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Title: Mineralogical and fluid characteristics of the fluorite-rich Monakoff and E1 Cu-Au deposits, Cloncurry region, Queensland, Australia: implications for regional F-Ba-rich IOCG mineralisation

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Keywords: IOCG, Monakoff, E1, fluorite, REE geochemistry, fluid inclusions.

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Abstract: The Monakoff iron oxide-Cu-Au (IOCG) deposit, located to the north east of Cloncurry within the Eastern Succession of the Mount Isa Inlier, Queensland, Australia, is characterised by high concentrations of F and Ba, with a host of other enriched elements including Co, Ag, Mn, REE, U, Pb, Zn and Sr. This gives the deposit a characteristic gangue assemblage dominated by fluorite, barite and calcite. The nearby E1 deposit, located 25 km to the NNE of Monakoff, and the large Ernest Henry deposit, 3 km to the west of E1, also contain abundant fluorite, barite and calcite in late stage assemblages. The three deposits, therefore, constitute a distinct group of IOCG deposits within the district, based on their F-rich geochemical and mineralogical affinities.

The Monakoff ore zone is hosted in dilational openings along a shear zone developed within metasediments and metavolcanic rocks at the boundary between competent hangingwall rocks of the Toole Creek Volcanics and footwall rocks of the Mount Norna Quartzites. Four stages of alteration and mineralisation are recognised: Stage 1 garnet-biotite alteration; Stage 2 biotite-magnetite alteration; Stage 3 main F-Ba-ore mineralisation; and a Stage 4 pyrite-alloclasite Au-Co-As overprint. The E1 deposit has a more complex history, but Stage 5 has veins of fluorite-barite-carbonate that are comparable to Monakoff's main stage. The Stage 3 assemblage at Monakoff comprises a sheared groundmass of fluorite, barite, manganoan calcite, magnetite, chalcopryrite, pyrite, galena and sphalerite, with coarser grained pods of the same mineralogy interpreted to be dilational structures infilled during syn-ore deformation. Accessory minerals include U-Pb-oxides, REE-F-carbonates and Ag-Pb-Bi-sulfosalts, with no discrete Au minerals. The sulfosalts are interpreted to have formed from an immiscible Bi-melt within the mineralising fluid at temperatures higher than the melting point of Bi. The Stage 4 overprint at Monakoff contains pyrite and alloclasite. Laser ablation analyses of the sulfide minerals at Monakoff reveal that Stage 3 sulfides contain only trace amounts of Au (0.04 ppm in pyrite), although galena and chalcopryrite contain significant concentrations of Ag. Stage 4 pyrite and alloclasite, however, contain ~1 ppm Au in solid solution and mass balance calculations indicate the majority of bulk rock Au to be present in these minerals, although the majority of bulk Ag is present in Stage 3 sulfides. The Stage 5 veins at E1 have an identical gangue and accessory mineralogy to Stage 3 at Monakoff and differ in the sulfide mineralogy only in the lack of galena and sphalerite.

Four fluid inclusion populations are identified within the fluorite at Monakoff: Group 1 are CO₂ rich; Group 2 are complex solid-liquid-vapour inclusions, with two groups based on homogenisation

temperature (>450°C and 300-375°C). Laser ablation-ICP-MS analyses indicate these inclusions contain Cu, Pb, Zn, Fe, Mn, Mg, Ag, REE, U and Ba, but significantly no S, Se or Au; Group 3 are solid-liquid-vapour inclusions with a Th of 200-275°C, and contain Ba, Na, Mg, K and Br; and Group 4 are low salinity liquid-vapour inclusions. Group 1, 2 and 4 inclusions are also present in fluorite at E1. The REE geochemistry of fluorite from Monakoff and E1 is comparable and is characterised by a distinct positive Eu anomalies in all analyses, interpreted to indicate oxidising conditions at the time of high temperature ore deposition. The presence of abundant fluorite and barite is indicative of fluid mixing due to the insolubility of barite and fluorite and thus Ba and S, and Ca and F must have been introduced via different fluids. We propose that the oxidised fluid represented by the Group 2 inclusions and containing F, Ba, REE, U and base metals, mixed with a reduced, S-bearing fluid in a zone of dilation in the host shear zone that acted as a conduit for fluid flow during D3 deformation. The source of the metal and F-rich fluid is likely to be the nearby granitic intrusions of the Williams-Naraku batholith, probably the Malakoff granite. This granite is also likely to be the source of the CO₂ represented by Group 1 fluid inclusions, and the REE, U, base metals and possibly Au, although the high Pb and Zn content of Monakoff and not E1 may suggest a local input of those elements at Monakoff. Stage 4 mineralisation overprints the F-Ba stage and is characterised by a Co-As-Au signature. At present it is unclear if this is a late stage, more reduced, evolution of the main ore fluid, or a separate mineralising event entirely.

The presence of this F-Ba-metal-rich fluid has produced a distinctive style of IOCG mineralisation in the area to the north of Cloncurry. The probable link to the Malakoff granite implies that similar deposits may be present within several kilometres of the granite in suitable structural traps. Monakoff illustrates that although structurally controlled, the presence of Na-Ca alteration and 'red rock' K-alteration and brecciation are not key exploration criteria for these deposits. In addition, the presence of the overprinting As-Co-Au assemblage may indicate that this is a separate mineralising episode that may be present at other localities in the district. This study has also shown that fluorite can provide a powerful tool for determining ore forming conditions in F-rich IOCG systems.

**Mineralogical and fluid characteristics of the fluorite-rich Monakoff and
E1 Cu-Au deposits, Cloncurry region, Queensland, Australia:
implications for regional F-Ba-rich IOCG mineralisation**

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HIGHLIGHTS:

- F-Ba-rich IOCG mineralisation in Cloncurry region formed from F-rich fluid
- F-Ba-REE-U-base metal-rich fluid sourced from Williams-Naraku granites
- Mixing of fluids in dilational structures forms distinct fluorite-barite-rich ores
- Identification of a late stage As-Co-Au overprint that carries the majority of Au
- Fluorite used as a proxy for ore forming conditions in IOCGs for the first time

Mineralogical and fluid characteristics of the fluorite-rich Monakoff and E1 Cu-Au deposits, Cloncurry region, Queensland, Australia: implications for regional F-Ba-rich IOCG mineralisation

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1. Introduction

Iron-oxide-copper-gold (IOCG) deposits comprise a diverse range of hydrothermal ore systems, and are currently major resources of Cu, Au, and a wide range of other associated metals, including rare earth elements (REE) and U (e.g. Williams et al., 2005; Groves et al., 2010; Porter 2010). It has been recognised for some time that many of these deposits are enriched in carbonate, Ba, P, or F-bearing minerals and contain anomalous to economic concentrations of REEs (e.g. Hitzman et al., 1992). A key subgroup of these deposits have evidence of F-rich hydrothermal fluids and are rich in Ba, U and REE, and include the giant Mesoproterozoic Olympic Dam deposit, in South Australia (Roberts and Hudson, 1983; Reeve et al., 1990; Ehrig et al., 2013); and a number of Mesoproterozoic deposits in the Cloncurry area of the Mount Isa Inlier, Queensland, Australia, including the Ernest Henry, Monakoff and E1 deposits (Mark et al., 2006a,b; Davidson et al., 2002; Williams et al., 2013; Case et al., 2013). Fluorine, as one of the most reactive and electronegative of all elements, is a powerful ligand for metal transport (including U and REE) in hydrothermal systems (Seward and Barnes, 1997; Wood and Samson, 1998). However, there are relatively few settings where F is sufficiently abundant to be an important ligand in hydrothermal fluids (e.g. Aiuppa et al., 2009), although a notable exception may be large F-rich silicic igneous provinces (McPhie et al., 2011). As such, IOCG deposits linked to such provinces of F-rich silicic intrusions may be characterised by metals that are preferentially transported by fluoride. Recent work by McGloin et al. (2013) has identified that temperature, oxidation state, and CO₂ content of fluoride-bearing fluids determine the capacity to transport, and form deposits of, Cu, Au, U, Th and REE. The Monakoff and E1 deposits, the focus of this paper, plus the nearby Ernest Henry deposit, contain abundant barite, fluorite and carbonate gangue, with a wide range of associated metals including Cu, Au, Ag, Pb, Zn, Co, U, REE and As (Davidson, 1998; 2002; Mark et al., 2005b, Williams et al., 2013; Case et al., 2013) and potentially represent a distinct style of IOCG mineralisation dominated by the effects of F-rich fluids.

The Eastern Succession of the Proterozoic Mount Isa Inlier, NW Queensland, is one of the world's most productive mineral provinces, recognised for its diversity in IOCG styles within a relatively small area, all of which formed during the period 1.5-1.6 Ga (see review by Mark et al., 2006a). Some of the major deposits are shown in Figure 1A, and include Glencore-Xstrata's Ernest Henry Mining Operation and the recently mined Monakoff and E1 deposits (Fig. 1A,B). Monakoff and E1 form two of several smaller, but economic systems, with the Monakoff deposit containing a resource of 1.5 Mt @ 1.39% Cu and 0.44 g/t Au (Xstrata Copper internal report, 2013). Monakoff lies ~15 km ENE of Cloncurry, and the E1 deposit is located ~25 km to the NNE of Monakoff and ~8 km E of Ernest Henry (Fig. 1B). Whilst Ernest Henry has been the focus of many studies over the past 20 years (e.g. Mark et al., 2000; Oliver et al., 2004; Mark et al., 2006b; Kendrick et al., 2007), the Monakoff, and recently discovered E1 deposits are less well understood. Previous work conducted on the Monakoff deposit by Davidson et al. (2002) focused on the petrology and structural history of the deposit and presented a model of ore genesis involving the mixing of two distinct fluids, based on mineralogical relationships, in a structural dilational site. No direct temperature or fluid compositional constraints have been reported previously and in this paper we build on the earlier work by presenting new fluid inclusion and mineral chemistry data.

Fluorite, present at Monakoff, E1 and to a lesser extent at Ernest Henry as disseminations and in veins, provides a powerful tool for assessing ore forming processes through identifying, and providing insights into, fluid compositions, temperatures and redox conditions (e.g. Gagnon et al., 2003; Schwinn and Markl, 2005). Fluorite may contain trace amounts of REE, which can be quantitatively analysed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) techniques (Gagnon et al., 2003). Together with other techniques for determining some of the ore forming conditions (e.g. temperature from fluid inclusion microthermometry), the REE geochemistry of fluorite constitutes a powerful tool in understanding ore forming processes. However, to date, the majority of REE studies on hydrothermal fluorite have focussed on low-temperature (<250°C) deposits (e.g. Constantopoulos, 1998; Smith et al., 2000; Schwinn and Markl, 2005), and there has been no comprehensive work reported on fluorite in IOCGs, which are typically formed at temperatures of 200-600°C (e.g. Williams et al., 2005; Porter, 2010).

This paper characterises the style of F-Ba-rich IOCG mineralisation at Monakoff and analogous F-Ba-rich veins at E1, focusing on the gangue, base metal, precious metal and U-REE mineralogy, including a laser ablation study of Au distribution in sulfides. The fluid characteristics which give rise to these assemblages are investigated using a combination of fluid inclusion microthermometry, laser ablation analysis of sulfide minerals and fluid inclusions, and REE geochemistry of fluorite. From this, a number of constraints on ore forming conditions from these deposits have been determined, including fluid compositions, temperatures and oxidation state. The implications of these results are discussed regarding potential fluid and metal sources, and provide insights on the development and diversity of regional F-Ba-(U-REE)-rich mineralising systems in the Mount Isa Inlier.

2. Regional and local geological setting

The Mount Isa Inlier, Queensland, is divided into three N-S trending tectonic zones, defined by bounding faults, lithology, metamorphic grade and deformation styles (Hatton and Davidson, 2004). These are: the Western Fold Belt, the Kalkadoon Leichhardt Belt and the Eastern Fold Belt/Succession (Fig. 1A), which is further subdivided into the Mary Kathleen, the Malbon and the Selwyn Zones (Rubenach et al., 2008). Proterozoic aged (~1.74-1.66 Ga) basement rocks form the majority of the Eastern Succession, which have been subject to a complex tectonic history (Austin and Blenkinsop, 2009). These have since been overlain by three major supracrustal sequences, in which the IOCG deposits occur: Cover Sequences One, Two and Three (Fig. 1A), which consist of sedimentary (siliclastic and calc-silicate sediments) and bi-modal volcanic rocks. These were deposited at 1.89 Ga and 1.67-1.61 Ga (Blake, 1987), in intracontinental rift basins (Davidson et al., 2002). The Isan Orogeny was a major contractional deformation event in the Mount Isa Inlier, at 1610-1490 Ma (Austin and Blenkinsop, 2009) and was coincident with the emplacement of the major granitic, magnetite-bearing, A-type Williams and Naraku Batholiths between 1550-1500 Ma (Page and Sun, 1998). These granites, shown in Figure 1A, include the Malakoff granite, located to the west of Ernest Henry and Monakoff; the small Mount Margaret granite, to the east of E1; and a number of granites to the south of Cloncurry including the Wimberu, Saxby, Mount Angelay, Squirrel Hills, Mount Dore and Yellow Waterhole granites (Page and Sun, 1998; Pollard et al., 1998; Wyborn 1998).

2.1. IOCG mineralisation in the Cloncurry area

The eastern succession of the Mount Isa Inlier around Cloncurry is host to a number of deposits spread over an area within a 100 km radius of Cloncurry (Fig. 1A). Williams and Skirrow (2000); Williams and Pollard (2001) and Mark et al. (2006a), and references therein, provide overviews of the characteristics of a number of the main deposits in the region, including Ernest Henry, Osborne, Mount Elliot, Starra, Eloise, Great Australia and Mount Dore (Fig. 1A). Many of the deposits are broadly coeval with regional granitic magmatism, are structurally controlled and are associated with extensive brecciation, albitisation and Na-Ca alteration (Mark et al. 2006a). Based on geochronological studies, several of the deposits have been dated as being post-peak metamorphism, synchronous with the emplacement of the Williams and Narku batholiths at 1.55-1.50Ga (Perkins and Wyborn, 1998; Duncan et al., 2011) and with regional alteration (1.59-1.50 Ga; Oliver et al., 2004), leading many researchers to invoke at least a partial magmatic-hydrothermal fluid source in some of these deposits. However, some deposits, including Osborne, yield ages of ~1.59 Ga which predate batholith emplacement (Perkins and Wyborn, 1998), implying that a magmatic fluid source is not essential in the genesis of all IOCGs within the region (Kendrick et al., 2007) or at least is not the sole causative mechanism (Oliver et al., 2008).

In general, fluid inclusion studies on the Cloncurry deposits have indicated the presence of high temperature, (300-500°C), highly saline (up to 70 wt% NaCl equivalent) and CO₂-bearing fluids, which in many cases are thought to be related to magmatic-hydrothermal source (Williams et al., 2001; Mark et al., 2006a,b; Kendrick et al., 2006; Kendrick et al., 2007; Fisher and Kendrick, 2008; Rusk et al., 2010). However, fluid mixing between at least two fluids is thought to be responsible for mineralisation at several of the deposits such as Ernest Henry (Mark et al., 2000; Oliver et al., 2004; Rusk et al., 2010), Monakoff (Davidson et al., 2002) and Starra (Williams et al., 2001). The range of ages of IOCG mineralisation suggests they are the result of not only single, but in some cases, multiple or evolving, regional scale hydrothermal systems. The diversity in the style of mineralisation between deposits in the district has been proposed to be due to differing structural settings, depth of emplacement, host rock lithologies and fluid-rock interactions, fluid compositions, fluid sources and physiochemical conditions such as temperature, pH and oxidation state (e.g. Mark et al., 2006a).

2.2. Local geological setting of Monakoff and E1

The dominant stratigraphic units in the Monakoff area are Proterozoic basement rocks of the Corella Formation of the Mary Kathleen Group of the ~1740 Ma (Page, 1988) Cover Sequence Two and the Soldiers Cap Group of the ~1680-1660 Ma, (Page and Sun, 1998) Cover Sequence Three (Fig. 2). The Monakoff deposit is hosted by the Soldiers Cap Group which consists of a carbonate-poor succession including the Mount Norna Quartzite Formation (1654 Ma, Rubenach et al., 2008) and the Toole Creek Volcanics (1658 Ma, Rubenach et al., 2008; Derrick et al., 1976). The Monakoff ore body, dated at $\sim 1508 \pm 10$ Ma via Ar-Ar methods on hydrothermal biotite (Pollard and Perkins, 1997) is located within a reactivated bedding parallel, D₁ shear zone on the northern limb of the D₂ Pumpkin Gully Syncline (Fig. 2), where the Mount Norna Quartzite is in sheared tectonic contact with the Toole Creek Volcanics (Ashley, 1983; Davidson and Davies, 1997, Davidson et al., 2002). Banded ironstones, represented by stratiform BIFs, metasomatic BIFs, and magnetite-hematite replacement deposits, are common, although laterally impersistent in the area (Fig. 2), and their origins and temporal relationship to Cu-Au mineralisation remain controversial (Davidson, 1996; Hatton and Davidson, 2004; Austin et al., 2013). The

Monakoff ore zone is associated with, although not directly located within, a banded magnetite ironstone which flanks the northern edge of the orebody (Davidson et al., 2002; Fig. 2).

Monakoff's outcropping oxide minerals were discovered and worked by prospectors at the turn of the 20th Century and the deposit was investigated and sporadically drilled between 1954-1997 by numerous companies, including Gold Mines of Australia, Mount Isa Mines, Esso Minerals and Cloncurry Mining (Davidson et al., 2002), and was mined by Xstrata Copper during 2013. Several different models have been proposed for the formation of the Monakoff deposit. A primary syngenetic origin as a seafloor exhalative deposit was suggested by Ashley (1983) and this was supported by Derrick (1996); however, Laing (1991) described Monakoff as an epigenetic ironstone-hosted system at a structural intersection. Davidson and Large (1998) interpreted it as an epigenetic system, associating it with the other IOCG deposits of Australia, and Davidson et al. (1998) classified it as a stratabound, ironstone-associated deposit. The only comprehensive work on Monakoff was carried out by Davidson et al. (2002), who proposed that the mineralisation is epigenetic, and is structurally controlled, forming within a dilational shear zone. They documented four main structural events, D₁, D₂, D_{2.5} and D₃, which correlate with the regional Isan Orogeny, although D_{2.5} and D₃ are now referred to as D₃ and D₄ (Austin and Blenkinsop, 2010). In this model, the main shear zone formed as a result of a dextral D₁ shear and Cu-Au mineralisation is synchronous with D₃ deformation that created dilational jogs in the D₁ shear. A recent study of remnant magnetisation at Monakoff by Austin et al. (2013) suggested that the ore formed in a zone of dilation sub-perpendicular to the NE-SW shortening direction during D₃ which also formed the NW-SE trending strike slip faults (Fig. 2). The deposit clearly shows at least two dilational jogs that host mineralisation (Fig. 2).

The E1 Group is located 8 km east of Ernest Henry (Fig. 1B), and consists of three deposits: E1 North, East, and South. The deposits are hosted primarily by metasilstone, psammite, marble, and, to a lesser extent, meta-volcaniclastic tuffs, meta-andesite, meta-basalt, and hydrothermal breccias similar to those in the Corella Formation. The total resource is 47 Mt @ 0.71% Cu and 0.21 g/t Au. Mineralisation is hosted within a series of steeply dipping and folded calcareous meta-sediments and intermediate meta-volcanic units of the Soldiers Cap Group, with barren intermediate/mafic meta-volcanics and altered hydrothermal breccias (Porter Geoconsultancy Website, 2012). Although these three deposits exhibit slightly different structural controls, the style of mineralisation within meta-sandstones, siltstones and volcaniclastic breccias/tuffs, including fluorite and sulfide bearing veins, is similar, and the highest Cu-Au grades are associated with zones with abundant late-stage fluorite-barite-carbonate veining (Case et al., 2013).

3. Methods

Twenty grab samples were collected from the Monakoff historic open pit mine and surrounding outcrops in August 2012 (Fig. 2), before large scale mining of the deposit commenced. In addition, 18 samples of quarter core were collected from diamond drill hole EMKDD011 (Fig. 2), covering each lithology at ~5 m intervals, increasing to ~1 m intervals within the ore zone (Fig 3). Five representative samples from late stage fluorite-rich veins within the high grade zones at E1 were gathered from drill holes EMM003, EMM008 and EMM016 in order to provide a reconnaissance-level comparison of the mineralogical and fluid characteristics associated with the fluorite-rich ores at Monakoff.

Samples were crushed using a steel fly press and milled using agate planetary mills at the University of Leicester and bulk rock geochemical analysis of all Monakoff core samples was undertaken by ALS Minerals Laboratories, Ireland, with the exception of bulk F, which was undertaken at ALS's Vancouver laboratory, Canada. Major elements were analysed by X-ray Fluorescence, due to the anomalously high Ba contents, which constitutes a major element within the ore zone. Bulk rock S was analysed by LECO combustion furnace, base metals by four acid digest followed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and other trace elements, including the REE by Li borate fusion followed by ICP-mass spectrometry. The volatile elements As, Bi, Hg, Sb, Se and Te were analysed by aqua regia digest followed by ICP-MS, and Au was determined by fire assay followed by atomic absorption spectrometry. Bulk rock F was determined by fusion selected ion electrode methods. The limits of detection, and method used for each element, are listed in Table 1.

Fluid inclusion microthermometry was undertaken on samples of fluorite at the University of Leicester using a Nikon Labophot microscope and Linkham MDS 600 freezing-heating stage and software. The fluid inclusions were located within fluorite and the method was applied to 52 separate fluid inclusions. Microthermometry methodology followed that of Shepherd (1985). All homogenisation temperature measurements were made on heating and repeat readings (using a slow rate of 4°C/min for at least one repeat) were taken for each fluid inclusion, unless the inclusion leaked. Heating was stopped at ~450°C which was the upper limit of the equipment. The fluid inclusions analysed were of a size (>10 µm) that phase changes could be observed accurately and were well formed. Primary, pseudo-secondary and secondary inclusions were analysed. There was also a possible bias towards the larger more workable fluid inclusions, although, a range of inclusion morphologies were attempted where possible.

Laser ablation-ICP-MS (LA-ICP-MS) was carried out at Cardiff University on a number of representative sample blocks from the Monakoff ore zone and E1 fluorite veins, to analyse both fluorite and sulfides. This technique was used to establish: (1) the REE geochemistry of fluorite; (2) the composition of fluid inclusions within fluorite; and (3) the presence of trace elements within sulfides. The laser was operated using a 40 µm diameter beam with a frequency of 20 Hz and a pulse energy of 1-2 mJ. Samples were analysed by ablating lines for an acquisition time of between 100-140 seconds. The first 20 seconds constituted a blank before the laser was switched on, with the remainder of the time used for data acquisition. The fluorite samples were analysed quantitatively for the REE as well as several other isotopes to establish the presence of any inclusions of ore minerals, identified during petrological analysis, and to qualitatively determine the compositions of any fluid inclusions. The sulfides were analysed for base, precious and semi-metals to determine the concentrations of trace elements within each sulfide mineral. The full suite of isotopes analysed was: ²³Na, ²⁴Mg, ²⁹Si, ³³S, ³⁹K, ⁴⁴Ca, ⁵⁵Mn, ⁵⁶Fe, ⁶⁵Cu, ⁶⁶Zn, ⁷⁹Br, ⁸²Se, ⁸³Kr, ⁸⁸Sr, ¹⁰⁷Ag, ¹²⁷I, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁹⁷Au, ²⁰⁸Pb, ²⁰⁹Bi, ²³²Th, ²³⁸U, ³³S, ⁵⁷Fe, ⁵⁹Co, ⁶¹Ni, ⁶⁵Cu, ⁶⁶Zn, ⁷⁵As, ⁸²Se, ¹⁰⁹Ag, ¹²¹Sb, ¹²⁵Te, ¹⁸⁵Re, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁶Pb, ²⁰⁹Bi. For fluorite analysis, a stoichiometric concentration of Ca in ideal fluorite was applied as an internal standard for the calculation of the trace-element abundances. This has been deemed acceptable as commonly fluorite comprises over 99% CaF₂. Elements which

can readily substitute for Ca, including Ce, Sr and Y have been found to generally occur at total concentrations of less than ~0.4 wt. % (Gagnon et al. 2003). Thus, applying a stoichiometric Ca standard here is considered suitable. Calibration of the fluorite analyses was accomplished using the NIST 610 and 612 glass standards with certified USGS basalt glass BHVO-2G used as an unknown to verify the accuracy of the analysis. Calibrations for the concentrations of Fe, Cu, Zn, Ag, As, Sb, Te, Re, Au, Pb and Bi in the sulfides were performed using the Fe-Ni-Cu sulfide standards documented in Prichard et al. (2013) plus a homogenous galena, and using S as an internal standard. The conversion of ICP-MS output data (counts/sec) to concentrations (µg/g) including all blank and internal standard corrections was accomplished using the Thermo Plasmalab software.

4. Monakoff mineralisation

4.1. Monakoff host rock petrology and field relations

The Monakoff ore zone is ~15 m thick and structurally controlled, formed within a D₃ dilational jog in an E-W trending, D₁ shear zone (Figs. 2,3). Mineralisation is hosted within meta-sediments and meta-volcanics between two relatively competent units (Fig. 3A,B): the Toole Creek Volcanics in the hangingwall (Fig. 3A-D) and volcanics of the Mount Norna Quartzite Formation in the footwall (Fig. 3A,B,G-I). The ore zone is dominated by pyrite, chalcopyrite, barite, fluorite and carbonate (Fig. 3E,F). Adjacent to the main ore zone, meta-sedimentary units are replaced by magnetite and sulfides, which are in turn oxidised to azurite and malachite within the zone of weathering (Fig. 3D).

The hangingwall is composed of the Toole Creek Volcanics and associated meta-sediments (Fig. 3A-C). The Toole Creek Volcanics are fine-grained, altered and predominantly consisting of amphibole, plagioclase, chlorite, clinopyroxene, biotite, magnetite and porphyroblastic garnet. The associated meta-sediments (Fig. 3A,B,D) display a brown/grey colour, are fine-grained and consist of quartz, biotite, magnetite, chlorite and porphyroblastic garnets. Garnets are metasomatic and Mn-rich spessartine in composition (Davidson et al., 2002) and represent the first stage (Stage 1) of alteration. These are in turn overprinted by magnetite and biotite, which constitutes the second stage (Stage 2) of alteration. Sulfides related to the main mineralising event (Stage 3) overprint garnet and magnetite alteration assemblages.

The Mount Norna Quartzite Formation that makes up the footwall consists of meta-basalt volcanics (Davidson et al., 2002) including a rheologically competent, massive, garnet-rich felsic unit (Fig. 3I) and, adjacent to the ore zone itself, fine grained meta-sediments forming the footwall lithology (Fig 3B). The garnet rich felsic unit (Fig. 3I) consists of porphyroblastic garnet, quartz, biotite, plagioclase, amphibole and magnetite. Magnetite also occurs around garnets, and overprints them in places. The meta-sediments are fine-grained and sheared, consisting predominantly of quartz, garnet, biotite, calcite and magnetite and contain two distinct marker units. A thin metasedimentary unit containing abundant pyrrhotite is present in the footwall adjacent to the garnet-rich unit, which contains pyrrhotite and coeval magnetite in sheared, ribbon-like discontinuous bands (Fig. 3B,G). A few metres from the ore zone, a well banded meta-sediment is present that contains slightly discontinuous bands rich in magnetite that overprint porphyroblastic garnets. Magnetite-poor bands contain quartz, calcite and some barite and fluorite that represent alteration from the main ore stage event (Fig. 3H). The magnetite bands are folded into tight isoclinal folds which imply deformation post-magnetite formation. This is the banded ironstone

described by Davidson et al. (2002), although we interpret it to be a replacive ironstone, rather than having a primary sedimentary origin, as the magnetite is metasomatic and overprints garnets from the first stage of alteration.

4.2. Monakoff geochemistry

Whole rock geochemical data for 18 samples from drill core EMKDD011 (Fig. 2) are given in Table 1 and selected elements through the hangingwall-ore zone-footwall sequence are shown in Figure 4. The ore zone is characterised by consistent concentrations and ratios of the majority of elements and there is no evidence of any systematic variations across the main ore zone (Fig. 4). The ore zone is very distinct and metal abundances rise sharply in the 10 m thick ore zone intersection (Fig. 4). Average metal concentrations for the five ore zone samples from drill core EMKDD011 are 0.66 ppm Au, 78.4 ppm Ag, 3.2% Cu, 0.97% Zn, 0.64% Pb, 1270 ppm Co, 145 ppm Mo, and 125 ppm W (Fig. 4A-C). This correlates with high S, Se, Te (Fig. 4D) and other semi metals, including very high As. Uranium is enriched in the ore zone, with average contents of 242 ppm U, whereas Th is strongly depleted relative to the host rocks (Fig. 4E). The LREE are enriched, but the HREE are depleted relative to the host rocks (Fig. 4F, Table 1). The ore zone is also particularly enriched in BaO (26.1%), F (6.9%), Sr (3638 ppm; Fig. 4F) and MnO (2.4%), which reflect the dominant gangue mineralogy of fluorite, barite and Mn-bearing carbonate. Conversely, depletions in Y, Sc, Zr and Cr (Fig. 4G) across the narrow ore zone are also present.

The bulk rock geochemistry also highlights that the hangingwall Toole Creek Volcanics exhibit a basic composition, representing basalts and trachy-basalts. In contrast, the Mount Norna Quartzite Formation garnet rich footwall unit exhibits a more felsic composition, however only SiO₂, Al₂O₃ and Fe₂O₃ are present as significant major elements, and other than a high Zr content (Table 2), the rocks are extremely depleted in most other elements. Clearly the rock has undergone some significant metasomatism and depletion of most mobile elements. Davidson et al. (2002) suggested that the unit was a porphyroblastic garnet-biotite schist of partly intrusive, partly extrusive igneous origin, with a dacitic to andesitic parentage.

4.3. Monakoff ore mineralogy and alteration

In line with the geochemistry, the Monakoff ore zone has a fairly homogenous mineralogy, dominated by gangue fluorite, barite, carbonate and some quartz, albite, biotite and apatite. However, some textural differences are present and the ore zone shows evidence of three distinct textures of ore mineralisation which follow the more widespread garnet (Stage 1) and magnetite-biotite (+pyrrhotite) (Stage 2) alteration mentioned above. The major ore forming stage (Stage 3) of mineralisation has produced a fine grained, groundmass aggregate of fluorite, barite, manganoan calcite (containing 1-4 wt % Mn, and 0.5-1.5 wt % Fe), quartz, with pyrite, chalcopyrite, galena and sphalerite, which display textures consistent with co-precipitation (Fig. 5A-F), plus magnetite which is likely to be a remnant from earlier alteration. There is a crude, but consistent fabric to the groundmass assemblage (Fig. 5A,B), which is in line with pods of fluorite that appear to show shear fabrics (Figs. 3F, 5B). This is consistent with synchronous deformation at the time of mineralisation (as suggested by Davidson et al., 2002 and Austin et al., 2013), and the lack of deformation of the ore minerals indicates no significant post-mineralisation deformation. The only precious metal-bearing minerals identified are very small

($<5\text{ }\mu\text{m}$) Ag-Bi-Pb sulfosalts (which contain $\sim 2\text{ wt\% Au}$) with a composition close to *treasureite* ($\text{Ag}_7\text{Pb}_6\text{Bi}_{15}\text{S}_{32}$) that are included in both sulfides and fluorite (Fig. 5F). Uranium minerals consist of U-Pb-oxides, such as *richetite* ($\text{Pb}(\text{UO}_2)_4\text{O}_5 \cdot 4\text{H}_2\text{O}$) and several U-silicates, generally as inclusions or at grain boundaries in Stage 3 assemblages (Fig. 5D). Rare earth minerals ($\sim 2\text{--}400\text{ }\mu\text{m}$) are mainly La-Ce fluoro-carbonates such as *bastnäsitite*-La ($(\text{La, Ce})(\text{CO}_3)\text{F}$), which are also texturally associated with Stage 3 assemblages (Fig. 5E). The fine grained groundmass, based on this textural distinction, is referred to as Stage 3A.

Pods of much coarser grained fluorite, barite, calcite and quartz with sulfide, U, and REE minerals occur throughout the central part of the ore zone and are commonly aligned along the general fabric of the ore zone (Figs. 3E,F, 5A). These are typically a few mm to a few cm in width, and up to 15 cm in length (Fig. 3F) and differ mineralogically from the Stage 3A assemblages only in a lack of magnetite. The coarse grained pods do not cross cut the groundmass (Figs. 5B,G), and there is no textural evidence to suggest the pods are significantly later than the main stage, and may represent dilational zones created during the latter parts of Stage 3 mineralisation during synchronous deformation. Based on the clear textural difference to the main groundmass, and also the lack of magnetite in these pods, we distinguish this as Stage 3B. However, we do not believe that Stage 3A and 3B assemblages are chronologically distinct and are grouped together on the paragenetic sequence (Fig. 6A). Instead, we interpret the textural difference to be a result of syn-ore shearing (c.f. Davidson et al., 2002; Austin et al., 2013). This, and field evidence indicates that the pods occur in dilational structures within the ore zone (Fig. 3F) without magnetite. The magnetite is likely to be a remnant feature of Stage 2 alteration, and therefore present in the Stage 3A assemblages as a remnant feature but not precipitated in the coeval dilational features.

Stage 4 mineralisation is identified as an overprint of the Stage 3 assemblages by fine-grained aggregates of pyrite, as well as aggregates of large euhedral pyrite crystals (Fig. 5G), and *allockasite* ($(\text{Co,Fe})\text{AsS}$) (Fig. 5H). In places, galena is associated with the fine grained aggregates of pyrite, forming around the margins of individual pyrite grains and in the spaces between them. The paragenesis for Monakoff is summarised in Figure 6A.

5. E1 mineralisation

The E1 deposits have a complex, multi-stage paragenesis (Fig. 6B), and a comprehensive mineralogical and alteration study will be reported elsewhere. In this paper, we focus on one specific stage of mineralisation at E1, characterised by fluorite-barite-carbonate-sulfide veins as a direct analogue to the main stage mineralisation at Monakoff (Stage 5, Fig. 6B). The following section presents the geological context and setting of these veins within the E1 deposit group.

5.1. E1 host rock petrology

The bulk of E1 Group mineralisation is bounded to the northwest and southeast by northeast-trending fault zones. E1 North is the most structurally complex deposit of the E1 Group. It is composed of steeply-dipping and discontinuous ore lenses in tightly folded and sheared metasediments, including black shales, and meta-volcanics, and is bounded by meta-basalt to the south and porphyritic meta-andesite to the north. E1 South is

connected to E1 North by a stratabound, ~20 m ore lens between the meta-basalt and meta-andesite, and forms an apparent synform of three stratabound lenses. E1 East occurs as three steeply-dipping ore lenses open at depth and surrounded by metabasalt. E1 East host rocks are mainly heavily-altered Corella Formation marble and breccia. High-grade (>1% Cu) mineralization at each deposit is dominated by mostly stratabound magnetite-sulfide±barite±fluorite±carbonate banded replacement and minor veining, with carbonate-fluorite-barite-chalcopyrite veining dominant on the ore zone periphery.

5.2. E1 ore mineralogy and alteration

Mineralisation and alteration paragenesis at E1 is more complex than at Monakoff, with five major stages recognisable, including two major mineralization events (Fig. 6B), and several minor substages. Stage 1 is characterized by pervasive albite-quartz-hematite alteration, and may correspond to early, regional Na-alteration. Stage 1 is rarely preserved in the main ore body. Stage 2 is comprised of localized K-feldspar, biotite, magnetite, pyrite, and chalcopyrite alteration, and is most abundant within the main ore zone. Renewed, but less abundant, albite-hematite veining and alteration comprises Stage 3. Most mineralization occurs in Stage 4, which is dominated by Fe-rich carbonate, magnetite, chalcopyrite, pyrite, barite, fluorite, quartz, chlorite, and minor albite, biotite, apatite, arsenopyrite and pyrrhotite alteration and veining. Gold occurs as electrum within sulfides, or in Bi-sulfosalts. Alteration is fine- to coarse-grained, is generally layer-controlled, and is most abundant in psammite, meta-siltstone and layered meta-volcanics. Sideritic calcite, ±dolomite, ±quartz, ±barite, ±fluorite, chalcopyrite, ±chlorite veining is moderate in the ore zones, but abundant in the meta-volcanics, and is accompanied by widespread chlorite alteration. Finally, Stage 5 is characterized by voluminous manganoan-calcite, fluorite, ±barite, chalcopyrite, ±pyrite, ±quartz, ±chlorite, ±sericite, ±epidote veining, with widespread sericite alteration.

5.2.1. Stage 5 fluorite-barite-carbonate-sulfide veins

The gangue mineralogy of Stage 5 assemblages is dominated by high abundances of fluorite and barite, accompanied by quartz, calcite, manganoan calcite (~2 wt% Mn), quartz, albite, biotite and apatite (Fig. 7A,B). The fluorite in the veins exhibits variations in colour from, pale to dark purple (Fig. 7A). The ore mineralogy of the fluorite-rich assemblage at E1 is similar to that at Monakoff. Sulfides are dominated by pyrite and chalcopyrite (Fig. 7B), although contain less sphalerite, galena and magnetite. As at Monakoff, U minerals (~<1-5 µm) consist of U-Pb-oxides, including richetite and U-silicates, commonly found as inclusions in pyrite (Fig. 6C); and REE minerals (~3-90 µm) include La-Ce REE minerals such as bastnäsite-La, which occurs as inclusions in calcite and fluorite gangue (Fig. 7B). Precious metal minerals are only present as Ag-Bi-Pb sulfosalts (<3 µm), generally included in chalcopyrite and pyrite (Fig. 7D), but also in fluorite, as they are at Monakoff.

6. Trace metal contents of sulfides at Monakoff by LA-ICP-MS

Laser ablation-ICP-MS was used to investigate the precious and semi metal contents of sulfide minerals at Monakoff. A key aim of this was to document the occurrence of Au, which was not identified in SEM studies, other than minor concentrations in the very small grains of Ag-Pb-Bi sulfosalts in Stage 3 assemblages, which does not account for the bulk rock Au grades of around 0.6 ppm Au (Table 2). Laser ablation-ICP-MS was

conducted on Stage 3 pyrite, chalcopyrite and galena and Stage 4 pyrite and alloclasite, including two textural generations of Stage 4 pyrite: coarse euhedral, and fine aggregated (Fig. 5G). Concentrations of a selection of precious, base and semi metals in these analyses are shown in Table 2, and time resolved analysis (TRA) spectra of representative individual analyses are shown in Figure 8.

6.1. Stage 3 assemblages

Stage 3A (groundmass) pyrite has low concentrations of most base, precious and semi-metals (Table 2, Fig. 8A), with very low mean Au contents of 0.04 ppm, and low As (779 ppm) and Co (2115 ppm). Contents of Se, Sb, Te and Bi are also very low, and represent the lowest concentrations of these elements in all of the sulfides analysed (Table 2). Individual grains of pyrite are, however, zoned with respect to the semi-metals and Co (Fig. 8A), with As and Co mirroring each other, whereas Se, Bi and Te display differing behaviour within a single grain (Fig. 8A).

For chalcopyrite, with the exception of Te, all elements are slightly more enriched in Stage 3A chalcopyrite compared with Stage 3B chalcopyrite, though there are no major differences in metal ratios between the two and chalcopyrite from Stage 3A and 3B associations can be considered to be comparable. This is particularly true for Ag content, which is present in concentrations of 43 – 173 ppm Ag (Table 2). The Ag is present in solid solution with a lack of any zonation throughout each chalcopyrite grain analysed (Fig. 8B). Peaks in Ag concentration in the TRA spectra in Figure 8B correspond to peaks in Pb and Bi and indicate the presence of inclusions of Ag-Pb-Bi-sulfosalts.

Stage 3A galena is highly enriched in Ag, Se, Te and Bi and the four analyses performed returned remarkably consistent analyses for these elements (Table 3). Mean concentrations of these elements are around 4500 ppm Ag, 1800 ppm Se, 13,000 ppm Bi and 80 ppm Te. All elements are evenly distributed in solid solution within the galena, as seen by the smooth, parallel profiles on the TRA spectra (Fig. 8C).

We performed a mass balance calculation to calculate the proportions of bulk rock Ag in Stage 3 sulfides. Average bulk rock contents of Pb (0.76 wt%) and Cu (6.11 wt%) in the ore zone samples from Table 1, and stoichiometric wt % contents of Pb and Cu in galena and chalcopyrite, were used to calculate mass fractions of galena and chalcopyrite in the ore zone. This is possible as Pb and Cu are almost entirely hosted by galena and chalcopyrite, respectively. The mass fraction of galena in the Monakoff ore zone was calculated to be 0.00878, and the mass fraction of chalcopyrite, 0.176. Using the average Ag contents in galena of 4485 ppm and chalcopyrite of 76 ppm, the amount of bulk rock Ag contained in galena is 39.4 ppm, and in chalcopyrite is 13.4 ppm. This gives a total of 52.8 ppm in Stage 3 galena and chalcopyrite. The average bulk Ag grade of the ore zone is 86.1 ppm, and therefore 39 % of the bulk rock Ag is not accounted for by Stage 3 galena and chalcopyrite. This will include the Stage 3 Ag-Pb-Bi sulfosalts, although the volume of these is probably not sufficient to account for the deficit of about 33 ppm of bulk rock Ag, and so one possibility is that Stage 4 sulfides may contain significant Ag as well, or that other minerals we have not analysed contain some Ag.

Similarly, mass balance calculations for the Au content of Stage 3 sulfides is quantifiable, with an average Au content in galena of 0.088ppm and chalcopyrite of 0.129 ppm, equating to 0.0008ppm of the whole rock Au present in galena and 0.023ppm of the whole rock Au in chalcopyrite. This equates to 0.03 ppm of the bulk rock as Au in galena and chalcopyrite, plus a negligible amount in Stage 3 pyrite. Therefore, to account for the bulk rock values of around 0.6 ppm Au (Table 1), without any significant Au minerals, some other phases must carry significant Au concentrations that are not part of the Stage 3 assemblage.

6.2. Stage 4 assemblages

Pyrite and alloclasite in the later Stage 4 assemblages contain Au contents up to a few ppm Au (Table 2), which provides at least a partial explanation of the discrepancy in the Au mass balance for Stage 3 above. The coarse euhedral pyrite and fine grained aggregated pyrite (Fig. 5G) appear to be genetically related but are distinguished here due to their obvious textural differences, although their compositions are comparable (Table 2, Figs. 8D,E). Both types of pyrite are considerably more enriched in As and Co relative to Stage 3 pyrite by an order of magnitude, with As and Co contents around 10,000 ppm for each element (Table 2). The semi-metals, Sb, Bi, Te and Se are also present in concentrations one to two orders of magnitude higher than the Stage 3 pyrite. Zonation in As, Co, Au and the other semi-metals is common within Stage 4 pyrite (Fig. 8D,E) and in general Co and As have divergent behaviour from Se, Sb and Au (Fig. 8D). Nevertheless, the highest Au contents are present in grains that also have the highest As and Co overall. Silver, not present at all in Stage 3 pyrite, is present in Stage 4 pyrite in concentrations of several hundred ppm, which can account for the discrepancy in the mass balance performed for Stage 3 sulfides above. Two analyses of Stage 4 alloclasite contained 0.3 and 1.1 ppm Au in solid solution within moderately zoned crystals (Fig. 8F), with Au, Ag, Sb, Bi, Te, Ni and Se all present in solid solution.

7. Fluorite

The mineralised zone at Monakoff contains abundant fine-grained fluorite located throughout the Stage 3A groundmass (Fig. 5B,C,H). Colour variations in this fine-grained fluorite are not obvious. In addition, coarse Stage 3B fluorite, which exhibits colour variations and zonations from dark purple cores to pale purple rims, occurs as crystals a few centimetres in size (Figs. 3E,F, 5G). The Stage 5 veins at E1 contain coarse, variably zoned dark to pale purple fluorite (Fig. 6A).

7.1. Fluorite fluid inclusions

7.1.1. Microthermometry

Fluid inclusion microthermometry has been conducted on fluorite, from both Monakoff and E1, in order to identify the fluids involved in ore genesis and to investigate whether these two deposits share comparable fluid characteristics. This represents the first fluid inclusion to be undertaken on Monakoff and E1. Four fluid inclusion groups have been identified in a reconnaissance study of 52 fluid inclusions from four samples of fluorite from Monakoff and E1 (full microthermometry data is presented in Table 1A – supplementary data):

Group One: Relatively pure CO₂-rich fluid inclusions with homogenisation temperatures (T_h) of CO₂ ~21.5°C and melting temperatures ($T_{m\text{CO}_2}$) of ~-56°C, close to the -56.6°C typical melting point of pure CO₂ (Shepherd

1985). The $T_{h\text{CO}_2}$ is lower than the critical homogenisation temperature of 31.1°C, with homogenisation into the vapour phase, indicating relatively low density. These inclusions are found as isolated inclusions and are interpreted to be primary.

Group Two: Complex, high salinity, multi-phase, liquid-vapour-solid fluid inclusions (Fig. 9A-C), present in all generations of fluorite that we studied. These occur as well formed, euhedral inclusions (Fig. 9A,B) interpreted to be primary inclusions, and as isolated and trails of amorphous inclusions (Fig. 9C) interpreted to be pseudo-secondary given their similarity to the primary inclusions and presence in trails parallel to growth zones. Group 2 inclusions display the most variation in terms of the degree of fill and the number of solid phases (Fig. 9A-C). In addition, the behaviour of the solid phases during heating and freezing is complex. The majority of fluid inclusions contain one or more well-formed cubic daughter minerals at room temperature (Fig. 9A,B), which do not behave consistently throughout all inclusions during heating and freezing. The vapour phase is air in most cases, although some inclusions show two distinct bubbles that show the presence of some CO_2 in the vapour phase (Fig. 9C). Figure 9C shows an example of one such inclusion which at room temperature contains a single, cubic phase like that shown in Fig. 9A. After freezing, upon heating, the first melting occurs around 27°C (Fig. 9C) to produce several solids which condense into a single phase which then alters in shape on heating, forming elongated laths before melting at ~104°C. On cooling to room temperature, the lath shapes are sometimes preserved. When more than one solid phase is present, some of the other solids do not alter in shape or melt by 450°C, whereas, others were observed to melt at ~67°C, ~200°C and ~280°C. Temperatures of homogenisation range from 300°C up to at least 450°C, where heating was stopped. Although 27 Group 2 inclusions were analysed, many decrepitated before a T_h was observed (see Table, supplementary data), however, 10 T_h measurements of Group 2 inclusions were possible (Fig. 10). Group 2 inclusions can be divided into lower temperature (T_h ~317-370°C) and higher temperature (T_h >450°C) populations (Fig. 10). On this basis, this group has thus been subdivided into Group 2A (lower T_h) and Group 2B (higher T_h).

Group Three: Multi-phase, liquid-vapour-solid secondary fluid inclusions present in trails cross cutting fluorite growth zones with a large degree of solid fill ~40-50% (Fig. 9D,E) and a T_h ~232°C (Fig. 10), present in both stages of fluorite at Monakoff. Salinity data was not calculated as ice melting was not observed accurately. These inclusions were not identified in the fluorite veins we studied at E1. The euhedral solid phases did not alter during the heating and freezing process.

Group Four: Lower salinity, lower temperature, aqueous liquid-vapour secondary fluid inclusions. Salinities are in the range of 3.42-11.64 wt. % eq. NaCl (mean 5.48 wt. % eq. NaCl) (Bodnar, 1993, after Hall et al., 1998). The T_h varies ranging from 183.6-295.4°C (mean 235.3°C) (Fig. 10).

The compiled histogram (Fig. 10) displays the latter three groups and highlights the comparability between the fluorite-hosted fluid inclusions at Monakoff and E1, especially with regards to the Group 2 inclusions.

7.2. LA-ICP-MS of fluid inclusions

A series of 25 line analyses were performed by LA-ICP-MS through areas of fluorite that contained fluid inclusions in order to qualitatively determine the presence and association of elements in the inclusions. The solid-liquid-vapour Group 2 and 3 fluid inclusions in fluorite samples from Monakoff and E1 were analysed by traversing the laser along a line that contained inclusions in the upper 10-20µm of the sample wafer. Due to the common occurrence of clusters or trails of inclusions of the same type, it was not possible to quantify the concentrations of elements present, as more than one inclusion may have been ablated at the same time. However, care was taken to ensure that where trails and clusters did occur, they contained inclusions of just one type. In addition, whilst a range of metals and other elements were detected, Cl and F were not detectable in our analysis technique, and Ca (and F) were unquantifiable in the inclusions due to the host mineral being fluorite.

Over 40 inclusions were identified in the laser traverses. The results from three representative line analyses of fluorite from Monakoff and E1 are shown as TRA spectra in Figure 11. Laser ablation of fluorite is rough, due to its perfect cleavage. Therefore, the laser beam bursts the surface regardless of its orientation to the cleavage. This results in the mineral particles entering the plasma simultaneously and ionizing, recording high intensities in the spectrum that decrease and become more stable with time. As a consequence, the TRA spectra in Figure 11 generally show a large peak at the beginning as the laser is turned on, typically ablating a large pit initially, followed by a smoother trench (Fig. 5G). Undulations seen in the signature for Ca, for example (Fig. 11A), are a result of unequal amounts of material being ablated due to this effect. Inclusions are picked out in the TRA spectra as concurrent peaks in several elements not present within the fluorite crystal lattice.

Line analyses that ablate Group 2 inclusions in fluorite from both Monakoff (Fig. 11A) and E1 (Fig. 11B) show very similar element associations, being characteristically enriched in U and LREE, metals such as Cu, Pb, Zn, Mn and Mg, plus some Bi, K, Na and Ba. Group 2 inclusions occasionally contain some detectable Si and Ag (e.g. Fig. 11B) but not in all cases (e.g. Fig. 11A). Notably, there is no detectable S, Se, Th or Au in any of the analyses of these fluid inclusions. With the exception of S, Se and Au, the elements found in these inclusions are representative of the ore body as a whole (Fig. 4). The only noticeable difference between the analyses from Monakoff and E1 is the distribution of Sr, which at Monakoff mirrors Ca and is located within fluorite (Fig. 11A,C), whereas at E1 it appears to be present in lower concentrations in the fluorite, but also present in the inclusions themselves (Fig. 11B). It is important to note that visually, there is no difference between Group 2A and B inclusions, and homogenisation temperature is not possible to determine along with LA analysis. Therefore subtle variations between LA analyses in terms of the presence of certain elements may be a result of sampling the two sub populations, which would imply that the two temperature-defined sub populations may have slightly distinct chemistries.

The Group 3 inclusions are very different and do not contain any U, REE and significantly less base metals (Fig. 11C), with only a trace of Cu and Zn detectable, and no Pb, Bi, Au, Ag or Si. However, these inclusions are highly enriched in Ba, Na, Mg, K, and also contain detectable Br. The analysis line shown by Figure 11C shows a large Group 4 inclusion hit at around 25-30 seconds, followed by a smaller one (with smaller peaks) at 55 seconds. A peak in Na at around 77 seconds with no other concurrent peaks, probably represent a Group 4 aqueous-NaCl fluid inclusion. The REE signal is low in the inclusion at 25-30 seconds and then rises, reflecting

its presence in the fluorite. Overall, we have not identified a fluid inclusion population using this technique that is S-bearing.

7.3. REE geochemistry of fluorite

We undertook a total of 40 line analyses of fluorite using LA-ICP-MS. Time slices from each ablation that gave a consistent signature (i.e. away from cleavage pits and inclusions) were used to calculate the REE contents of fluorite from Stage 3A (groundmass) and Stage 3B (pod) fluorite from Monakoff, and from Stage 5 fluorite veins at E1 for comparison. Results from individual analyses are shown in Table 3.

7.3.1. Monakoff

Both Stage 3A and 3B Monakoff fluorite REE concentrations are characterised by a large, distinct positive Eu anomaly, a steep and slightly concave-up LREE profile and a flat to arched HREE chondrite-normalised pattern (Fig. 12A,B). All Monakoff fluorite samples display extremely similar fluorite REE geochemistry in terms of profile shape, although the Stage 3A fluorites are slightly more enriched in REE in general, and the LREE in particular. The positive Eu anomaly is present in every analysis from Monakoff and Stage 3A fluorite samples display a Eu/Eu* range from 5.58-23.1 (mean 10.7), and Stage 3B fluorite shows a similar Eu/Eu* range from 3.11-15.2 (mean 8.9). La_n/Yb_n ratios have also been determined to quantify the overall slope of the profiles. Stage 3A fluorite have a large La_n/Yb_n range from 3.64-1689 (mean 236), which reflects the large LREE enrichment in two of the fluorite grains analysed (Fig. 12A). Stage 3B fluorite have a much tighter constrained slope profile with a range in La_n/Yb_n ratios of 0.37 to 18.7 (mean 3.9). However, aside from the two Stage 3A fluorite analyses with anomalously high LREE enrichment, the REE profiles for Stage 3A and Stage 3B fluorite are almost indistinguishable (Fig. 12A,B).

7.3.2. E1

Figure 12C displays the chondrite-normalised REE profiles for Stage 5 fluorite veins at E1 for comparison with Monakoff. E1 fluorites are not as enriched in REE overall, with Figure 12C showing most elements to be in the range of 1-10 times chondrite, whereas Monakoff fluorite has REE abundances up to an order of magnitude higher (also Table 3). Overall though, the REE pattern of E1 late stage vein fluorite is very similar to the Monakoff fluorite, with a concave up LREE profile, a positive Eu anomaly and a flat-to-arched HREE pattern (Fig. 12C). The shape of the mean values is almost identical to that of Stage 3B at Monakoff (Fig. 12B), although the positive Eu anomaly is smaller. Eu/Eu* values are in the range 1.03-3.11 (mean 1.8). The overall slopes of the E1 fluorite REE profiles are similar to Monakoff with La_n/Yb_n ratios in the range 0.07 to 75.8 (mean 11.1). Two analyses show a La_n/Yb_n ratio of less than 1, indicating relative HREE enrichment or LREE depletion, however, the other 12 analyses all have La_n/Yb_n ratios of greater than 1.

7.3.3. Core/rim and colour variations

It is known that variations in colour, and thus trace element composition across fluorite grains can indicate changing compositions of the fluid and REE concentrations are known to increase from early precipitation in the cores to later precipitation in the rims (Schwinn and Markl 2005), although the overall profile shape does not necessarily change. A number of our analyses of Stage 3B Monakoff and E1 fluorite were performed on cores

(purple) and rims (pale purple), to assess variations within each deposit. No consistent relationships were found, although in general, fluorite rims at both locations exhibit a greater abundance of REE and a slightly greater Eu anomaly compared to the cores (e.g. Eu/Eu* Rim-9 is 12.41 compared to 9.63 in Core-8, Fig. 12D), although they have comparably shaped profiles. This is consistent with precipitation from a single fluid that is progressively enriched in incompatible REE with evolution, leading to enrichment in the later rims relative to the cores. However, other fluorites show near exact patterns between cores and rims (Fig. 12D), which may indicate fast precipitation and some of the E1 fluorites show considerable variation in pattern shape from core to rim (Fig. 12D), which may indicate variation in fluid composition or multiple fluid pulses.

8. Discussion

The results of this study have highlighted several key new mineralogical and fluid characteristics of the F-Ba-rich IOCG mineralisation at Monakoff. As such, any genetic mineralisation model for Monakoff must take into account the following features determined by this, and previous work:

1. A gangue mineralogy dominated by fluorite, barite and carbonate;
2. Gold present predominantly in solid solution in late Stage 4 pyrite and allocasite and only as a minor constituent in the main Stage 3 as Ag-Pb-Bi sulfosalts;
3. The presence of high temperature (>450°C) U-REE-base metal-rich, S- and Au-poor fluid inclusions in all textural categories of fluorite;
4. The presence of almost pure CO₂ fluid inclusions;
5. The presence of at least two populations of lower temperature fluid inclusions;
6. Very similar REE profiles in all textural categories of fluorite characterised by positive Eu anomalies.

Using this data, plus the results of previous work (Davidson et al., 2002), it is possible to determine, or at least suggest, some key constraints on the conditions of ore formation at Monakoff, which have implications for the distribution of such mineralisation in the area, and possible fluid and metal sources. In addition, we have demonstrated from our initial results that late stage F-Ba-rich veins at E1 show comparable mineralogy, fluid inclusions and fluorite REE geochemistry to Monakoff. Although the two deposits are separated by 25 km, and have very different structural settings and host rocks, the commonality of many of these characteristics constitute compelling evidence that the deposits share at least some common factors in ore genesis which are discussed in the following sections.

8.1. Characterisation of mineralisation style and links between Monakoff and E1

The style of mineralisation at Monakoff is distinct from many of the other IOCG deposits in the Cloncurry district (Williams and Skirrow, 2000). The characteristically high F and Ba contents and similar mineralogy of Monakoff and E1 distinguish them from most of the other IOCG deposits in the district and suggest a possible link in fluid sources and compositions. In addition, Monakoff has by far the widest range of enriched elements of all the deposits in the area, being particularly enriched in Pb, Zn, Co, Sr, REE and U, plus many other metals and semi-metals (Fig. 4). In contrast, the ore zone is heavily depleted in most of the immobile elements such as Zr, Ti, Al, HREE and Cr (Table 1), indicating that the ore zone was deposited from fluids that carried a wide range of mobile elements, and that the ore zone is representative of those fluids, without a significant host rock input into the bulk geochemistry.

The presence of significant Pb and Zn at Monakoff is atypical for IOCGs, but accessory minerals include U-Pb-oxides, bastnäsite-La and Ag-Pb-Bi sulfosalts (Figs. 5,6) are also common at E1 and therefore can be considered to be analogous to Monakoff. Given the proximity to Ernest Henry, it is pertinent to also assess the possible links between it and Monakoff and E1. Ernest Henry also contains significant fluorite and barite with carbonate in late stage assemblages (Mark et al., 2006b), and although not as voluminous as Monakoff and E1, the presence of fluorite and barite at Ernest Henry suggest similarities in the nature of at least some of the fluids in these deposits. Further similarities between Monakoff and E1 are present in the fluid inclusion compositions and temperatures (Figs. 9-11), and REE patterns in fluorite (Fig. 12). As such, we consider Stage 3 at Monakoff and Stage 5 at E1 to be analogous, and this will be explored below.

Our mineralogical results have identified that there is a significant late-stage assemblage at Monakoff, characterised by Co- and As-rich pyrite and alloclasite, both of which contain the majority of the Au in the deposit. This is a distinct stage that overprints the main F-Ba-Cu assemblages, and although how much later this was formed is unclear, it does show that Monakoff displays evidence of a distinct Co-As-Au sulfide signature, not currently recognised elsewhere, which is later than Cu mineralisation.

8.2. Gold and silver mineralogy

At Ernest Henry, Mark et al. (2006b) note the presence of native Au and electrum and Foster et al. (2007) demonstrate that almost all of the bulk rock Au at Ernest Henry is present as such, with very low concentrations in solid solution in chalcopyrite and pyrite (< 400 ppb). They interpret that Au was deposited electrochemically on pyrite surfaces, and was closely associated with chalcopyrite deposition. Native Au is also recorded as being present at Starra (Rotherham, 1997). In contrast, no electrum or native Au were observed in our SEM studies, and although minor amounts of Au are present within Ag-Pb-Bi-sulfosalts at Monakoff and E1, the LA analysis of sulfides suggests that at Monakoff, Au is present primarily within Stage 4 pyrite and alloclasite. Silver, in contrast, is present predominantly within Stage 3 sulfides, with some also in the Stage 4 sulfides.

8.2.1. Au in sulfosalts

The presence of Au and some Ag as sulfosalt inclusions in sulfides and fluorite in Stage 3 Monakoff mineralisation, and the F-rich veins at E1 is likely to be indicative of certain conditions of ore formation. Documentation is sparse regarding the presence of sulfosalts within IOCG deposits and in general, sulfosalts within other deposit types are low temperature phenomena, whereas our fluid inclusion data suggests temperatures of at least 450°C. However, the dominant theory in explaining Ag-Bi-Pb sulfosalt association with Au is via the ‘liquid bismuth collector’ model, proposed by Douglas et al. (2000) and further refined by Tooth et al. (2008). At temperatures above the melting point of Bi (271°C), Bi can divide from the hydrothermal fluid forming separate Bi-melt (Douglas et al., 2000). The liquid melt can effectively scavenge Au, even from fluids undersaturated in this element (Tooth et al., 2008). This theory has been applied to efficiently explain Au deposition in deposits of magmatic affiliation (Ciobanu et al., 2009), including the epithermal-porphyry transition at Larga (South Apuseni Mountains), Romania (Cook and Ciobanu, 2004) and Bi-Au skarn prospects in NW Tasmania (Cockerton and Tomkins, 2012), both consistent with temperatures of >400-500°C. Our fluid

inclusion microthermometry clearly indicate formation of Stage 3 at Monakoff and stage 5 at E1, in which chalcopyrite and fluorite are formed containing inclusions of sulfosalts, at temperatures of $>450^{\circ}\text{C}$. Therefore, we suggest that the presence of Au and Ag-bearing sulfosalts as inclusions in the F-rich Stage 3 Monakoff and Stage 5 E1 mineralisation is a result of the presence of a small amount of Bi-melt in the high temperature mineralising fluid.

8.2.2. Au in pyrite and other sulfides

One of the most significant findings of this work is the identification that the majority of the Au at Monakoff is located in solid solution within Stage 4 arsenian pyrite and alloclasite, which overprints the main F-Ba-Cu stage. Concentrations of Au in Stage 4 pyrite and alloclasite are around 1 ppm Au, but range up to a few ppm, with correspondingly high As and Co (Table 2, Fig. 8). This is in contrast to Ernest Henry, where Foster et al. (2007) report a mean of 77 ppb Au in pyrite and 56 ppb Au in chalcopyrite, representing around 2% of the bulk grade. It is well established from both experimental and analytical studies of natural samples, that high concentrations of Au in pyrite (above 1 ppm) are always correlated with As-rich compositions, and Au-bearing arsenian pyrite has been identified in a wide range of hydrothermal deposits (e.g. Cook and Chryssoulis, 1990; Fleet et al., 1993; Tauson, 1999; Pals et al., 2003; Reich et al., 2005; Deditus et al., 2011).

The identification of a separate, late stage event that hosts the majority of Au at Monakoff indicates a potentially important mineralisation stage in the district that has a characteristic Au-As-Co signature. Furthermore, it implies that although the main stage was highly enriched in a wide range of elements, it may actually have been relatively poor in Au, as seen by our analysis of fluid inclusions (Fig. 12A). Experimental data on the solubility of Au in chalcopyrite by Simon et al. (2000) predicts that at the temperatures determined by our fluid inclusion data of $400\text{--}500^{\circ}\text{C}$, chalcopyrite should contain around 1-10 ppm Au, if it is available. Mean values for Stage 3 chalcopyrite are 0.13 ppm Au, indicating that the bulk amount of Au available during precipitation of chalcopyrite may have been low, consistent with the Au-poor nature of the Group 2 fluid inclusion data.

8.3. Fluid characteristics

Our combined mineralogical, fluid inclusion and fluorite REE geochemical study provides some insights into the fluid characteristics at Monakoff and the analogous Stage 5 veins at E1. This includes: fluid redox state from REE geochemistry in fluorite; evidence of fluid mixing from the mineralogical relationships; fluid compositions from fluid inclusion laser ablation and fluorite REE geochemistry; and fluid temperatures from microthermometry. The following discussion addresses these aspects in turn.

8.3.1. Oxidation state and REE geochemistry of fluorite

The REE patterns in fluorite can provide information on source rocks, fluid compositions, and redox conditions at the time of deposition (e.g. Gagnon et al., 2003; Schwinn and Markl, 2005). The most striking characteristic of the REE geochemistry of fluorite we studied is a distinct positive Eu anomaly in all analyses. Europium anomalies can be propitious indicators of fluid temperature and $f\text{O}_2$ (Sasmaz et al., 2005) as Eu^{2+} is larger in ionic size than Eu^{3+} , Eu^{3+} can substitute for Ca^{2+} within the fluorite crystal lattice, whereas, Eu^{2+} is excluded (Constantopoulos, 1988). It is this Eu^{3+} substitution which results in the distinct positive Eu anomaly

documented within fluorite. Sverjensky (1984) and Bau (1991) applied calculations of molal Gibbs free energies of formation at elevated temperatures and pressures, to investigate factors affecting $\text{Eu}^{3+}/\text{Eu}^{2+}$ potential. With increasing temperature, the predominance field of Eu^{3+} relative to Eu^{2+} shifts to significantly higher $f\text{O}_2$, whereas, it is only slightly affected by pH and almost totally unaffected by pressure (Bau, 1991; Fig. 13).

Schwinn and Markl (2005) suggested that crystallisation temperatures are required to be below 200°C if fluorite is to display the positive Eu anomaly of the fluid due to crystallographically controlled fractionation during precipitation, based upon the thermochemical reduction of Eu^{3+} to Eu^{2+} at elevated temperatures. However, in this study the majority of fluid inclusion homogenisation temperatures are $>200^\circ\text{C}$ and most of the Group 2 inclusions are at least 450°C . Therefore, other explanations for this positive anomaly need to be explored. Kolonin and Shironosova (2007) offer an alternative explanation for Eu anomalies based on whether a mineral formed early or later in the mineralogical paragenesis, with negative Eu anomalies replaced by a positive one in REE patterns of late-stage minerals. Our data however does not support such an origin for the Eu anomalies, with cores and rims all exhibiting very similar, distinct positive Eu anomalies despite colour variations (Fig. 12D), implying that mineral paragenesis is not a significant controlling factor upon Eu anomalies at Monakoff and E1.

It is important to note, that the $f\text{O}_2$ of the environment is, in addition to temperature, another major $\text{Eu}^{3+}/\text{Eu}^{2+}$ controlling factor. It is possible that the positive Eu^{3+} anomaly can be preserved at temperatures $>200^\circ\text{C}$ if the environment is sufficiently oxidised and strong positive Eu anomalies, correlated with high fluid inclusion temperatures ($\sim 390\text{--}430^\circ\text{C}$), from fluorite deposits in Central Turkey, have similarly been explained via high $f\text{O}_2$ values (Sasmaz et al., 2005). Referring to the phase relations of Bau (1991) shown in Figure 13, and by applying a temperature of 450°C , for Eu to be in the Eu^{3+} state, it requires a highly oxidised environment, equivalent to a minimum $\log f\text{O}_2$ of around ~ 0 to 5. There is an abundance of sulfides and sulfates in the ores, and the sulfate-sulfide transition is close by to the conditions estimated from the fluorite data (Fig. 13), but at those temperatures, Fe^{2+} is stable, which is consistent with the presence of magnetite rather than hematite. All of these observations support the presence of an oxidised conditions during deposition of fluorite.

The similarity between the overall REE profiles at Monakoff and E1 provide evidence for a similar chemistry fluid(s) precipitating fluorite at each locality. There is, however, variance in the overall REE concentrations and the magnitude of Eu anomalies, within each individual deposit and between Monakoff and E1, which has been noted in previous studies, even within the same deposit (Sasmaz et al., 2005; Eppinger and Closs, 1990), and can be the result of a number of processes including host rock effects, chemical complexation and sorption processes (Schwinn and Markl, 2005). The magnitude of the Eu anomaly at E1 is less than that at Monakoff ($\text{Eu}/\text{Eu}^* \sim 9$ at Monakoff; ~ 2 at E1), which may reflect differences in the oxidation state, with possibly a lower $f\text{O}_2$ at E1, which is possible given the presence of black shales in the E1 area, which would act as a chemical reductant. Additionally, it is important to note that co-precipitation of REE minerals, sequestering certain REE preferentially, will locally affect the fluid composition and hence alter the REE content within co-precipitated fluorite (Gagnon et al., 2003). The Monakoff ores and E1 fluorite veins are enriched in La- and Ce-bearing minerals (including bastnäsité-La) and so variability in the enrichment of LREE in the fluorite may be related to

the relative timing of REE-mineral precipitation. Alternatively, the total REE content of fluorite can decrease in correlation to increasing distance from the source, due to fractionation (Eppinger and Closs, 1990; Sasmaz et al., 2005), and thus if this were the case, E1 may be interpreted to be further from the source of REE than Monakoff..

8.3.2. Fluid compositions and evidence for fluid mixing at Monakoff and E1

There is abundant evidence that several hydrothermal systems operated within the Mt Isa Inlier during its 250 Ma evolution (Oliver et al., 2008) and fluid mixing has been proposed as a fundamental process in many, if not all of the IOCGs in the Cloncurry district (Fu et al., 2003; Baker et al., 2008), including Monakoff (Davidson et al., 2002), Ernest Henry (e.g. Mark et al., 2006b; Kendrick et al., 2007; Rusk et al., 2010), Starra (Williams et al., 2001) and Osborne (Fisher and Kendrick, 2008). Evidence for fluid mixing in these studies includes multiple fluid inclusion populations with: wide ranges in salinity and temperature; differing halogen ratios indicating multiple sources; and variable $^{40}\text{Ar}/^{36}\text{Ar}$ values. In addition, fluid unmixing, especially of CO_2 , is thought to be common in the IOCG deposits of the Cloncurry area (Fu et al., 2003; Williams et al., 2001).

At Monakoff, geochemical and mineralogical associations support the presence of more than one fluid at the time of ore deposition. This interpretation is based upon a number of parameters; primarily, the abundance of co-precipitated barite and fluorite in the ores. Davidson et al. (2002) proposed that the Monakoff ores formed from the mixing of (1) an oxidised, sulphate-rich, metal-bearing, high temperature, F-rich fluid of likely granite derivation; and (2) a reduced, saline, Ca-K-Fe-Mn-Ba and CO_2 -rich fluid. The reasoning given by Davidson et al. (2002) is summarised as follows. Barium and S can rarely be transported within the same fluid, due to the low solubility of barite. Similarly, due to fluorite's low solubility, F and Ca must be transported separately. Furthermore, within oxidised fluids, Ba and Mn also exhibit minimal solubility (Cooke et al., 2000), and so Davidson et al., (2002) proposed that the Ba and Mn were most likely to have been transported in a reduced fluid and that this was likely to be a K-Ca-Ba-Mn-Cl-rich. Mixing of F- and S-bearing fluid (1) with Ca- and Ba-bearing fluid (2) then precipitated the abundant fluorite and barite.

With our new data on the composition and microthermometry of fluid inclusions within the fluorite, we are able to develop this two fluid mixing model further in terms of the composition of the two proposed fluids. Our fluid inclusion data suggest that the high temperature fluid, represented by Group 2 inclusions, is enriched in many metals, including Cu, Pb, Zn, U, REE, Ba, Fe and Mn, but does not contain significant S. An oxidised, F-rich, base metal-rich, U- and REE-bearing fluid of granitic derivation seems likely for fluid (1) seems likely, though our data does not support this being S-bearing. Uranium conveyance is often favoured by saline and oxidised fluids (Hitzman and Valenta, 2005), hence, it is purported to have been transported in fluid (1). Work by McGloin et al. (2013) supports the notion of U and Cu being transported in oxidised F-rich fluids, and our fluid inclusion analysis is consistent with the presence of a high temperature, U-REE-base metal-F-rich fluid. Most significantly, our data also shows Ba to be present in Group 2 fluid inclusions, but no S, contrary to the proposed fluid compositions of Davidson et al. (2002). Cooke et al. (2000) indicate that there is no significant Ba transfer > 100 ppm in oxidised conditions, and thus Ba is unlikely to be transported in an oxidised fluid. However, an exception to this is if the fluid is highly acidic with a pH of 2 or less (Cooke et al., 2000).

Therefore, given the evidence for the presence of Ba in the oxidised fluid, we infer that this fluid was probably acidic as well as oxidised. At temperatures of >450°C, this would make for a highly corrosive fluid, which would have the ability to leach and transport a wide range of metals, as seen in the varied metal content of Group 2 inclusions, although this noticeably does not include detectable Au. Furthermore, the presence of Ba in fluid (1) precludes the presence of oxidised S in this fluid. Our LA-ICP-MS analysis shows no evidence of S within the Group 2 inclusions (Fig. 11A,B), and so we propose that S was carried in a different fluid, possibly as reduced S in fluid (2).

Williams-Jones et al. (2000) document REE transport within F-rich magmatic fluids, predominantly as fluoride complexes and U and REE exhibit the propensity to partition strongly into F-rich fluids (Keppler and Wyllie, 1991). Mineralogical observations indicate that REE and U are associated with the fluorite rich stage (Fig. 5,6) at both Monakoff and E1 and subsequently are likely to have been transported within a F-rich fluid, thus supporting their probable presence within fluid (1). The mixing of fluid (1) and (2) at the site of deposition would result in a sudden drop in F activity (owing to Ca mixing), depositing fluorite and causing the destabilisation of REE fluoride complexes, resulting in REE deposition, including bastnäsite (Williams-Jones et al., 2000), plus the destabilisation of other complexes to precipitate barite and other ore minerals.

It is possible that the Group 1, pure CO₂ inclusions exsolved from one of the main ore forming fluids, especially given that there is evidence that some Group 2 inclusions contain some CO₂ (Fig. 9C). Kendrick et al. (2007) suggest that CO₂ rich inclusions at Ernest Henry are unlikely to be sourced from the Paleoproterozoic igneous rocks and thus can be most easily explained by a post-peak metamorphic origin during the regional magmatism and Na-Ca alteration. Unmixing of CO₂ and hypersaline brines from magmatic fluid phases is known from the Cloncurry district (Perring et al., 2000). It is argued that fluid inclusion data from IOCG deposits supports the presence of a hypersaline brine and coexisting CO₂ rich fluid, which have been interpreted to have evolved via unmixing, of an original H₂O, CO₂, NaCl +/- CaCl₂ fluid, derived from granitoid magmas (Pollard, 2001). Oliver et al. (2008) suggest CO₂ was released from the mantle or mafic magmas, into the felsic magmas, and this was carried into volatile fluids released during emplacement of the Williams-Naraku batholith.

Davidson et al. (2002) suggest that CO₂ was present in the reduced fluid at Monakoff, but we suggest that it is more likely that the CO₂ came from the oxidised and granite-derived F-rich as suggested by the studies by Perring et al. (2000), Pollard (2001) and Oliver et al. (2008). Furthermore, S isotope work on sulfide-sulfate pairs at Monakoff by Davidson and Davis (2002) indicates a common, and likely magmatic source of S for both, and that this supported a model of decompression of CO₂-bearing magmatic fluids. Additional support for a magmatic CO₂ source comes from the relative amounts of U and Th in the Monakoff ores. Whilst Monakoff is enriched in U (~200-300 ppm; Table 1; Fig 4), Th is highly depleted with only around 1-2 ppm Th in the ores, which is lower than the host rock background values (Table 2; Fig. 4). McGloin et al. (2013) note that fluoride effectively mobilises both U and Th, and thus both should be expected to be transported by a F-rich fluid and although high *f*O₂ conditions favour U mobility over Th, this alone is unlikely to produce the extremely low Th/U ratios seen in deposits such as Monakoff. Keppler and Wyllie (1991) demonstrate that adding CO₂ to a F-rich fluid allows the complexing of U with carbonate, but not Th. Therefore, the presence of CO₂ in the F-rich

fluid is consistent with the low Th/U ratios of the Monakoff ores if U is complexed by CO₂ and the possibility that CO₂ exsolved from this fluid to form Group 1 and 2 fluid inclusions.

The nature of fluid (2) is less clear, but it is inferred to be S- and Ca-bearing in order to mix with the Ba- and F-rich fluid (1) to form the abundant barite and fluorite, plus base metal sulfides. We do not, however, have any evidence from our LA-ICP-MS analysis of a S-bearing fluid, and at this stage, the presence of fluid (2) is based on the mineralogical implications outlined above. Whilst a circulating basinal brine origin is possible, the S isotope work of Davidson and Davis (2002) and Williams et al. (2013) does however, indicate that the sulfides and sulfates at Monakoff have S consistent with a magmatic source, and so the source of S and the fluid in which it was transported remains poorly constrained.

8.4. Fluid history at Monakoff

Following the early two alteration stages of garnet and magnetite-biotite ($\pm$ pyrrhotite), there is a distinct two-stage history of ore mineralisation at Monakoff. As a result of the parameters discussed above, we therefore propose that Monakoff formed from the mixing of the following fluids:

1. A high temperature (>450°C), oxidised, CO₂-bearing F-U-REE-Cu-Ba-Pb-Zn-Bi-Ag fluid (Group 2 inclusions). There is no evidence that significant Au was brought in with this fluid, and it is likely a Bi-melt co-existed with the hydrothermal fluid. The CO₂ exsolved and was trapped as pure CO₂ inclusions in fluorite (Group 1 inclusions). This fluid was most likely derived from the nearby Williams-Naraku granites;
2. A reduced, Na-K-Ca-S-rich fluid, possibly sourced from basinal brines.

In addition to this, we have evidence of at least three other fluids at Monakoff:

3. The fluid responsible for the Stage 4 Au-As-Co overprint;
4. A moderate temperature (200-250°C), Na-K-Mg-Ba-Sr saline fluid represented by Group 3 inclusions;
5. A low-moderate temperature (175-300°C) low salinity aqueous fluid represented by Group 4 inclusions.

Perhaps most significant is the textural and mineralogical evidence of an overprinting stage of Au-As-Co-rich (Stage 4) mineralisation that contains most of the bulk Au. It may be possible that Stage 4 represents a late stage evolution of the main ore forming fluids. At Starra, Rotherham et al. (1998) suggest that Au was deposited as a result of a decrease in temperature, coupled with a decrease in fO_2 due to interaction with magnetite, and an increase in pH following the precipitation of calcite decreasing the CO₂ content of the fluid. An analogous process of precipitation of oxidised minerals, with Au complexed as chlorides, followed by an increase in pH and evolution to a more reduced nature and the precipitation of Au and Fe sulfides may account for the Stage 4 assemblage at Monakoff. However, if this was the case, Au would be expected to be present in the Group 2 fluid inclusions, which it is not. Therefore we favour introduction of Au with As and Co as a separate, later event.

The Group 3 fluid inclusions record a Na-K-Mg-Ba-Sr and Br-rich fluid. Although not analysed in our LA analysis, given the presence of Br, it is likely this fluid also contained Cl and other halogens in a saline fluid. It

is unlikely that this represents fluid (2) above, as the inclusions are clearly secondary, have lower trapping temperatures, do not contain any S, and also contain substantial Ba. We interpret this fluid to represent a later stage, lower temperature fluid not present at E1. The low salinity aqueous fluid represented by Group 4 inclusions, which do not contain any significant metals are likely to be circulating meteoric waters. Previous studies conducted in the area report the presence of lower salinity, lower temperature fluid inclusions (Kendrick et al., 2006; Kendrick et al., 2007), similar to Group 4 inclusions that are interpreted to represent later surficial fluids.

8.5. Potential fluid and metal sources at Monakoff and E1 and links to other IOCGs in the region

Our work has identified several distinct fluid inclusion populations; a feature common to many of the deposits in the Cloncurry area and are testament to multiple fluid sources (Rotherham et al., 1998; Mark et al., 2000; Williams and Skirrow, 2000; Williams et al., 2001; Williams and Pollard, 2001; Kendrick et al., 2007; Mark et al., 2006b; Baker et al., 2008; Fisher and Kendrick, 2008; Marshall and Oliver, 2008; Oliver et al., 2008; Rusk et al., 2010). In a review of the fluid inclusion studies of the district, Williams and Pollard (2001) proposed that hypersaline fluid inclusions were trapped prior to or contemporaneously with Cu-Au mineralisation at temperatures generally $>300^{\circ}\text{C}$, and typically co-exist with $\text{CO}_2\pm\text{CH}_4$ vapours and our fluid inclusion study is consistent with this general characterisation. It is widely accepted that these high temperature, ultra-saline fluids, recorded in the majority of major IOCG deposits and also linked to significant amounts of metals, represent the ore forming fluid (Bertelli and Baker, 2010).

Although the link between magmatism and Cu-Au mineralisation in the Mount Isa Inlier is compelling in many cases, several authors have noted that a magmatic source of fluids is not necessarily required to produce the IOCG mineralisation in the district (e.g. Williams et al., 2005; Fisher and Kendrick, 2008; Duncan et al., 2011), and Baker et al. (2008) suggest that metals may be leached directly from crustal rocks during large scale alteration events, as well as exsolving directly from magmatic fluids (Baker et al. 2008). There is evidence within the region for large scale non-magmatic fluid flows, with some researchers supporting this model as it is a credible way to explain how the Osborne deposit may have formed prior to the emplacement of granite intrusions within the region (Fisher and Kendrick, 2008). However, given the various evidence discussed above, we favour a magmatic source for at least the F- and metal-rich fluid at Monakoff.

8.5.1. The role of granites as a source of fluids and metals

As stated earlier, the clear F-signature in the Monakoff ores, plus the inferred composition of the main ore forming fluid from our REE geochemistry and fluid inclusion studies of fluorite suggest at least fluid (1) being linked to the nearby post-peak metamorphic, oxidised, F-rich, A-type granites of the Williams and Naraku Batholiths (Fig. 1A). Page and Sun (1998) report a U-Pb zircon age for the Malakoff granite of 1505 ± 5 Ma. The only current geochronology for Monakoff is an Ar-Ar biotite date of 1508 ± 10 Ma from Pollard and Perkins (1997). This is within error of the date for the granite, although some caution should be taken as it may simply record a thermal resetting and therefore records a minimum age at least. The evidence for a direct magmatic-hydrothermal origin of the fluids at the Monakoff deposit is therefore still equivocal, however, there is certainly good evidence from other IOCG deposits in the Cloncurry district for at least a magmatic-hydrothermal input in

some (but not all) deposits. Furthermore, a connection between Monakoff and a magmatic association is supported by S isotope data (Davidson and Davis, 2002; Williams et al., 2013). As such, the source of the F-rich fluid at Monakoff is most likely the Naraku batholith. In addition, the granites are also potential sources for many of the metals that have been deposited at Monakoff.

Baker et al. (2008) documented that these batholiths generated an oxidised, ultra-saline, high temperature fluid, which is consistent with fluid inclusion Group 2 documented here. These intrusions can also provide an enrichment in U, REE and F (Pollard, 2000; Pollard, 2006), offering a potential provenance for these elements at Monakoff and E1. Although ultra-saline brines have also been linked to evaporite sequences in some terrains (Barton and Johnson, 1996), much of the literature, particularly in the Mount Isa region, favours a magmatic origin, which also provides a plausible explanation for the high U, REE and F abundances. The presence of CO₂ rich fluid inclusions have also been related to magmas emplaced during the Williams-Naraku igneous event (e.g. Kendrick et al., 2007; Bertelli and Baker, 2010). Strong affiliations between these Williams and Naraku Batholiths and Olympic Dam A-type granites, which are enriched in U and REE (Keppler and Wyllie, 1991) and interpreted as an efficient U source at Olympic Dam, have been documented (Haynes et al., 1995). As such, the F-U-REE-rich fluids interpreted to have been expelled by the Williams-Naraku granites in the Cloncurry area, evident at Monakoff, have parallels to the ore forming fluids at Olympic Dam.

In order to assess the potential link with the granites, the bulk REE geochemistry from the Williams and Naraku Batholith and the local host rocks at Monakoff are plotted in Figure 14, together with the average for the ore zone samples. The positive Eu anomaly and overall profile shape recorded in the fluorites is also evident in the bulk rock, and this does not appear to translate to the immediate host rocks, implying that the latter may not be the origin of REE (e.g. Schönerberger et al., 2008). The hangingwall metadolerites have flat REE profiles, with a negative, or flat Eu anomaly, and the footwall unit that is thought to have a dacitic or andesitic origin exhibits a gently sloping profile with a small negative Eu anomaly. Data for the local granites is sparse, and full REE analyses are not available, however Pollard et al. (1998) present data for La, Ce, Sm, Eu, Tb, Yb and Lu for the Mount Angeley and Saxby granites ~25km south of Cloncurry (Fig. 1A) that exhibit steep sloping LREE and flat HREE patterns, with a distinctive negative Eu anomaly (Fig. 14). The negative Eu anomaly in the granites may be consistent with the ore forming fluids being sourced from the granites, which have undergone feldspar breakdown and alteration.

An effective source for a positive Eu anomaly is via the alteration and decomposition of feldspars, as plagioclase and K feldspar typically exhibit positive Eu anomalies, due to a high abundance of Eu²⁺ (Constantopoulos, 1988). This suggests that the fluid responsible for fluorite deposition was involved in the decomposition of feldspars, transporting the Eu anomaly. The Eu²⁺ will be converted to Eu³⁺ in oxidising conditions and will thus be incorporated into the fluorite to exhibit a positive Eu anomaly. This is a plausible mechanism within the district, with extensive alteration and decomposition of feldspar reported (Kendrick et al., 2007). Although speculative, it is inferred that a positive Eu anomaly in the granite leachate can be produced via the breakdown of its feldspars, at high temperatures (which is reported within the Inlier: Laukamp et al., 2011), leaving a resultant negative Eu anomaly within the granite (Schwinn and Markl, 2005). This positive Eu

anomaly is then transferred within the hydrothermal fluid to the site of deposition, whereby oxidising conditions preserve Eu^{3+} in fluorites.

Similarly, the breakdown of feldspars may be a potential source of Ba in the ores. Monakoff does not have a significant K-feldspar alteration stage in the host rocks as many other deposits in the region do, and thus if breakdown of feldspars is a major contributor to the Ba content of the Monakoff ores, it must be sourced from elsewhere and transported with the mineralising fluid. Williams et al. (2001) report Ba-Cu-Zn-Pb-rich fluid inclusions at Starra, which is known to pre-date granite magmatism (Duncan et al., 2011), and suggest that the metal bearing fluids had a primitive mantle source, and so the Ba may not necessarily be of a granitic source. For Monakoff, the extremely high Ba contents are such a characteristic feature of the F-rich stage of mineralisation, and our fluid inclusion data shows that this fluid was Ba-rich, such that Ba must have been introduced in significant amounts with this probable granite-derived fluid. Whether the Ba was stripped from wall rocks, leached from feldspars, or whether it was sourced from the granite itself is unclear. However, the local granites are Ba-rich and Wyborn (1998) reports Ba contents from the nearby Malakoff granite (Fig. 1A) of around 250-850 ppm Ba and the Mount Margaret granite (Fig. 1A) has between 300 and 900 ppm Ba (Page, 1988; Wyborn, 1998), and the Saxby and Mount Angelay granites from 25 km south of Cloncurry have Ba contents in the range from around 150 to over 1600 ppm (Blake, 1986; Pollard et al., 1998), and thus constitute a possible Ba source.

The source of Cu has also been attributed to the Williams-Naraku granites with Baker et al. (2008) proposing that the generation of a high temperature, ultrasaline, Cu-rich magmatic fluids exsolved from the Williams and Naraku batholiths. This was then channelled through structures to sites where it could mix with nonmagmatic fluids, which had lower Cu contents and evaporitic-like halogen signatures. Oliver et al. (2008) suggest that the widespread oxidised, CO_2 -rich brines associated with the granites in the area may have had varying effects on ore genesis in terms of Cu; either mobilising pre-existing IOCG deposits, without adding significant Cu themselves; adding Cu from the granites to earlier reduced assemblages; or provided oxidised Cu-rich fluids that mixed with one or more different fluids to trigger ore formation. Furthermore, Oliver et al. (2008) state that rocks encountered during fluid-rock interaction may have provided a host of elements such as Fe, Ca, REE and various alkali earth elements. Given our constraints about the highly oxidised and likely acidic nature of the magmatic fluid, it is possible that significant metals may have been leached by what would have been a very caustic fluid. The anomalously high Pb and Zn contents at Monakoff, may lend support to these elements at least being partially leached from country rocks during fluid flow through the local crustal rocks. The ores at E1 have considerably less Pb and Zn, though the fluids are consistent in almost every other aspect, and therefore discrepancies in the bulk amount of any particular metal may reflect local fluid-rock interactions.

8.6. Mineralisation model for Monakoff

Davidson et al. (2002) proposed that the bedding-parallel D_1 shear zone present between the Toole Creek Volcanics and Mount Norna Quartzite were reactivated during D_3 as dilational, features that allowed for fluid flow and mixing at Monakoff. Austin et al. (2013) also interpret emplacement in a dilational zone sub-perpendicular to D_3 NE-SW shortening. Davidson et al. (2002) suggest that Fe-K-Mn enrichment event occurred

at 1651-1640 Ma (Davidson et al., 2002), with mineralisation significantly later. We largely agree with the structural aspects of these models, and given the deformed and folded nature of the magnetite bands in the metasediments, movement along this shear zone also occurred after Stage 2 magnetite alteration. Furthermore, the crude fabric defined by the groundmass assemblages in the Stage 3 ore, together with the dilational pods filled with barite-fluorite-carbonate-sulfide indicate deformation during Stage 3 ore formation.

As the structural trap is along a bedding parallel shear zone that is, in turn, folded by the D₂ Pumpkin Gulley syncline (Fig. 15, inset), it implies that the D₁ shear zone does not extend to depth beneath the syncline. However, any fluids sourced from below this must have been fed by a fluid feeder system or structure that intersects the base of the Pumpkin Gulley syncline beneath the present day surface. However, given the occurrence of the Malakoff granite just a few kilometres to the west, (Fig. 2), a lateral direction of fluid expulsion is possible. Nevertheless, it is the dilational opening of this structure during D₃ that is the key structural control on fluid flow and mineral deposition.

Figure 15 summarises our model for the emplacement of mineralisation at Monakoff. Following the early stages of alteration that produced Stage 1 garnet and Stage 2 biotite- magnetite alteration, D₃ deformation focussed on the pre-existing shear occurred, opening up dilational jogs in the main D₁ structure. This was coincident with granite magmatism and the emplacement of the Naraku batholith at around 1505 Ma, with oxidised, carbonic, F-U-REE-Ba-Cu rich fluids being expelled from the crystallising granite, which transported a range of metals, and also leached metals from the surrounding country rocks. At Monakoff, this includes the incorporation of anomalously high Pb and Zn contents. These fluids mixed with circulating non-magmatic brines in the dilational traps, precipitating the main Stage 3 mineralisation. At E1, the same F- and metal-rich granite-derived fluid mixed with a similar brine to form the late stage veins, which overprint the pre-existing main stage mineralisation, and also impart a F-Ba-rich alteration signature. Later stage fluids at Monakoff then form an overprint of Au-bearing arsenian pyrite and alloclasite, possibly as a result of reduction of the main ore forming fluid, or as a separate, late stage event.

8.7. Implications for regional F-Ba-IOCG metallogenesis

The wide variety in a number of controlling factors has produced a district of deposits with some common characteristics, but a great deal of complexity and diversity in most of their features. These include structural setting, rheological contrasts, host rock lithologies, fluid compositions, fluid temperatures, the number of fluids present and the depth of emplacement. In addition, the source of both the fluids and the metals in the Cloncurry deposits is as controversial as it is in any IOCG province in the world. Given this variability, it is not surprising that each deposit is unique in certain ways and therefore attempts to generalise are fraught with difficulty. However, our identification of a ‘Monakoff style’ of F-Ba-rich IOCG mineralisation allows for a number of general constraints to be made about the extent of this style of mineralisation in the Cloncurry district, which is dominated by the effects of a F-rich fluid.

The most important control on this style of mineralisation is the presence of a F-rich, metal bearing fluid, most likely derived from the Naraku batholith – probably the Malakoff and/or Mount Margaret granites, given that

this style is not as prominent to the south of Cloncurry. As such, this gives mineralisation formed from this a distinct, oxidised mineralogical assemblage that includes abundant fluorite, carbonate and barite, and also a geographic control. Not only does granite fluid source imply that such deposits are likely to be present only within a certain radius of where such granites occur, it also raises the possibility of a proximal-distal control of the nature of mineralisation formed from such fluids. The total REE content of fluorite can decrease in correlation to increasing distance from the source, due to fractionation (Eppinger and Closs, 1990; Sasmaz et al., 2005), and thus the lower REE contents of fluorite at E1 could be interpreted to be a result of E1 being further from the source of REE than Monakoff. The apparent extent of the signature of this F-rich fluid is from the Pumpkin Gulley syncline in the south, north to E1 and Ernest Henry, although these latter deposits are undercover so the true extent is unknown and could be extended much further (Fig. 1A).

A key feature of Monakoff is the clear structural control, with mineralisation present within dilations along a shear zone (Fig. 2) focussed in metasediments and volcanics located between two structurally competent units. All of the deposits in the district are structurally controlled in some way, and the nearby Ernest Henry deposit is also bounded on both sides by shear zones. However, in contrast to Ernest Henry, plus some other exploration targets in the area, early Na-Ca alteration is not present and none of the hydrothermal breccias common in many deposits (Oliver et al., 2006), with associated K-feldspar alteration are present at Monakoff. This illustrates that the presence of breccias and 'red-rock' alteration is therefore not essential, nor is Na-Ca alteration signature, at least for relatively small deposits. Davidson et al. (2002) note that the F alteration signature in the wall rocks extends for at least 130 m across strike, representing a F-enriched zone more than ten times the width of the orebody itself. Although this represents a valuable geochemical signature for this type of mineralisation, the expense and difficulty in assaying for F somewhat inhibits its practical use as a geochemical exploration tool.

Perhaps the most intriguing of the results from this study is the identification of a late-stage Au-As signature at both Monakoff and E1. Monakoff exhibits a late stage overprints of As-Co-Au-rich sulfides suggesting much more reduced conditions than the F-rich stage. Interestingly, the Lorena Au deposit, just to the southeast of Monakoff, in the Pumpkin Gulley Syncline area (Fig. 1B) is comprised of Au-rich arsenopyrite with pyrrhotite, pyrite and very minor chalcopyrite (Lawrence et al., 1999). It may be possible that the main mineralisation stage at Lorena is analogous to the late stage overprint at the nearby Monakoff. As such, this fluid may also be regionally extensive, utilising some of the same structural traps as the earlier Cu-rich mineralisation.

From our work at Monakoff we are able to define some constraints about where would be prospective for similar F-Ba-IOCG mineralisation, and what the likely characteristics of such deposits will be. These are:

- (1) the presence of a granite-derived F-Ba-rich oxidising fluid, that can carry a diverse range of elements;
- (2) the extent of this fluid is at least 25km along strike, although how far this extends laterally from the granite is unclear but is at least a few kilometres;
- (3) deposits that are formed from such fluids are rich in fluorite, barite and carbonate, giving a distinctive F-Ba, and also REE-U-Mn geochemical signature
- (4) breccias are not necessarily important, but structural controls, such as dilations are, especially as zones for fluid mixing;

(5) targets will be magnetic due to the amount of magnetite, but laterally extensive ironstones do not necessarily hold a control on the presence of mineralisation;

(6) the late stage Au-Co-As stage gives a distinct geochemical signature and mineralogy of Au.

Overall, IOCGs in the area are the result of mixing of two or more fluids with potentially several overprints and there is clearly a history of multiple fluid phases in the area, and the interaction of any one of these, with one or more of the others in structural traps in a range of host rocks have formed a diverse set of deposits.

8.8. Implications for the use of fluorite in interpreting F-rich IOCGs

Fluorine-rich fluids are a fundamental feature of some IOCG deposits, some of which are associated with granite magmatism, such as Olympic Dam (McPhie et al., 2011). Whilst this produces deposits with fluorite as a common gangue mineral, the role fluoride has in transporting certain elements under certain conditions means that such deposits have a characteristic enrichment in REE and U. The work by McGloin et al. (2013) demonstrates that the ability of such fluids to transport U, Th, REE, Cu, Au, Zr and any combination thereof, are determined by the oxidation state, temperature and the presence of CO₂, with evidence from the Mount Isa Inlier showing a lack of Cu and Au in fluoride fluids that are reduced in nature. The characteristic REE geochemistry of fluorite, together with other techniques which determine some of the ore forming conditions (e.g. temperature and CO₂ content from fluid inclusions) means that fluorite represents a unique proxy for determining fluid compositions, temperatures and redox conditions (Bau, 1991; Schwinn and Markl, 2005; Gagnon et al., 2005)

Our work shows that this approach can be effectively applied to fluorite-bearing IOCGs, illustrating how the combined use of fluid inclusions and REE geochemistry in fluorite provide insights into these key ore forming conditions, as well as potential sources of fluids and metals, and also the relative proximity to source. In addition, the Sm-Nd isotopic system can be used to date fluorite and provide further constraints on fluid sources such as granites (Chesley et al., 1993). Being able to constrain these conditions is critical to determine if a particular hydrothermal system has the potential to host significant resources of any of these elements, and also the particular element associations that may be present. As such, there is potential to use fluorite as a proxy for not only fluid conditions and fluid sources, but also a geochemical vectoring tool in F-rich magmatic-hydrothermal systems.

9. Conclusions

Monakoff is a structurally controlled IOCG deposit, characterised by the presence of very high concentrations of Ba and F. It is interpreted to have formed from the mixing of a high temperature, oxidised, CO₂-bearing, F-rich, metal rich brine of granitic origin, with a reduced S-bearing fluid in a structural trap to produce a highly exotic mineralogy enriched in a large range of elements. The main F-rich fluid that formed Monakoff also formed the late stage veins at E1, which have comparable fluid inclusions, fluorite REE geochemistry, and mineralogy. The majority of Au however, does not appear to be in the main stage at Monakoff, but in a late overprint of Co-As sulfides, with Au present at ppm level in sulfides rather than as electrum. The source of the F-rich fluid is likely to be the nearby granites of the Naraku batholith, and the extent of this fluid is at least 25 km in strike length along the batholith margin, and may extend for several kilometres outwards. The source of metals is also likely

to be, in part at least, the granites; although leaching of some metals, such as Pb and Zn is likely to have occurred locally along structural pathways through the diverse range of crustal rocks in the region. This work has highlighted that fluorite geochemistry and fluid inclusions can be used to identify key temperature, compositional and redox constraints on the ore forming fluids, which are all factors that determine the mobility of Cu, Au, U and REE in F-rich fluids. As such, fluorite can be used as a geochemical vectoring tool in F-dominated hydrothermal systems.

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Table 1. Bulk rock geochemistry across the hangingwall, ore zone and footwall lithologies at Monakoff from drill hole EMKDD011. Analytical technique abbreviations: XRF (X-ray fluorescence); CF (combustion furnace); FSIE (fusion, selected ion electrode); 4A ICP-AES (four acid digest, inductively coupled plasma mass spectrometry-atomic emission spectrometry); FA-AAS (fire assay, atomic absorption spectrometry); AR-ICP-MS (aqua regia, inductively coupled plasma mass spectrometry-mass spectrometry); LBF (lithium borate fusion). bd = below detection limit; ad = above detection limit.

Also submitted as Excel file.

		SAMPLE: Depth (m)	14.4	19.4	23.0	29.2	33.0	41.9	48.3	49.6	50.2	51.0	52.3	53.2	55.8	60.2	63.9	65.5	67.2	76.0
		Rock type	Toole Creek Volcanics	Toole Creek Volcanics	Sulphide rich vein	Toole Creek Volcanics	Meta-sediment	Meta-sediment	Ore Zone	Ore Zone	Ore Zone	Ore Zone	Ore Zone	Quartz-sulphide vein	Banded ironstone	Meta-sediment	Meta-sediment	Meta-sediment	Mount Norma Quartzite	Mount Norma Quartzite
Analyte	Units	Technique (detection limit)																		
SiO ₂	wt%	XRF (0.01-100)	46.6	47.8	23.9	49	59.4	27.4	20.7	6.92	2.76	4.97	2.34	81.6	24.1	33.5	42	72	66.5	68.6
TiO ₂	wt%	XRF (0.01-100)	0.97	1.12	0.28	1	0.74	1.29	0.3	0.07	0.03	0.08	0.02	bd	0.03	0.34	0.46	0.59	0.93	0.91
Al ₂ O ₃	wt%	XRF (0.01-100)	13.6	15.55	9.81	14.7	20.2	16.15	8.37	1.72	0.74	1.54	0.47	0.08	0.72	8.26	11.35	15.35	11.9	11.15
Fe ₂ O ₃	wt%	XRF (0.01-100)	17.18	17.79	26.33	13.54	5.88	28.1	31.76	12.76	16.45	19.94	14.6	11.96	52.76	33.75	31.35	3.86	12.51	11.42
MnO	wt%	XRF (0.01-100)	1.06	0.66	2.13	1.32	0.41	2.09	0.87	1.6	1.44	4.06	2.34	0.1	1.84	9.93	2.66	0.11	1.64	0.92
MgO	wt%	XRF (0.01-100)	8.24	7.01	0.75	7.94	1.7	6.07	1.5	0.35	0.3	0.41	0.2	0.02	0.14	1.13	0.81	0.29	0.59	0.45
CaO	wt%	XRF (0.01-100)	3.99	3.15	19.55	5.65	0.55	9.31	14.2	13.6	13.75	13.2	14.4	0.07	10.85	4.28	1.15	0.4	1.72	1.6
Na ₂ O	wt%	XRF (0.01-100)	3.74	5.23	0.72	3.89	0.86	0.03	1.84	0.29	0.19	0.15	0.1	0.03	0.04	0.03	2.35	0.52	2.02	1.92
K ₂ O	wt%	XRF (0.01-100)	0.33	0.25	0.19	1.21	5.73	0.71	2.28	0.6	0.2	0.51	0.02	0.01	0.21	1.44	2.29	4.49	2.11	2.07
P ₂ O ₅	wt%	XRF (0.01-100)	0.07	0.08	0.31	0.07	0.28	0.1	1.44	0.32	0.27	0.25	0.23	bd	0.61	2.83	0.5	0.17	0.27	0.27
Cr ₂ O ₃	wt%	XRF (0.01-100)	0.03	0.03	0.01	0.03	0.01	0.04	0.01	0.01	0.01	bd	0.01	bd	bd	bd	bd	0.01	bd	bd
SiO	wt%	XRF (0.01-100)	0.02	0.02	0.19	0.04	bd	0.01	0.04	0.47	0.41	0.41	0.44	bd	0.05	0.01	0.01	bd	0.01	bd
BaO	wt%	XRF (0.01-100)	0.04	0.04	1.52	0.35	1.81	0.39	1.41	26.8	24.8	23.1	29.8	0.1	0.09	0.23	0.26	0.34	0.18	0.16
LOI	wt%		2.38	2.07	4.33	0.91	2.32	5.69	6.73	0.24	-1.83	1.53	-0.47	5.19	4.93	3.51	3.62	1.8	0.41	0.57
Total	wt%		102.55	101.05	97.71	99.97	100.65	98.5	99.27	89.25	85.53	89.29	87.47	109.55	96.78	102.55	109.4	100.05	101.6	100.45
S	wt%	CF (0.01-50)	0.87	0.02	3.46	0.02	0.27	0.31	4.12	11.6	13.75	9.34	10.4	8.98	0.12	1.15	10.3	0.04	0.27	0.13
F	wt%	FSIE (0.01-100)	0.07	0.05	0.03	0.07	0.19	0.12	0.56	6.21	7.48	6.56	7.35	0.02	0.06	0.27	0.12	0.09	0.08	0.06
Ag	ppm	4A, ICP-AES (0.5-100)	bd	bd	bd	bd	bd	bd	2.8	56.9	86.1	81.8	88.7	6.6	bd	0.9	6.7	bd	bd	bd
Cd	ppm	4A, ICP-AES (0.5-1000)	26.3	0.7	18.9	0.7	bd	1.3	8.9	16.9	31.5	41.2	45.6	0.9	2.4	1.3	bd	bd	bd	bd
Co	ppm	4A, ICP-AES (1-10000)	47	37	59	51	44	23	593	1110	1520	1590	867	602	bd	30	366	2	14	6
Cu	ppm	4A, ICP-AES (1-10000)	30	3	87	30	33	120	1640	25100*	61100*	24000*	19250*	5620	38	88	1550	18	37	18
Mo	ppm	4A, ICP-AES (1-10000)	bd	bd	bd	bd	32	1	33	197	99	157	125	1	50	22	47	bd	bd	1
Ni	ppm	4A, ICP-AES (1-10000)	111	111	25	109	39	105	69	104	118	118	89	18	bd	43	125	1	bd	bd
Pb	ppm	4A, ICP-AES (2-10000)	10	4	39	46	10	38	405	4940	7600	7410	5640	22	20	37	74	11	6	14
Sc	ppm	4A, ICP-AES (2-10000)	36	41	6	39	14	40	4	1	1	1	bd	bd	bd	8	8	14	17	15
Zn	ppm	4A, ICP-AES (2-10000)	17050*	835	8820	787	121	964	2400	4180	8220	11950*	14400*	240	442	187	101	21	87	131
Au	ppm	FA-AAS (0.005-10)	bd	bd	bd	bd	bd	0.072	0.747	0.656	0.667	0.572	0.006	bd	0.015	0.074	bd	bd	bd	bd
As	ppm	AR, ICP-MS (0.01-250)	1.9	1.3	16.8	1.6	33.1	3.2	ad	ad	ad	ad	ad	134	6.8	7.7	9.3	1.1	46.7	54.9
Bi	ppm	AR, ICP-MS (0.01-250)	0.09	0.05	4.92	0.66	2.55	0.72	37.7	ad	ad	ad	193.5	2.68	0.37	3.56	86.2	0.1	0.22	0.3
Hg	ppm	AR, ICP-MS (0.01-250)	2.77	0.058	1.415	0.046	0.026	0.045	0.477	1.62	3.45	5.57	8.62	0.181	0.189	0.024	0.025	0.01	0.016	0.011
Sb	ppm	AR, ICP-MS (0.005-250)	0.71	0.66	4.95	1.37	1.85	0.33	3.88	11.85	18.15	12.55	10	0.91	0.89	2.72	5	0.43	0.77	1.34
Se	ppm	AR, ICP-MS (0.02-250)	1.4	bd	1.6	0.3	1.4	0.4	3.3	22.4	25.2	18.9	17.4	3.1	0.7	1.7	5.3	0.4	1	1.2
Te	ppm	AR, ICP-MS (0.01-250)	0.02	0.02	0.71	0.07	1.04	0.04	0.35	3.27	3.79	3.33	2.63	0.06	0.06	0.45	1.28	0.01	0.01	bd
Ce	ppm	LBF, ICP-MS (0.5-10000)	4.2	23.7	42.8	10.8	72.3	12.6	73.1	1020	1435	814	795	8.6	35.3	64.4	113.5	56.5	85.7	80.3
Cr	ppm	LBF, ICP-MS (0.1-10000)	260	280	40	260	90	270	40	10	10	10	10	bd	10	60	60	70	10	10
Cs	ppm	LBF, ICP-MS (0.01-10000)	1	0.77	0.16	6.1	7.96	1.68	11.6	0.54	0.19	0.22	0.01	0.04	0.17	1.91	3.75	3.61	2.41	2.25
Dy	ppm	LBF, ICP-MS (0.05-1000)	2.37	3.82	4.9	3.39	7.64	3.35	1.26	1.11	0.7	0.57	0.49	0.07	0.97	8.49	4.37	5.33	8.42	7.87
Er	ppm	LBF, ICP-MS (0.03-1000)	1.69	1.85	2.97	2.1	5.47	2.41	0.87	0.59	0.41	0.39	0.26	bd	0.46	3.94	2.19	3.42	4.91	4.65
Eu	ppm	LBF, ICP-MS (0.03-1000)	0.33	0.8	2.91	1.01	1.23	0.78	1.65	12.8	14.9	11.25	12.5	0.12	1.22	3.67	2.55	1.47	2.27	2.26
Ga	ppm	LBF, ICP-MS (0.1-10000)	17.4	17.2	23.8	17.3	27.2	22.6	24.9	21.6	16	21.5	11.5	0.7	2.4	14.7	19.2	30.4	22.9	22
Gd	ppm	LBF, ICP-MS (0.05-1000)	1.86	5.62	5.8	3.18	6.19	2.5	1.23	1.74	1.54	1.16	0.78	0.14	1.5	11.6	7.7	6.35	10.25	10
Hf	ppm	LBF, ICP-MS (0.2-10000)	1.2	1.5	2	1.6	6.2	2	2.4	0.6	0.5	0.5	0.6	bd	0.3	2.7	3.5	4.7	7.7	7.4
Ho	ppm	LBF, ICP-MS (0.01-1000)	0.56	0.7	1.11	0.77	1.75	0.76	0.28	0.2	0.11	0.11	0.05	bd	0.16	1.59	0.85	1.18	1.7	1.59
La	ppm	LBF, ICP-MS (0.5-10000)	1.8	8.6	24.1	5	33.8	8.7	85.4	1395	2050	1175	1135	11	32.2	36.9	69.8	27.8	41.2	36.6
Lu	ppm	LBF, ICP-MS (0.01-1000)	0.33	0.27	0.3	0.28	0.74	0.36	0.15	0.11	0.07	0.08	0.05	bd	0.02	0.4	0.34	0.54	0.78	0.81
Nb	ppm	LBF, ICP-MS (0.2-2500)	3	3	5.8	3	17.5	4.7	6.4	2.2	0.9	1.9	0.5	bd	0.7	7.2	10.3	12.8	14.9	15.1
Nd	ppm	LBF, ICP-MS (0.1-10000)	3.5	17.5	21.2	7.8	30.9	6.3	9.5	70.4	91.3	51.1	47.1	1.2	10.2	31.5	43.9	27.4	43.5	44.6
Pr	ppm	LBF, ICP-MS (0.03-1000)	0.63	3.64	5.06	1.6	8.36	1.45	4.46	48.1	66.9	38	37	0.49	3.17	7.71	12	6.84	10.55	10.4
Rb	ppm	LBF, ICP-MS (0.2-10000)	14.5	10.1	9.1	77.1	320	32.9	155	20.8	6.8	16.1	0.7	1	6.7	76.6	129.5	193.5	105	103.5
Sm	ppm	LBF, ICP-MS (0.03-1000)	1.31	4.79	4.76	2.45	6.08	1.78	1.09	2.81	2.68	1.71	1.49	0.12	1.76	8.56	8.3	5.79	9.97	10.25
Sn	ppm	LBF, ICP-MS (1-10000)	bd	bd	1	bd	4	3	5	16	26	14	12	bd	1	4	2	6	2	2
Sr	ppm	LBF, ICP-MS (0.1-10000)	95.1	158	1515	332	34.3	86.5	309	3920	3780	3250	3600	11.6	369	66.2	48	26.1	36.3	31.4
Ta	ppm	LBF, ICP-MS (0.1-2500)	0.2	0.2	0.6	0.2	1.5	0.4	0.6	0.2	0.1	0.3	0.1	bd	0.1	0.7	0.9	1.2	1.2	1.3
Tb	ppm	LBF, ICP-MS (0.01-1000)	0.37	0.78	0.82	0.61	1.16	0.51	0.19	0.28	0.24	0.17	0.12	bd	0.2	1.72	0.96	0.98	1.53	1.5
Th	ppm	LBF, ICP-MS (0.05-1000)	0.64	0.65	8.38	0.7	21.7	1.24	7.65	2.91	1.28	2.01	0.87	0.46	0.89	8.83	13.1	15.3	9.63	10.3
Ti	ppm	LBF, ICP-MS (0.5-1000)	bd	0.5	bd	1.3	2.4	1	6.6	4.1	2.2	2.4	0.8	bd	0.7	1.9	1.7	2.7	1.5	1.4
Trm	ppm	LBF, ICP-MS (0.01-1000)	0.25	0.25	0.42	0.29	0.83	0.32	0.13	0.08	0.05	0.03	0.03	bd	0.03	0.52	0.34	0.52	0.77	0.75
U	ppm	LBF, ICP-MS (0.05-1000)	0.26	0.23	3.55	0.27	11.95	2.58	18.9	262	277	205	225	0.57	5.25	33.6	18.2	3.57	3.02	2.94
V	ppm	LBF, ICP-MS (5-10000)	324	372	269	329	126	271	123	87	78	102	101	5	80	188	147	97	16	15
W	ppm	LBF, ICP-MS (1-10000)	bd	bd	1	bd	8	28	66	104	78	128	190	bd	27	7	4	7	11	5
Y	ppm	LBF, ICP-MS (0.5-10000)	15.5	18.1	35.8	18.8	52.8	20.9	7.7	11.4	8.6	7.3	8.3	bd	6.4	41.3	22.2	34.1	43.8	40.2
Yb	ppm	LBF, ICP-MS (0.03-1000)	1.85	1.56	2.42	1.														

Table 2. LA-ICP-MS analysis of sulfides from Stage 3 and 4 mineralisation at Monakoff.

			¹⁹⁷ Au	¹⁰⁹ Ag	⁶⁵ Cu	⁶¹ Ni	⁶⁶ Zn	²⁰⁶ Pb	⁵⁹ Co	⁷⁵ As	⁸² Se	¹²¹ Sb	¹²⁵ Te	²⁰⁹ Bi
			ppm	ppm	%	%	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm
Pyrite groundmass	n=3	Mean	0.038	<1	0.03	0.08	444	0.01	2115	779	64.50	5.49	3.90	17
Stage 3A		Max	0.044	<1	0.03	0.20	1290	0.02	3775	1132	64.50	5.49	7.63	20
		Min	0.031	<1	0.03	0.02	15	0.01	456	151	64.50	5.49	1.07	15
Groundmass chalcopyrite	n=5	Mean	0.259	80.78	21.64	0.02	14595.72	0.34	27.60	65.73	99.88	3.33	3.72	143
Stage 3A		Max	1.133	160.30	23.28	0.02	65310.00	1.04	72.92	159.20	120.00	9.49	8.11	454
		Min	0.014	48.13	20.21	0.02	599.10	0.01	1.62	10.15	79.76	0.85	1.37	3
Coarse chalcopyrite	n=10	Mean	0.064	73.94	24.53	0.01	2637.46	0.17	5.28	7.35	51.82	2.61	14.70	45
Stage 3B		Max	0.191	173.70	27.64	0.07	5751.00	1.22	20.03	20.64	105.20	9.70	81.23	177
		Min	0.008	43.71	20.94	0.01	988.60	0.00	0.07	0.59	16.21	0.70	-2.53	2
Galena	n=4	Mean	0.088	4484.75	0.02	0.01	435.64	80.19	0.26	5.68	1818.25	9.01	347.13	12860
Stage 3A		Max	0.102	5046.00	0.08	0.02	1694.00	86.63	0.38	16.65	1876.00	11.03	387.10	13030
		Min	0.073	3967.00	-0.07	0.00	0.86	73.65	0.14	0.07	1759.00	7.54	301.50	12590
Alloclasite	n=2	Mean	0.695	3.46	0.04	0.99	79	0.05	323700	509150	92.77	37.44	7.40	62
Stage 4		Max	1.096	3.46	0.04	1.10	86	0.06	361700	549800	108.20	45.59	8.58	89
		Min	0.293	3.46	0.03	0.87	71	0.05	285700	468500	77.34	29.29	6.22	36
Aggregated pyrite	n=5	Mean	0.534	129.09	0.04	0.04	196	1.41	11515	10694	110.00	11.37	15.79	441
Stage 4		Max	1.193	202.10	0.05	0.06	655	4.64	23750	20490	157.00	22.73	24.63	985
		Min	0.084	9.56	0.03	0.03	28	0.02	4305	5014	63.14	3.48	7.90	28
Coarse Pyrite	n=10	Mean	1.223	242.80	0.03	0.16	454	2.37	8081	7862	194.14	19.97	19.45	741
Stage 4		Max	3.080	872.80	0.05	1.15	2673	12.04	15220	17040	595.60	64.44	41.97	3154
		Min	0.048	6.32	0.03	0.03	20	0.00	1800	84	60.02	1.68	2.32	2

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Table 3. REE contents of fluorite from Monakoff and E1 as determined by LA-IPC-MS

Analysis	Deposit	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Stage	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
50A L3	Monakoff 3A	10.776	13.18	0.7296	2.87628	0.67379	3.6632	1.292	0.24	1.983	0.496	1.468	0.203	1.343	0.163
50A L5	Monakoff 3A	268.38	237.7	9.7584	17.8308	1.66764	6.9502	6.558	0.385	2.453	0.587	1.652	0.218	1.208	0.177
12A L12	Monakoff 3A	13.932	17.13	1.0146	3.48428	0.63947	4.4764	3.405	0.201	1.543	0.347	1.017	0.129	0.838	0.09
12A L13	Monakoff 3A	27.048	50.61	1.91672	6.12756	1.30442	8.3828	5.306	0.303	2.218	0.47	1.326	0.221	1.35	0.129
12A L2	Monakoff 3A	8.8	11.66	1.73	7.34	1.29	13.34	2.35	0.61	4.72	1.27	2.99	0.35	1.65	0.27
12A L3 80	Monakoff 3A	8.4	10.71	1.79	6.67	0.72	12.59	7.44	0.56	3.53	0.84	1.89	0.29	1.48	0.14
12A L4	Monakoff 3A	23.8	29.72	4.41	14.87	2.73	21.70	9.90	0.62	6.07	0.85	2.63	0.62	2.06	0.28
12A L5	Monakoff 3A	3499.0	1586.00	76.17	119.90	5.25	17.75	9.75	0.30	2.28	0.55	1.30	0.18	1.41	0.11
12B L1 core	Monakoff 3B	1.5216	2.133	0.24396	0.92916	0.33917	2.21084	1.013	0.196	1.619	0.375	1.097	0.141	0.556	0.04
12B L2 core	Monakoff 3B	27.72	25.67	0.9766	3.27832	0.73957	3.98164	6.018	0.321	2.351	0.583	1.57	0.205	1.009	0.075
12B L2 rim	Monakoff 3B	2.8038	2.993	0.247	1.44368	0.41496	2.34004	1.1933	0.197	1.533	0.365	1.009	0.118	0.579	0.059
12B L3 rim	Monakoff 3B	9.846	10.12	0.78584	2.41116	0.60372	3.92464	2.545	0.279	2.616	0.547	1.299	0.164	0.743	0.071
12B L4	Monakoff 3B	4.4232	10.28	0.399	1.12144	0.39351	2.67292	5.544	0.191	1.804	0.396	1.219	0.122	0.612	0.053
12B L5 core	Monakoff 3B	1.7694	2.794	0.23104	1.73932	0.36491	2.59084	1.063	0.203	1.768	0.395	1.166	0.125	0.554	0.055
12B L6 rim	Monakoff 3B	2.0598	3.446	0.19532	1.0082	0.42783	2.43352	1.794	0.198	1.91	0.367	1.075	0.136	0.607	0.056
12B L7core	Monakoff 3B	3.3558	9.272	1.03132	3.33988	1.03844	5.76384	2.835	0.316	2.592	0.593	1.699	0.205	0.929	0.115
12B L8 rim	Monakoff 3B	19.476	30.99	3.44888	13.02	2.52707	13.4748	4.276	0.481	4.215	0.891	2.521	0.212	1.514	0.232
12B L9 core	Monakoff 3B	10.752	16.26	1.20308	3.43488	0.85397	5.4036	1.366	0.195	1.262	0.302	0.977	0.157	0.797	0.109
49B L11	Monakoff 3B	5.1756	6.405	0.45524	1.4946	0.98267	2.7018	2.594	0.406	3.24	1.032	2.887	0.442	2.502	0.28
49B L12	Monakoff 3B	3.1878	11.07	0.27284	1.18604	0.72527	2.13256	1.012	0.251	2.761	0.701	2.164	0.257	1.689	0.229
49B L2	Monakoff 3B	2.1594	5.679	0.665	2.77368	1.22434	3.56668	2.664	0.488	4.436	1.242	3.735	0.574	3.876	0.563
49B L5	Monakoff 3B	15.066	9.292	0.5472	2.836	1.49747	4.06068	3.042	0.377	5.233	1.267	3.688	0.554	3.799	0.653
50B L12	Monakoff 3B	1.9206	4.722	0.77292	2.38608	0.67808	3.9216	1.33	0.232	2.366	0.672	2.016	0.283	1.672	0.206
50B L11	Monakoff 3B	1.7994	5.391	0.67792	3.01156	0.9984	4.29476	1.688	0.313	2.636	0.675	2.116	0.316	1.885	0.266
50B L2 core	Monakoff 3B	4.4232	5.599	0.59432	2.65588	1.03272	4.46424	1.531	0.326	2.474	0.622	1.962	0.254	1.58	0.233

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50B L3 rim	Monakoff 3B	3.5256	11.07	0.72732	2.53732	0.81965	3.4656	1.352	0.299	2.158	0.655	1.67	0.209	1.549	0.19
50B L3 core	Monakoff 3B	1.6782	4.9	0.6308	2.78128	0.93548	4.44904	1.663	0.312	2.601	0.62	2.034	0.281	1.662	0.239
197 L1	E1 Stage 5	0.2136	0.305	0.02964	0.15244	0.06175	0.02508	0.071	0.026	0.121	0.033	0.11	0.0105	0.049	0.003
197 L2	E1 Stage 5	4.1172	3.86	0.36784	0.62896	0.3263	0.5586	1.956	0.173	1.315	0.37	1.004	0.063	0.4	0.029
197 L3 core	E1 Stage 5	5.9148	6.083	0.35948	0.81592	0.30096	0.33896	0.367	0.072	0.516	0.153	0.264	0.017	0.053	0.013
197 L4 rim	E1 Stage 5	18.36	34.25	1.58384	3.6112	1.0842	0.82688	1.162	0.166	1.111	0.263	0.972	0.091	0.511	0.041
197 L5	E1 Stage 5	0.5358	0.972	0.057	0.44428	0.1105	0.04712	0.174	0.014	0.123	0.039	0.093	0.011	0.026	0.005
197 L6 rim	E1 Stage 5	3.1842	4.238	0.22496	0.85468	0.5551	0.4978	1.202	0.205	1.88	0.48	0.953	0.131	0.587	0.032
197 L7 core	E1 Stage 5	0.1134	0.281	0.04332	0.21248	0.19045	0.15352	0.419	0.085	0.915	0.244	0.631	0.057	0.217	0.017
197 L8 rim	E1 Stage 5	0.2478	0.357	0.0304	0.15244	0.06604	0.03648	0.055	0.01	0.078	0.01	0.035	0.003	0.013	0.001
197 L9	E1 Stage 5	0.1698	0.246	0.02888	0.157	0.07891	0.05548	0.09	0.022	0.112	0.047	0.086	0.009	0.067	0.007
163 L1	E1 Stage 5	5.0862	5.856	0.23332	0.898	0.16042	0.13908	0.453	0.078	0.696	0.244	0.787	0.1	0.607	0.07
163 L2	E1 Stage 5	2.5092	3.839	0.32908	0.727	0.20761	0.22116	0.618	0.084	0.754	0.234	0.739	0.072	0.421	0.036
163 L5	E1 Stage 5	0.7458	1.588	0.10488	0.35612	0.18473	0.54416	1.081	0.281	1.762	0.422	1.199	0.12	0.431	0.053
163 L7	E1 Stage 5	0.9942	1.526	0.095	0.48456	0.23764	0.14896	0.524	0.078	0.726	0.227	0.855	0.089	0.499	0.046

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Figure captions:

Fig. 1. A: Geological map of the eastern succession of the Mount Isa Inlier showing the location of major IOCG deposits and mines, and granites of the Williams-Naraku batholith (modified after Mark et al. 2006a). B: magnetic map of the area north of Cloncurry, including the Monakoff, E1, Ernest Henry and Lorena deposits. Note that Ernest Henry, Monakoff and E1 are all associated with strong magnetic highs.

Fig. 2. Geological map of the Monakoff deposit within the Pumpkin Gulley Syncline, showing the proximity to outcropping Malakoff granite. Inset shows the schematic geology of the Monakoff deposit, with the main ore zone located within sheared metasedimentary and metavolcanic rocks between competent hangingwall and footwall lithologies. Grab sample locations and the drill hole sampled in this study are shown.

Fig. 3. Field relationships, generalised geological section and rock types of the Monakoff deposit. A: typical section facing west across the orebody showing the nature of the hangingwall and steeply dipping ore zone; B: geological log of drillhole EMKDDH011, representative of the deposit as a whole. Samples collected for this study are shown at the corresponding depths with an asterisk; C: Hangingwall Toole Creek Volcanic rocks made up largely of green amphibole (amp), with phenocrysts of plagioclase (pl) and prophyroblastic garnet (gt); D: Low grade hangingwall mineralisation comprising lamination-replacement of metasediments; E: typical fine grained fluorite (fl), barite (bar), calcite (cc), sulfide (sul), magnetite (mt) ore zone with coarse pods of fluorite; F: large pod-like fluorite showing kinematic indicator consistent with the overall sense of shear indicated in Figure 2; G: footwall pyrrhotite-bearing sheared metasediment, made up of quartz (qtz), biotite (bi) and porphyroblastic garnets. Note the wispy ribbons of pyrrhotite (po) that follow the sheared fabric; H: Footwall banded ironstone containing bands of replacement magnetite, porphyroblastic garnets and bands of carbonate (carb) and quartz with minor fluorite and barite alteration; I: Footwall unit of garnet skarn derived from Mount Norna Quartzite Formation volcanics. The rock is totally replaced by quartz, biotite and metasomatic spessartine garnets.

Fig. 4. Geochemical variations through the Monakoff ore zone, hangingwall and footwall. A: Au and Ag; B: Cu, Co and Mo; C: Pb, Zn and Cd; D: S, Se and Te; E: U and Th; F: selected REE; G: F, BaO and Sr; and H: Zr and Cr.

Fig. 5. Monakoff ore mineralogy: A: core sample from (EMKDDH011, 49.6 m) showing typical fine-grained Stage 3A groundmass made up primarily of fluorite (fl), barite (bar), manganoan calcite (cc), sulfides (sul) and magnetite (mt), with coarser pods of Stage 3B chalcopryrite (cpy), sphalerite (sph), fluorite, barite and calcite; B: Reflected and transmitted light photograph showing typical groundmass Stage 3A assemblage of fluorite, barite, calcite, chalcopryrite, magnetite and pyrite with a roughly defined fabric (left), Stage 3B coarse chalcopryrite, sphalerite, barite, calcite and fluorite (centre), overprinted by Stage 4 pyrite (right); C: Reflected and transmitted light photograph showing Stage 3B chalcopryrite, sphalerite and galena (gn) showing textures consistent with co-precipitation with fluorite, calcite and barite; D: SEM backscattered image of typical association of fine-grained inclusions of U-Pb-oxide within barite in a Stage 3A assemblage; E: SEM backscattered image of typical association of REE minerals with Stage 3A assemblages, with bastnäsité-La (bst) together with fluorite, barite and sulfides; F: SEM backscattered image of inclusions of Ag-(Au)-Pb-Bi-sulfosalts in fluorite in a Stage 3A assemblage; G: Reflected and transmitted

light photograph of Stage 4 pyrite, as euhedral grains and aggregated masses overprinting both Stage 3A groundmass (top left) and Stage 3B coarse pods of fluorite, barite and calcite. Note the lack of cross cutting relationship between Stage 3A and 3B textures; H: Reflected and transmitted light photograph of Stage 4 allosilite (al) and aggregates of pyrite, overprinting Stage 3A and 3B assemblages.

Fig. 6. Summary of paragenesis for A: Monakoff (this study); and B: E1 (modified from Case et al., 2013).

Fig. 7. E1 ore mineralogy of Stage 5 F-Ba-rich veins. A: core sample showing typical cross cutting nature of purple fluorite (fl), white manganoan calcite (cc) and red barite (bar) veins. Chalcopyrite (cpy) is the main sulfide. The veins cross cut the main stage ore assemblage of fine grained pyrite (py), chalcopyrite, and magnetite (mt); B: chalcopyrite, with minor pyrite and magnetite in a calcite-fluorite vein, with an inclusion of bastnäsite-La (bast) in calcite; C: typical association of U-Pb-oxide minerals as inclusions in pyrite. Also shown is accessory apatite (ap) together with calcite and barite; D: An inclusion of Ag-Pb-Bi sulfosalt within zoned pyrite within a calcite-fluorite-barite vein.

Fig. 8. Representative laser ablation TRA spectra (line analyses) of sulfides from Monakoff. A: Stage 3A pyrite from the groundmass assemblage, showing no significant detectable Au and slight variation across the grain with respect to Co and As. The two peaks in Ag at the start and end of the laser line are traces picked up from adjacent chalcopyrite; B: Stage 3A chalcopyrite showing Ag in solid solution, but also as distinct peaks with Bi and Pb, representing inclusions of Ag-Pb-Bi-sulfosalts; C: Stage 3A galena showing Ag, Se, Bi, Sb and Te in homogenous solid solution across the grain. Minor Au is also present in solid solution; D: Stage 4 euhedral pyrite grain showing Au in solid solution, but a distinct zonation of Co-As rich rims, and an Sb-Se-Au-Ag-rich core; E: Stage 4 aggregated pyrite showing strong Co-As zonation, with minor inverse Se-Sb correlation. Gold is present in solid solution relatively homogeneously; F: Stage 4 allosilite showing Au in solid solution and correlating well with the Fe, Bi, Sb and Ag content across the grain. The peak in Ag at the end of the line is related to the incorporation of some adjacent chalcopyrite.

Fig. 9. Morphology, composition and behaviour of Group 2 and 3 fluid inclusions in fluorite. A: Group 2 solid-liquid-vapour inclusion at room temperature; B: Group 2 two solid-liquid vapour inclusion at room temperature; C: behaviour of solid phases during heating of a Group 2 solid-liquid-vapour inclusion. Note that the vapour bubble (*) is CO₂-bearing as seen by two bubbles below room temperature; D: typical morphology of Group 3 inclusions from Monakoff; E: trail of Group 3 inclusions in Stage 3B fluorite from Monakoff.

Fig. 10. Histogram of homogenisation temperature data for Group 2, 3 and 4 fluid inclusions in fluorite from Monakoff (M) and E1.

Fig. 11. Laser ablation TRA spectra of line analyses through fluorite containing fluid inclusions. Each ablation is shown as a pair of plots along the same axes to illustrate a range of elements. A: Ablation of fluorite from Monakoff containing Group 2 (G2) fluid inclusions. The ablation of the inclusions is marked by concurrent sharp peaks in U, REE, Cu, Ba, Pb, Zn, Mg, Mn, Na, K, Fe and Bi, but notably not Si, S or Au (Au not shown as no counts were detected). Note Sr in this Monakoff analysis mirroring Ca, and thus being predominantly in fluorite, rather than the inclusions; B: Ablation of fluorite from E1 containing two distinct Group 2 inclusions, with almost identical element signatures to those at Monakoff in A. Note

these also contain Ag, and Sr is predominantly detected in the inclusions, rather than the host fluorite; C: Ablation of fluorite from Monakoff containing Group 3 (G3) and Group 4 (G4) inclusions. The Group 3 inclusions show distinct concurrent peaks in Na, Ba, Mg, Br and K, with very minor peaks in Cu and Zn (compared with G2 inclusions), and no S, Fe, U or Si. Note La is present within the fluorite host in greater abundance than in the inclusions. An example of the trace of the laser path in C is shown before ablation. Focus is in the upper ~10µm to illustrate what was to be ablated by the laser trench.

Fig. 12. Chondrite-normalised REE profiles (ranges and mean values) for fluorite from A. Monakoff Stage 3A groundmass, B. Monakoff Stage 3B pods; C. E1; and D: example of core/rim effects from Monakoff (sample 12B) and E1 (sample 197).

Fig. 13. The $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox equilibrium as a function of temperature and $\log f\text{O}_2$ in a mildly acidic environment (pH 3) and pressures of 500-1000 bar (Bau, 1991). The dashed line represents the highest fluid inclusion homogenisation temperature recorded, of at least 450°C, correlating with a minimum $\log f\text{O}_2$ of ~0 to 5.

Fig. 14. Comparison of primitive-mantle normalised REE patterns from Monakoff and granites from the Williams-Naraku batholith. Data shown are mean values from Table 1 for the Monakoff ore zone, the Toole Creek Volcanics and metasediments, and the Mount Norna Quartzite rocks from this study. Data for the Cloncurry Supersuite and Eureka Supersuite granites are from Pollard et al. (1998). Normalising values from Sun and McDonough (1989).

Fig. 15. Composite model for the emplacement of Monakoff. See text for explanation.

Figure 1
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Figure 2
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Legend to map above

- Residual soil and colluvium; sand, gravel and clay
- Dissected high level alluvial sheets and fans; sand, gravel and clay
- Meta-dolerite of various ages
- Williams and Naraku Granite Batholiths; Granite, granodiorite and albitised granite
- Guided Rose Chaotic Breccia
- Mary Kathleen Group: Corrella Beds**
 - Well-bedded calcareous meta-sediments, limestone, marble
 - Predominantly brecciated equivalent

Soldiers Cap Group:

Toole Creek Volcanics:

- Amphibolite, metamorphosed chert and siltstone, phyllite, slate
- Amphibolite, meta-basalt, meta-dolerite
- Banded-Iron Formation

Mount Norma Quartzite:

- Fine grained quartzite, metamorphosed greywacke, siltstone, chert and limestone
- Amphibolite, meta-basalt, meta-dolerite
- Banded-Iron Formation

Syncline

Anticline

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**Mineralogical and fluid characteristics of the fluorite-rich Monakoff and
E1 Cu-Au deposits, Cloncurry region, Queensland, Australia:
implications for regional F-Ba-rich IOCG mineralisation**

Megan R. Williams, David A. Holwell, Richard M. Lilly, George N.D. Case and Iain
McDonald

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RESPONSE TO REVIEW (1 review) of the paper:

Mineralogical and fluid characteristics of the fluorite-rich Monakoff and E1 Cu-Au deposits, Cloncurry region, Queensland, Australia: implications for regional F-Ba-rich IOCG mineralisation

By Megan Williams et al

Firstly, we appreciate this very thorough and highly constructive review, and take on board all of the comments raised and have found it most useful in improving the quality and focus of the manuscript. We are particularly pleased that the amount and presentation of the data is recognised to be good, and that the major issue is style, rather than anything fundamentally wrong with the science.

Our responses to the original comments are presented in order below in bold italics.

Note to Editor: We note that on the Word file, the initials RGS are shown, which we take to be Roger Skirrow. As such, we have acknowledged Roger in the revised manuscript, however, if the review was supposed to be anonymous; then by all means, change that to ‘an anonymous reviewer’.

General comments

The Cloncurry district in northwest Queensland hosts a wide range of Cu-Au deposits attributed to the IOCG family of deposits, and the district has received considerable research attention over the past two decades. The Monakoff deposit and recently discovered E1 deposit are two small IOCG resources with distinctive, high F-Ba, mineralogy associated with Cu-Au mineralisation. Previous research work on the Monakoff deposit was carried out by Davidson et al. (2002), whereas no previous work has been reported on the E1 deposit. The contribution by Williams et al. builds on the work by Davidson et al. (2002) by presenting new fluid inclusion, whole rock geochemical and mineral chemical data within a new paragenetic framework. Comparisons are presented with other IOCG deposits in the district and a genetic model is presented for the formation of the Monakoff deposit.

The high-F-Ba geochemistry of these IOCG deposits is an intriguing feature that is also present in several other IOCG deposits, including the nearby Ernest Henry deposit and the Olympic Dam deposit in South Australia, although in both cases (and unlike the Monakoff and E1 deposits) much of the fluorite and barite are relatively late with respect to the main phases of Cu-Au (U) mineralisation. The subject of the manuscript therefore should be of interest to readers of Ore Geology Reviews as the work has potential to shed light on aspects of the geochemistry and origins of a distinctive sub-group of IOCG deposits.

In general the quality and quantity of the new data are good, and are presented adequately. However, fluid inclusion microthermometry was carried out on a relatively small number of

inclusions, at least as recorded in Figure 7 (27 inclusions in two deposits). The microthermometry observational data are not presented in detail, and should be presented in a table (appendix?). The paragenetic relationships of the fluid inclusion populations within fluorite also are not adequately documented, and I am unconvinced as to whether certain specified populations are indeed “primary” or “pseudosecondary” in origin as stated. This is important because much emphasis is placed on the laser ICPMS analyses of the fluid inclusions in latter, interpretative, parts of the manuscript.

One reason for the apparently small number of analyses was the depiction in Figure 7 of homogenisation temperature only, whereas many of the inclusions decrepitated and thus Th was not recorded. As such, many more inclusions were actually analysed (note we stated in the Methods section that 52 were analysed). As suggested below in point 8, we have added in a table of microthermometry data (for an appendix) which shows the amount of inclusions analysed, and also those that decrepitated before a Th was recorded. So we hope that the inclusion of a table of microthermometry data goes to satisfactorily addressing this concern. The petrology aspect is addressed below.

The major problems with the manuscript are the length and quality of the English. The manuscript is written in a verbose and loose, colloquial, style which is not appropriate for this international journal. As a reviewer, I was disappointed and irritated at times by the lack of attention to detail in the writing, making the reviewer’s job more difficult than it need be. The manuscript reads in parts as a first draft, including typos, repetition, mis-use of capitals, and inconsistent use of hyphens, commas etc. Expressions such as “in terms of . . .” at the start of sentences are symptomatic of poorly constructed sentences. Figures were not numbered, and the model figure is out of order, in the pdf I worked on. I have tried to make corrects and suggest alternative expressions as annotations on the manuscript, but by the fluid inclusion section I was less inclined to make all the necessary changes. This distracts from the scientific content and colours the overall impression of the work, unfortunately.

We concede the Figures were not numbered on upload and that was a mistake on our part. Plus, as a multi-authored paper some sections were written by different authors perhaps leading to inconsistencies in style. So, we have, in the revised manuscript, paid particular attention to the writing style and made sure it is consistent throughout and are confident that the revised manuscript reads much better, and is more concise.

We have also made typographic and phrasing changes as suggested by the reviewer on the annotated script where appropriate.

I suggest the manuscript is shortened by at least 30% in total, particularly the Discussion which amounts to almost 16 pages. The writing must be much more succinct with more attention to detail. It may be possible to move some of the information into tables, and figure captions.

The manuscript is long, but as there are multiple datasets to be presented (field relations, petrology, mineralogy, geochemistry, fluid inclusion microthermometry, fluid inclusions laser ablation and sulfide laser ablation... on two deposits!), then we do feel a longer than average paper is justified and is one of the reasons for submitting to Ore Geology Reviews. As such the results sections have not been shortened significantly. However, we agree that the discussion can

be shortened and focussed, so we have done this, reducing the number of words in the discussion from 9500 to 7700, which amounts to a shortening of 20% in the discussion, which we feel is appropriate, without undermining the discussion of what are a wide range of points.

Numbered points

1. Must state the type of mill used in pulverising the samples – chrome steel, tungsten carbide?
This has now been added to the second paragraph of the methods section. The crushing and milling were performed at the University of Leicester and did not use a tungsten carbide mill, and thus the high W bulk rock values are real.
2. Basalts and dolerites are compositionally equivalent
This has been changed to meta-basalts
3. 'Skarn' is a mineralogical rather than compositional term
This has been removed to avoid confusion
4. What is evidence that these minerals were "sheared" as opposed to having grown within a pre-existing shear zone?
We have added in a sentence to this section (4.3) that now explains this more clearly. The fabric shown in the groundmass mineralogy show the same orientation as the shear fabrics shown by the fluorite pods in Fig 3D and Fig 5A. We also state co-precipitation of all ore minerals and interpret the fabric (and lack of deformation) to indicate synchronous deformation at the time of mineralisation (as also concluded by Davidson et al., 2002 and Austin et al., 2013). We also mention in the discussion that the pods are probably infilled dilational zones that open up during mineralisation, given their lack of magnetite (which is pre-main stage)
5. Origin and paragenesis of fluid inclusions needs more documentation, as noted above.
We have added a bit more description which explains the classification as primary, etc, and reference to Figure 9 (perhaps the reviewer missed this – it was mislabelled as Fig8?). Also complimenting this is the addition of a table of microthermometry as Supplementary Data.
6. Only 18 measurements from Monakoff and 9 from E1 (?) Need to present the actual observational data of microthermometry (temp and freezing point measurements), not just a summary histogram of homogenisation temperatures.
As mentioned above in response to the general comment, we analysed 60 fluid inclusions by microthermometry, however, as is the case with fluorite, many of them decrepitate on heating and therefore the homogenisation temperature is not always possible to record. We feel that the data depicted in the histogram is good enough as a pilot dataset, with some clear temperature differences. As mentioned above, the full data table of microthermometry is now included as a table for an appendix (we do not feel this should

be part of the main manuscript though, as the histogram gives the main data from this study)

7. Citation of McPhie et al (2013) is not appropriate for Olympic Dam fluids as they did not study nor report details of such. Haynes et al (1995) is a better reference, and also Oreskes and Einaudi (1992). Also, the origins of the fluids at Olympic Dam are controversial and there is certainly no consensus for fluids of “granitic derivation” in the formation of the Olympic Dam deposit.

We have now removed this reference from such contexts, and have added in some other references for Olympic Dam as suggested. This is the case for a number of occurrences of this throughout the manuscript.

8. Actually very few data presented in the MS to support or refute this claim, just 3 traverses of laser across 4 x Group 2, 2 x Group 3 and 1 x Group 4 inclusions. This is a useful reconnaissance dataset but inconclusive at this stage.

We acknowledge the reconnaissance nature of the fluid inclusion datasets, and have now emphasised this point in several places within the discussion. As such, our interpretations have become a little more cautious, in not wanting to place too much emphasis over limited datasets. However, this is data that is new, and the first of its kind, so gives valuable information and we feel we have now discussed its significance, with the required caveats, fairly.

We have also added in to the main results section the number of inclusions we hit, thus stating that the traverses in Figure 11 are representative of what we found. Given the qualitative nature of the data, we cannot present tables of concentrations, so the representative TRA spectra in Fig 11 we feel are suitable for the purpose.

9. “Fluid complexes” suggests a lack of understanding of metals and ligands in hydrothermal fluids. Need to specify which complexes could have transported U and REE: fluoro, chloro, hydroxyl, etc? While the proposed process of REE deposition seems reasonable, I am not convinced of the proposed model of barite deposition. If Ba is transported in an oxidised brine, as suggested, then it is true that the same brine could not have carried much S either as sulphate or sulphide. Mixing of the proposed S-bearing fluid (2) could have resulted in barite deposition via oxidation of reduced sulphur in fluid (2) to sulphate. Are S-isotope data available for the barite to test this mechanism? I believe Davidson did some S-isotopes studies, in AMIRA project, but some data may be published and available. Nevertheless, Ba transport in an oxidised fluid is unconventional and needs further justification as to why this fluid was oxidised and not reduced. As you note on page 22, Schwinn and Markl (2005) state that the positive Eu anomaly in fluorite is a feature restricted to <200°C, and yet your temperature estimates are well above this. That the signature can be preserved at higher temperature, even at very oxidised conditions as you propose, is unsubstantiated from the information presented in the MS. Hence the evidence for suggesting that the F- and Ba-rich fluid was oxidised is not strong.

The “fluid complexes” was a simple typo that should have, and now does, read “fluoride complexes”!

The major piece of evidence we show here to support this is the presence of lots of Ba in the fluid inclusions along with U, REE and base metals, but not S. As such, although we do agree that this appears at first less likely, this clear evidence we show is most consistent with the Ba being in the same fluid as the U and REE.

Davidson has done some S isotope work, though this has not been published yet. However, there is an abstract which we cite (Davidson and Davis 2002) that states that the S isotope systematics of sulfates and sulfides are similar, and that they support a model of decompression of a CO₂ rich magmatic fluid (see point 11). We now incorporate this into this part of the discussion.

As for the oxidised nature, we do feel that our explanation via the experimental work by Bau (Fig. 13) offers an explanation for the extremely characteristic positive Eu anomaly in ALL fluorites that we analysed. However, we have now offered a slightly more general interpretation saying that conditions of precipitation were oxidised (and that it is likely, though not certain), that Fluid (1) was oxidised.

10. Argument for low Th contents does not seem to work, because you propose the fluids were F-rich. Even if they were also CO₂-bearing, the F-rich composition should have permitted both U and Th transport, according to Keppler and Wyllie 1991. I think you have misinterpreted the results of the experimental work of K and W 1991. On the other hand, K & W 1991 say that U can be effectively chloro complexed whereas Th is not, and a key point of that paper is the possible partitioning of U from Th in some hydrothermal systems. It is possible this is behind the low Th at Monakoff, among other potential reasons. You also need to explain the low Yb and Zr in the same zones as low Th. Is this due to dilution of immobile Th, Yb and Zr in the original hostrock by hydrothermal minerals, or is it due to removal of these elements during hydrothermal leaching? A more in-depth assessment of your whole rock geochemical data may provide some further answers, applying the 'isocon' methods of Grant 1986 (Econ Geol).

Our arguments are based on new data by McGloin et al (2013), which is an extended abstract from the SGA meeting from last year, which the reviewer may not have had access to. In this work, it clearly states that CO₂ content can inhibit the transport of Th over U by fluoride rich fluids, so we have kept this argument. In terms of the K and W 1991 work, the addition of CO₂ to the fluoride liquid shows that U can complex with carbonate in such a fluid, but Th does not. Thus, the presence of CO₂ in a fluoride bearing fluid allows for U transport with carbonate, which is the argument put forward also by McGloin. We have rephrased the end of this paragraph to hopefully make the argument clearer.

Also, we have decided not to present an isocon analysis of the geochemistry – this is on the one hand due to the paper focussing on the mineralogy and fluid aspects, with support from the geochemistry – thus adding more on the geochemistry turns it into a much larger paper. But more importantly, this method requires 'least altered' samples to compare with. We do not have any relatively 'unaltered' rocks, and would need more field work to try and do this away from the large geochemical halo of the deposit. In fact, one could argue that there aren't any unaltered rocks in that part of the Mount Isa Inlier. So based on these two reasons, we argue this is not justified for this particular manuscript.

However, we have added in a small section in the first part of the discussion on the characterisation of the ores that covers the depletion in these elements.

11. The compositions of these fluids and their oxidation states is a key part of the MS, but I am unconvinced. For example, if fluid (1) contained CO₂, and this CO₂ exsolved, then the residual brine should contain a small amount of CO₂ and hence the vapour bubble in the fluid inclusions should be CO₂-bearing. No data are presented to verify this prediction. The issue of which fluid carried Ba was discussed above, as was the problem of oxidation state based on Eu anomaly of fluorite. In the absence of solid counter-evidence, I don't think there is strong justification for a mixing model different to that already proposed by Davidson et al (2002).

We feel this is more personal opinion than any significant error or flaw in our interpretation. As such, we are happy with our interpretation, but understand that the results of this work in places are equivocal, due in the most part to this being the first and only fluid study of the deposit. We have toned down the discussion in places to be more accepting of this fact and we feel our arguments fit with our data and that we define some important constraints, but agree that there is still considerable more work to be done. However, based on this comment, we have returned to our petrology and found some fluid inclusions to have some CO₂ in the vapour bubble – e.g. Fig. 8C.

As we state in section 8.3.1, fluorite with strong positive Eu anomalies, correlated with high fluid inclusion temperatures (~390-430°C), have similarly been explained via high fO₂ values from fluorite deposits in Central Turkey, (Sasmaz et al., 2005).

We have added reference to the Davidson and Davis S isotope work that support CO₂ derived from the decompression of magmatic fluids.

Also, we do not deviate from the Davidson mixing model, and instead are refining it with our new data – which includes the key point of Ba in the same fluid as the U and REE and Cu, and S not in this fluid. So we feel we have now argued our point, but remain open to other possibilities.

12. The similarity in the biotite Ar-Ar age to the zircon U-Pb age of the granites could be simply due to re-setting of the biotite age during granite magmatism, so the biotite age is simply a minimum age. The evidence for a direct magmatic-hydrothermal origin of the fluids at the Monakoff deposit is circumstantial, based on what is presented in the MS. However, there is certainly good evidence from other IOCG deposits in the Cloncurry district for at least a magmatic-hydrothermal input in some (but not all) deposits. However, it is the presence of a second, non-magmatic, fluid that seems to be also crucial in this and many other IOCG districts.

We have taken this comment into account and now include this in the discussion. However, we do note that S isotope constraints also point towards a magmatic source, so we feel the evidence (with all the F-U-REE geochemistry and hypersaline brines) is more than circumstantial.

13. Source of Ba – destruction of K-feldspar could be a regional or local source of Ba at Monakoff and E1, for example through hydrothermal leaching and replacement of K-

feldspar by albite or biotite. Both processes have been described in the district, the first as part of the widely observed (although not at Monakoff) regional Na-Ca alteration.

A new comment has been added to cover this possibility for the source of Ba