) is an additional factor, and perhaps composition is a third factor, similar to the synthesis given by González-Jiménez et al. (2014).

TABS are commonly associated with PGE in natural rocks. Here we show that Bi forms solid solution with PGM regardless of its concentration in the silicate melt. It is highly soluble as Bi$_2$O$_3$ (evident by the high Bi contents of glasses in some runs) and does not saturate, evident by the lack of any specific Bi mineral in our experiments. Yet, it still occurs as a major element in PGM and coarser nanonuggets, even when added as a trace constituent. This suggests that Bi in PGM is not controlled by Bi saturation but rather by the high stability of Bi–PGE metallic bonds. A similar process was suggested for PGE–As minerals observed in the Pindos ophiolite (Kapsiotis et al., 2011). Helmy et al. (2013) showed the common association of As (also a group 15 element) and Pt in nanoscale phases observed in experiments that did not achieve saturation in any particular Pt–As phase. This is in contrast to the accepted model that PGM saturate and crystallise out of cooling PGE-rich sulfide liquids (Barnes et al., 2006; Holwell and McDonald, 2010; Helmy et al., 2010). Furthermore, Hutchinson et al. (2015) claim that in the Merensky Reef and Platreef of the Bushveld, TABS extracted PGE out of the PGE-enriched sulfide to form TABS-bearing PGM, even without any saturation of any specific TABS element in both silicate and sulfide liquids. Another possibility is the formation of PGE-TABS eutectic melts, as suggested by Borisov and Palme (1997), but our experimental results suggest otherwise. The multitude of PGE types in a single locality is often given as evidence for late alteration and local fluctuations in various intensive parameters such as \( T \), \( P \), \( f\text{O}_2 \) and \( f\text{S}_2 \) (e.g. Cawthorn et al., 2002). However, in our experiments we also observe differing PGM phases in a single run where \( T \) and \( P \) were kept constant, \( f\text{O}_2 \) decreased to a constant, and sulfur was not present. Ag, Ag–Pd, Ag–Pd–Bi, Ag–Pd–Pt (in varying proportions) were all detected together using EDS, and the existence of Au and Ir bearing phases can be inferred from LA-ICP-MS analyses.

Médard et al. (2015) suggested that Ostwald ripening will cause coarsening of larger PGE phases at the expense of smaller nanonuggets. Their proposed mechanism is that Pt$^6$ atoms detach from nanonuggets, diffuse as ions through the silicate melt and then reattach to larger crystals. This requires that Pt (or any other noble metal) has a redox partner in their runs, they observed that nanonuggets appeared in Fe-poor synthetic compositions, but were absent in Fe-bearing natural compositions. They cited this as evidence for the role of Fe as a redox partner for nanonugget removal. Our results argue against this process. Run D2200 was completed in 48 h–longer than any other run, including runs with coarse PGM (D1996 and D2203, run for 40 and 38 h, respectively). While oxides Ostwald ripened (D2200 has some of the largest ilmenite crystals of all runs), noble metals did not. The noble metal assemblage is type 2 with 1–2 \( \mu \text{m} \) wide PGM and abundant nanonuggets of all colours dispersed in the glass, indistinguishable from other type 2 experiments run for only 3 or 4 h (e.g. D1943 and D1912). The starting mix contained about 15 wt% of Fe$_2$O$_3$, and as the run reduced there was no shortage of both Fe$^{2+}$ and Fe$^{3+}$ in the melt. This is inconsistent with the suggestion of Médard et al. (2015) that Fe is a redox partner that facilitates Ostwald ripening of noble metal nanonuggets.

5.2.3. Effect of Ti

The two runs containing 5 wt\% of TiO$_2$ (D2001 and C5068) indicate a possible control by the Fe–Ti oxide composition on PGM crystallisation. Whereas noble metal nanonuggets formed, we could not find any PGM. Instead, abundant aggregates of quench Ag nanonuggets and nanorods occur. Quench textures were common in oxidised runs, but these two runs were not particularly oxidised (Fig. 2). There are two explanations for this phenomenon: Firstly, TiO$_2$ is known to increase noble metal solubility in silicate melts (Borisov et al., 2004). Secondly, given two runs with identical \( f\text{O}_2 \), runs richer in Ti crystallise more Ti-rich oxide (in the mt-us and hm-il series), thus removing less Fe$^{2+}$ from the silicate melt. As a result, the melt is less reduced than runs that crystallise Ti-poor–Fe$^{3+}$-rich oxides. Both of these processes facilitate dissolution of more noble metals in the melt than in Ti-poor compositions. Therefore, the total amount of noble metals dissolved in the melt may reach the amounts present in oxidised Ti-poor runs, and their subsequent deposition as quench phases.

5.3. Implications for natural systems

5.3.1. Direct crystallisation of PGM: are sulfides necessary?

Our experiments show that PGM can crystallise directly from silicate melts, in agreement with previous experimental studies (e.g. Finnigan et al., 2008; Wijbrans et al., 2015). Direct crystallisation of PGM from silicate magma has been suggested to occur in some natural localities (Stockman and Hlava, 1984; Peck et al., 1992; Barnes, 1993; Melker et al., 1997; Mutanen, 1997; Garuti et al., 1999, 2003; Brennan and Andrews, 2001; Augé et al., 2005; Godel et al., 2007; Wang et al., 2008; Park et al., 2012; Kamenetsky et al., 2015), but paradoxically the PGE contents are sometimes in fact higher than what would be possible according to experimental determinations of PGE solubility in silicate melts (Augé et al., 2005; Naldrett et al., 2009; Maier et al., 2015). Sulfur-bearing yet sulfide-under saturated silicate melts may be capable of dissolving larger amounts of PGE, but experimental studies show contrasting results for different PGE: S$^2$ increases Ru solubility in the silicate melt, whereas Pd bonds with sulfur making an immiscible sulfide phase that depletes the silicate of Pd (Laurenz et al., 2013). Fonseca et al. (2009) and Mungall and Brennan (2014) claim that high sulfur and PGE contents in silicate melts are possible at sulfide saturation, but this may only be applicable in a few cases because it requires very little sulfide relative to silicate, and that both liquid phases are PGE saturated. Additional work by Mungall and Brennan (2014) showed that partition coefficients for PGE between sulfide and silicate are higher than previously thought and simple magma mixing can explain the anomalously high PGE tenors in ore deposits such as the
Bushveld. However, as stated above, much of the PGE are hosted as PGM inclusions in oxides and silicates. Sulfur-loss processes are thus invoked to explain the occurrence of S-absent PGE mineralisation. Curiously, some sulfide-hosted PGM are interpreted as PGE saturation in the silicate melt prior to sulfide saturation, with subsequent preferential trapping in a later immiscible sulfide liquid (Wirth et al., 2013; Junge et al., 2015; Barnes and Ripley, 2016). This suggests that in some cases sulfides only act as collectors that upgrade the PGE tenors of already PGM-saturated magmas by physically concentrating the PGE phases (Mutamnen, 1997; Bockrath et al., 2004b; Ballhaus et al., 2006). One possibility for the anomalously high PGE content in magmas is their transport as nanonuggets with additional stabilisation by TABS. This stands in contrast to the more prevalent explanation that sulfur was removed from the system. In many cases—particularly when the PGM are wholly included in oxides or silicates—there is no evidence for sulfur loss. Finnigan et al. (2008) showed that PGM can directly crystallise from silicate magmas during oxide growth. This hypothesis was subsequently confirmed in natural rocks by Gonzalez-Jiménez et al. (2009). Our study supports that model: we show that such phases (either in the form of nanonuggets or full-sized PGM) can form from silicate magma without sulfide saturation, thus a sulfur-loss process is not needed. PGE inclusions can also appear in oxidised rocks where sulfide would not be stable, for example in the Guli massif in which the occurrence of nanonuggets is interpreted as mixing of two PGE saturated magmas (Ryabchikov and Kogarko, 2012).

A common process invoked for PGM crystallisation in magnetitites is sulfide saturation by magnetite-induced reduction (Loucks and Glasscock, 1989; Prendergast, 2000; Bowles et al., 2013). As magnetite crystallises, Fe₂O₃ is removed from the melt reducing the /O₂, triggering sulfide saturation that scavenges PGE from the melt. However, this process shares the same problem observed in some other chromitite-hosted PGE deposits: where are the sulfides? Again, a sulfur-loss process is suggested (Prendergast, 2000; Bowles et al., 2013). In our experiments we show that neither sulfide saturation nor sulfur loss is required. PGM can crystallise in association with magnetite regardless of the presence of an immiscible sulfide phase in the system. Okrujin (2011) proposed a model for the concentration of PGE in immiscible Cr₂O₃ oxide melts, but in our study no immiscible oxide melt was observed and therefore liquid immiscibility is not needed to explain the association of PGE with oxide minerals.

5.3.2. Causes for nanonugget formation in nature

What causes saturation of PGE in the silicate melt and formation of nanonuggets in the first place? One possibility is that PGE-bearing sulfide liquid entrained in mantle-derived silicate melt may redissolve the immiscible sulfide phase due to increasing sulfide solubility during decompression (Mavrogenes and O’Neill, 1999), as suggested by Maier (2005), Bockrath et al., 2004a and Ballhaus et al. (2006). Decompression might also change the valence state of sulfur. Sulfide is stable at rather oxidising conditions at high pressure, but changes to sulfate upon decompression (Matjuschkin et al., 2016), releasing any PGE transported with it to the silicate melt.

A more compelling mechanism, suggested by our experimental results, does not require a sulfide phase whatsoever at all stages of magmatic evolution. There are regions in the mantle that host S-free PGE(±TABS) phases commonly interpreted as refractory residues after initial partial melting and sulfur removal, or metasomatism and refertilisation (Bird and Bassett, 1980; Luguete et al., 2007; Kogiso et al., 2008; Lorand et al., 2010, 2013; Fonseca et al., 2012; Ferraris and Lorand, 2015; König et al., 2015; Lorand and Luguete, 2016). A PGE undersaturated mantle melt generated in or percolating through these regions will dissolve PGE, ideally until saturation is reached.

PGE solubility depends to a large degree on /O₂, but it is also dependent on the S²⁻ (Laurenz et al., 2013) and Fe²⁺ content of the melt (Laurenz et al., 2010), with higher PGE contents possible at higher Fe²⁺ contents (Médard et al., 2015). TiO₂, silica depolymerisation, and H₂O contents also play a role in PGE solubility as mentioned previously. Oxide crystallisation will increase the relative proportion of Fe³⁺ in the melt and decrease Ti⁴⁺, whereas silicate crystallisation will reduce it. Redox and other compositional changes may also happen during magma mixing or assimilation processes. All of the above processes may cause fluctuations in the PGE solubility of a silicate magma close to PGE saturation, providing ample opportunities for the appearance of nanonuggets (e.g. Garuti et al., 2003). Once formed, nanonuggets will not redissolve in the silicate melt, even if solubility increases (as evident by runs D2203 and CS220). If a nanonugget bearing magma is then modified again such that PGE solubility increases, it will dissolve PGE from any coarse PGE alloys it encounters, rather than nanonuggets. The nanonuggets will not fractionate and be carried along with the melt owing to their small size. They may also stick to any oxides present in the magma or be trapped as inclusions in minerals. Therefore, this silicate melt will be richer in PGE than equilibrium solubility permits.

5.3.3. Applicability to natural systems

While it is true that our experiments had an ‘infinite’ metal source in the capsule, other metals were available only as trace constituents and were still mobilised to the nanonuggets and eventually coarser PGM. The presence of an ‘infinite’ capsule is not important. Once a silicate melt becomes PGE saturated, the amount of the saturated bulk phase (i.e. a PGM and not a nanonugget) has no thermodynamic significance. Two different silicate melts with identical properties and P-T-Xf/O₂ paths will behave similarly with respect to PGE whether the melt is enclosed in an experimental capsule or it exists in the mantle in the presence of PGM crystals.

It may be argued that our experiments, which incorporate silver and enhance nanonugget formation are not applicable to natural rocks, where PGE solubilities are orders of magnitude lower. We now present a simple calculation to show that abundant nanonuggets are not required to drastically change PGE contents in a melt. Consider a (100 μm)³ cube of silicate liquid of density 2800 kg/m³ with
10 ppb dissolved Pt. This cube has a mass of 2.8 μg and contains 28 fg of Pt. A single Pt nanonugget with a 50 nm radius has a mass of ~11.4 fg. Thus, only three such nanonuggets are required to more than double the total amount of Pt contained in the magma. Dozens to hundreds of nanonuggets occur in a similar volume in experiments D1906 and D2007, run in Pt and AuPd capsules, respectively (see online Supplementary files). Therefore, even in the absence of silver, orders of magnitude more nanonuggets than required to surpass equilibrium solubilities are present. Natural systems regularly have smaller δ/O2, lower overall /O2 and melt compositions that are less favourable for PGE dissolution and nanonugget formation. However, given that only a few nanonuggets are required to significantly enrich silicate magmas with PGE, it is not unlikely that this process occurs in nature.

5.4. Possible implications for core–mantle differentiation

It is currently accepted that PGE partitioned to Earth’s core during the core–mantle differentiation event. However, there are more PGE in the mantle than would be predicted from metal/silicate partition coefficients. The ‘late veneer’ theory solves this discrepancy by suggesting that meteoritic PGE were added to the mantle at a later stage (Righter, 2003). This theory is substantiated on very high metal/silicate partition coefficients measured experimentally. Previous studies were concerned on whether nanonuggets occurring in experimental charges are an ‘artifact’ and should be disregarded when deriving partition coefficients (Malavergne et al., 2016) or not (Cottrell and Walker, 2006). Very little consideration was given to the possible role of the nanonuggets themselves occurring in nature and the effect that this ‘experimental artifact’ may have on core–mantle differentiation processes. We suggest that nanonuggets could have remained in the mantle during core formation, thus retaining PGE in the mantle above equilibrium levels. We suggest this warrants further study.

6. CONCLUSIONS

1. Optical microscopy using a 100× oil immersion objective is a powerful technique that can reveal the three dimensional distribution of nanonuggets, and possibly their relative size and composition. We encourage all who work with these kinds of materials to examine their experimental runs with this method. Even though vivid colours are observed only with Au and Ag, other nano phases are visible nevertheless.

2. Nanonuggets can be a means to transport PGE at much higher concentrations than can be dissolved in silicate magmas. Because of their diminutive size, they are carried in colloidal suspension and do not fractionate or settle out mechanically.

3. PGE saturation in our experiments is a two stage process: initial saturation as nanonuggets followed by ‘proper’ PGM. Nanonuggets only appear when solubility decreases. We do not know why this is the case, and this issue requires novel experimental and analytical techniques to be developed in future studies.

4. Nanonuggets are consumed as PGE feedstock for coarser PGM, leaving no traces of their previous existence unless fortuitously trapped as inclusions in minerals (e.g. Merkle, 1992; Handler and Bennett, 1999; Ballhaus and Sylvester, 2000). Even then, they may be easily overlooked because of their small size, rarity, random distribution and simply because silicate minerals are usually not analysed for PGE in routine studies.

5. PGE solubility and partitioning experiments require removal of nanonuggets. We suggest that in cases where melt composition permits, cooling and heating of the run (possibly more than once) may remove nanonuggets and produce coarser metallic phases, which are more easily removed or avoided when analysing the glasses.

ACKNOWLEDGMENTS

Technical assistance for the piston cylinder runs was provided by Dean Scott, David Clark and David Cassar. Access to the facilities of the Centre for Advanced Microscopy (CAM), with funding through the Australian Microscopy and Microanalysis Research Facility (AMMRF), is gratefully acknowledged. We wish to thank Peter Tolland for his assistance with the LA-ICP-MS analyses, to Antony Burnham for his assistance with the Raman analyses, and Neil Bennett for his thorough review of the text. Michael Anenburg acknowledges the support of a Ringwood Scholarship from the Research School of Earth Sciences.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.08.010.

REFERENCES


Associate editor: Rajdeep Dasgupta
Chapter 6: Anenburg & Le Losq (II)—SNAppSci

Some of the experiments conducted for chapter 5 resulted in the surprising crystallisation of perrhenate sodalite: Na₈(AlSi)₆O₂₄(Re⁷⁺O₄)₂. The important points from these experiments are:

1. First demonstration of perrhenate sodalite crystallisation from silicate melts. All previous methods used low temperature wet chemistry or hydrothermal methods, usually below 200 °C. This proves the thermodynamic stability of perrhenate sodalite at these conditions.

2. Equilibrium coexistence of Re metal and Re⁷⁺: this shows the ability of sodium to stabilise high oxidation states of metals (most known is Fe³⁺). This is the first demonstration of a higher oxidation state by Na.

3. Re is occasionally used as an analogue for Tc, and sodalite is potentially used to retain volatile Tc/Re during nuclear waste vitrification. This shows that by adjusting the glass composition it is possible to stabilise sodalite over long durations.
Perrhenate sodalite growth from alkali silicate melts by noble metal catalysis

Michael Anenburg · Charles Le Losq

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Abstract
Perrhenate sodalite (Na₈Al₆Si₆Re₂O₃₂) which contains the perrhenate anion (ReO₄⁻) has been synthesised in equilibrium with Na–Fe-rich aluminosilicate melt and Re metal at 1100 °C and 500 MPa. Quenched glasses contain a homogeneous distribution of nepheline and magnetite, whereas sodalite only forms a crust on noble metal surfaces (Pt, Pt–Rh, Ag–Pd, and Re) in contact with the glass. The sodalite have been characterised by wavelength-dispersive X-ray spectroscopy and Raman spectroscopy. The experimental products contain both Re(0) and Re(VII), but other oxidation states of Re were not detected, suggesting the role of Na as a higher oxidation state stabiliser. Sodalite has potential uses for immobilising volatile Re and Tc during nuclear waste vitrification. Our study demonstrates the thermodynamic stability of perrhenate sodalite at Na-rich aluminosilicate melts at high temperature and pressure conditions.

Keywords Pertechnetate · Microporous · Mesoporous · Zeolite · Experimental petrology · Optical basicity

1 Introduction
Sodalite is a naturally occurring feldspathoid mineral with the formula Na₈Al₆Si₆O₃₂Cl₂, in which Si, Al and Na form a cage structure containing chloride anions [1, 2]. Sodalite anion chemistry is flexible due to the relatively large cage structure, and compounds incorporating halides (e.g., bromide and iodide) and oxyanions (e.g., tungstate, molybdate, permanganate, chlorate, perchlorate, nitrate, etc.) have been synthesised [3–11]. In particular, incorporation of perrhenate (ReO₄⁻) to the sodalite cage structure has been the focus of several studies due to its similarity to pertechnetate (TcO₄⁻) and applications in nuclear waste management [12–17]. Synthesis of perrhenate sodalite (referred to as Re-sodalite hereafter) has been achieved via a low temperature hydrothermal process (175 °C) involving preliminary solution chemistry methods [12–17]. Additionally, Re-sodalite has been shown to be stable in high temperature melts and retain its Re content [15]. This raises the possibility that Re-sodalite can crystallise directly from silicate melts, without an intermediate stage of low temperature solution and hydrothermal synthesis. As stabilisation of nuclear waste is done in glass matrices, improving incorporation of volatile Tc through optimisation of the glass composition and formation process is an important goal, for which Re has been proposed as an analogue [18–21]. Determining the conditions that favour the nucleation and growth of Re-sodalite crystals in silicate melts helps in this regard.

In this study we report high temperature and pressure experiments during which we observed crystallisation of Re-bearing sodalite from Na-rich silicate melts. The experiments were conducted at high pressure in order to avoid the problems of Re volatilisation from the silicate glass.
2 Experimental methods

Experimental details have been described in detail elsewhere [22]. In short, a silicate starting material was prepared by mixing sodium metasilicate (Na$_2$SiO$_3$), silica (SiO$_2$), hematite (Fe$_2$O$_3$) and alumina (Al$_2$O$_3$) in an agate mortar and pestle. The mixture was sintered and partly vitrified at 800 °C to produce a homogenous semi-glassy material containing 47.16 wt% SiO$_2$, 17.62 wt% Na$_2$O, 17.94 wt% Al$_2$O$_3$ and 17.28 wt% Fe$_2$O$_3$, corresponding to a 50:50 stoichiometric mixture of nepheline (NaAlSiO$_4$) and aegirine (NaFeSi$_2$O$_6$).

The silicate mix was loaded into a 2.3 $\varnothing$ mm noble metal capsule (either Ag–Pd alloy or Pt) together with a piece of Pt$_{94}$–Rh$_{70}$–Rh$_{6}$–30 alloy and a Re strip. The capsules were then loaded into a ½-inch (12.7 mm) pressure vessel via a MgO–graphite–Pyrex–NaCl–Teflon assembly. The pressure vessel was inserted into a 200-ton piston cylinder apparatus, in which pressure and temperature were increased simultaneously to run conditions. Three experiments were conducted, the details of which are given in Table 1. The experiments were quenched after the run duration, reaching room temperature in about 20 s. Temperature measurement was precise to 2 °C and pressure to less than 50 MPa.

After each experiment, the assembly was mounted in epoxy, and polished using sand paper to expose the interior of the noble metal capsule. The surface was then polished using diamond paste to prepare the samples for analysis.

3 Analytical methods

Backscattered electron (BSE) images, X-ray spectra scans, and quantitative compositions were acquired using a JEOL 8530F Plus electron probe microanalyser (EPMA) running with an accelerating voltage of 15 kV. X-ray scans were conducted using wavelength-dispersive spectrometers (WDS) with TAP (thallium acid phthalate), PET (penterythritol) and LIF (lithium fluoride) diffracting crystals, a 100 nA beam current, and a 5 µm defocused beam [23, 24]. Quantitative analyses were conducted using a 2 nA beam current with the following reference materials: albite (Na, Al, Si), hematite (Fe), Re metal (Re). The beam was defocused to 30 µm when analysing the silicate glass to avoid Na-migration under the beam.

For chemical analysis of Re-bearing silicates, WDS methods have an advantage over EDS (energy-dispersive spectroscopy) because of the Re M-lines interferences on the Si K-line, introducing uncertainties in the quantified composition. The higher energy resolution of WDS relative to EDS allows the overlap to be eliminated.

Raman spectra were recorded using a Renishaw InVia spectrometer, equipped with a Peltier-cooled detector, a 2400 l/mm grating and a confocal system. Samples were excited using a 532 nm laser line focused on sample surface using a × 50 Leica objective. The laser power on the sample was ~1.2 mW. The spatial resolution was ~1 μm, and the spectral resolution ~1.2 cm$^{-1}$. Raman spectra were processed with using the rampy library [25] in the programming language Python.

4 Results

All experiments resulted in a homogenous silicate glass with abundant dispersed crystals of magnetite and noble metal nanoparticles (Fig. 1). See [22] for a discussion of the nanoparticle significance. Crystals of Na-perrhenate (NaReO$_4$) and a Re-chloride phase of uncertain composition grew on the polished sample surface, particularly where pitted by scratches or imperfect polishing (Fig. 1b). Rare crystals of nepheline occur in experiments D1900-101 and D1906-103, whereas nepheline is abundant in experiment D1901-102 due to the lower run temperature. Rarely, Al–Fe spinel inclusions occur inside nepheline (Fig. 1c). We suspect it to be an unreacted relict from the sintered starting materials.

A crust of sodalite, 1–10 µm thick, formed on all noble metal surfaces present inside the capsule (Fig. 1). This includes the capsule itself, the Pt–Rh alloy and the Re strip. A gap exists between the glass and sodalite and the metal surface (now filled with epoxy resin), probably due to thermal contraction during quenching (Fig. 1c).

A WDS scan of a sodalite crystal from experiment D1906-103 shows that it contains Na, Al, Fe, Si and Re (Fig. 2). Spectra of other experiments are similar and not shown here. The height of the Na peak is abnormally low. This can be explained by the mobility of Na under the electron beam, causing significant migration during the 30-min scan duration [28]. Quantitative chemical
compositions of sodalite and silicate glass are given in Tables 2 and 3, respectively. The measured sodalite composition approximates that of stoichiometric Re-sodalite (Na₈Al₆Si₆Re₂O₃₂), with several minor differences. Re contents are consistently below 2 atoms per formula unit, suggesting that the cages are not fully occupied by perrenate anions. Alternatively, as perrenate is moderately volatile, it could have been mobilised under the electron beam. This could lead to an overestimation of the other calculated cation values as they are calculated assuming full occupancy and 32 oxygens. Contents of Si are consistently above 6, and it is not clear whether it results from the overestimation or whether it is real. Natural sodalites commonly contain greater than 6 Si atoms per formula unit [28–30], suggesting that our measured overoccupancy is real. It is possible that the excess Si is charge balanced by introduction of some divalent Fe via 2Al³⁺ → Fe²⁺ + Si⁴⁺, both occupying the Al tetrahedral site [28, 29]. This is consistent with the low Al contents in our samples (< 6 atoms per formula units). The low Al contents could also be explained by trivalent Fe substituting Al in the crystals (Al³⁺ → Fe³⁺ [29]). Similarly, Na contents are occasionally low (< 8), which could either result from Na mobility, or alternatively from the charge-balanced simultaneous Na⁺ and ReO₄⁻ vacancies in the crystal structure.

Our starting materials included Fe³⁺, imposing initially oxidised conditions, but Re metal remained in the experimental products, indicating overall reducing conditions during the run durations. There is no other reductant other than metallic Re to drive further reduction, indicating that the oxygen fugacity was buffered to values below but probably close to those determined by the Re–ReO₂ equilibrium [31]. Rhenium contents of the silicate glass are too low to be reliably analysed by EPMA (see Table 3), but are likely to be at a maximum on the order of magnitude of 1000–2000 µg/g. These values are within the range expected for silicate melts at this oxygen fugacity [32, 33].

Raman spectra of the glasses (Fig. 3a) show typical spectra of sodic Fe-bearing aluminosilicate glasses characterised by two broad peaks near 500 and 1000 cm⁻¹, due to intertetrahedral T–O–T vibrations and intratetrahedral T–O stretching vibrations in the glass structure (T = Si, Al, Fe³⁺), respectively (see [34] for a review and references cited therein). A small asymmetric peak, centred near 3590 cm⁻¹, is also observed and testifies for a small quantity of water dissolved in the glass. Quantification of its amounts from the Raman spectra yields a mean value of wt% H₂O = 0.36 ± 0.11 (1σ). This is consistent with the totals obtained from EPMA analysis (Table 3).

Raman spectra of the sodalite crystals show three peaks at 332, 922 and 976 cm⁻¹, and another peak near 422 cm⁻¹ (Fig. 3b). Those observations are in perfect agreement with previously reported Re-sodalite Raman spectra [16]. The peaks are assigned to vibrational modes of Re in tetragonal coordination [16]; the 332 cm⁻¹ peak is assigned to a pure bending mode (ν₂), the 922 cm⁻¹ to an asymmetric stretch mode (ν₃), the 976 cm⁻¹ to a symmetric stretch mode (ν₁) and the 422 cm⁻¹ peak to a combination of stretching and...
bending \( (\nu_4) \). Raman spectra of the crystals thus confirm that the reported crystals are a Re-sodalite phase.

Raman spectra of the silicate glass does not reveal any Re-related peak. It was previously reported that peaks of perrhenate only become distinguishable from the background glass signal at contents of several thousands of \( \mu g/g \) [35]. Therefore, our failure to detect any peaks related to Re is consistent with the chemical analysis showing Re contents equal to \( \sim 1500 \mu g/g \) at maximum.

**Table 2** Chemical composition of sodalites in oxide wt%. Atomic proportions calculated based on 32 oxygens

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
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<tr>
<td>( SiO_2 )</td>
<td>25.40</td>
<td>25.39</td>
<td>26.87</td>
<td>26.09</td>
<td>24.01</td>
</tr>
<tr>
<td>( Al_2O_3 )</td>
<td>19.88</td>
<td>20.05</td>
<td>19.12</td>
<td>19.01</td>
<td>18.78</td>
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<tr>
<td>( Fe_2O_3 )</td>
<td>2.60</td>
<td>2.36</td>
<td>3.11</td>
<td>2.31</td>
<td>1.79</td>
</tr>
<tr>
<td>( Na_2O )</td>
<td>16.05</td>
<td>15.06</td>
<td>16.42</td>
<td>17.42</td>
<td>16.37</td>
</tr>
<tr>
<td>( Re_2O_7 )</td>
<td>33.37</td>
<td>33.83</td>
<td>31.76</td>
<td>32.33</td>
<td>32.25</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td>97.30</td>
<td>96.69</td>
<td>97.28</td>
<td>97.16</td>
<td>93.20</td>
</tr>
<tr>
<td>( Si )</td>
<td>6.15</td>
<td>6.18</td>
<td>6.44</td>
<td>6.32</td>
<td>6.18</td>
</tr>
<tr>
<td>( Al )</td>
<td>5.67</td>
<td>5.76</td>
<td>5.40</td>
<td>5.43</td>
<td>5.70</td>
</tr>
<tr>
<td>( Fe )</td>
<td>0.47</td>
<td>0.43</td>
<td>0.56</td>
<td>0.42</td>
<td>0.35</td>
</tr>
<tr>
<td>( Na )</td>
<td>7.53</td>
<td>7.11</td>
<td>7.64</td>
<td>8.18</td>
<td>8.17</td>
</tr>
<tr>
<td>( Re )</td>
<td>1.92</td>
<td>1.94</td>
<td>1.82</td>
<td>1.86</td>
<td>1.85</td>
</tr>
<tr>
<td><strong>Cations</strong></td>
<td>21.74</td>
<td>21.42</td>
<td>21.86</td>
<td>22.20</td>
<td>22.25</td>
</tr>
</tbody>
</table>

**Table 3** Chemical composition of silicate glasses in oxide wt%

<table>
<thead>
<tr>
<th></th>
<th>101 (( n = 10 ))</th>
<th>102 (( n = 8 ))</th>
<th>103 (( n = 10 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean</strong></td>
<td><strong>SD</strong></td>
<td><strong>Mean</strong></td>
<td><strong>SD</strong></td>
</tr>
<tr>
<td>( SiO_2 )</td>
<td>49.81 0.36</td>
<td>54.47 0.56</td>
<td>48.84 1.40</td>
</tr>
<tr>
<td>( Al_2O_3 )</td>
<td>18.40 0.21</td>
<td>14.17 0.65</td>
<td>17.50 0.76</td>
</tr>
<tr>
<td>( Fe_2O_3 )</td>
<td>13.72 0.31</td>
<td>13.39 0.90</td>
<td>13.07 0.76</td>
</tr>
<tr>
<td>( Na_2O )</td>
<td>17.90 0.20</td>
<td>17.58 0.47</td>
<td>19.04 0.36</td>
</tr>
<tr>
<td>( Re_2O_7 )</td>
<td>0.06 0.06</td>
<td>0.08 0.09</td>
<td>0.13 0.06</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>99.89 99.69</td>
<td>99.69 98.58</td>
<td></td>
</tr>
</tbody>
</table>
5 Discussion

The presence of Re-sodalite in experiments run for 19 h at 1100 °C indicates that it is a thermodynamically stable phase at these conditions and melt composition. Rhenium was sourced from the Re strip placed in the capsules, and as such it was expected that sodalites would be more common adjacent to the strip. Surprisingly, Re-sodalite was found exclusively as crusts on metal surfaces regardless of the position in the capsule. This is in contrast with nepheline and magnetite that are distributed homogeneously throughout the capsule. The Re-sodalite crusts appear identical whether they were on Pt, Pt–Rh, Ag–Pd, and even on the Re metal itself. This indicates that the noble metals catalysed the Re-sodalite crystallisation.

The silicate glass contains up to 1000 ppm of Re, whereas the Re-sodalite contain ~25% Re. This represents a 2500-fold increase in Re concentration in the solid phase relative to the liquid. This confirms the exceptional potential of sodalite to extract Re from silicate melts (and by analogy, Tc [15]). Most nuclear waste glasses are not as sodic as our starting materials and contain abundant B2O3 (e.g., [36]), which may explain the lack of sodalite crystallisation even though the glasses are commonly prepared in noble metal crucibles. This indicates that Re-sodalite may not be a thermodynamically stable phase in these melts. Therefore, their retention (e.g., [15]) is likely promoted by slow dissolution kinetics of Re-sodalite in the liquid, which does not proceed to completion in the rapid heating and subsequent quenching during nuclear waste vitrification.

As mentioned above, our runs were buffered close to the Re–ReO2 oxygen fugacity buffer, in which the oxidation state of Re in the oxide is 4+. Yet, sodalite contains Re6+ in perrenate. The higher oxidation state is an example of the general tendency of metals to adopt higher oxidation states with Na or other basic cations as next-nearest neighbours, as generally found in silicate melts [37, 38]. This effect has been described from solids such as aegirine (NaFe3+Si2O6 [39]), dyrnaesite–(La) (Na8Ce4+La2P6O24 [40, 41]), and sodic amphiboles (riebeckite and arfvedsonite [42]). Likewise, the oxidation state of Re in the glass is expected to be dominated by Re6+ and Re7+ [32, 43–45]. Remarkably, these higher oxidation states of Re are stable in equilibrium with metallic Re. NaReO4 has been observed as a stable phase at conditions similar to those of our experiments [44, 46, 47], but was not observed in the present case. However, as our samples were prepared by water-lubricated polishing, any exposed perrenate salts would immediately dissolve. The formation of perrenate salts on the surface of our polished sections may have resulted from remobilisation of crystalline NaReO4 through cracks in the glass during sample preparation [46].

6 Conclusions

Crystallisation of Re-sodalite from a sodic Fe-bearing aluminosilicate melt was observed at high temperature and high pressure. Crystallisation happened to be catalysed by noble metals and alloys during the experiments. Re-sodalite can thus be a stable phase in Na-rich silicate melts in equilibrium with Re-bearing alloys at high pressure and high temperature. Therefore, in addition to the hydrothermal path previously presented [16], high pressure and high temperature experiments are another path to Re-sodalite synthesis. Furthermore, the experiments suggest that the presence of a noble metal catalysts in Na-rich silicate melts may be another way to stabilise Re-sodalite to higher temperatures, inhibiting through this way Re (and by analogy, Tc) volatilisation during vitrification processes, or increased stability during glass alteration [48, 49].

Acknowledgements This work was supported by Australian Research Council grant FL130100066 to Hugh O’Neill. We acknowledge the...
facilities and technical assistance of Jeff Chen at Microscopy Australia, Centre for Advanced Microscopy, ANU.

Compliance with ethical standards

Conflicts of interest We declare no conflicts of interest.

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Conclusions

The collection of works presented in this thesis follow a common thread of understanding the critical metal groups—REE and PGE (inclusive of Re)—in carbonatitic and alkaline systems.

One of the major conclusions arising from these papers is the effect of carbonatite metasomatism on mass transfer of these metals. REE mineralisation in carbonatites is commonly considered as igneous or hydrothermal crystallisation within or adjacent to a carbonatite proper. However, Nolans Bore is an example of carbonatite metasomatism, without the “carbonatite” actually being present. This can process can be likened to hydrothermal quartz veins. There is no doubt that these veins crystallise from a hydrothermal fluid, dominated by H\textsubscript{2}O, with silica dissolved. However, the H\textsubscript{2}O is long gone, and quartz is all that remains. The former presence of H\textsubscript{2}O is not questioned, and the quartz vein formation is well understood in the context of this process. This is the point of view that should be adopted for carbonatites. The question should thus be—“what can carbonatites do?” rather than the commonly asked questions “how do carbonatites form?” or “how do carbonatites look like”? Returning to the topic of this thesis, REE-bearing apatite veins form by a similar process of carbonatite liquid reaction during transport through the crust, followed by migration of the liquid elsewhere. The ability of carbonatites to flux Mo and Re is another contribution to answering the wider question of “what can carbonatites do?”. For example, many metasomatised mantle xenoliths contain disrupted Re–Os ratios, but the metasomatising agent is not always clearly identified. Carbonatites have been suggested, along with C–H–O–S fluids or silicate melts. The work presented here demonstrates that carbonatites should be taken into consideration seriously in such cases. Apart from cases where such processes lead to economic mineralisation (such as Nolans Bore), carbonatite metasomatism can cause significant mass transfer in the crust, particularly in deep granulite-facies rocks. Currently, identification of these metasomatic zones is challenging, but this work opens the door into future studies, both experimental and observational, allowing to discern these processes.

Carbonatites are commonly associated with alkaline systems. The work here showed that high Na contents enhance PGE+Re mobility. Future research directions might
explore similar relationship at mixed alkali–carbonatite melts (e.g., at high pressure). Additionally, igneous alkali complexes are usually considered to host REE and HFSE mineralisation. However, these results suggest that these complexes can host PGE as well. The possibility of such an occurrence is indeed an exciting hypothesis that should be explored, both experimentally and in the field.

Finally, applying any models developed by experimental methods requires correct description of the natural rocks. REE deposits, in particular those containing apatite are challenging to properly characterise. This work shows a multi-approach petrographical and analytical method to acquire high quality data on apatite. This involves an innovative correction method of interfering masses during LA-ICP-MS analysis based on REE shape coefficients (the “lambda” method). It also involves correct analysis of F, and a way to determine whether any “excess” F is true or not by cross-validation with FTIR to measure the charge-balancing carbonate. Finally, numbers may only be as good as the textural interpretation, and I show how the combination of electron microscopy, cathodoluminescence, and X-ray CT allows three-dimensional reconstruction of different apatite generations.