Diagenetic francolite (carbonate fluor-apatite) occurs as overgrowths on detrital apatite grains in sandstones from the Lower Jurassic Statfjord Formation of the North Sea. The francolite overgrowths are considerably more enriched in the rare-earth elements (up to 1 wt% CeO2), Sr and F than the detrital cores. These elements were carried in aqueous solution, probably in the form of complex ligands involving organically sourced carbon and halogens. It is possible that reported aberrant neodymium isotope model ages within the Statfjord Formation are the result of mobilization and relative fractionation of Sm and Nd during diagenesis, rather than a result of changes in provenance.

**Keywords:** North Sea, diagenesis, francolite, rare earths, 144Nd/143Nd.

It is becoming accepted that the assumption that the rare-earth elements (REE) are immobile in aqueous systems is not always valid. Banfield & Eggleton (1989) reported REE mobilization and fractionation resulting from the dissolution of apatite on a very small scale during weathering of a granite. Hole et al. (1992) demonstrated that the REE, Zr, Nb and Y were mobilized during late diagenesis within permeable sandstones of mixed fluvial/aeolian origin, transport within aqueous fluids at <200°C probably being enhanced by formation of halogen complexes. Rasmussen & Glover (1994) described early diagenetic florencite (Ce, La, Al phosphate) and xenotime (YPO4) preserved by later bitumen envelopes within sandstones. Additionally, Ohr et al. (1994) came to the general conclusion that the REE can be fractionated by diagenetic and prograde metamorphic processes in argillaceous rocks.

Variations in the modal abundances of detrital ‘heavy’ minerals within clastic sedimentary rocks are commonly used as a tool in aiding the correlation of hydrocarbon reservoirs (Morton & Hurst 1995). Consequently, it is important to differentiate between diagenetic heavy mineral phases and original detrital grains, a process that is not always straightforward. Apatite (Ca10(PO4)6(OH,F,Cl)) is a common component of detrital heavy mineral suites and, together with other heavy minerals such as monazite, zircon, garnet and titanite, is potentially a site for a large proportion of the total REE budget of a clastic sedimentary rock. Apatite can be dissolved by low-pH meteoric fluids during early diagenesis (Morton 1984, 1986), and consequently the stability of apatite during diagenesis is likely to have a strong influence on the behaviour of the REE. Furthermore, Sm–Nd isotopes are used in sedimentary provenance and hydrocarbon reservoir correlation studies. However, the use of Nd model ages requires the assumption that a system has remained closed to REE fractionation, at least on a sample scale, since deposition (e.g. Mearns et al. 1989). If the REE are mobile and fractionated during late diagenesis, then there is the potential for the ‘resetting’ of Nd-model ages (Awwiller & Mack 1991), which carries strong implications for the use of Sm–Nd isotope systematics in reservoir correlation.

In this paper, we describe in detail the occurrence and REE geochemistry of diagenetic francolite (a carbonate fluor-apatite containing CO2 and F > 1 mol%; McConnell 1973) overgrowths on detrital apatite cores from the Jurassic Statfjord Formation (North Sea). We show that the REE are greatly enriched in the overgrowths relative to cores and that REE transport is likely to have occurred over a considerable distance. This enables the distinction of diagenetic and detrital apatite grains. In addition, we demonstrate that transport and fractionation of the REE during diagenesis can potentially have a profound influence on Nd model ages.

**Data and analytical techniques.** The Statfjord Formation (Brent Field, northern North Sea) is the lower member of the Upper Triassic to Lower Jurassic Banks Group. It is a continental fluvial sequence comprising channel sands and overbank flood deposits on which palaeosols with variable maturities characteristic of an arid climate have developed (Dalrymple et al. in press). The diagenetic apatite species described here is from a medium-grained channel sand within part of the sequence dominated by stacked channel sands. Similar material occurs throughout the Statfjord Formation.

Polished grain mounts prepared from heavy mineral separates were initially investigated using SEM backscattered imaging (BSE-SEM); (see Lloyd 1987 for review). On the basis of this, several points on 2–3 grains from each sample were chosen for wavelength dispersive electron microprobe analysis (EPMA). Importantly, analysis of individual mineral grains avoids the problem of averaging of chemical characteristics, which occurs when bulk samples are studied (e.g. Dill 1994). Analyses were performed on a Cambridge Instruments Microscan 5 electron microprobe using a beam accelerating voltage of 15 kV, a current of 20 nA (Ca and P) or 50 nA (other elements), and a focused spot of approximately 2–5 μm diameter. Total counting times (peak plus background) were between one and two minutes, depending on the abundance of the element being analysed. Raw count data were matrix corrected using Link Analytical ZAF-4/FLS software. All analyses except carbon were conducted using a carbon sample coating. For the analysis of carbon, the initial carbon coating was removed and the sample recoated with aluminium.

Classification of apatite and francolite requires the determination of F, Cl, OH and C concentrations. The light elements (F, O, C) have characteristic X-rays of very long wavelength making it difficult to separate these lines for analysis using conventional diffracting crystals. Analyses for F and C were therefore conducted using a synthetic multilayered dispersion element (MLDE) with a 2d spacing of 62.2 Å. Potts & Tindle (1989) describe the use of such a MLDE for the quantitative analysis of F and show that the third order reflection of the phosphorus Kα line, which is a potential problem in the analysis of fluorine in apatite, is absent. Carbon contamination by oil condensed on the sample surface from oil reservoirs within the microprobe vacuum diffusion pumps is a
potential problem in quantitative carbon analysis by EMPA (Potts 1987). The presence of a build up of carbon at the point of analysis was checked for by measuring the intensity of the carbon Ka line for ten minutes (much longer than the time required for analysis) without moving the beam position. Over this time period no change in peak count intensity was observed suggesting that any carbon build up was insignificant relative to the carbon concentrations of the mineral grains being studied. However, the possibility that the earlier carbon coating was not completely removed, coupled with poorly known matrix correction coefficients for carbon, and the possibility of C build up at the sample surface, means that the carbon analyses should be considered as semi-quantitative only. Representative analyses are given in Table 1, together with the appropriate EPMA lower limits of detection and standard errors.

Mineral chemistry. Figure 1 shows a BSE-SEM image for a single grain (12636.9 ap#1) from the Statfjord Formation. The grain consists of a small (detrital) core (black) which has been overgrown by the euhedral (bright) diagenetic overgrowth. Vague sector twins and growth zones which are clearly observable under transmitted cross polarized light microscopy can be seen as very subtle brightness variations within the overgrowth. Numbered points on the BSE-SEM image represent EPMA analysis points (Table 1).

As implied by the BSE-SEM image there is a major difference in chemistry and also mineralogy between the detrital core and the diagenetic overgrowths. Figure 2 is a plot of phosphorus concentration against total (OH + F + CI) for 18 analyses from three grains in the same sample superimposed on the compositional fields for apatite and francolite plotted from analyses given by Deer et al. (1962). The overgrowths have fluorine concentrations in excess of the stoichiometric maximum (>2 formula units) for fluorapatite and show a trend of decreasing phosphorus content as this excess fluorine concentration increases. The observed compositional fields suggest that the detrital cores are near stoichiometric fluor(chlor)apatites and the overgrowths are francolite.

The francolite overgrowths contain appreciable concentrations of REE (up to 1.1 wt% Ce2O3; Table 1). Chondrite-normalized REE profiles for the overgrowth,.., 4

Table 1. Representative analyses of diagenetic and detrital apatite

<table>
<thead>
<tr>
<th>12636.9 ap#1</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tr>
<td>CaO</td>
<td>5.52</td>
<td>51.21</td>
<td>51.09</td>
<td>52.67</td>
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<td>0.27</td>
<td>0.30</td>
<td>0.25</td>
<td>0.26</td>
<td>0.07</td>
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<td>Y2O3</td>
<td>1.55</td>
<td>1.51</td>
<td>2.13</td>
<td>1.64</td>
<td>2.26</td>
<td>bd</td>
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<tr>
<td>La2O3</td>
<td>0.27</td>
<td>0.28</td>
<td>0.24</td>
<td>0.12</td>
<td>0.22</td>
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</tr>
<tr>
<td>Ce2O3</td>
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<td>1.02</td>
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<tr>
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<tr>
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<tr>
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<td>P2O5</td>
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<td>36.33</td>
<td>36.64</td>
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<tr>
<td>CO2</td>
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<td>2.62</td>
<td>2.36</td>
<td>2.23</td>
<td>1.69</td>
</tr>
<tr>
<td>F</td>
<td>4.48</td>
<td>4.79</td>
<td>4.66</td>
<td>4.80</td>
<td>4.77</td>
<td>2.41</td>
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<tr>
<td>Cl</td>
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<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
</tr>
<tr>
<td>Total</td>
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<td>99.63</td>
<td>99.65</td>
<td>100.52</td>
<td>99.89</td>
<td>100.55</td>
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<tr>
<td>F = O</td>
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<td>2.02</td>
<td>1.96</td>
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Formula units (10 Ca etc.)

<table>
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<tr>
<th>Ca</th>
<th>Sr</th>
<th>Y</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>P</th>
<th>C</th>
<th>F</th>
<th>Cl</th>
<th>O</th>
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<td>9.66</td>
<td>0.02</td>
<td>0.14</td>
<td>0.02</td>
<td>0.07</td>
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<td>0.01</td>
<td>0.02</td>
<td>5.45</td>
<td>0.60</td>
<td>2.43</td>
<td>23.76</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 shows the positions of analyses, 1-5 are from the diagenetic overgrowth, analysis 6 is from the detrital core. Probe operating conditions are given in the main text. Lower limits of detection (3 sigma oxide wt%) for the trace elements are: SrO 0.03; Y2O3 0.09; La2O3 0.07; Ce2O3 0.06; Nd2O3 0.14; Sm2O3 0.08; Gd2O3 0.10; CO2 0.25; F 0.12. Oxygen is calculated by stoichiometry. bd, below detection.

Figure 1. BSE-SEM image of an apatite/francolite grain (grain 12636.9 ap#1). Numbered points represent positions of analyses whose results are presented in Table 1.
Francolite contains (by definition) concentrations of P, F, REE mobility. Francolite is more usually associated with enhanced through formation of complexes with ligands such as fluorides, phosphates and carbonates (Wood 1990). These species could have been responsible for enhanced enrichment observed in the later diagenetic overgrowths (up to 20x relative to cores) would require the dissolution of considerably more apatite than was re-precipitated as francolite. This suggests that the detrital apatite is unlikely to be the sole source of REE. Alternatively the REE could have been derived through dissolution of other detrital apatite cores in this sample are very small indicating another channel sand sample (not shown here) have an early phase of extensive corrosion. Similar grains from fig. 3) are generally flat (average Ce/Y = 1.37), with absolute REE abundances around 10 000× chondrite. The detrital cores contain low REE concentrations and only Ce is consistently detectable. EPMA is unable to distinguish the subtle variations in chemistry responsible for the slight sector and growth zonation.

**Discussion.** Diagenetic francolite overgrowths on detrital apatites can readily be identified by BSE-SEM, as they are chemically very different from their detrital cores. The detrital apatite cores in this sample are very small indicating an early phase of extensive corrosion. Similar grains from another channel sand sample (not shown here) have chemical compositions that are indistinguishable from the grains described here, but have only slightly corroded detrital cores and considerably smaller authigenic overgrowths. The corrosion of the detrital grains was probably caused by low pH meteoric waters relating to soil-forming processes during the time the sediments were stored on the fluvial floodplain. The later precipitation of the francolite overgrowths with their high REE, Sr, and F concentrations is likely to have occurred as conditions changed as the sediments were buried. These overgrowths are also clear evidence that the REE were present in diagenetic fluids and therefore mobile at the time of francolite crystallization.

The early dissolution of detrital apatite grains is liable to have released some REEs to the fluids. However, the REE enrichment observed in the later diagenetic overgrowths (up to 20× relative to cores) would require the dissolution of considerably more apatite than was re-precipitated as francolite. This suggests that the detrital apatite is unlikely to be the sole source of REE. Alternatively the REE could have been derived through dissolution of other detrital REE-bearing minerals. REE mobility is likely to be enhanced through formation of complexes with ligands such as fluorides, phosphates and carbonates (Wood 1990). Francolite contains (by definition) concentrations of P, F and C and therefore it is conceivable that any combination of these species could have been responsible for enhanced REE mobility. Francolite is more usually associated with phosphorite deposits and black shales (see Jarvis *et al.* 1994 for a recent review), both of which have organic associations. It is possible therefore that the REEs present in the diagenetic francolite were derived from organic components and that organic species may have been responsible for complexing. However Jarvis *et al.* (1994) note that francolite associated with organic mudrocks tend to have lower CO₂ and F concentrations than those from carbonate associated phosphorites. The sector growth observed in these francolites indicates disequilibrium between the mineral and fluid during growth, making it difficult to relate trace elements within the mineral to fluid compositions. Dissolution of apatite and other detrital phosphate phases may have controlled the amount of phosphorus available in the fluids, thus limiting the amount of francolite which could re-precipitate.

Mearns *et al.* (1989) successfully used Sm-Nd isotopes to distinguish different provenance areas for the Upper Triassic Lunde and Lower Jurassic Statfjord Formations in the Snorre Oil Field (northern North Sea), and to subdivide the Statfjord Formation on the basis of discontinuities in the patterns of Nd-isotope model ages. However, Mearns *et al.* (1989) also document that some samples have anomalously high or low Sm/Nd ratios, and that some closely spaced sample pairs have widely different model ages. Mearns *et al.* (1989) accounted for these variations by changes in provenance, although they recognized the possibility that fractionation of Sm relative to Nd could have occurred between the coarse- and fine-grained lithologies.

The diagenetic francolite described here has approximately 7000 ppm Nd and 1700 ppm Sm giving an Sm/Nd ratio of c. 0.24. Such high REE concentrations coupled with relatively high Sm/Nd ratios, means that the addition or removal of very low abundances of authigenic francolite in a sample will produce large variations in bulk Sm/Nd ratios. Figure 4 shows that the addition of trace concentrations of
authigenic francolite of the composition described here can produce large variations in the calculated model age of a bulk sample. If the remobilization was on only a sample scale then any perturbation of the isotope system would not be reflected in bulk sample analysis. However, if mobilization and fractionation occurred on a scale greater than that of sampling, as the significant concentrations of REE observed in these francolites would seem to require, then the Nd model age of bulk sample will reflect a than that of sampling, as the significant concentrations of Nd observed in these francolites would seem to require, then the Nd model age of bulk sample will reflect a Nd isotopic signature. We therefore suggest that the precipitation of even minor amounts of diagenetic francolite in porous and permeable sedimentary rocks could account for the aberrant model ages observed in some provenance studies (e.g. Mears et al. 1989). In addition, because it is clear that diagenetic effects can have profound effects on apatite dissolution and recrystallization, the use of REE fingerprinting of bulk apatites for correlation purposes (e.g. Dill 1994) should be treated with caution.

The REE-rich diagenetic francolites described here provide a potential means of investigating the migration of fluids through a hydrocarbon reservoir during diagenesis, and their influence on bulk sample REE profiles. If apatite crystallization was relatively early during diagenesis then variations in REE profiles between different authigenic francolite samples within the Statfjord Formation may be useful as a tool for reservoir correlations. Alternatively they may hold information enabling reservoir connectivity during diagenesis to be assessed.

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References


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