

Independent ages of magmatic and hydrothermal activity in alkaline igneous rocks: The Motzfeldt Centre, Gardar Province, South Greenland

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Received: 31 May 2011 / Accepted: 16 November 2011 / Published online: 30 November 2011
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Abstract The Motzfeldt Centre is one of four major alkaline centres belonging to the Igaliko complex, part of the Mid-Proterozoic Gardar province of South Greenland. Motzfeldt comprises syenites and nepheline syenites displaying complex magmatic and subsolidus histories. Ta, Nb and REE-rich zones are associated with a pervasive hydrothermal alteration process in the North and East of the complex, part of a subdivision of the Centre called the Motzfeldt Sø Formation (MSF). The zircons from the MSF show textures that are both magmatic and altered, whereas the textures of pyrochlore have a predominantly subsolidus chemistry. We compare and contrast the radiogenic isotope geochemistry of the zircon and pyrochlore to obtain independent age estimates of the magmatic and hydrothermal episodes. Selected analyses of magmatic zircons are

concordant with an age of $1,273 \pm 6$ Ma. Altered zircons are normally discordant with one intercept at $1,261 \pm 28$ Ma and the other at 349 ± 49 Ma. This younger age would appear on face value to date the hydrothermal event at Motzfeldt to ~ 900 Ma after the magmatism. However, the Pb–Pb isotope systematics from altered pyrochlore define an isochron age of $1,267 \pm 6$ Ma for isotopic closure of the pyrochlore following alteration during the subsolidus. There is no known magmatic event in Southern Greenland at ~ 350 Ma and discordant points have high common lead. We therefore infer that the younger intercept age is spurious. The overlap between the magmatic U–Pb zircon and the Pb–Pb pyrochlore age suggests that alteration of the Motzfeldt centre occurred shortly after magmatism.

Keywords Alkaline · Geochronology · Zircon · Pyrochlore · Lead isotopes · Hydrothermal alteration · Gardar Province · Greenland

Communicated by J. Blundy.

Electronic supplementary material The online version of this article (doi:10.1007/s00410-011-0709-1) contains supplementary material, which is available to authorized users.

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Introduction

Alkaline magmas account for a small portion of igneous rocks in the Earth's crust, but there is great interest in them and a substantial amount of literature devoted to their study because of their economic importance. Alkaline rocks are often enriched in high-field-strength elements (HFSE) such as Zr, Nb, Ta, Y and REE and host a substantial volume of the world's strategic reserves of these elements. In addition, alkaline rocks often have significant post-magmatic hydrothermal activity, which in many cases can be shown to import, export and remobilise elements, enhancing the grade of many economic deposits. Many studies of alkaline rocks assume that this hydrothermal phase is a single event that immediately post-dates the magmatic

history. However, it is also possible that hydrothermal activity in an area is multiphase, particularly where an area has been the focus of repeated activity with a significant hiatus between episodes (e.g. Finch 1995; Liégeois et al. 2005). Determining robust, but independent, age estimates for the magmatic and hydrothermal stages of the evolution of alkaline rocks is a significant analytical challenge, particularly where the hydrothermal alteration has the potential to open isotopic systems and produce inaccurate age estimates. However, such analysis is essential to understand fully the nature, origins and development of mineral deposits in alkaline rocks.

The present study considers the Motzfeldt Centre in the Gardar alkaline province of South Greenland. Motzfeldt is the site of one of the world's largest potential Ta reserves (Armour-Brown 2001), yet the origin of the mineralisation and its relationships to the magmatic and subsolidus evolution of the centre are unclear. In Motzfeldt, Ta and other high-field-strength elements are intimately associated with areas showing pervasive hydrothermal alteration (Tukiainen et al. 1984; Tukiainen 1988). Therefore, understanding the timing of alteration and the role fluids have played in the evolution of the centre is important to the overall history. The hydrothermal history of the Motzfeldt Centre shows evidence for multiple phases of activity which may be separated by significant periods of time (McCreath 2009). The role of hydrothermal phases on the mobilisation, introduction and redistribution of elements within the system must therefore be examined independently from the magmatic history. Here we examine the ages and isotopic signatures of zircon and pyrochlore from the Motzfeldt Centre and use the data to understand the processes occurring during the magmatic and hydrothermal events at Motzfeldt.

Geological setting

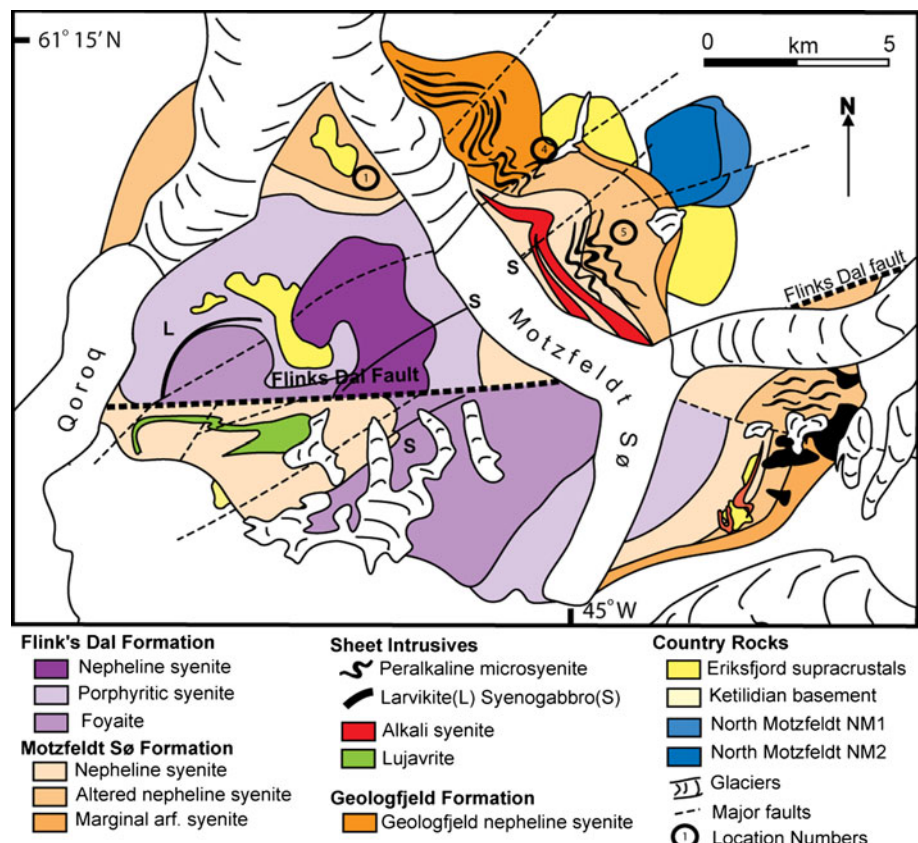
General overview

The Motzfeldt Centre is one of four major alkaline centres belonging to the Igaliko complex of South Greenland. The complex is in the north-east of the mid-Proterozoic Gardar province, which represents the products of repeated rift-related alkaline magmatism during the interval ~1,300–1,140 Ma (Blaxland et al. 1978; Upton and Emeleus 1987; Upton et al. 2003). The centre was emplaced into Ketilidian age (1,900–1,700 Ma) subduction-related I-type granites, belonging to the Julianehåb batholith (Allaart 1976; Garde et al. 2002), by a combination of block stopping, ring fracture and partial ring dyke formation (Emeleus and Harry 1970; Jones 1980). The tensional stress regimes active during the Gardar can be inferred from the orientations of faults and dykes. At the earliest

rifting, tension was parallel to ENE-WSW and a series of NNW-SSE basic dykes ('the Brown Dyke 0' or BD0 swarm) resulted (Upton and Emeleus 1987). The Gardar rift soon adopted a dominant E–W sinistral transtension generating E–W faults and *en echelon* NE–SW dilation along which most Gardar dykes were intruded (see Upton et al. 2003 for a review and for a map placing Motzfeldt in the context of the Gardar province). The geography of SW Greenland is now dominated by a series of deep NE–SW fjords and it is inferred that these lie along the major Gardar vertical rifting. The earliest Gardar rocks are a sequence of interbedded clastic sediments, pyroclastics and lavas together called the 'Eriksfjord formation'. From both in situ exposures and the widespread presence of Eriksfjord xenoliths in Gardar central complexes, it is thought that the Eriksfjord once covered the majority of SW Greenland.

The Motzfeldt Centre covers an area of approximately 150 km² with excellent 3-dimensional exposure in steeply dissected glacial valleys. The rocks comprise syenite, nepheline syenite, syenogabbro and minor intrusives, ranging in composition from basic to evolved rocks and quartz normative to agpaitic (Emeleus and Harry 1970; Jones 1980; Tukiainen 1988). The general structure of Motzfeldt comprises steep-sided concentric intrusions whose marginal contacts dip outwards. The roof to the intrusion was the Eriksfjord Formation, and recent glaciation in the east of the centre may have exploited the sub-horizontal plane of weakness that the roof zone provided to leave a relatively flat land surface that is consistently within a few 10 s of metres from the roof. Initial mapping of Motzfeldt by Emeleus and Harry (1970) distinguished 5 major syenite and nepheline syenite units, prefixed SM and numbered 1–5 broadly in order of emplacement, and two main satellite syenites called the North and East Motzfeldt syenites. Jones (1980) later added an agpaitic syenite (SM6) and identified a heterogeneous facies of SM4 termed HY. Bradshaw (1985, 1988) and Tukiainen et al. (1984) produced a revised field description of the centre, using different terminology, dividing the centre into the Geogfjeld (GF), Motzfeldt SØ (MSF) and Flinks Dal Formations (FDF), within each of which are several subdivisions (Fig. 1). The SM1 and 3 units of Emeleus and Harry (1970) correspond to the MSF and GF; SM2, 4, 5 and 6 form the FDF. In detail, the correlations between old and new nomenclatures are few. SM2 and parts of SM4 together comprise the FDF—*Porphyritic syenite*; SM5 was subdivided into the FDF—*Nepheline syenite* and FDF—*Foyaite* (here used to mean a nepheline syenite with a well-defined lamination). HY does not appear in the new nomenclature. The earliest activity in Motzfeldt is interpreted as lying to the North and East; it comprises SM1 and SM3 of Emeleus and Harry (1970) and the GF and MSF of Bradshaw (1985, 1988). The East Motzfeldt syenite of

Fig. 1 Geological map of Motzfeldt alkaline centre (after Bradshaw 1988; Jones 1980; Tukiainen et al. 1984). Numbers in circles refer to locations identified by Angus & Ross plc during their exploration of the area



Emeleus and Harry (1970) is now recognised as an extension of the Motzfeldt SØ Formation, offset by the Flinks Dal Fault (Fig. 1), rather than a separate satellite intrusion. Younger activity, in the middle of the centre, cored out older syenites and now forms the FDF, which comprises the middle, south and west of the complex. The youngest activity is a series of sub-horizontal peralkaline sheets and syenogabbro and larvikite giant-dykes. The relative ages of these late-stage intrusives are not known, although they are inferred to be part of Motzfeldt.

The Motzfeldt Centre was cross-cut by both NE-SW and E-W faults, the most substantial of which is the E-W Flinks Dal Fault which bisects the intrusion (Fig. 1). The Flinks Dal Fault has a sinistral offset of ~6 km and, assuming the exposure levels of the Eriksfjord formation are broadly equivalent, up to 800 m vertical offset. The intersections of E-W and NE-SW faults are a major control on the siting of Gardar central complexes (Stephenson 1976). These faults may have been reactivated in post-Gardar times.

Motzfeldt SØ and Geologfjeld formations

The area East of Motzfeldt SØ lake has been the site of much interest since the early 1980s when detailed mapping commenced as part of the Syduran uranium exploration project

(Armour-Brown et al. 1983). It comprises the Geologfjeld (GF) and the Motzfeldt SØ Formations (MSF) of Bradshaw (1985, 1988). The MSF was subdivided into: *MSF—Marginal Arfvedsonite Syenite*, *MSF—Altered Nepheline Syenite* and *MSF—Nepheline Syenite*. Within the MSF are a number of late microsyenite sheets termed the *MSF—Peralkaline Microsyenite Suite* (Bradshaw 1988; Tukiainen 1988). SM1 corresponds to the *MSF—Altered Nepheline Syenite* and *Marginal Arfvedsonite Syenite*; SM3 broadly corresponds to the *MSF—Nepheline Syenite*, *Alkali Syenite* and *Peralkaline Microsyenite Suite*. The frequency and thickness of peralkaline microsyenite sheets increase towards the upper areas of the formation with associated increase in textural heterogeneity and degree of alteration. The *GF—Nepheline Syenite* is considered a ‘fresh’ variant of the *MSF—Altered Nepheline Syenite* which was impervious to alteration. Pervasive alteration within the Motzfeldt Centre is restricted to the MSF suggesting that the hydro-thermal activity was intimately associated with this unit.

Materials and methods

Field data and material for the present study were collected during 2005 and 2006 under the auspices of Angus and

Ross plc. Sample reference numbers refer to the collections of the University of St Andrews, UK, and sample locations (latitude and longitude) can be found in McCreath (2009). Fieldwork focussed on the areas to the N and E of Motzfeldt Sø and the samples in the present study derive from the MSF—Altered Nepheline Syenite unit in locations ‘1’, ‘4’ and ‘5’ (Fig. 1). The location numbers derive from target areas identified by Angus and Ross plc. The analysis spots for zircon separates are given on a supplementary electronic archive.

Samples for isotopic analysis were crushed using a steel jaw crusher and sieved to $<350\ \mu\text{m}$. Pyrochlore and zircon were then separated by a combination of Wilfley table washing, heavy liquid separation using tetrabromoethane (TBE) and magnetic separation, followed by hand picking under a binocular microscope. A total of 74 pyrochlore crystals were picked from the least magnetic, 1.3 and 1 A magnetic fractions. Pyrochlore separates were then mounted in epoxy blocks and polished for laser ablation microprobe-multi-collector inductively coupled plasma mass spectrometry (LAM-MC-ICPMS) analysis. The same procedure was followed for zircon, but these were picked only from the least magnetic fraction to avoid metamict grains. A total of 19 zircons were sampled and subject to isotopic analysis. Samples were examined using optical microscopy, back scatter electron imaging (BSEI) and cathodoluminescence (CL) imaging on thin sections and mineral separates. CL was performed on a Technocyn 8200 mk V cold-cathode luminoscope on a Nikon Optiphot microscope. Beam conditions were maintained at $\sim 600\ \mu\text{A}$ and $\sim 15\ \text{kV}$ corresponding to a power density of $50\ \text{kW m}^{-2}$. The CL images were collected with a DVC high sensitivity CCD camera using EPIX software. Typical exposure times were 8 s and the images were enhanced after collection using Adobe Photoshop.

Microchemical analysis of zircon separates was carried out at the Department of Earth Sciences, University of St Andrews, UK, by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a Thermo Electron X-Series2 quadrupole ICP-MS. A New Wave UP213 laser ablation microprobe was used for spot analyses of zircons. The laser delivered 213 nm UV light from the 5th harmonic of a Nd:YAG laser. Samples were ablated in He gas which was mixed with Ar in a Teflon mixing cell prior to entry into the plasma torch. Analyses were carried out using a stationary beam and a spot size of $\sim 40\ \mu\text{m}$ with a pulse frequency of 10 Hz operating at 33% intensity. A single laser ablation analysis of zircon included a 40 s on-peak background measurement with the laser turned off, followed by 80 s of ablation and 40 s washout time. Operating conditions were optimised before each analytical session using continuous ablation of NIST SRM 612 reference glass in order to provide maximum signal intensity and stability. The NIST SRM 612 standard was analysed in

duplicate at the beginning and end of each analytical session and at regular intervals during analyses.

Data reduction was performed using the GEMOC-developed GLITTER software (Van Achterbergh et al. 2001). Raw signal counts were carefully studied in order to exclude from calculations portions of signal deviating from a flat profile. Because of the time dependence of elemental fractionation during ablation, we selected GLITTER settings that optimised the precision of the standards and provided consistency in approach. Net background-corrected count rates for each isotope were used for sample calculation. Under such conditions, precision is typically $\pm 10\text{--}15\%$ at 95% confidence.

All isotopic analyses were carried out at the Laboratory of Isotope Geology, Mineralogical-Geological Museum, University of Oslo, using a Nu Plasma HR mass spectrometer equipped with a U–Pb collector block (e.g. Simonetti et al. 2005). U–Pb analyses were made in static mode, with masses 204, 206 and 207 in ion counters and 238 in a Faraday cup, positioned by adjusting the magnetic field and zoom lens voltages. Masses 235 and 232 were monitored in Faraday cups, but the counting statistics on the low intensity signal on mass 235 were insufficient for precise measurement, and ^{235}U was instead estimated from the signal on mass 238 using $^{238}\text{U}/^{235}\text{U} = 137.88$ for natural uranium. The sensitivity at ^{238}U was ca. $10^{-4}\ \text{V/ppm}$. A New Wave/Merchantek LUV213 laser ablation microprobe was used for the spot and raster analyses. The laser delivered 213 nm UV light from the 5th harmonic of a Nd:YAG laser. Samples were ablated in He in a specially built ablation cell. The He aerosol was mixed with Ar in a Teflon mixing cell prior to entry into the plasma. This gas mixture was optimised daily for maximum sensitivity and the laser beam focussed in aperture imaging mode with a circular spot geometry. U–Pb analyses on zircon were carried out using a stationary beam and a spot size of $\sim 40\ \mu\text{m}$ with a pulse frequency of 10 Hz operating at 33% intensity delivering an energy of $0.1\ \text{J/cm}^2/\text{pulse}$. Ablation depth during a 60 s run with static beam is ca. $40\ \mu\text{m}$. A single laser ablation analysis of zircon included a 30 s on-peak background measurement with the laser turned off, followed by 60 s of ablation. Three natural zircons were used as calibration standards: GJ-01 ($609 \pm 1\ \text{Ma}$; Belousova et al. 2006), 91500 ($1,065 \pm 1\ \text{Ma}$; Wiedenbeck et al. 1995) and A382 ($1,876 \pm 2\ \text{Ma}$, Patchett and Kouvo 1986, H. Huhma, personal communication). These were analysed in duplicate at the beginning and end of each analytical session, and at regular intervals during analyses. A Tl correction for Pb isotope mass discrimination was not used for the analysis of zircons. A high background signal on mass 204 (typically ca. $10^3\ \text{cps}$), due to Hg contamination of the He and Ar gas, was observed. However, there was no excess ionisation of Hg during ablation at the laser and microscope light settings used, so that common

lead in the zircons could be monitored at mass 204. Raw data from the Nu Plasma time-resolved analysis program were imported into a Microsoft Excel/VBA spreadsheet program (UPSB, written by T. Andersen) for interactive selection of isotopically homogeneous integration intervals, background correction, calibration to standards and calculation of ages. To minimise laser-induced fractionation of U from Pb, we follow Jackson et al. (2004) in combining data for isotopically homogeneous intervals of the time-resolved signal of an unknown with the corresponding depth intervals on the standards, assuming similar ablation rates for standards and unknowns.

The raw data from the calibration standards were fitted to the relationship:

$$y = x(a + bx + ct)$$

where y is the true isotope ratio, x is the observed ratio for the relevant depth interval, t is time since the first standard analysis in a series, and a , b and c are coefficients determined by the built-in linear regression algorithms of Microsoft Excel 2003. The second-order term was necessary to compensate for an observed deviation from linearity of the ion counters at high counting rates.

Laser ablation lead isotope analysis of pyrochlore was done in line-scan mode, using a 40–50 μm laser beam focused in aperture imaging mode, a frequency of 10 Hz and energy of ca. 0.12 J/cm²/pulse. Masses 202, 203, 204, 205, 206, 207 and 208 were measured in Faraday collectors. A dilute thallium solution was aspirated through a desolvating nebuliser during ablation runs, and lead isotope ratios were corrected for mass bias relative to $^{203}\text{Tl}/^{205}\text{Tl} = 2.3889$. The value of $^{203}\text{Tl}/^{205}\text{Tl}$ ratio is determined from long-term relationship between Pb fractionation and Tl fractionation for laser analysis of NIST SRM 610, NIST SRM 610 was used due to lack of an pyrochlore isotope standard. Analyses were made in time-resolved mode, using 20 s on-peak background measurement for Pb and ^{202}Hg , followed by 20 s background measurement for Tl with the ion beam deflected by the electrostatic analyser. Data were reduced using the NU Plasma time-resolved analysis software. NIST SRM 610 was run at 10 Hz frequency using a 100 μm spot and energy of 12–20 J/cm²/pulse at regular intervals to monitor the performance of the machine. Isoplot 3.00 (Ludwig 2003) was used to plot all of the radiogenic isotope data and for calculating U–Pb zircon ages and pyrochlore Pb–Pb isochron ages.

Results

Field studies

The MSF—Altered Nepheline Syenite is typically brick-red syenite with widespread textural and mineralogical

variation over metre scales. Despite the facies name (Bradshaw 1985, 1988), the rock in location 5 (Fig. 1) is typically a coarse feldspathic syenite with little nepheline—the nepheline present is heavily altered. The mafic phases are dominated by black arfvedsonite and needle-like green aegirine. Several samples show secondary dark micas after amphibole. A striking feature of the Motzfeldt SØ Formation is the high degree of alteration of the rock, expressed as (a) the breakdown of primary mafic minerals to Fe–Ti oxides and secondary micas, (b) intensive oxidation of feldspars and permeation of the feldspar by haematite giving the rock (and the whole MSF) a striking brick-red appearance. The altered units are also particularly rich in fluorite (up to 10 modal %) occurring as an intergranular accessory mineral and vein fluorite.

We infer that the late-magmatic history of the MSF—Nepheline syenite involved repeated sheeting of magma into hot, partially crystallised syenite. The re-melting of contacts resulted in modal variability without obvious chilled margins, and variations in thermal gradient and composition (particularly volatiles) gave rise to rocks with strikingly variable grain-size (mm to cm grains) over m-scales. The assimilation of Eriksfjord arenite from the roof may account for some of the textural and compositional variability, particularly the relatively low modal amounts of nepheline in this area and the transitional to silica-oversaturated pegmatites. The MSF units (including Nepheline Syenite and Altered Nepheline Syenite, Fig. 1) are not rocks with a single characteristic mineralogy and texture, but rather are definable suites of syenitic variants. An objective of fieldwork was to provide materials for precise age dating of the MSF. For that purpose, particular attention was paid to two syenitic variants within the MSF—Nepheline syenite: (a) a *pyrochlore microsyenite* and (b) a *zircon-rich pegmatite*. These lithologies are from field relationships synchronous with the major episodes of magmatism and are particularly rich in datable minerals.

The final magmatism was the MSF—Peralkaline Microsyenite Suite. These are substantial (m-thick) units with sharp but unchilled boundaries against the MSF—Nepheline Syenite and Altered Nepheline Syenite. Late-stage peralkaline minor intrusives occur across NE Igaliko, and include SM6 of Jones (1980) and NM3 of Finch et al. (2001a). They may represent a widespread phase of peralkaline magmatism across the whole of the Motzfeldt region.

Petrology of the pyrochlore- and zircon-bearing rocks

Pyrochlore is found throughout the MSF as an accessory, though some facies show particular enrichment. The pyrochlore microsyenite is encountered in drill cores across

location 5 (Fig. 1) and cross-cuts heavily altered units approaching the roof zone of the centre. This variant is common in the roof zone of the intrusion around location 5 (Fig. 1), where alteration is most extreme and fluorite most abundant. It occurs in inclined sheets typically 10–20 cm wide without chilled contacts, demonstrating that this magma was part of the multiple episodes that gave rise to the MSF—Altered Nepheline Syenite. It is a component of the late-magmatic repeated sheeting across the whole of location 5 and contemporaneous with it. The pyrochlore microsyenite is widespread but laterally discontinuous; individual sheets cannot be mapped across the terrain, nor correlated between drill cores. Rather it forms a swathe of minor intrusives across the whole of location 5. Although all Motzfeldt syenites are relatively enriched in HFSE, the pyrochlore microsyenite is particularly enriched with high concentrations of Nb, Ta, Th, U, Zr and LREE. It is the primary focus of the commercial interest in HFSE at Motzfeldt. Pyrochlore microsyenite comprises euhedral pink alkali feldspar crystals that are typically 1–3 mm in length, showing coarse perthite textures with an elongate tabular habit and strong mineral alignment. The modal amount of mafic minerals in the rock is typically <10%. The primary mafic mineral, usually amphibole, is largely replaced by granular clusters of Fe–Ti oxide minerals and secondary micas. Pyrochlore typically occurs as fine euhedral to subhedral crystals disseminated throughout the rock or as rare pyrochlore-rich veinlets. Crystals occurring in the enriched veinlets are typically 100–300 µm, compared to an average of approximately 100 µm for the disseminated pyrochlore. Pyrochlore typically occurs <15%, though in some particularly enriched samples can make up approximately 25% of the rock's mineralogy.

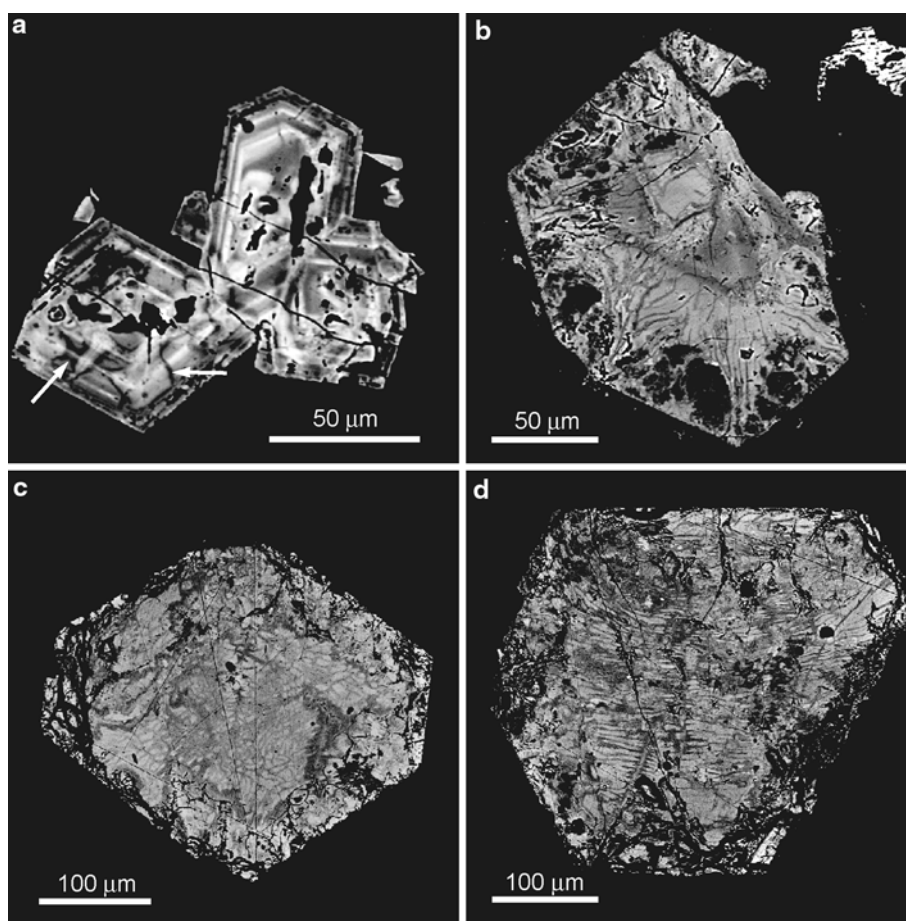
Zircon within the MSF is extremely variable occurring as euhedral accessory minerals in many facies of syenite. Zircon solubility in silica-undersaturated alkaline melts is high (Watson and Harrison 1983), but it is a common accessory in Motzfeldt syenites. However, zircon is largest and most abundant in transitional to silica-oversaturated pegmatites. The zircon-rich pegmatites are a series of irregular inclined sheets with transitional to silica-oversaturated compositions. These comprise arfvedsonite, pink alkali feldspar, zircon, magnetite and relict astrophyllite ± quartz and are petrographically similar to pegmatites in the Nunarsuit complex dated by Finch et al. (2001b). Feldspars and astrophyllite are typically 2–3 cm across with massive magnetite and amphibole crystals as large as 10 cm. The zircons are typically 3–8 mm in size. The altered nature of feldspar is consistent with the pegmatites having experienced the same hydrothermal episode that gives the MSF its characteristic pink colour in hand specimen.

Pyrochlore occurrence and composition

Pyrochlore minerals are generally characterised by their octahedral habit and strong honey-yellow colour in transmitted light. However, crystals from the MSF show varying states of alteration, being dark reddish-brown to opaque in transmitted light. The chemistry of pyrochlore group minerals varies greatly though may be expressed by the general formula $A_{2-m}B_2O_{6-w}Y_{1-n}pH_2O$, where $A = Na, Ca, Mn, Fe^{2+}, Sr, Cs, Ba$, rare earth elements (REE = Sc, Y and lanthanides), Pb, Bi, Th, U or site vacancies; $B = Al, Nb, Ta, Ti, Fe^{3+}$; $Y = OH, F$ or site vacancies (Hogarth 1977). Altered pyrochlore may also be stabilised by the incorporation of H_2O molecules and OH groups.

Pyrochlore crystals in the MSF show complex internal textures. In a few cases, some primary concentric growth zoning can be preserved, overprinted by alteration textures penetrating the crystal in a 'watermark' texture from its margins (Fig. 2a). However, the vast majority of pyrochlores have textures inconsistent with primary growth zonation. We describe such features as 'tortoise shell' or mosaic pattern in BSEI (Fig. 2). Many show evidence for alteration along a network of microfractures penetrating the crystal. In some samples this gives the crystal an appearance similar to exsolution lamellae (e.g. Fig. 2d). These styles of texture are observed widely in the MSF—Altered Nepheline Syenite, but are particularly well displayed in the pyrochlore microsyenite where the crystals tend to be larger. We infer these textures are the result of fluid–mineral interaction, although it is difficult to rule out the possibility that some may be fluid-assisted exsolution textures. Whatever the mechanisms for their formation, they clearly indicate that the pyrochlore is almost entirely recrystallised in the subsolidus. Lumpkin and Ewing (1992, 1995) showed that secondary alteration in pyrochlore is strongly fracture-controlled and often associated with the alteration of feldspars and formation of iron oxides. In the MSF the character of alteration in both pyrochlore and their host rocks is consistent with this suggestion. However, in samples where alteration is less intense, intracrystalline diffusion has likely been the principal control of alteration, giving way to microfracturing as alteration intensified. Chemical changes accompanying fluid–mineral interaction vary depending on the degree of alteration. In a large number of samples the alteration is so intense that it becomes difficult to distinguish primary chemical variations in magmatic parts of the crystal from those which have experienced chemical exchange in the subsolidus. In many instances the latter dominate the crystal, masking evidence of the magmatic history of the crystal. Textural and microchemical analyses of pyrochlore minerals from the Motzfeldt centre are presented in McCreath (2009).

Fig. 2 BSE images of pyrochlore group minerals showing various states of alteration. **a** Cluster of oscillatory zoned pyrochlore crystals showing development of ‘watermark’ alteration front (*dark line*) with lighter more diffuse altered areas. **b** Pyrochlore with penetrating network of microvein alteration penetrating weak primary (oscillatory) zoning. **c**, **d** Heavily altered pyrochlore crystals with intense network of microfractures penetrating the whole crystal (*dark grey* BSE) primary textures are masked by intense alteration



where the reader is referred for more detailed interpretations on the mode of alteration.

Zircon occurrence and composition

Preliminary analysis of several pegmatites was performed as part of the present study. Two (GJM06-29 and -15) provided superlative, transparent zircons up to several millimetres in size from which the zircons analysed here were separated. These crystals are typically 500–700 μm in size but occur up to several mm. These have euhedral crystal habit terminating in perfect pyramidal faces with typical aspect ratios around 2. A total of 19 zircons were separated from MSF samples and subject to isotopic analysis. All of the crystals sampled have a brown to reddish-brown rim with a light sky-blue core and are typically turbid-translucent with slightly cloudy or opaque cores in PPL. BSEI shows the zircons to have complex internal textures (Fig. 3). None of the samples, with the exception of GJM06-18, show oscillatory zoning in BSE and CL imaging. Instead, samples show relatively homogeneous BSE textures with weak broad zoning and slight contrasts between the core and rim. All of the samples show

evidence of late to post-magmatic modification, indicated by discordant patches of alteration penetrating into the crystal from its margins and cross-cutting any magmatic features (Fig. 3). We infer that homogeneous, magmatic parts of the crystal have experienced post-magmatic alteration in the presence of a fluid phase. The altered areas are characterised by lower BSE intensities and bright blue CL colours compared to the higher BSE and dark blue CL emission retained in magmatic areas of the crystal (Fig. 3). The percentage of the total crystal that has experienced such alteration is highly varied, ranging from a narrow mantle on the margin of the crystal to pervasive alteration as in Fig. 3, where up to 40% of the crystal has been altered.

Representative chemical analyses of zircons from the Motzfeldt Sjø Formation are given in Table 1. Chemical changes in U, Th, Pb and REE concentrations have been investigated using LA-ICPMS analyses on unaltered areas and areas interpreted as having experienced late- to post-magmatic modification. Altered areas are depleted in U and Th when compared to areas preserving magmatic textures (Table 1, Fig. 4). U and Th contents of the unaltered areas range from 357 to 1,880 ppm for U and 170 to 2,622 ppm

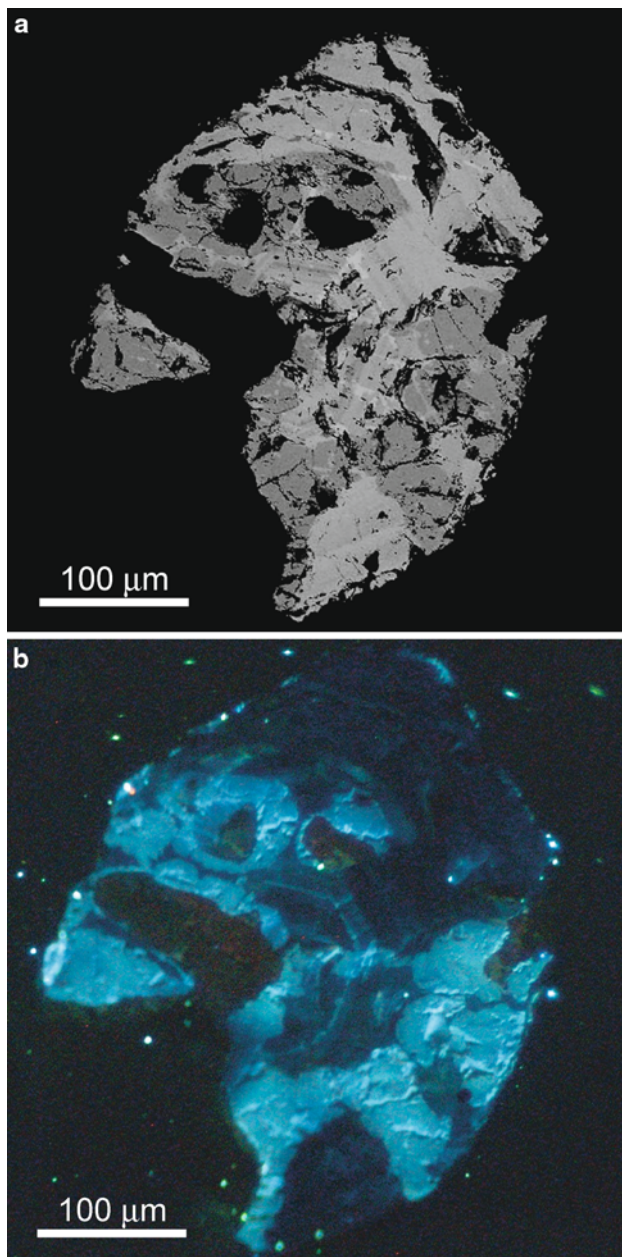


Fig. 3 Back scatter electron image (a) and Cathodoluminescence (b) image of zircon GJM06-18-1 from the Motzfeldt centre showing discontinuous areas of alteration, with dark grey BSE and bright blue CL emissions, cutting a primary oscillatory zonation pattern with int. grey BSE and dark blue CL emissions

for Th, defining a trend. The pattern for altered areas spans a similar range for U, though Th contents are almost half those found in the unaltered samples and show a much more scattered distribution.

The REE content also shows notable differences in the altered and unaltered areas (Fig. 4). The overall REE content of the altered zircon samples is lower than the unaltered samples; this is particularly evident for the lighter REE's up to Gd which are typically lower by up to 1 order

of magnitude. The heavier REEs (Gd–Lu) show little systematic difference. La appears to be enriched in the altered domains giving the REE profile a relatively flat pattern compared to that of unaltered areas, which show a notable positive Ce anomaly. Such Ce enrichment is typical of unaltered natural zircons (Hoskin and Ireland 2000). Pr similarly also shows a slight increase, which further enhances the relatively flat REE pattern of the altered areas. The slope of the REE pattern for elements heavier than Sm in altered areas matches well with the REE pattern for areas which show no evidence for alteration, suggesting little involvement of the HREEs during alteration. This interpretation is supported by the preservation of the Eu anomaly for both magmatic and altered areas.

Zircon U–Pb isotope systematics

A total of 51 spot analyses were made from 19 zircons. Zircons from the MSF show a broad range of isotopic compositions obtained using LA-MC-ICPMS (Table 2 and Supplementary Electronic Archive). These are plotted in Fig. 5 as a Tera-Wasserburg Concordia plot. The analyses are subdivided according to whether they were made from areas of the zircon interpreted as preserved magmatic zones or from regions altered during post-magmatic events. The Concordia diagram shows a range of isotopic compositions with a strong grouping of points at $\sim 1,300$ Ma and a significant number of points plotting outside this cluster, defining a Discordia line between 350 and $\sim 1,300$ Ma (Fig. 5b). Restricting the dataset to only magmatic zones with minimum discordance yields a Concordia age (Ludwig 2003) of $1,273 \pm 6$ Ma (Tera-Wasserburg plot, Fig. 5a). The Rb–Sr isochron age for Motzfeldt by Blaxland et al. (1978) dated the centre at $1,282 \pm 30$ Ma (2σ , recalculated using decay constants of Steiger and Jäger 1977), although those data show significant scatter, with an MSWD of 18.06. Finch et al. (2001a) noted that the residuals from the Motzfeldt isochron of Blaxland et al. (1978) are greatest for samples collected N of Motzfeldt SØ (i.e. the MSF) and suggested that these samples either have significantly different initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to the FDF, or that the FDF and MSF have different ages. Removal of samples belonging to the MSF gave a more robust Rb–Sr isochron age of $1,287 \pm 4$ Ma for the emplacement of the FDF. The greater spread of ages from the Rb–Sr system are to be expected since most Rb and Sr in the rocks are hosted in feldspar and this mineral is heavily altered in most MSF samples. Hence the precision on the Rb–Sr age estimate is a larger value, and the accuracy may be suspect.

The Concordia diagram also shows a number of normally discordant points plotting along a Discordia line (Fig. 5a). These points broadly correlate with analyses

Table 1 Representative LA-ICPMS compositions of zircons from the Motzfeldt Sjø formation

ppm	Unaltered zircon						Altered zircon					
	18-1d	29-4a	29-8c	29-10a	29-16c	29-17d	18-1c	29-3c	29-5b	29-14a	29-18c	29-20b
La	1.02	14.56	9.57	10.78	69.29	67.05	3.43	23.22	27.24	34.20	26.57	44.72
Ce	16.13	141.06	233.62	73.31	836.51	687.00	8.68	43.42	69.14	103.05	75.92	57.54
Pr	1.10	12.71	35.45	9.09	108.28	83.93	1.26	11.94	15.09	17.13	7.08	17.49
Nd	13.29	75.21	242.29	50.07	619.13	436.01	7.61	59.29	75.42	87.63	31.46	83.32
Sm	21.57	56.98	112.40	39.03	293.40	246.07	5.67	30.91	43.86	52.73	12.67	32.04
Eu	2.73	9.55	18.54	5.35	37.83	50.40	1.046	5.31	5.94	7.45	1.58	4.02
Gd	86.16	153.37	169.16	85.12	439.32	359.76	18.06	55.55	93.65	133.27	30.49	54.02
Tb	27.68	46.85	39.73	24.76	100.93	84.65	6.76	17.37	28.96	41.31	9.72	18.65
Dy	328.46	521.20	379.28	287.16	911.15	698.29	76.61	196.24	319.34	461.59	105.88	203.10
Ho	106.04	154.53	98.13	81.69	228.81	156.83	21.06	55.47	87.56	132.78	32.95	55.62
Er	431.02	596.38	355.53	318.92	795.17	519.58	80.67	213.72	327.41	525.47	130.23	209.64
Tm	83.89	109.23	63.24	59.10	133.65	87.74	14.94	38.93	57.62	95.66	24.16	37.01
Yb	650.11	835.45	475.40	451.82	948.16	633.25	118.05	277.58	422.78	730.28	193.26	258.63
Lu	97.78	116.91	66.97	60.99	132.79	82.38	17.42	32.09	56.33	101.30	29.74	30.62
Pb	25.12	63.60	91.42	73.68	104.08	100.08	12.17	20.44	152.11	78.59	29.89	27.22
Th	169.61	928.50	1,319.0	554.77	1,559.4	1,785.5	59.1	375.67	384.01	687.21	173.09	311.44
U	357.59	1,219.2	1,376.6	800.68	1,619.5	1,670.9	61.01	300.37	439.51	975.34	306.52	292.91
²⁰⁷ Pb/ ²⁰⁶ Pb	1,248	1,205	1,278	1,245	1,200	1,244	670	962	835	615	665	732

made from altered areas of zircon showing homogeneous textures. Figure 5a shows a simplified illustration of zircon sample GJM06-18-1 in CL, with dark blue luminescent, oscillatory zoned, magmatic zircon and bright blue luminescent, homogeneous patches of alteration. The analysis of ‘magmatic’ and ‘altered’ zones is expressed in Fig. 5a as dark blue and light blue ellipses, indicative of the CL colour observed at that spot. Note that these results are an amalgamation of data from the many grains analysed in the present study, rather than a detailed dissection of one single crystal—the diagram is illustrative of how dark blue and light blue points from individual crystals plot. Figure 5 provides a visual illustration of the correlation between areas of alteration and isotopic discordance. The Tera-Wasserburg plot (Fig. 5d) includes a line for modern lead loss with points lying above and below the line. Of the 35 dark blue luminescent (magmatic) zones analysed, 17 (49%) have >10% discordance whereas of those from the light blue altered zones, 15 (of 16 = 93%) are similarly discordant (Table 2). There is an isotopic distinction in the populations between altered and unaltered zircon. The fact that the populations do not perfectly correlate may indicate that some dark blue zones are truly discordant (i.e. discordance can be introduced without changes to CL). Alternatively it may be that the CL of the surface does not exactly correspond to the nature of the microvolume analysed by ICPMS, which ablates to significant depth.

The upper intercept age of discordant zircon ($1,261 \pm 28$ Ma) is within error of the concordant age from magmatic zircon analyses. A lower intercept age on the Concordia diagram (349 ± 60 Ma) is often considered to record a secondary event during which most or all of the radiogenic Pb accumulated since the time of isotopic closure is lost from the zircon (e.g. Geisler et al. 2007; Harley and Kelly 2007 and Wetherill 1956, 1963). Therefore, the lower intercept value potentially records the age of an episodic Pb-loss event, assuming the zircon lost all previously accumulated radiogenic Pb. Given the textural relationship between hydrothermal alteration and the discordant points in the zircons of the present study, the lower intercept age might provide an age for the hydrothermal event (cf. e.g. Soman et al. 2010). Taking these discordant data at face value suggests that a hydrothermal alteration event is substantially (~ 900 Ma) younger than the magmatism. However, it is also possible that the lower intercept is a spurious age relating to open system behaviour. It may be that alteration and damage to structural domains in the zircon, associated with the alkaline hydrothermal phase, has resulted in partial and steady diffusive loss of radiogenic Pb (Tilton 1960) in confined domains of the zircon, resulting in a series of variably discordant analyses spread out along a single Discordia. Although the exact control over the isotopic discordance is uncertain, it is clear that hydrothermal activity has played an important

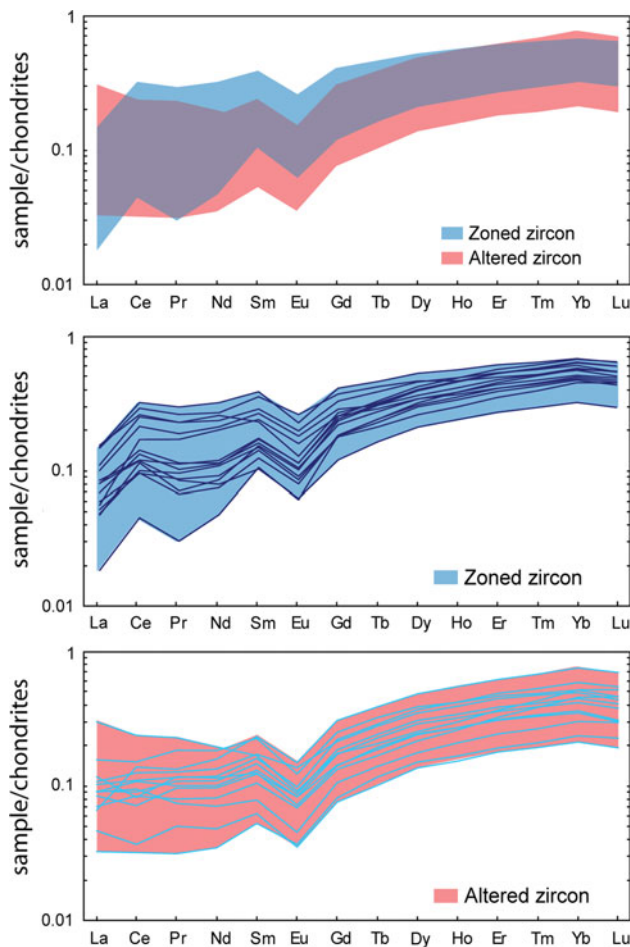


Fig. 4 Plot of chondrite normalised REE profiles from altered (red) and unaltered (blue) areas of zircons from the Motzfeldt Sjø formation. Individual profiles are plotted at the bottom and the fields are compared at the top

role in the isotopic systematics of the MSF zircon population.

Pyrochlore Pb–Pb systematics

LA-MC-ICPMS data for pyrochlore display a large range of isotopic compositions (Table 3 and Supplementary Electronic Archive). Uranogenic lead ($^{207}\text{Pb}/^{204}\text{Pb}$) shows a range from 15.52 to 112.06 with a $^{206}\text{Pb}/^{204}\text{Pb}$ range of 17.08–1,183.54. Data for pyrochlore uranium are plotted in Fig. 6. When the pyrochlore data are regressed, a Model 2 age of $1,267 \pm 6$ Ma is obtained (MSWD = 4.5, Ludwig 2003). This age is indistinguishable from the concordant U–Pb zircon age ($1,273 \pm 6$ Ma).

The pyrochlores have a relatively constant $^{208}\text{Pb}/^{204}\text{Pb}$ at variable $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, ranging from 37.65 to 68.42 with one anomalously high sample at 103.06. The independent behaviours of thorogenic and uranium lead may represent fractionation of U over Th during crystallisation

of the parental magma from which the pyrochlores crystallised. However, the textural analysis of the pyrochlores (Fig. 2; McCreath 2009) shows that they are almost entirely recrystallised. Alternatively, the separation of uranium and thorogenic lead might be interpreted as mobilisation of Th in the subsolidus. Airborne gamma spectrometry surveying during the SYDURAN project revealed significant Th anomalies in several localities in the roof zone of the MSF (Tukiainen et al. 1984) and notable thorium anomalies were identified during the surface sampling program of Angus and Ross plc (Armour-Brown 2001), suggesting that Th may be localised in the roof zone of the centre through ponding of residual fluids. It is therefore plausible that in addition to U, which may be mobilised when oxidised to the 6+ state, Th may also be mobilised during the subsolidus and locally concentrated in unidentified Th-rich phases within the high-level units of the formation. Although thorium is usually considered immobile in the geochemical environment, Keppler and Wyllie (1990) demonstrated that partitioning of Th (and U) into a fluid phase can occur in the presence of fluorine and/or chlorine. In the Gardar, Goodenough et al. (2000) also showed that Th, U and other trace elements are mobilised by F-rich fluids and the Motzfeldt centre has been shown by Finch et al. (1995) to have been associated with late-stage fluids containing some of the highest fluorine contents of all Gardar centres. This is supported by the high modal abundance of fluorite in these rocks where it can make up 10%. Additionally, localised fluorite mineralisation is found in the preserved roof zone of the centre suggesting ponding of F-rich fluids. Varied complexing of U and Th with fluorine-rich fluid ligands in the subsolidus is therefore a plausible explanation for the geochemical separation of U and Th. Although the exact process responsible for the independent behaviours of thorogenic and uranium lead remain unclear, it is likely that the intense subsolidus activity associated with the MSF, in particular the elevated activity of F-rich fluid ligands, played an important role in contributing to the isotopic character of pyrochlore from the MSF.

Discussion

Timing of Motzfeldt magmatism and its regional significance

The Gardar province was initially interpreted in terms of three major episodes of rifting and associated alkaline magmatism occurring at 1,350–1,300, 1,280–1,260 and 1,180–1,140 Ma (Upton and Blundell 1978). Advances in U–Pb age determinations further constrained these periods in favour of two main episodes of igneous activity at

Table 2 U–Pb data for zircons from the Motzfeldt SØ formation

	$^{206}\text{Pb}/^{204}\text{Pb}$	1σ	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ
<i>Fresh areas sample name</i>								
GJM06-18-2A	51,853	22,794	0.08250	0.00093	2.500	0.045	0.2181	0.0031
GJM06-18-2B	1,975	385	0.09314	0.00136	2.826	0.058	0.2200	0.0031
GJM06-18-2C	50,494	6,019	0.08238	0.00093	2.504	0.046	0.2205	0.0032
GJM06-29-03A	34,424	13,415	0.08214	0.00092	2.553	0.047	0.2254	0.0033
GJM06-29-03B	1,075	194	0.08175	0.00099	2.462	0.046	0.2184	0.0031
GJM06-29-04A	3,091	363	0.08579	0.00101	2.384	0.046	0.2016	0.0031
GJM06-29-04C	615	8.8	0.08165	0.00092	0.772	0.013	0.0686	0.0009
GJM06-29-05A	1,344	42	0.08049	0.00089	1.300	0.022	0.1154	0.0016
GJM06-29-06A	795	18	0.07988	0.00088	0.881	0.014	0.0800	0.0010
GJM06-29-06B	1,045	26	0.08151	0.00091	1.139	0.021	0.1014	0.0015
GJM06-29-06C	44,262	6,586	0.08209	0.00101	2.581	0.045	0.2281	0.0028
GJM06-29-07C	13,284	2,752	0.08303	0.00092	2.477	0.044	0.2164	0.0030
GJM06-29-07D	86,587	29,163	0.08196	0.0009	2.499	0.044	0.2212	0.0031
GJM06-29-07E	5,150	468	0.08398	0.00094	2.561	0.046	0.2212	0.0031
GJM06-29-08A	3,676	202	0.08556	0.00081	2.606	0.036	0.2209	0.0022
GJM06-29-09A	2,031	214	0.08892	0.00097	2.284	0.037	0.1863	0.0022
GJM06-29-10A	1,960	96	0.08848	0.00075	2.656	0.033	0.2177	0.0020
GJM06-29-11A	2,781	251	0.08756	0.00081	2.650	0.035	0.2195	0.0020
GJM06-29-11B	1,408	157	0.09313	0.00083	2.740	0.034	0.2134	0.0019
GJM06-29-11C	324	7.0	0.12299	0.00142	3.749	0.057	0.2211	0.0022
GJM06-29-11D	74,505	22,433	0.08238	0.00065	2.503	0.030	0.2203	0.0020
GJM06-29-12A	43,621	14,011	0.08314	0.00069	2.547	0.032	0.2222	0.0021
GJM06-29-12B	1,986	108	0.08923	0.00079	2.629	0.033	0.2137	0.0019
GJM06-29-12C	2,610	195	0.08697	0.00076	2.491	0.032	0.2077	0.0019
GJM06-29-13C	989	10	0.07880	0.00063	1.037	0.013	0.0955	0.0009
GJM06-29-13D	514	52	0.16820	0.0154	2.320	0.230	0.1000	0.0038
GJM06-29-14A	16,130	4,876	0.08295	0.00056	2.500	0.028	0.2184	0.0019
GJM06-29-14B	74,536	35,345	0.08177	0.00084	2.473	0.035	0.2194	0.0021
GJM06-29-14C	27,961	6,565	0.08290	0.00058	2.458	0.027	0.2150	0.0018
GJM06-29-14E	5,476	292	0.08315	0.00067	2.256	0.026	0.1968	0.0017
GJM06-29-15A	62,335	9,475	0.08196	0.00055	2.297	0.031	0.2033	0.0024
GJM06-29-16C	593	15	0.10315	0.00095	2.842	0.036	0.1999	0.0017
GJM06-29-17C	17,424	5,945	0.08200	0.00083	2.519	0.038	0.2228	0.0025
GJM06-29-20	915	12	0.07547	0.00055	0.753	0.008	0.0723	0.0006
GJM06-29-20A	1,718	106	0.08437	0.00072	1.631	0.035	0.1402	0.0027
GJM06-29-7A	1,354	24	0.08313	0.00092	1.430	0.024	0.1248	0.0015
<i>Altered areas sample name</i>								
GJM06-29-07B	692	12	0.08791	0.00109	1.248	0.026	0.1030	0.0018
GJM06-29-19A	1,058	17	0.07089	0.00051	0.679	0.007	0.0694	0.0005
GJM06-29-19B	917	15	0.07725	0.00068	0.841	0.014	0.0790	0.0011
GJM06-29-18A	1,764	22	0.07928	0.00060	1.382	0.015	0.1264	0.0010
GJM06-29-17A	1,697	31	0.07792	0.00058	1.399	0.015	0.1302	0.0010
GJM06-29-17B	1,645	39	0.07941	0.00059	1.423	0.019	0.1299	0.0014
GJM06-29-05B	464	18	0.10612	0.00170	2.271	0.058	0.1552	0.0031
GJM06-29-13A	12,037	3,843	0.08758	0.00119	2.713	0.044	0.2246	0.0020
GJM06-29-13B	592	66	0.12189	0.00708	1.952	0.115	0.1162	0.0009
GJM06-29-14D	1,090	25	0.07214	0.00047	0.700	0.006	0.0657	0.0005

Table 2 continued

	$^{206}\text{Pb}/^{204}\text{Pb}$	1σ	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ
GJM06-29-15B	1,114	357	0.0952	0.00110	1.847	0.043	0.1407	0.0028
GJM06-29-15C	815	15	0.07735	0.00059	0.703	0.008	0.0660	0.0005
GJM06-29-16E	220	11	0.13801	0.00392	1.640	0.065	0.0862	0.0024
GJM06-29-16B	665	15	0.08141	0.00063	0.778	0.008	0.0693	0.0005
GJM06-29-04B	883	15	0.08386	0.00095	1.044	0.018	0.0903	0.0011

Further details are in the supplementary information. Errors in $^{206}\text{Pb}/^{204}\text{Pb}$ are based on internal counting statistics

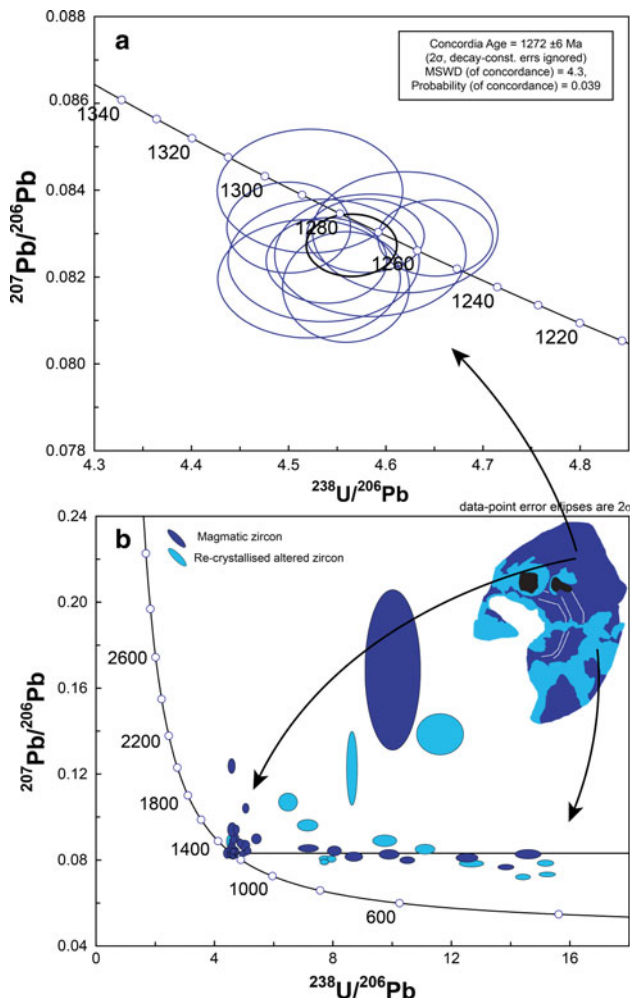


Fig. 5 Tera-Wasserburg Concordia diagrams shown with $\pm 2\sigma$ error ellipses. **a** Concordant, common Pb free zircon analyses of magmatic zircon dated by U–Pb LA-MC-ICPMS defining a Concordia age of $1,273 \pm 6$ Ma. **b** All zircon analyses are shown to illustrate the correlation between discordant points displaying bright blue CL emission (dark BSE) interpreted to have experienced alteration and recrystallisation during the subsolidus. Analyses from areas representing preserved magmatic zones generally provide concordant ages. The horizontal black line in **b** represents the compositions followed by recent lead loss

~1,280 Ma and 1,180–1,140 Ma (Upton et al. 2003). Motzfeldt is regarded as one of the oldest centres in the Gardar province. Blaxland et al. (1978) reported a whole-rock Rb–Sr

age of $1,282 \pm 30$ Ma for the centre (recalculated using decay constants of Steiger and Jäger 1977), which has been regarded as an estimate of the age of emplacement for the Motzfeldt centre. However, feldspar and mica, usually the host of Rb in igneous rocks, have experienced intense alteration in the Motzfeldt Centre which would permit significant opening of the isotopic system. Discrepancies between U–Pb age estimates from zircon and those from Rb–Sr isotope studies have been reported by, for example, Finch et al. (2001b) in the Gardar Nunarsuit pegmatite.

Finch et al. (2001a) obtained a Rb–Sr isochron age of $1,226 \pm 27$ Ma for the nearby North Motzfeldt centre, a small satellite intrusion north-east of the MSF, and inferred from cross-cutting relations that the North Motzfeldt centre predates the emplacement of the MSF. If North Motzfeldt predates the Motzfeldt Centre, as was suggested by Emeleus and Harry (1970), then the MSF must be significantly younger than the age estimate of Blaxland et al. (1978). From this observation, Finch et al. (2001a) tentatively suggested that Motzfeldt be divided into two periods of magmatism termed ‘Early’ and ‘Late’ Motzfeldt separated by a significant hiatus. Early Motzfeldt would comprise the FDF and be of Early Gardar age with Late Motzfeldt (including the MSF and GF) post-dating the emplacement of the North Motzfeldt syenites. However, the U–Pb age of $1,273 \pm 6$ Ma (Fig. 5c) obtained from preserved magmatic zones of zircon provides an age for magmatism within the MSF. Therefore, the MSF is older than the North Motzfeldt complex and is the oldest record of Igaliko magmatism. We therefore infer that the whole of Motzfeldt (FDF, MSF, GF) is early Gardar in age.

Timing and duration of alteration

The rock types of the Motzfeldt Centre, their textural relations, mineralogical and chemical characteristics are all indicative of extreme differentiation and evolution of a highly fractionated peralkaline melt. The geological history of the MSF is particularly complex, encompassing both a convoluted magmatic history and an extended halogen-rich hydrothermal phase (Finch et al. 1995). The differentiation

Table 3 Pb–Pb data from pyrochlores from the Motzfeldt SØ formation

Pyrochlores	$^{208}\text{Pb}/^{204}\text{Pb}$	1σ	$^{207}\text{Pb}/^{204}\text{Pb}$	1σ	$^{206}\text{Pb}/^{204}\text{Pb}$	1σ
GJM06-18-1a	46.4597	0.2800	27.0723	0.4800	160.7250	5.9000
GJM06-18-1b	45.3652	0.0910	23.7075	0.1700	119.5320	2.1000
GJM06-18-1c	46.9089	0.1400	28.8965	0.1800	182.8300	2.2000
GJM06-18-2a	53.0037	0.7200	51.0972	2.2000	448.2760	27.0000
GJM06-18-2b	52.1801	0.5600	45.1822	1.6000	377.4420	19.0000
GJM06-18-3a	46.7132	0.0930	28.6910	0.1600	181.8910	2.0000
GJM06-18-4	44.7638	0.0540	27.2137	0.4400	162.9110	5.4000
GJM06-18-5	50.3323	0.2700	31.7982	0.6300	217.4280	7.6000
GJM06-18-6	48.5686	0.2900	28.5604	0.7100	179.9220	8.6000
GJM06-18-7a	45.9751	0.1100	29.4253	0.5300	189.7130	6.4000
GJM06-18-7b	46.7490	0.1000	25.2098	0.2500	138.1900	3.2000
GJM06-18-9a	47.4807	0.1100	34.1151	0.2000	245.9780	2.3000
GJM06-18-9b	47.8124	0.4400	35.3298	1.2000	260.2530	14.0000
GJM06-18-9c	47.5678	0.6500	34.5665	1.7000	250.3040	21.0000
GJM06-18-10	103.0580	0.3100	65.8644	0.5500	632.2430	5.2000
GJM06-18-13	47.7688	0.0830	31.0498	0.3900	208.4230	4.7000
GJM06-18-15	45.1189	0.1100	22.5040	0.2300	105.4390	2.8000
GJM06-18-17	47.1050	0.2500	28.0492	0.6600	172.1790	8.1000
GJM06-18-19	47.6747	0.3300	35.0554	0.7300	256.9130	8.7000
GJM06-18-24	54.0890	0.3700	35.0997	0.5900	259.2370	7.3000
GJM06-64-6a	54.4784	0.1800	66.1778	0.8100	632.7460	9.7000
GJM06-64-6b	67.3031	0.2100	111.1490	0.4200	1174.4100	5.1000
GJM06-64-7	68.4211	0.2200	112.0580	0.6200	1183.5400	7.9000
GJM06-64-8	62.8806	0.2600	100.4850	0.7500	1044.0500	9.0000
GJM06-64-10	37.6506	0.0180	21.5885	0.0610	92.9251	0.7500
GJM06-64-13	39.0508	0.0720	26.5540	0.2500	153.2910	3.0000
GJM06-64-14	61.1372	0.3000	91.1593	0.9100	931.2140	11.0000
GJM06-64-17	52.0623	0.8300	60.6166	2.6000	565.2730	32.0000
GJM06-64-19a	59.9687	0.5400	87.8031	1.6000	895.1380	19.0000
GJM06-64-19b	48.5539	0.4000	52.3165	1.5000	465.5930	18.0000
GJM06-64-22	61.3027	0.8100	69.9746	1.6000	675.6040	19.0000
GJM06-64-23	63.0179	0.1200	101.6560	0.4400	1060.5200	5.5000
GJM06-64-25	65.2969	0.1200	96.6401	0.2900	998.9340	3.6000
GJM06-64-26	44.6401	0.1000	40.5179	0.3000	336.1280	3.1000

Further details are in the supplementary information

of each phase is often poorly constrained owing to the continuum from the magmatic phase into the hydrothermal phase. In the MSF the temporal evolution of a volatile-enriched residual fluid extended the crystallisation interval of the MSF and gave rise to multiple phases of hydrothermal alteration (McCreath 2009). This alteration is particularly well expressed in pyrochlore group minerals from the highly evolved and extremely altered units of the formation, which show complex textural and microchemical features that indicate fluid–rock interaction during the late magmatic to hydrothermal stages of the centre’s history (McCreath 2009).

Many studies assume that hydrothermal activity is immediately post-emplacement, and therefore effectively synchronous (within the errors of radiometric age dating) with the timing of emplacement. In the MSF, however, multiple phases of hydrothermal alteration have been encoded in pyrochlore group minerals associated with the evolution of an alkaline hydrothermal residuum (McCreath 2009 and Fig. 2). In another part of the Igaliko complex, South Qôroq (Finch 1995), younger fluids from one episode of magmatism overprinted the chemistry of older rocks. Hence it is credible that the age of the pervasive hydrothermal alteration that characterises

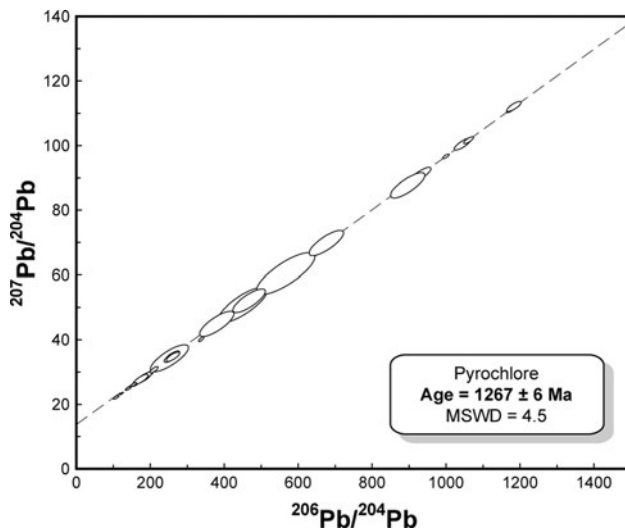


Fig. 6 Pb–Pb systematics for pyrochlore separates from the Motzfeldt centre. Analyses are shown as $\pm 2\sigma$ error ellipses. The line is a regression and the *inset* shows the resultant age estimate

present-day MSF rocks is significantly younger than MSF magmatism.

In the present study, one particular objective has been to develop methods to date the magmatic and hydrothermal episodes independently. We use a combination of luminescence petrography of zircons with selected area LAM-MC-ICPMS to examine pristine and altered parts of zircon crystals. The magmatic zircons are generally concordant giving a robust age estimate for the emplacement of the MSF as $1,273 \pm 6$ Ma. Analysing the altered zircons and interpreting the data at face value suggests that magmatism took place at $1,261 \pm 28$ Ma and a process of hydrothermal alteration took place in Motzfeldt at 349 ± 60 Ma, ~ 900 Ma later. The younger intercept on the Discordia line could represent a subtle crustal uplift or reheating episode at that time, but it could be a spurious age estimate. The age period identified in the altered zircons overlaps with the very end of fault movement in the Greenland Caledonides (Gilotti and McClelland 2008). The Laurentian plate margin was $\sim 1,000$ km E of current exposure in Southern Greenland before the opening of the Atlantic (Henriksen and Higgins 2008) and the closest surviving Caledonian rocks to Motzfeldt are now the Caledonides of NW Scotland and Ireland (Leslie and Higgins 2008). The collision of Laurentia and Baltica (the Scandian orogeny) is dated as ~ 430 Ma and was followed by subduction-related magmatism up to the Early Devonian (400 Ma). There are very few constraints on the timing of faults that cross-cut the Gardar centres and it is difficult to rule out the possibility that they express post-Scandian orogenic collapse directed towards the foreland. Such movement may have reactivated older Gardar fault systems (cf. Liégeois et al.

2005). However, analysis of common lead (from $^{206}\text{Pb}/^{204}\text{Pb}$ data, Table 1) may also provide insights into the origins of the ‘Caledonian’ intercept. The discordant points have higher common lead values (expressed as lower 206/204 ratios). Analyses without significant common lead (e.g. $206/204 > 5,000$) are almost exclusively concordant points. This introduces the possibility that hydrothermal alteration of the zircons, by geochemically opening the zircon system, has introduced common lead. This correlation may suggest that introduction of common lead is the cause of the apparent ‘Caledonian’ intercept.

The data from zircon have been compared and contrasted with the Pb–Pb isotope systematics from pyrochlore. Pyrochlore textures by BSEI show them to be almost entirely recrystallised in the late-stage hydrothermal environment during (Fig. 2) and U contents are frequently enhanced during alteration (McCreath 2009). Hence isotopic opening of the system during the alteration is inferred. The pyrochlores define a good ($\text{MSWD} = 4.5$) isochron age of $1,267 \pm 6$ Ma, which, given the widespread alteration, we consider an age for the hydrothermal event. This age is within error of the magmatic age of $1,273 \pm 8$ Ma obtained from magmatic zircons.

We have compared the data from zircon to pyrochlore. Taking the zircon data on face value, the hydrothermal alteration at Motzfeldt took place at 349 ± 60 Ma and yet that of the pyrochlores ($1,267 \pm 6$ Ma) occurred within error of the magmatism ($1,273 \pm 8$ Ma). However, the alteration of zircon (Fig. 3) was achieved by an aggressive hydrothermal fluid that mobilised HFSE such as Zr, Nb, Ta, U and Th. Such fluids are inferred to be F-rich and are characteristic of alkaline igneous rocks (Finch et al. 1995). Hence we infer that the fluid interaction expressed in the zircon is unlikely solely to result from a process of fault reactivation and must be Gardar in age. It may be that the alteration that in Gardar times modified the zircon structure such that it was more susceptible than pyrochlore to reheating associated with fault movements at ~ 350 Ma. However, the most likely conclusion is that the ‘Caledonian’ intercept on the Discordia line in zircon is a spurious age caused by open system behaviour and/or inadequacies in the common lead corrections. The overlap of the magmatic age and the hydrothermal age in pyrochlore indicates that the magmatism and associated mineralisation of the MSF, the target of the present study, cannot be distinguished in time. Importantly, the F-rich hydrothermal activity was not a secondary event of significantly younger origin, as it is in the case of the South Qôroq/Igdlerfigssalik centres (Finch 1995), but was effectively synchronous with the emplacement and evolution of the centre. We conclude that analysis of altered (discordant) and magmatic (concordant) zircon has proved to be in this field area an unreliable route to determine the ages of hydrothermal

activity. This is consistent with [Geisler et al. \(2002\)](#), [Hansen and Friderichsen \(1989\)](#), [Pidgion \(1992\)](#), [Pidgion et al. \(1998\)](#), [Sinha et al. \(1992\)](#) who all show that the U–Pb system in zircon is susceptible to isotopic exchange in the subsolidus. Detailed textural analysis of pyrochlore and zircon in the same intrusions followed by precise radiogenic isotopic analysis has provided a route to deconvolute the magmatic and hydrothermal ages of these igneous rocks.

Conclusions

Geochemical and isotopic analyses of zircons and pyrochlores from the highly altered units of the Motzfeldt Sø Formation (MSF), part of the Motzfeldt complex in the Gardar Province encode information relating to the primary magmatic and secondary hydrothermal phases of the centre's history, providing independent age estimates of each of these events. Using the U–Pb system in zircons, a new age estimate of the magmatic emplacement of the centre has been obtained at $1,273 \pm 6$ Ma. Pb–Pb isotope systematics from pyrochlore minerals, which show textural and microchemical evidence for polyphase fluid interaction, define an isochron age of $1,267 \pm 6$ Ma for the age of isotopic closure of the pyrochlore following alteration during the subsolidus. These dates overlap, suggesting that the hydrothermal alteration encoded in the pyrochlore of the MSF is a product of the alkaline hydrothermal phase, within ~ 6 Ma of the magmatic phase. However, in many centres, multiphase hydrothermal activity may significantly post-date the magmatic history of the area, associated with repeated magmatism centred about, or close to, the same focus. Such settings provide excellent opportunity to study the timing of textural and chemical changes associated with fluid–rock interactions in polyphase hydrothermal systems.

Fluid–mineral interaction during the hydrothermal phase resulted in pervasive alteration of the MSF, including zircon which is often considered isotopically closed under extreme geological environments. However, we show that the stability of the U–Pb system was susceptible to isotopic exchange (cf. [Geisler et al. 2002](#); [Hansen and Friderichsen 1989](#); [Pidgion 1992](#); [Pidgion et al. 1998](#); [Sinha et al. 1992](#)) at Motzfeldt. Zircons from the MSF show isotopic discordance from altered areas of the crystal. Nevertheless, concordant age estimates can be obtained from selective analysis of unaltered, magmatic parts of the same zircon crystals. This has implications for bulk zircon chronology in alkaline igneous environments where late-stage fluid activity is common. Ages obtained in bulk zircons mix material from magmatic and altered zircon. Such material may provide age estimates that mix concordant with discordant zircon material, which has experienced opening of

the U–Pb system. Such ages may not truly represent the magmatic crystallisation and alteration will give progressively younger ages. Therefore, in environments where fluid–rock interaction is evident, a detailed textural and microchemical approach must be made prior to isotopic age determinations.

Acknowledgments Work for the present study was carried out during tenure of a postgraduate studentship funded by Angus and Ross plc. The assistance of Tom Andersen with isotopic determinations is gratefully acknowledged. Field assistance was provided by Johannes Schönenberger, Teal Riley and Malcolm Wilkinson. The manuscript was greatly improved by detailed and constructive comments from Kathryn Goodenough and Jean-Pierre Liégeois. The present manuscript is contribution no. 26 from the Isotope Geology Laboratory at the University of Oslo.

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