Recycling Argon through Metamorphic Reactions: the Record in Symplectites

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Recycling argon through metamorphic reactions: The record in symplectites

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Abstract
The 40Ar/39Ar ages of metamorphic micas that crystallized at high temperatures are commonly interpreted as cooling ages, with grains considered to have lost 40Ar via thermally-driven diffusion into the grain boundary network. Recently reported laser-ablation data suggest that the spatial distribution of Ar in metamorphic micas does not always conform to the patterns predicted by diffusion theory and that despite high metamorphic temperatures, argon was not removed efficiently from the local system during metamorphic evolution. In the Western Gneiss Region (WGR), Norway, felsic gneisses preserve microtextural evidence for the breakdown of phengite to biotite and plagioclase symplectites during near isothermal decompression from c. 20–25 to c. 8–12 kbar at ~700 °C. These samples provide an ideal natural laboratory to assess whether the complete replacement of one K-bearing mineral by another at high temperatures completely ‘resets’ the Ar clock, or whether there is some inheritance of 40Ar in the neocrystallized phase. The timing of the high-temperature portion of the WGR metamorphic cycle has been well constrained in previous studies. However, the timing of cooling following the overprint is still much debated. In-situ laser ablation spot dating in phengite, biotite-plagioclase symplectites and coarser, texturally later biotite yielded 40Ar/39Ar ages that span much of the metamorphic cycle. Together these data show that despite residence at temperatures of ~700 °C, Ar is not completely removed by diffusive loss or during metamorphic recrystallization. Instead, Ar released during phengite breakdown appears to be partially reincorporated into the newly crystallizing biotite and plagioclase (or is trapped in fluid inclusions in those phases) within a close system. Our data show that the microtextural and petrographic evolution of the sample being dated provides a critical framework in which local 40Ar recycling can be tracked, thus potentially allowing 40Ar/39Ar dates to be linked more accurately to metamorphic history.

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1. Introduction

⁴⁰Ar/³⁹Ar dating is commonly used to constrain the timing and the rate of cooling in high temperature metamorphic terranes via the closure temperature (Tc) formulation suggested by Dodson (1973). This formulation is underpinned by a number of assumptions: (1) that the mineral in question (re)crystallized with an insignificant initial ⁴⁰Ar concentration; (2) that thermally-activated volume diffusion, observing Fick’s 2nd law, redistributed Ar within the mineral after its production, (3) that the grain boundary network surrounding the mineral had a sufficiently low Ar concentration and high connectivity to act as an infinite reservoir (i.e. an ‘open’ grain boundary system) during the time at which temperatures were high enough for efficient diffusion, and (4) that the grain crystallized at temperatures high enough for diffusion to initially be efficient. Furthermore, the formulation requires a cooling path of 1/T shape.

Many studies document equivocal metamorphic ⁴⁰Ar/³⁹Ar muscovite, phengite (high pressure (HP) muscovite) and biotite ages that are ‘too old’ to be interpreted as representing the timing of cooling when assessed within a chronological framework defined by higher closure-temperature chronometers such as U—Pb zircon (e.g. Baxter et al., 2002; Li et al., 1994; Warren et al., 2012b). These results are most commonly documented in HP metamorphic terranes, where the temperature was relatively low (< 600 °C), the timescales of metamorphism commonly short (< 10 Ma), and fluid availability and permeability is low, thus limiting the efficiency of diffusion and efficiency of Ar removal from the grain boundary network. There has been much debate about whether the “too old” ages are the result of contamination with ‘excess’ or ‘inherited’ ⁴⁰Ar (decoupled from parent K or inherited from an earlier generation of mineral growth), whether they represent the timing of mineral crystallization, or a combination of the above (e.g. Allaz et al., 2011; Beltrando et al., 2013; de Sigoyer et al., 2000; Di Vincenzo, 2006; Hacker et al., 2003; Li et al., 1999; Putlitz et al., 2005;
2. Methods

2.1. Electron microprobe analysis

Major phases were characterized by back-scattered electron images and electron-microprobe analyses of polished thin sections on the Cameca SX100 (5 spectrometer) Electron Microprobe (EMP) at the Open University. Operating conditions were set to 15 kV and 20 nA, with a defocused beam of 10 μm. A ZAF matrix correction routine was applied and a selection of national standards was used for calibration. Unknowns were bracketed by analyses of internal secondary standards; uncertainty on major element concentrations is <1%. X-ray element maps of Al, Ca, Mg, Si, and Ti in phengite, biotite, and symplectites; and Al, Ca, Fe, Mg, and Si in garnet were obtained from polished thin sections scanned in mosaic mode (4 × 7 grid) with operating conditions of 20 kV and 20 nA. Dwell time was set at 5 ms with a step size of 20 μm. Chemical formulae were calculated stoichiometrically based on 12 oxygens for garnet, 8 for plagioclase, 22 for phengite and biotite, and 23 for amphibole. Representative core-rim analyses of phengite, biotite and plagioclase are shown in Table 1. Full geochemical analyses are provided in Supplementary Table S.1. Minerals abbreviations used in the tables, figures and text are after Whitney and Evans (2010).

2.2. Bulk chemistry determination

Major elements were determined using sample-glass discs prepared by fusing a 5:1 ratio mix of lithium metaborate/tetraborate flux (Spectroflux 105) and powdered samples prepared by jaw crushing and temna mill. Aliquots of ~3 g of sample powder were dried overnight in porcelain crucibles in an oven at ~100 °C. 3.59 g of flux and 0.7 g of sample powder were weighted into platinum crucibles and stirred with a glass rod to ensure homogeneity, before being fired in a furnace at 1100 °C for ~20 min. Sample mixtures were stirred every 5 min to remove gas bubbles and promote homogeneity. The melt was poured into a pre-heated brass mold and formed using a sprung press. Discs were left to cool prior to analysis. 1.2 g of sample powder from the dried
aliquots was weighed to four decimal places into pre-ignited alumina crucibles. Samples were ignited in the furnace at 1000 °C for 1 h, cooled for 15 min and reweighed to four decimal places. The difference in weight before and after ignition was used to assess the mass loss on ignition for each sample. Trace elements were determined from pressed sample powder pellets formed by thoroughly mixing approximately 9.5 g of sample powder with 0.9 ml of Polyvinylpyrrolidone (PVP)-methyl cellulose binder using the "bag technique" (Watson, 1996). The mixture was emptied into a hardened steel mold and formed into a pellet using a hydraulic press.

Table 1
Representative mineral chemistry of phengite, biotite, plagioclase, and amphibole.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Phengite</th>
<th>Idioblastic biotite</th>
<th>Symplectic biotite</th>
<th>Plagioclase</th>
<th>Amphibole</th>
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<tr>
<td></td>
<td>Core</td>
<td>Rim</td>
<td>Core</td>
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<tr>
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Trace elements were determined from pressed sample powder pellets formed by thoroughly mixing approximately 9.5 g of sample powder with 0.9 ml of Polyvinylpyrrolidone (PVP)-methyl cellulose binder using the “bag technique” (Watson, 1996). The mixture was emptied into a hardened steel mold and formed into a pellet using a hydraulic press.
press. The sample pellets were dried overnight in the oven at ~100 °C prior to analysis. Results of XRF analyses are presented in Supplementary Material S.2.

2.3. Thermodynamic modelling

Symplectites form from the breakdown of unstable HP phases (e.g. phengite and pyroxene) into two or more minerals at lower P-T conditions. Symplectites provide evidence that textural and compositional equilibrium was attained only on a domainal scale. This lack of textural equilibrium represents a challenge when modelling the metamorphic evolution of the sample. In the present case, a simplified approach was used to constrain the P-T evolution of the major phases:

(i) the whole rock composition, determined by XRF, was used to model the growth of the HP assemblage as well as the symplectites. Microstructural evidence suggests that amphibole, biotite, and plagioclase formed from the breakdown of phengite and pyroxene (most probably omphacite, e.g. Wain et al., 2000). Garnets were replaced by fine grained aggregates of biotite and plagioclase. Following previous work (e.g. Godard and Mabit, 1998; Groppo et al., 2015) we have assumed the whole rock volume was chemically involved and behaving as a closed-system during symplectite formation;

(ii) the retrograde formation of amphibole–plagioclase symplectites was constrained by the plagioclase–hornblende thermobarometer (temperatures using the calibration of Blundy and Holland, 1990; Holland and Blundy, 1994 and pressures using the calibrations of Anderson and Smith, 1995; Schmidt, 1992);

(iii) the reconstructed metamorphic evolution was compared with published P–T paths for the WGR.

The evolution of sample was modelled in the simplified MmNCfKfMfSfMf system using Perple_X (version 6.6.8. Connolly, 1990). The pseudosection was calculated using the internally consistent thermodynamic database (hp04ver.dat) and the equation of state for H2O of Holland and Powell (1998) and Holland and Powell (2011). Solid solution models include garnet (Holland and Powell, 1998), omphacite (Holland and Powell, 1996), plagioclase (Fuhrman and Lindsley, 1988), phengite (Holland and Powell, 1998), biotite (Tajčmanová et al., 2009), chlorite (Holland et al., 1998), amphibole (Dale et al., 2000), staurolite (Holland and Powell, 1998), chloritoid (White et al., 2000), and melt (Holland and Powell, 2001; White et al., 2001). Additionally, quartz, aluminosilicates, zoisite, lawsonite, titanite, rutile, and ilmenite were included as pure phases.

2.4. Diffusion modelling

In order to determine the expected 40Ar/39Ar ‘cooling’ ages of phengite, biotite and plagioclase for a purely diffusive, open system given the best-fit post-crystallization P–T–t history, diffusion ages were modelled using DiffArg, which incorporates the pressure-dependance of Ar diffusion in muscovite (modified from DiffArg after Wheeler, 1996; Warren et al., 2012a). All models were calculated for cylindrical diffusion geometry, with a Crank–Nicholson time integration solver, and a time step of 10 (Wheeler, 1996).

On the basis of petrographic observation constraints, 1 mm radius phengite was modelled as crystallizing at peak pressure conditions of 23.5 kbar and 710 °C. It then decompressed to 12 kbar (at 680 °C) over 12 Ma (calculated from the difference between the youngest published U–Pb zircon, and the weighted average titanite age (Root et al., 2004; Spencer et al., 2013) followed by linear cooling at rates of 10, 25, 50, 70, and 100°C Ma−1. Current estimates for the cooling rates of the WGR range from 20 to 90°C Ma−1 based on the assumption that 40Ar/39Ar ages represent cooling through the muscovite closure temperature of ~450 °C (Hacker et al., 2010; Kylander-Clark et al., 2008; Root et al., 2004, 2005; Walsh et al., 2013). Decompression set so that P reached zero at the same time as T.

For modelling purposes, biotite and plagioclase were assumed to have crystallized at conditions of 12 kbar and 680 °C. Cooling initiated immediately in the models and multiple models were run with the same cooling rates as the white mica models. Idioblastic biotite was modelled using a grain radius of 0.5 mm while the symplectitic biotite and plagioclase were modelled with a grain radius of 0.25 mm.

To determine the possible affects of variations in the model starting temperatures, pressures, grain sizes, and cooling rates, a sensitivity analysis was performed. Muscovite peak temperatures and pressures were modelled at ±50 °C and ±1.5 kbar, to reflect uncertainties in the modelled peak metamorphic conditions. Amphibolite-facies conditions for muscovite, biotite, and plagioclase were also modelled at ±50 °C and ±5 kbar. Grain size was modelled at 0.25–1.5 mm for each mineral at the above mentioned cooling rates.

Model results and sensitivity analysis (Table 3a, b, and Supplementary Tables S.4) are reported as bulk (area-integrated) age differences between the timing of cooling initiation based upon the U–Pb zircon and titanite ages, and the modelled grain age.

2.5. 40Ar/39Ar analysis

Polished thick sections (~250 μm thick, Fig. 2D) were prepared by adhesion to glass slides with cyanoacrylate (“super glue”). Sections were removed from the glass by soaking in acetone for up to 24 h and then cut into 5 × 5 mm squares, washed in acetone or methanol and distilled water, and packed into aluminum foil packets, which were irradiated at McMaster University Reactor, Ontario.

High spatial resolution single spot and traverse analyses on polished thick sections were achieved using a New Wave Systems Nd-YAG 213 nm ultraviolet (UV) laser coupled to a Nu Instruments Noblesse gas mass spectrometer run in single-collector mode. Prior to analysis, samples were loaded into an ultra-high vacuum laser port, warmed under a heat lamp for 8 h to reduce atmospheric background levels and left to pump down for at least 48 h. Analyses consisted of ablating 50/30/15 μm diameter spots for 90 s followed by 90 s gettering time. Active gas species were gettered using two SAES AP10 Zr-Al getters (one at room temperature and the other at 450 °C). Peaks of 40Ar, 39Ar, 38Ar, and 36Ar were scanned ten times each and the data extrapolated back to the inlet time (time zero).

Irradiation flux was monitored using the biotite standard CA-1550 with an age of 99.74 ± 0.10 Ma (Renne et al., 2011). Sample J values and uncertainties are given in Supplementary Table S.3 and were calculated by linear interpolation between two bracketing standards. The following corrections were applied to the standards: (39Ar/37Ar)Ca = 0.00065 ± 0.0000033, (36Ar/37Ar)Ca = 0.0002654 ± 0.0000013, (40Ar/39Ar)K = 0.0085 ± 0.0000425 based on analyses of Ca and K salts; only the K correction was applied to the analyzed samples due to negligible Ca in the sample micas. Background (blank) measurements bracketed every 1–2 sample measurements. Analyses were corrected for mass spectrometer discrimination using an assumed value of 295, determined from regular analysis of modern glass.

Data were reduced using the in-house software package ArMaDiLo using a decay constant of 5.530 × 10−10 ± 0.013 a−1 (Renne et al., 2011). Age uncertainties are reported to 2σ; uncertainties on the isotopic measurements are reported to 1σ. The maximum and minimum phengite, biotite, and plagioclase 40Ar/39Ar ages are reported in Table 2. The full dataset is provided in Supplementary Table S.3.

3. Results

3.1. Petrography and mineral chemistry

Sample NF42 is a medium-grained, unfoliated and highly symplectized gneiss containing quartz, garnet, biotite, symplectites of
biotite-plagioclase and amphibole-plagioclase, and phengite (Figs. 2 and 3, and Supplementary Material S.5). Accessory phases include kyanite, chlorite, rutile, apatite, and zircon. There is no petrographic evidence for partial melting in this sample (Peterman et al., 2009; Wain et al., 2000).

Phengite relics make up ~5–6% of the sample (Fig. 2A). Grain radii vary from 300 μm to 1100 μm (Fig. 2A, Table 1). Si concentrations range from 6.8 atoms per formula unit in the geographic core to 6.6 at in narrow (<50 μm) rims (Fig. 3A). Grains are commonly replaced at their rims by biotite-plagioclase symplectites.

Biotite crystallizes in two different microstructural, and textural domains: (i) in symplectites pseudomorphing phengite, with the grain size coarsening outwards from core to rim (40–200μm laths, Fig. 3C), and (ii) randomly oriented aggregates of grains within the matrix (300–1200 μm, Fig. 3B). The biotite–plagioclase symplectites make up approximately ~50 vol% (Fig. 2B). Biotite in the symplectites is Mg-rich with XMg (Mg/(Mg + Fe) values of 0.65–0.70 and Ti contents ranging from 0.12–0.31 apfu (Table 1). Geochemical analysis and maps (Fig. 3C) show that each grain is homogeneous in geochemistry; and that the variability seen is between individual grains within the symplectite (detailed geochemical maps are supplied Supplementary Material S.5).

Idioblastic biotites form approximately 10 modal% of the sample (Fig. 2C) and are found in the matrix, occasionally adjacent to garnet and quartz, but never adjacent to phengite. They are similar in composition to the symplectic biotites, with XMg values of 0.67–0.73 and Ti contents ranging from 0.21–0.32 apfu (Table 1). Geochemical maps show that these grains are relatively homogeneous cores and narrow (<5 μm) rims (Fig. 3D). The idioblastic grains contain inclusions of plagioclase (Fig. 2C), suggesting that they formed by coarsening of the symplectite biotites.

Plagioclase is found within the symplectic domains associated with biotite or amphibole and forms anhedral grains with a typical grain

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Mineral</th>
<th>n*</th>
<th>Oldest age (Ma ± 1σ)</th>
<th>Youngest age (Ma ± 1σ)</th>
<th>Wtd Mean age (Ma ± 1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF42</td>
<td>Krokkenakken</td>
<td>Phengite</td>
<td>41</td>
<td>517.7 ± 2.8</td>
<td>388.8 ± 2.3</td>
<td>398.1 ± 1.3</td>
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<tr>
<td></td>
<td></td>
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<td>25</td>
<td>398.8 ± 3.1</td>
<td>385.6 ± 4.7</td>
<td>392.2 ± 1.1</td>
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<tr>
<td></td>
<td></td>
<td>Symplectic Biotite</td>
<td>10</td>
<td>391 ± 11</td>
<td>375 ± 20</td>
<td>384.8 ± 2.4</td>
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<tr>
<td></td>
<td></td>
<td>Symplectic Plagioclase</td>
<td>12</td>
<td>434 ± 42</td>
<td>378 ± 65</td>
<td>392.0 ± 7.5</td>
</tr>
</tbody>
</table>

n* = number of spots
Sample Location 61°54′53.73″ N 005°20′16.49″ E
size of 80–140 μm (Fig. 2B). X-ray compositional maps (Fig. 3B) show that the grains are compositionally zoned, with low-Ca cores (An_{11}Ab_{39}Or_{50}) and higher-Ca rims (An_{43}Ab_{14}Or_{50}).

Garnet crystals form 10–15% of the sample, are sub-to anhedral in shape and range from 0.5–15 mm in diameter. Garnets contain abundant, randomly-oriented inclusions of quartz, rutile, white mica, and apatite. Minor replacement of garnet by biotite and plagioclase (Fig. 2A-C) is visible at grain rims. Grains are zoned in X_{Fe} (0.66 in the core to 0.50 in the rim) and X_{Mg} (0.14 in the core to 0.31 at the rim), whilst X_{Ca} is more homogeneous, varying from 0.18 in the core to 0.19 at the rim. Some grains show a high-Ca annulus between the core and rim at X_{Ca}~0.23. X_{Mn} is low throughout garnet at 0.01–0.02 (Supplementary Material S.5).

Fine-grained amphibole is associated with plagioclase in symplectites that form ~10 modal % of the sample. Amphiboles are magnesio-hornblende in composition with X_{Mg} = 0.68–0.74 (Table 1).

Rare small kyanite crystals (50–100 μm) are present in the matrix (mostly at the contact with garnet rims) whilst rutile, zircon, and apatite are present in both the matrix and included in garnet (Supplementary Material S.5).

### 3.2. Pressure-temperature path

The pseudosection in Fig. 4a shows the modelled metamorphic assemblages for the considered bulk composition between 2.5 and 25 kbar and 300–900 °C. The model shows that the compositions of phengite and garnet rim (S_{ph} = 3.35–3.37; F_{gr} = 0.54–0.46 M_{gr} = 0.26–0.34 C_{gr} = 0.15–0.22) overlap in fields where the high-pressure phengite is stable with garnet + omphacite + rutile + quartz ± kyanite ± amphibole between 660 and 760 °C and 22–25 kbar (Fig. 4b).

During decompression from the HP stage, at an approximate T of 700 °C, the pseudosection suggests that feldspar becomes stable at <16 kbar and biotite at <12 kbar. This marks the beginning of symplectite formation; phengite is no longer stable at conditions below 7–11 kbar and <660 °C. The X_{Mg} and X_{Na} compositions of biotite and plagioclase help to constrain the conditions of phengite replacement by biotite-plagioclase symplectites. The modelled isopleths in biotite and plagioclase suggest that the symplectites formed at T < 720 °C and P < 12 kbar following (near) isothermal decompression from peak pressures (Fig. 4b).

The compositions of amphibole and plagioclase in equilibrium in symplectic domains constrain the PT conditions of replacement of earlier pyroxene. The amphibole-plagioclase thermometer (Anderson and Smith, 1995; Blundy and Holland, 1990; Holland and Blundy, 1994; Schmidt, 1992) suggests crystallization at 660 ± 70 °C and 7.9 ± 1.1 kbar.

### 3.3. Diffusion modelling

Diffusion modelling results are summarized in Table 3a. The model results suggest that in an open, purely diffusive system, 1 mm radius phengite grains should yield bulk ages that are 29.1–13.2 Ma younger than the time at which cooling started (Δt), depending on the cooling rate (10–100 °C/Myr −1). A conservative estimate for the cooling rate of 25 °C/Myr −1 suggests Δt = 11.1 Ma. Furthermore, the models suggest that 0.5 mm biotite grains should yield Δt = 12.5 Ma at 25 °C/Myr −1, 32.9 Ma at 10 °C/Myr −1, and 2.9 Ma at 100 °C/Myr −1. 0.25 mm biotite grains cooling at 25 °C/Myr −1 should yield Δt = 13.4 Ma, and 0.25 mm plagioclase grains should yield Δt = 13.2 Ma (slower and faster cooling at 10–100 °C/Myr −1 should yield age differences of 35.0–3.1 and 34.6–3.1 Ma, for 0.25 mm biotite and plagioclase respectively).

### 3.4. 40Ar/39Ar laser spot dating

Forty-one spots on 5 phengite grains yielded ages varying from 517.7 ± 5.6 Ma to 388.8 ± 4.6 Ma (Fig. 5A). Age distributions are patchy, with clusters of ‘older’ ages in regions that are neither associated spatially with the geographical nor the geochemical cores of the phengite (Fig. 5A). Ten spots on 3 different symplectite biotite grains yielded ages from 488 ± 36 Ma to 329.8 ± 9.2 Ma (Fig. 5 B1, B2). Twelve spots on 12 different symplectite plagioclase grains yielded highly variable 40Ar/39Ar ages from 687 ± 36 to 93 ± 10 Ma (Fig. 5 B1, B2). Three analyses had 39Ar measured/39Ar background measurements <2 (analyses GM7, GM11, and GM12). The calculated ages have large errors, are therefore not considered robust and are ignored for the purposes of further discussion. Ignoring these three analyses, the plagioclase yielded ages ranging from 434 ± 84 Ma to 378 ± 130 Ma. Twenty-six spots on 6 grains of idiomorphic biotite yielded a range of ages from 448 ± 8 to 376.6 ± 6.4 Ma. There is no systematic distribution of age within the grains (Fig. 5C).

### 4. Discussion

#### 4.1. Metamorphic evolution

Three main metamorphic stages have been recognized in the Krokkenakken gneisses based on microtextural relationships, crystal chemistry, conventional thermobarometry and pseudosection modelling.
The first stage occurs under prograde conditions with the growth of garnet. The major element zoning in the garnets core and rim are interpreted as reflecting this prograde growth. Peterman et al. (2009) have also documented prograde-zoned garnet at this locality. Eclogite-facies conditions followed the prograde growth of garnet and are characterized by the assemblage phengite + garnet + omphacite + quartz + rutile + amphibole ± kyanite. Because of the poor preservation of eclogitic mineral relics such as omphacite, this stage can only be loosely constrained at 20–25 kbar and 670–770 °C (Fig. 4b). The white mica solution model (Holland and Powell, 1998) correctly predicts the stability field of K-rich white micas but does not incorporate the right amount of Na. The main consequence of this is the modelled appearance of paragonite (Pg in Fig. 4a).

Although amphibole, interpreted as part of the HP assemblage, has not been observed in the sample, the model shows that the amount of it stable in these fields corresponds to <2 vol.%. Therefore, we cannot exclude that amphibole was part of the high-pressure assemblage and it was subsequently replaced by later phases. Kyanite probably once included in garnet rims later replaced by biotite + plagioclase aggregates (Supplementary Fig. S.5), has been interpreted as part of the same assemblage. The calculated HP conditions overlap with the data presented for the same area (e.g. Cuthbert et al., 2000; Wain, 1997).

Peak pressure conditions were followed by (near-)isothermal decompression to amphibolite-facies conditions of T = 700 °C and P < 12 kbar as documented by the growth of biotite-plagioclase and amphibole-plagioclase symplectites developed after phengite and pyroxene respectively. The association of amphibole and plagioclase in fine-grained symplectites has been documented in other HP gneisses from the WGR (e.g. Wain et al., 2000) and has been interpreted as forming from the breakdown of an HP pyroxene (e.g. omphacite). The pseudosection constraints presented here provide similar PT estimates to those previously presented for the WGR gneisses (e.g. Cuthbert et al., 2000; Engvik et al., 2007; Hacker, 2007; Johnson et al., 2007; Labrousse et al., 2004; Root et al., 2005; Terry et al., 2000; Terry and Robinson, 2003; Wain, 1957; Wain et al., 2000; Walsh and Hacker, 2004). These calculated conditions indicate that the amphibole-plagioclase symplectites most probably re-equilibrated at lower P–T conditions after formation.

The timing of titanite crystallization plays an important role in the interpretation of the 40Ar/39Ar age patterns, as the titanite U–Pb age has been used to constrain the amphibolite-facies recrystallization across the WGR (Krogh et al., 2011; Schärer and Labrousse, 2003; Spencer et al., 2013; Tucker et al., 1987). The conditions of titanite crystallization are controlled primarily by the bulk rock Ca/Al ratio (Frost et al., 2001). In rocks with high Ca/Al ratios, titanite can be stable up to granulite-facies conditions (Frost et al., 2001). However, in orthogneiss, such as those from the WGR, titanite is only stable at much lower P–T conditions (Frost et al., 2001). A large dataset of titanite U–Pb ages from across the WGR accompanied by pseudosections of different titanite-bearing rocks showed both that the ages are widely variable and that titanite is stable across a broad range of PT conditions depending on the bulk composition (Spencer et al., 2013). The titanite stability field in the pseudosection presented here (Fig. 4b) overlaps with the titanite-in reactions published by Spencer et al. (2013) for comparable bulk compositions at T < 500 °C and P < 12 kbar. Therefore, we suggest that titanite crystallization occurred syn- to post-symplectite formation.

4.2. Modelled vs. observed age ranges: Are the “ages” cooling ages?

The diffusion modelling predicts that at cooling rates of 25°CMa⁻¹, the phengite, idioblastic biotite, symplectite biotite and symplectite plagioclase grains should yield Δt of 11.1, 12.5, 13.4, and 13.2 Ma respectively.

The model results are variably sensitive to a number of uncertainties, many of which have previously been discussed in detail (Warren et al., 2012b). Most of the model input parameters affect the whole population, and would not generate a spread of ages, rather they would just shift the model age to older or younger values. For example uncertainties in the activation energy (Ea) and the diffusion coefficient (D) lead to an uncertainty of ±4 Ma on the resulting model age.

In the phengite models, varying the starting temperature and pressure by ±50 °C and ±1.5 kbar, respectively, showed no change in resulting modelled ages. Varying the amphibolite-facies temperature and pressure conditions by ±50 °C and ±5 kbar, respectively, leads
to an uncertainty on the resulting model age of ±5.3–0.6 Ma and 1.5–0.2 Ma for cooling rates from 10°CMa−1 to 100°CMa−1 (Table 3b).

For biotite and plagioclase models, varying the model starting temperature by ±50 °C results in uncertainties on the model ages of 5.0–0.2 Ma for cooling rates from 10°CMa−1 to 100°CMa−1 for both minerals (Table 3b).

For all other parameters being equal, the variation between the modelled age of grains between 1.5 mm to 0.25 mm yields a ±2.5 Ma and a ±1.5 Ma uncertainty on the final age of the plagioclase models, ±2.5–0.3 Ma uncertainty on the biotite models, and ±2.9–0.4 Ma uncertainty on the plagioclase models for cooling rates between 10°CMa−1 and 100°CMa−1 (Table 3b).

Dependent upon the bulk rock composition, titanite either crystallizes after the symplectite growth (as documented here), or may be contemporaneous with symplectite growth (Spencer et al., 2013). The reported U–Pb titanite ages for the Nordfjord area range from 399 to 379 Ma, with a weighted mean of 393 ± 4 Ma (Spencer et al., 2013). Since the diffusion models are calculated relative to the U–Pb zircon (Fig. 6), the phengite 40Ar/39Ar ages are mostly older than those predicted by diffusion models, regardless of whether the weighted mean or the youngest age is compared with the model results. The phengite ages are also generally older than the reference titanite age, suggesting that phengite displays little diffusive resetting despite the high temperatures (700–750 °C). Overall the phengite 40Ar/39Ar ages are not therefore interpretable as cooling ages, a conclusion also reached by previous studies (McDonald et al., 2016; Warren et al., 2012a).

Biotite ages are consistently younger, with a smaller spread than phengite, though the ages are still overall older than expected from the diffusion models (Fig. 6). There is little consistent difference in age between the smaller, earlier-crystallized biotite in the symplectite and the larger, later, idioblastic grains, although the idioblastic grains yield a wider range but with overlapping errors. The similar ages yielded by biotites across a range of grain sizes either suggests that diffusive loss of Ar was inefficient, even at temperatures >680 °C (and therefore

A) Diffusion modelling results. Shown are the predicted model 40Ar/39Ar ages for phengite, biotite, and plagioclase for various cooling rates given various starting ages for the timing of peak metamorphism (U–Pb zircon) and amphibolite-facies cooling (U–Pb titanite). The modelled time difference between the start of the model and the resulting age (Δt) for each of the minerals is shown at varying cooling rates. B) Results of sensitivity testing showing the standard deviation of the model age output by varying the peak temperature and pressure (Peak T, Peak P) of the phengite models, and the temperature and pressure of the the amphibolite-facies conditions (Amp T, Amp P) for phengite, biotite, and plagioclase.
that most of the ages cannot be considered true “Dodson” cooling ages), or that the rate of cooling experienced by this sample was fast enough to yield little difference between the biotite age of differing grain sizes.

The plagioclase ages also span a considerable range (434–378 Ma). The plagioclase has low K concentrations (average 0.1 wt%), and consequently some of the variability may be due to low measured 39Ar concentrations and the presence of fluid inclusions. It is therefore plausible that the elevated plagioclase 40Ar/39Ar ages represent either crystal-lattice-hosted or fluid-inclusion-hosted contamination by excess 40Ar.

Despite the uncertainty in the timing of initiation of cooling of the WGR, there is clearly a disparity between both the observed 40Ar/39Ar ages (and age ranges) and the modelled ages derived from DiffArg_P. Overall the data suggests that a diffusion model for Ar distribution that includes a fully open grain boundary network and a zero-concentration crystallization state is inadequate for the interpretation of the phengite, biotite, and plagioclase ages as cooling ages.

5. Implications: crystallization vs. contamination

As the 40Ar/39Ar phengite, biotite, and plagioclase ages measured in the WGR cannot be interpreted as simple thermally-activated diffusive loss in an open system, they may instead reflect either the timing of their crystallization, ‘contamination’ with excess 40Ar, inefficient diffusive loss or a combination.

5.1. Phengite

The pseudosection in Fig. 4 and petrographic textures (Fig. 2A) indicate that phengite crystallized at P < 25 kbar and T < 770 °C. The timing of peak metamorphism has been constrained by U–Pb zircon at c. 410–400 Ma (Kylander-Clark and Hacker, 2014; Root et al., 2004; Young and Kylander-Clark, 2015). Therefore, if the 40Ar/39Ar phengite ages represent the timing of their crystallization, they should be similar. The model results suggest that to be consistent with open system
cooling, the phengite ages should be 21–3 Ma younger than the timing of crystallization, depending upon the cooling rate.

The observed phengite $^{40}$Ar/$^{39}$Ar ages span a range of c. 518–389 Ma, far greater than the spread expected for crystallization ages. The ages between c. 400–389 Ma imply that these grains lost some $^{40}$Ar, but not enough compared to the loss expected for a fully open system. The ages $>$410 Ma suggest contamination that occurred during decompression, with Ar having diffused into the phengite from either the grain boundary fluid, adjacent grains, or incorporated into the phengite crystal lattice during crystallization. The data do not allow these two scenarios to be separated. The ‘old’ ages within the phengite crystals are concentrated in patches that are not associated with the geographic cores of the grains. Chemical maps (Fig. 3A) do not indicate the presence of zoning within the grains. The contaminating $^{40}$Ar may therefore be held within microstructural defects in the phengite.

5.2. Biotite

The pseudosection suggests that the biotite crystallized during near isothermal decompression at $P <$ 12 kbar, $T$–700 °C and pre-dates titanite formation. Therefore, the timing of biotite crystallization is constrained by the youngest U–Pb zircon age (400 Ma) and the weighted mean titanite age (393 Ma).

The symplectite biotite ages lie between c. 488–330 Ma, a greater-than-expected spread given the grain size variation for a fixed regional cooling rate (Fig. 6). The larger idioblastic biotites range in age from c. 449–377 Ma; which is also greater than that predicted from simple open system cooling models (Fig. 6). Furthermore, the symplectite biotite is texturally older than the idioblastic biotite, yet yields ages that are less dispersed but lie within the same range. We therefore suggest that the idioblastic biotite ages show patchy evidence for $^{40}$Ar contamination. This contamination mostly likely occurred during crystallization and growth, but may also have occurred during exhumation and cooling.

5.3. Plagioclase

Evidence for the presence of fluid that is enriched in $^{40}$Ar comes from the dates yielded by the plagioclase that co-crystallized with the biotite during symplectization of HP phengite. The plagioclase yields very scattered and generally “old” ages that are considerably older than the ages yielded by the co-crystallizing biotite (Fig. 6). The source of the contaminating $^{40}$Ar was most probably the reacting phengite. The ‘excess’ $^{40}$Ar measured in the plagioclase implies that the grain boundary network was poorly interconnected, at least on the local scale.

6. Conclusions

Textural evidence for the reactions between different K-bearing minerals within the same sample combined with spatially-detailed in-situ $^{40}$Ar/$^{39}$Ar analyses can offer insights into how efficiently Ar is removed or recycled during high temperature metamorphism. In the WGR, gneisses that reached eclogite facies (~20–25 kbar) conditions...
at c. 410–400 Ma followed by isochronal decomposition to <12 kbar, record mineralogical evidence for all these stages. In-situ laser ablation 40Ar/39Ar data from phengite and the biotite–plagioclase symplectites that replace it yield wide age ranges that help to constrain how Ar behaves during recrystallization.

Phengite which grew at 20–25 kbar and 670–770 °C and which subsequently partially broke down during decomposition yields ages ranging from 518 to 389 Ma. Heterogeneous Ar distributions within and between grains suggest little diffusive resetting despite the high temperatures experienced after crystallization. Ages older than the estimated timing of crystallization suggest 40Ar contamination during crystallization or decomposition.

Symplectites that grew from phengite during decomposition at <12 kbar document the partial redistribution of phengite-hosted Ar. 40Ar/39Ar ages of symplectite biotite grains that are “older” than those predicted from diffusion modelling suggest that either they incorporated Ar during their growth, or that they degraded inefficiently. The plagioclase that co-crystallized with the symplectite biotite yields ages that reflect contamination and incorporation of 40Ar, possibly in fluid inclusions and not related to K in the plagioclase lattice. These data point towards plagioclase acting as a sink for the 40Ar released by phengite during breakdown. 40Ar/39Ar ages of idiomorphic biotite that grew at <12 kbar, show that as biotite coarsened following initial crystallization, Ar released during the breakdown of phengite was still present in the rock volume and that the grain boundary network within the rock was partially closed to Ar loss. These lines of evidence combine to indicate that the grain boundary network was partially closed during exhumation and symplectite-formation.

None of the measured ages can be reconciled with models of simple thermally-activated diffusion during cooling in a purely open system. Instead the ages of the phengite reflect contamination (which may have occurred during either crystallization or along the decomposition path) and inefficient Ar loss. The plagioclase and biotite ages reflect continuing contamination by Ar released during the breakdown of phengite, within a grain boundary network with very restricted advection of either Ar or hydrous fluids.

Overall, these data demonstrate that even at high temperature metamorphic conditions, Ar may not diffuse efficiently out of micas unless there is sufficient advection of the grain boundary fluids. These datasets show that 40Ar/39Ar ages, and their interpretation may vary from sample to sample and mineral to mineral, even in the same terrain. The petrographic evolution of each rock should be carefully documented in order to provide a (relative) temporal framework in which to interpret the 40Ar/39Ar data. Furthermore, the analysis of multiple minerals aids the determination of how Ar has behaved during metamorphic recrystallization. Overall this approach allows 40Ar mobility and distribution to be more precisely linked to a samples metamorphic evolution. Supplementary data to this article can be found online at https://doi.org/10.1016/j.lithos.2017.11.028.

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