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Surface expression of Late Caledonian magmatic lithium concentration, in the Rhynie Chert, UK

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Abstract: The Lower Devonian plant-bearing Rhynie Chert, Aberdeenshire, UK, consists of sinters deposited by a hot spring system. Like many modern hot springs, the Rhynie geothermal system was lithium-rich, and its silica deposits are richer in lithium than other current or fossil sinters. Twenty samples of Rhynie sinter have a mean content of 255 ppm lithium. The high values imply exceptional lithium contents in the spring waters. Together with pegmatites and granites in the same region, the chert is related to a lithium-rich Late Caledonian magmatic suite, of which it is a surface expression. The measurements suggest that ancient hot spring deposits could provide valuable data during the exploration for lithium.

Keywords: lithium; Caledonian; Rhynie Chert; Devonian; caesium

Supplementary material: Supplementary Table 1 (compositional data for Late Caledonian granites) is available at https://doi.org/10.6084/m9.figshare.c.6756506

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Large resources of lithium are needed for the foreseeable future, in particular for batteries in electric vehicles (Diouf and Pode 2015; Xu *et al.* 2020; Masias *et al.* 2021). Much exploration for the required lithium resources is in pegmatites and related granite plutons (Bradley *et al.* 2017), and geothermal waters with associated clay deposits (Kesler *et al.* 2012; Bowell *et al.* 2020). These alternatives are represented by different reservoirs of lithium in time and space. The plutonic rocks formed deep sub-surface in the geological past, some as old as the Precambrian. The geothermal deposits are in many cases young (Miocene to modern) hot spring systems and their clay deposits, at the Earth's surface (Benson *et al.* 2017; Bowell *et al.* 2020). Exploration strategies are accordingly very different. Plutons are not commonly associated with deposits at the contemporary surface. However, in the British Caledonides, a well-preserved Lower Devonian hot spring deposit coeval with a metal-rich batholith allows a possible coupling of the two exploration plays. In the Grampian region of NE Scotland, the Rhynie Chert, a hot spring deposit dated at 407.6 ± 2.2 Ma (Mark *et al.* 2013) occurs within 30 km of lithium mica granite, also dated at about 408 Ma (Smith *et al.* 2002). The established lithium enrichment in the granite (Webb *et al.* 1992) suggests the possibility of a lithium enrichment in the coeval geothermal deposit at Rhynie.

Lithium in the Caledonides

Pegmatites rich in critical elements (LCT, lithium–caesium–tantalum; NYF, niobium–yttrium–fluorine) occur along the Caledonides suture zone from eastern Canada to northern Norway, encompassing the boundaries between Laurentia and both Avalonia/Gondwana and Baltica (Fig. 1). The Brazil Lake LCT pegmatite in Nova Scotia intruded within the interval 410–395 Ma (Kontak 2006). In central Newfoundland, numerous LCT pegmatite prospects have been identified (Magyarosi 2020), in a zone where many granites and pegmatites date at 410–390 Ma (Kerr *et al.* 2009). NYF-rich pegmatites on the Baltica margin are dated 410–400 Ma (Hetherington *et al.* 2021).

In Britain and Ireland, the Late Caledonian (Late Silurian to Early Devonian) granite suite is similarly partly lithium-rich. Commercial prospectivity is evident in lithium pegmatite resources in the Leinster Granite (Barros *et al.* 2022; Wall Street Journal 2022), exploration for lithium pegmatites in the Grampian region (British Geological Survey 2016) and exploration of lithium-rich brine related to the Weardale Granite (Whitfield 2021; Jasi 2023). While exploration for lithium has focused on plutonic rocks, Late Caledonian magmatism also yielded large volumes of approximately coeval lavas. Similar ages for Late Caledonian granitic plutons and andesitic/rhyolitic volcanic rocks reflect a genetic relationship between them and imply that much volcanic rock of this age was eroded away (Neilson *et al.* 2009). Loss of the surface volcanics would, however, leave roots in the underlying basement. Late Caledonian dykes of mixed breccia and igneous rock (tuffisites and similar) are widespread in Britain and Ireland, reflecting pathways for magmatic fluids and degassing that reached the surface (e.g. Rock *et al.* 1986; Hunt and Mohr 2007). This activity would have involved interaction with the hydrosphere, and generated hot springs and other phreatomagmatic phenomena. The Early Devonian sedimentary record shows evidence of such interactions (Kokelaar 1982; Hole *et al.* 2013), including the hot spring system which formed the Rhynie Chert (Rice and Trewin 1988; Rice *et al.* 1995). Hot springs in particular play a role in the lithium cycle today.

Lithium in hot spring systems

The waters of active geothermal systems are a potential source of commercially viable lithium. Hot springs are enriched in lithium at many sites globally (Goldberg *et al.* 2020; Stringfellow and Dobson 2021; Wang *et al.* 2021; Sanjuan *et al.* 2022). Spring waters have the advantages as a resource of being renewable, and of containing lithium and other elements already in a form convenient for processing. Chemical sediments deposited from the spring waters (siliceous sinters, travertine carbonates) may also carry the lithium-rich signature, and they can even include lithium mineral precipitation (Bargar *et al.* 1973). The hot spring sediments may be commercially exploited for caesium, which commonly accompanies lithium (Trueman *et al.* 2020). Data for hot spring deposits are largely limited to relatively young (Miocene to recent) sediments, and they are rare in ancient equivalents. Exploration

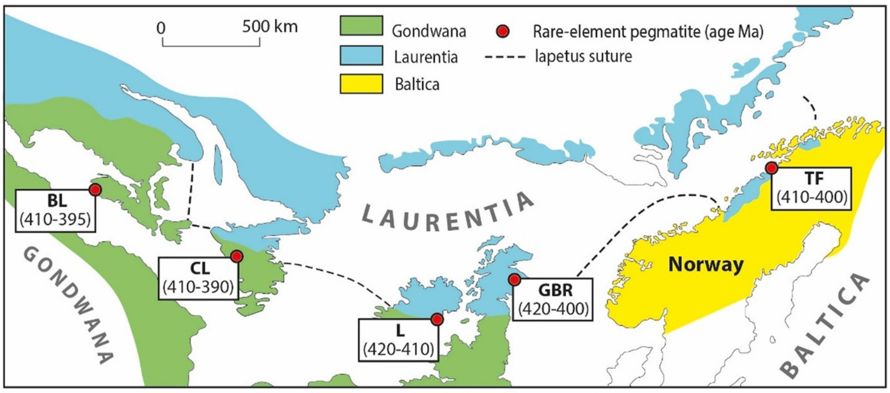

Fig. 1. Location of Rhynie Chert, and pegmatites rich in rare elements, along Caledonides suture between Laurentia, Gondwana and Baltica. Map modified from Dokken *et al.* (2018).

for gold in the Lower Devonian Rhynie Chert, UK, shows that siliceous sinters which constitute the chert contain the trace element signature of an ancient hot spring system (Rice and Trewin 1988; Rice *et al.* 1995). The metalliferous spring deposits are attributed to a source in underlying andesitic magmas and/or granite (Rice *et al.* 1995; Parry *et al.* 2011). The Rhynie Chert is therefore suitable for assessment of lithium concentration in ancient sinter deposits, and also the surface expression of lithium concentration during late Caledonian magmatism.

This study assesses:

(i) comparison of the lithium content of the Rhynie Chert with other lithologies in the surrounding region, to determine if the chert values are anomalously high;
(ii) determination if the lithium content in the whole region is anomalous relative to the crustal mean composition;
(iii) comparison of the lithium content of the Rhynie Chert with siliceous sinters in modern and ancient hot spring deposits.

Data are also reported for caesium, which accompanies lithium due to their comparable chemistry.

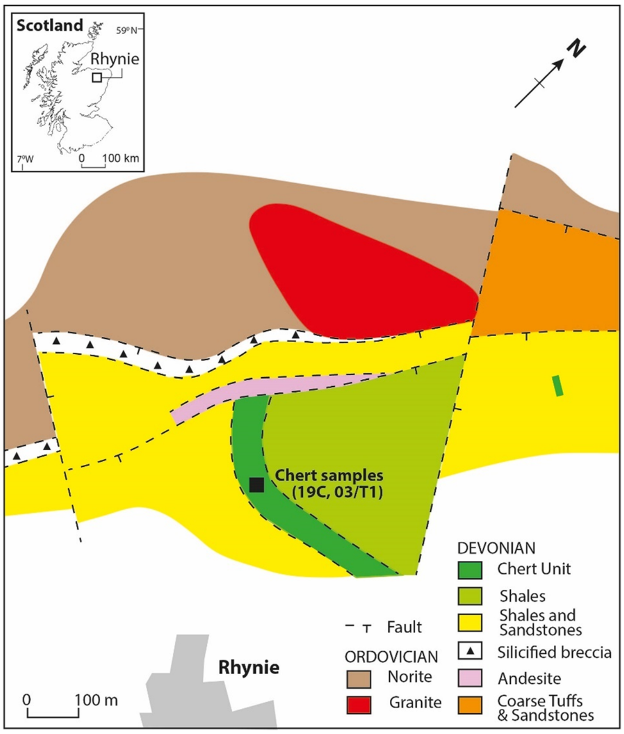

Fig. 2. Geological map of Rhynie, showing locations of chert samples, and immediately adjacent andesite, tuff and granite. Map modified from Rice *et al.* (2002).

Geological setting

The Rhynie Chert (Fig. 2) is a Lower Devonian (*c.* 410 Ma) lagerstätte of early plants and their accompanying biota (Trewin and Fayers 2015), preserved by early silicification from adjacent hot springs at the faulted margin of a small continental basin. The margin itself is marked by quartz vein rock and silicified breccias. The deposit constitutes the world's oldest preserved terrestrial ecosystem. Multiple episodes of hot spring activity resulted in siliceous sinters, which are interbedded with shales and sandstones in a section about 35 m thick (Rice *et al.* 2002). The chert is underlain by andesite, and sandstones with interbedded tuffs. These rocks are part of a Lower Devonian section in a basin (the Rhynie Basin) which developed on a surface composed of Neoproterozoic metasediments (Dalradian Supergroup), Ordovician intrusions ('Newer Gabbros') and Late Caledonian granite–norite. Together, the Late Caledonian plutonic rocks and the andesites belong to a magmatic suite which is probably related to slab break-off following NW-directed subduction below the Iapetus Ocean (Neilson *et al.* 2009; Archibald *et al.* 2022). The Rhynie Chert is one expression of widespread Lower Devonian geothermal activity in Scotland and Ireland, along with gold and iron–manganese mineralization, all associated with the magmatism (Nicholson 1989; Rice *et al.* 2002; Tanner 2014; Hill *et al.* 2015). The geothermal activity is exceptional in including surficial deposits at Rhynie.

Methodology

Samples of sinter were taken from a borehole (19C) drilled in 1988 and a logged trench section (03/T1) excavated in 2003 (Trewin and Fayers 2015), supplemented by float material in the trench and immediately adjacent ground. In addition to 20 samples of sinter, samples from Rhynie also included basin margin fault rock from the adjacent basin margin, and andesite/tuff from the underlying succession. The fault rocks included three samples collected from surface blocks at the trace of the margin, and a sample at the faulted sediment/basement boundary in borehole 97/2, depth 210.44 m (Rice *et al.* 2002). Andesite was sampled from the surface and from borehole 97/8, depth 51.4 m (Rice *et al.* 2002).

The geochemistry of Rhynie Chert sinter samples (Table 1) was compared with mean values for Late Caledonian granites from Britain and Ireland (Supplementary Table 1). Trace element contents were measured in samples using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled emission spectroscopy at the ALS Minerals Loughrea Laboratory, Ireland, using method ME-MS61L. Samples of *c.* 30 g rock were milled and homogenized, and 0.25 g digested with perchloric, nitric, hydrofluoric and hydrochloric acids to near dryness. The residue was topped up with dilute hydrochloric acid, and analysed using a Varian 725 instrument. Samples with high concentrations were diluted with hydrochloric acid to make a solution of 12.5 ml,

Table 1. *Composition and element ratios for cherts and volcanic beds, and feeder zone rocks at basin margin*

	Description	Li ppm	Cs ppm	Rb ppm	Li/Rb	Cs/Rb	Nb ppm	Ta ppm	Nb/Ta	Mg %	Mg/Li	S %	Al %
Cherts													
RCS1	Trench 03/T1/float 5	102.0	4.9	7.2	14.21	0.68	0.16	0.02	7.85	0.01	0.98	0.01	0.33
RCS2	Trench 03/T1/bed 1	141.0	20.2	14.4	9.79	1.40	2.47	1.80	1.37	0.04	2.84	0.12	0.76
RCS3	Float D50	146.5	20.0	57.8	2.53	0.35	3.56	1.41	2.52	0.08	5.46	0.15	1.69
RCS4	Float R47	153.0	7.2	30.8	4.97	0.23	3.09	2.20	1.40	0.05	3.27	0.03	1.15
RCS5	Float RJ101	155.0	8.1	41.4	3.74	0.20	2.98	0.40	7.45	0.07	4.52	0.04	1.40
RCS6	Borehole 19C/8.35 m	158.5	20.5	33.5	4.73	0.61	2.44	1.46	1.67	0.14	8.83	0.28	1.26
RCS7	Float WHS J1	164.0	16.8	38.7	4.24	0.43	2.64	2.18	1.21	0.06	3.66	0.02	1.21
RCS8	Trench 03/T1/bed 9i	170.5	10.9	17.2	9.91	0.63	0.28	0.05	5.56	0.03	1.76	0.15	0.76
RCS9	Float WHS17	173.5	8.2	37.4	4.64	0.22	1.93	0.33	5.85	0.05	2.88	0.02	1.18
RCS10	Trench 03/T1/bed 11	205.0	14.0	24.2	8.47	0.58	0.90	0.15	6.02	0.04	1.95	0.03	0.72
RCS11	Trench 03/T1/bed 13	205.0	7.1	8.9	23.16	0.80	0.93	1.20	0.78	0.01	0.49	0.07	0.33
RCS12	Trench 03/T1/bed 3	219.0	19.3	35.7	6.13	0.54	2.86	1.17	2.44	0.06	2.74	0.02	1.22
RCS13	Trench 03/T1/bed 5	261.0	21.0	70.6	3.70	0.30	5.41	1.90	2.85	0.10	3.83	0.10	2.21
RCS14	Trench 03/T1/bed 9ic	267.0	35.9	86.3	3.09	0.42	7.31	1.02	7.17	0.18	6.74	0.09	3.44
RCS15	Float RDA111	276.0	31.4	75.7	3.65	0.41	6.33	1.99	3.18	0.10	3.62	0.06	2.20
RCS16	NHM ID 0-1	301.0	6.0	4.4	68.25	1.36	0.13	0.01	13.40	0.01	0.33	0.02	0.44
RCS17	Trench 03/T1/float 6	381.0	19.7	29.9	12.74	0.66	3.85	1.14	3.38	0.08	2.10	0.06	1.88
RCS18	Trench 03/T1/bed 14	485.0	25.2	37.1	13.07	0.68	4.87	1.52	3.20	0.08	1.65	0.23	2.46
RCS19	Float RCSS1	506.0	17.8	36.8	13.75	0.48	5.36	1.48	3.62	0.09	1.78	0.03	2.38
RCS20	NHM ID 10-11	637.0	17.4	32.9	19.36	0.53	6.09	1.58	3.85	0.10	1.57	0.17	2.79
RCSM1	Borehole 19C/19.4 m	133.5	43.7	68.8	1.94	0.64	5.43	1.17	4.64	0.30	22.47	0.81	2.88
Volcanic beds													
	Andesite WHA1	115.5	1.7	94.6	1.22	0.02	17.25	1.05	16.43	1.82	157.58	0.01	7.98
	Andesite 102F	170.5	7.1	250.0	0.68	0.03	18.10	1.40	12.93	0.54	31.67	0.01	6.57
	Tuff 97/5 23.6 m	25.5	15.6	321.0	0.08	0.05	25.20	2.00	12.60	0.05	19.61	0.48	8.13
Feeder system													
	Quartz veinrock MRT 54	177.0	7.4	219.0	0.81	0.03	10.55	2.08	5.07	0.09	5.08	0.03	4.49
	Quartz veinrock QV1	126.0	1.5	31.5	4.00	0.05	0.06	0.06	1.00	0.03	2.38	0.01	0.81
	Quartz veinrock QV2	207.0	3.5	61.1	3.39	0.06	4.42	1.73	2.55	0.27	13.04	0.01	2.39
	Cherty Breccia (97/2 210.44 m)	276.0	3.8	74.4	3.71	0.05	4.64	1.23	3.77	0.84	30.43	0.10	2.67

homogenized, then analysed by ICP-MS. Results were corrected for spectral inter-element interferences. The limits of detection/resolution are 0.05 and 10 000 ppm. Geological Certified Reference Materials (CRMs) utilized included MRGeo08 (mid-range multi-element CRM), GBM908-10 (base metal CRM), OGGeo08 (ore grade multi-element CRM) and GEOMS-03 (multi-element CRM). Results for CRM analysis were within the anticipated target range (upper and lower bound) for each metal and standard. Duplicate analysis of samples produced reported values within the acceptable range for laboratory duplicates.

Scanning electron microscopy (SEM) was conducted in the Aberdeen Centre for Electron Microscopy, Analysis and Characterization facility at the University of Aberdeen using a Carl Zeiss Gemini SEM 300 VP Field Emission instrument equipped with an Oxford Instruments NanoAnalysis Xmax80 Energy Dispersive Spectroscopy detector, and AZtec software suite. Measurement of metallic elements was made using factory elemental standards. The content of tungsten in titanium oxide grains was measured, and recorded on a ternary plot, as an indicator used in gold exploration (Agangi *et al.* 2019; Sciuba and Beaudoin 2021).

Results

The 20 samples of sinter (Table 1) yielded lithium contents from 102 to 637 ppm (mean 255 ppm, median 205 ppm). The sinters included several different chert beds in the logged trench 03/T1 (Fig. 3). The four fault rock samples contained 126 to 276 ppm lithium. Two andesite samples contained 116 and 171 ppm lithium. The Rhynie samples were plotted in comparison to published data sets for modern and fossil sinters (Table 2; Fig. 4). The Rhynie samples were also compared with other samples in the Grampian region (Fig. 5). The regional samples included the main rocks that constitute the basement to the Rhynie Basin: Dalradian Supergroup, Newer Gabbros and Caledonian granites. Most notably, four samples of zinnwaldite-bearing granite at Gairnshiel, Aberdeenshire, yielded 723 to 2030 ppm lithium (mean 1381 ppm). The number of comparative data sets was limited by the exclusion of lithium from many analytical surveys.

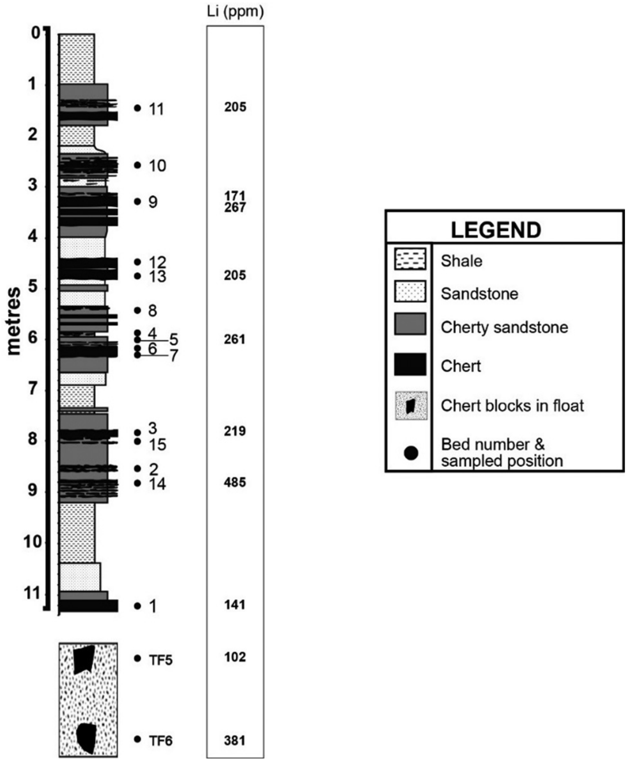

Fig. 3. Section of Rhynie Chert exposed in trench 03/T1, recording lithium contents in individual numbered chert beds and detached blocks in the underlying float. Section after Trewin and Fayers (2015).

In addition to the lithium data, SEM observations showed that many titanium oxide grains in the Rhynie sinters contain measurable tungsten contents. Previous observations in the cherts show that pyrite grains are arsenic-rich and contribute to whole rock values up to 600 pm arsenic (Parnell *et al.* 2022), and synchysite mineralization represents the availability of rare earth elements and fluorine (Parnell *et al.* 2023).

Discussion

Rhynie sinter samples

Globally there is abundant evidence of lithium enrichment in hot spring systems, and spring waters generally (Seidel *et al.* 2019; Neves *et al.* 2020). High lithium contents imply high degrees of water–rock interaction (Tomascak 2004; Dugamin *et al.* 2021). Both modern and fossil sinters show lithium enrichment from the spring waters. The fossil sinters in Table 2 and Figure 4 are not completely representative, as they have been analysed in support of mineral exploration (gold or caesium). However, there is no reason to think that this makes them less likely to be lithium-rich. Indeed, the Rhynie Chert sinters are both gold-bearing (Rice and Trewin 1988; Rice *et al.* 1995; Parnell *et al.* 2022), and lithium-rich. The evidence for high arsenic and fluorine contents is consistent with deposition from a geothermal system (Bundschuh and Maity 2015; Morales-Arredondo *et al.* 2016).

The lithium values for the Rhynie sinter samples are higher than all the mean values determined for modern sinters, including well studied deposits in Yellowstone National Park (USA), Chile, New Zealand and the Tibetan Plateau. The values for the fault rock are also greater than most values from hot springs elsewhere. Data for other fossil sinters are also lower than in the Rhynie Chert. The high values imply that the lithium content of the hot spring waters at Rhynie was exceptional. The relationship between lithium contents in sinters and their parent fluid would depend upon the rate of sinter deposition and other factors. However, it is probable that the content in the Rhynie fluid exceeded the mean values for El Tatio (Chile), Yellowstone and the Tibetan Plateau (36.3, 2.4, 32.8 mg Li/l, respectively; Nicolau *et al.* 2014; Havig *et al.* 2021; Wang *et al.* 2021), where sinters were much less lithium-rich than at Rhynie (15, 41, 63 ppm). For reference, a cut-off value of 25 mg Li/l is adopted for commercial production from brines in China (Wang *et al.* 2021), implying that the Rhynie brine would have been of commercial value today.

The Rhynie lithium values are higher than almost all published values for British rocks. Measurements of the most lithium-rich granites in Cornwall, where commercial lithium exploration is undertaken, exceed 1000 ppm (Simons *et al.* 2017), as does the zinnwaldite-bearing Caledonian granite at Glenshiel, Aberdeenshire. Hitherto, the next most lithium-rich rocks reported are the other Late Caledonian granites. The Shap and Skiddaw granites in northern England have mean values of 117 and 118 ppm Li, respectively, although the mineralized Skiddaw greisen is richer (O'Brien *et al.* 1985; Cooper *et al.* 1988). Also, in northern England, the Weardale Granite sampled from the Rookhope borehole has a mean content of 141 ppm Li (Holland 1967). Some measurements of the Late Caledonian granites in NE Scotland exceed 100 ppm (Plant *et al.* 1980; Gould 2001), and associated lithium pegmatites are very rich. Other Late Caledonian granites have lower lithium contents. For example, mean values for the Cheviot Granite, Helmsdale Granite and Etive Granite are 70, 12, and 24 ppm respectively (Plant *et al.* 1980; Batchelor 1987; Hines *et al.* 2018).

Table 2. *Published data for lithium and caesium contents in hot spring deposits*

Data set	Location	Lithology	Range Li (ppm) (*n*)	Range Cs (ppm) (*n*)	Mean Li (ppm)	Mean Cs (ppm)	Reference
MS1	Solomon Islands	Sinter, travertine	0.5–31.6 (22)		5.4		Smith *et al.* (2011)
MS2	Los Geysers, Mexico	Sinter	3.3–9.1 (17)	8.7–53.7 (17)	5.9	28.5	González-Guzmán *et al.* (2022)
MS3	Yellowstone Lake, Wyoming, USA	Sinter	3–60 (10)		12.5		Shanks *et al.* (2007)
MS4	El Tatio, Chile	Sinter	6.4–24.8 (62)	52.6–532.3 (62)	14.5	165.4	Wilmeth *et al.* (2020)
MS5	Utah, USA	Sinter, soil	2–66 (21)		17.2		Bamford *et al.* (1980)
MS6	Dagejia, Tibet	Sinter	11.4–29.8 (4)	2034–10 662 (4)	19.4	4299	Wang *et al.* (2019)
MS7	Nevada, USA	Sinter	13–34 (3)		20.0		Rimstidt and Cole (1983)
MS8	Kyushu, Japan	Sinter (induced)	0.9–74.3 (15)		25.4		Yokoyama *et al.* (1993)
MS9	Yellowstone, Wyoming, USA	Sinter	1–208 (29)		41.0		Havig *et al.* (2021)
MS9a	Yellowstone, Wyoming, USA	Sinter		0.3–5.2 (15)		2.8	Churchill *et al.* (2021)
MS10	Tibetan Plateau	Sinter	1–331 (7)	0–4331 (10)	62.7	540.7	Feng *et al.* (2014)
MS11	Gulu, Tibet	Sinter	52.4–83.3 (3)	536.4–1256 (3)	66.9	809.7	Elenga *et al.* (2021)
MS12	Virginia, USA	Sinter	Not known (30)		75.6		Nolde and Giannini (1997)
MS13	Puchuldiza, Chile	Sinter	1–954 (61)		131.3		Sanchez-Yanez *et al.* (2017)
MS14	Waiotapu, New Zealand	Sinter (selected sample)	Not known		149		Jones *et al.* (2001)
FS1	Taron, Argentina	Fossil (Miocene) sinter	10–182 (1239)	52–15 763 (1239)	37	1406	Trueman *et al.* (2020)
FS2	Massif Central, France	Fossil (Permian) sinter	0–112 (65)		44.4		Marcoux *et al.* (2004)
FS3	Coromandel Volcanic Zone, New Zealand	Fossil (Miocene) sinter	1.2–151.5 (18)	0.1–17.1 (18)	51.6	4.9	Hamilton *et al.* (2019)
FS4	Drummond Basin, Australia	Fossil (Devonian) sinter	10–149 (12)	1–52 (12)	58.4	15.6	Uysal *et al.* (2011)

The high lithium values in the sinters may be engendered by a high content of clays. Lithium is commonly resident in detrital clay minerals (Starkey 1982; Benson *et al.* 2017). The cherts contain sediment rich in micas and clays between masses of silicified plant fossils (Fig. 6). Electron microscopy shows that the clays contain oxide precipitates which have adsorbed other trace elements (Fig. 6), and they may also be the residence of the lithium. A broad correlation of lithium and aluminium (Fig. 7) further implies that the lithium is resident in phyllosilicates (clays, micas).

Regional lithium data

Each of the other main rocks in the NE, the Dalradian Supergroup, the Ordovician gabbros and the Late Caledonian granites, have all

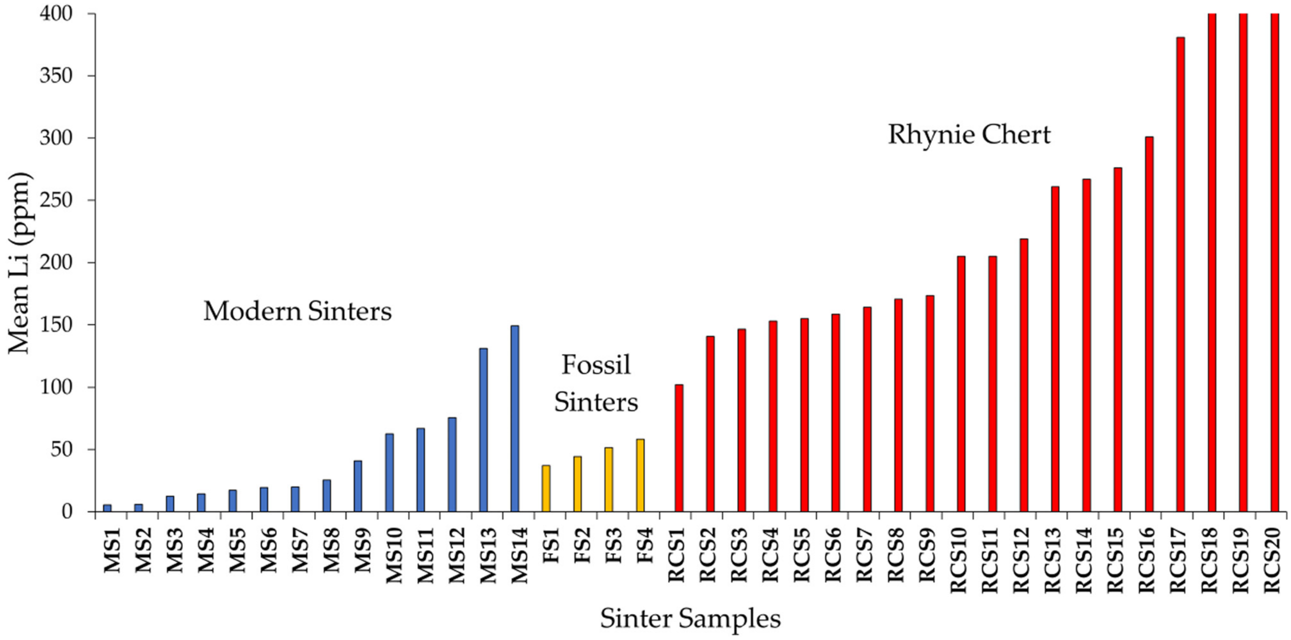

Fig. 4. Lithium contents of Rhynie Chert samples, compared to mean values for modern and fossil sinters. Data sources in text. Rhynie Chert has consistently higher content. Contents capped at 400 ppm Li for clarity, but extend to over 600 ppm Li.

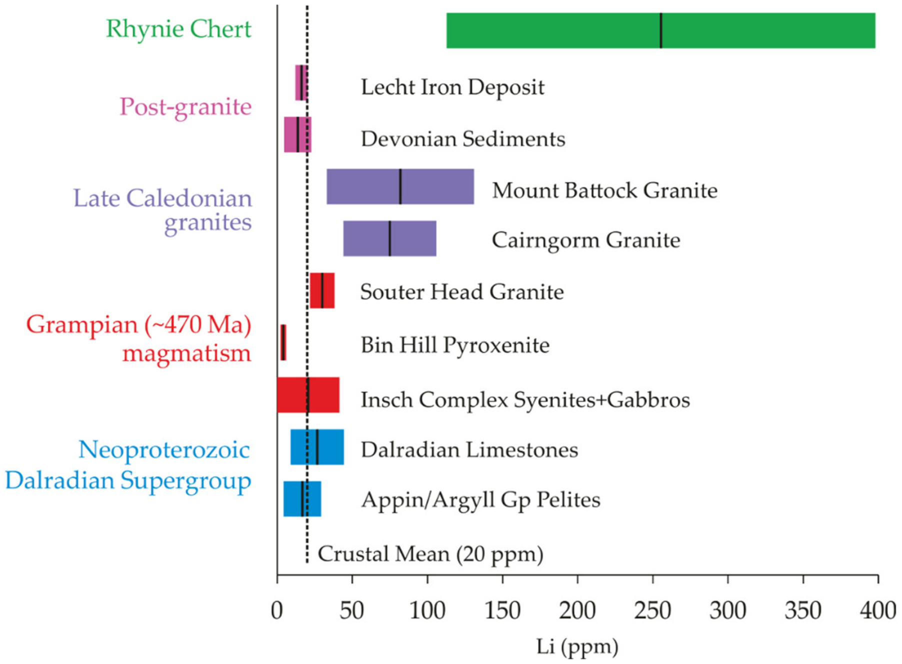

Fig. 5. Mean lithium content (ppm) of Rhynie Chert samples, compared to mean values for other rocks in NE Scotland, and upper crustal average. Data from Nicholson (1987), Nicholson and Anderton (1989), Plant *et al.* (1980), Read and Haq (1963), Rice and Mark (2020) and this study. Data ranges show standard deviations for each rock type. Data for Mount Battock granite show full range, as reported by Gould (2001). Global upper crustal mean (20 ppm Li) from McLennan (2001).

yielded lower lithium contents than in the Rhynie sinters. The finer-grained part of the Dalradian Supergroup succession, the Appin and Argyll subgroups, had a mean Li value of 16.8 ppm ($n = 14$) for samples within 20 km of Rhynie. The Ordovician rocks yielded a mean content of 20.4 ppm Li ($n = 11$), in syenites and gabbros of the Insch Complex to the east of Rhynie (Read and Haq 1963).

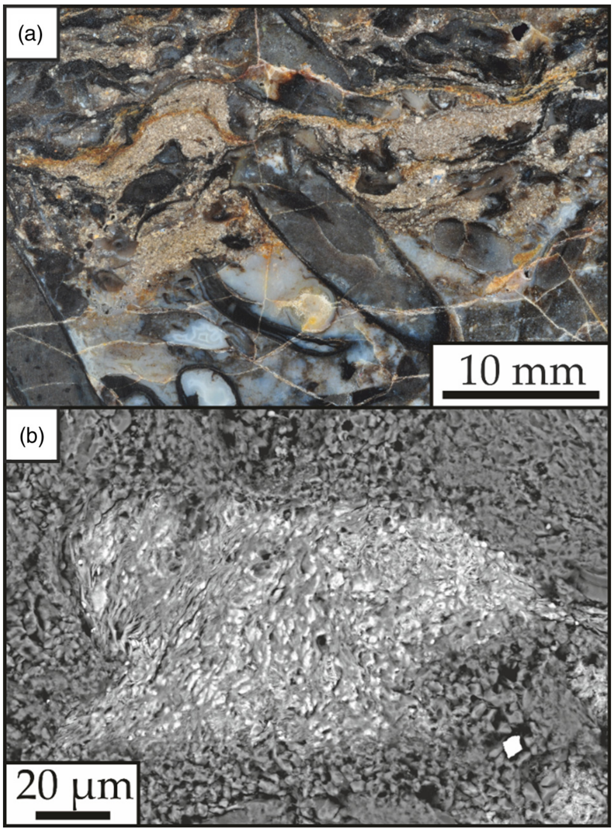

Fig. 6. Clay in chert samples. (**a**) Polished surface of Rhynie Chert showing patches of silicified plant remains, and intervening sediment rich in clays and micas. (**b**) Scanning electron micrograph of clay showing oxide precipitates which have adsorbed trace elements (bright), and may also be the residence of the lithium.

Pyroxenites yielded 4.1 ppm Li ($n = 11$) (authors' unpublished data). The Caledonian granites, including the Cairngorm, Ballater, Mount Battock and Bennachie plutons, are tin–uranium granites which are enriched in lithium relative to other Caledonian granites elsewhere in Scotland (Plant *et al.* 1990). The mean value determined for the Cairngorm Granite is 75 ppm (Plant *et al.* 1980). Values determined for the Mount Battock Granite range from 33 to 131 ppm (Gould 2001). The composition of the Late Caledonian granites in NE Scotland is related to melting of protoliths with a high proportion of magmatic material, rather than assimilation of metasediments (Steinhoefel *et al.* 2008), i.e. the relative enrichment in lithium is a magmatic signature. A range of other Devonian sedimentary samples, including sandstones, conglomerates and calcretes, all have low lithium contents (mean 13.7 ppm, $n = 13$), indicating that the anomaly is not a characteristic of the surface environment in general. Stream sediment data for NE Scotland confirm that there is anomalous lithium in the catchment area of the granites (British Geological Survey 1991; Lipp *et al.* 2020). The spatial resolution of the stream sediment data does not highlight the Rhynie Chert, which has a footprint of much less than a square kilometre (Rice and Ashcroft 2004; Trewin and Fayers 2015).

Data for the lithium content in the Late Caledonian plutons of Britain and Ireland distinguish a group with high lithium and rubidium but low barium and strontium, and a group with low lithium and rubidium but high barium and strontium (Plant *et al.* 1980; Fowler *et al.* 2001, 2008). The former group are more extensively mineralized, including tin enrichment in the granites of NE Scotland (Plant *et al.* 1980, 1990). Notably, there is a link between tin-bearing granites and availability of lithium elsewhere, due to the occurrence of both elements in relatively volatile fluids (Swanson 2012; Hofstra *et al.* 2013). Consequently, mining companies co-explore for both commodities in pegmatites and granites in the same licenced ground (e.g. Creamer 2023; TinOne Resources Inc. 2023).

Exploration for lithium and rare earth elements in felsic rocks makes use of an assessment of 'fertility', represented by the Mg/Li ratio. Typically, a Mg/Li ratio from <30 to <10 is regarded as indicating a high degree of fractionation of rare elements from other elements (Černý 1989; Breaks *et al.* 2003; Selway *et al.* 2005). Commercial surveys use a cut-off as high as Mg/Li = 50. The Mg/Li

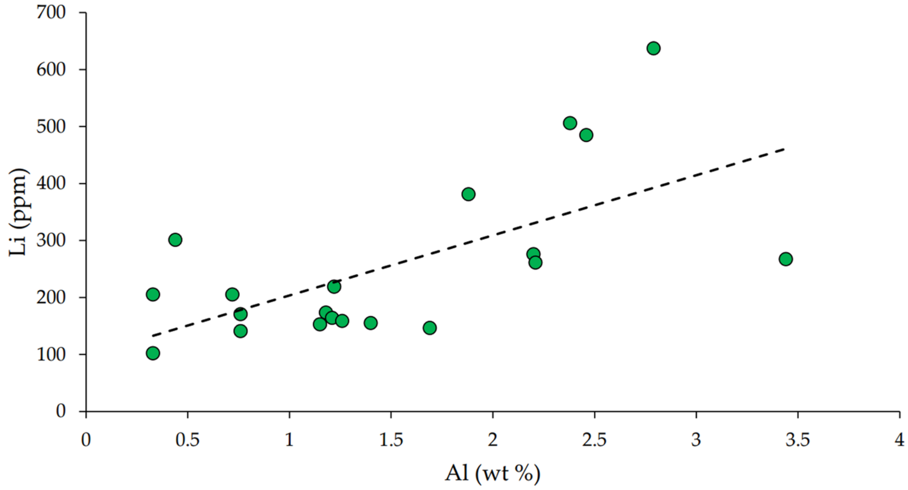

Fig. 7. Cross-plot of Li and Al for 20 Rhynie Chert samples, showing a broad positive correlation, which implies residence of Li in clays/micas.

values for the Rhynie Chert are consistently very low, ranging from 0.3 to 8.8 (mean 3.1), which indicate a system fertile for lithium.

Fertile granites also have a distinctive range of ratios for Nb/Ta <8 (Selway *et al.* 2005). The samples of Rhynie Chert have values consistently <8. The two element ratios are used in combination during exploration (Breaks *et al.* 2003; Selway *et al.* 2005; Lima *et al.* 2019). A cross-plot of the ratios shows that Rhynie Chert samples lie in the fertility field (Fig. 8). The Cairngorm granite has notably low ratios of Mg/Li and Nb/Ta (Plant *et al.* 1990), and similarly plots in the field, together with two granodiorites from the lithium-prospective Leinster pluton. The cross-plot is intended to fingerprint granite samples, but the preferential distribution of chert samples in the fertility field emphasizes that they are unusually lithium-rich.

Data for niobium and tantalum can also be plotted to distinguish degrees of fractionation (Fig. 9). The curve of evolving composition on a plot of Nb/Ta ratio against tantalum content (a typical 1/*x* against *x* curve) represents progressive fractionation in granites and transition from magmatic to hydrothermal activity (Ballouard *et al.* 2016, 2020; Yin *et al.* 2022). A Nb/Ta ratio of about 5 is suggested to mark the transition to hydrothermal (Ballouard *et al.* 2016). The data for Late Caledonian granites in Britain and Ireland show a limited number have reached the hydrothermal stage (Fig. 9). A majority of the Rhynie Chert samples plot in the hydrothermal field, which is consistent with their purported deposition by hydrothermal processes. A previous plot for a Late Caledonian plutonic suite in Newfoundland shows fractionation culminating in lithium-rich pegmatites (Magyarosi 2020). Both chert and pegmatites represent late stages in the fractionation process.

Contents for caesium were measured in addition to lithium. The group 1 alkali metals lithium, rubidium and caesium are all enriched in hot springs, and in the Late Caledonian granites of NE Scotland. A plot of Li/Rb against Cs/Rb (Fig. 10) shows that lithium and caesium are relatively enriched in the hot spring system to different degrees. The fault vein rock feeding the hot springs shows an enrichment in lithium compared to the granite, but the chert shows an additional enrichment in caesium (Fig. 10). Modern hot springs can similarly show substantial enrichment in caesium (Table 2). Caesium concentration from hot springs on the Tibetan Plateau has been attributed to microbial activity (Wang *et al.* 2012), and it reflects a wider role for biology in caesium fractionation in surface environments (e.g. Kuwahara *et al.* 2011).

Lithium in hot spring systems is commonly accompanied by tungsten, also of magmatic origin. Lithium-bearing hot springs in New Zealand, Yellowstone and Tibet all have high tungsten contents, up to 1600, 4000 and 1100 times the mean global river content respectively (data in Gaillardet *et al.* 2003; Ullrich *et al.* 2013; Guo *et al.* 2019; Planer-Friedrich *et al.* 2020), and brines in the Great Basin, USA, are exploited for both lithium and tungsten (Ririe 1989). Similarly, the lithium-rich cherts at Rhynie are also tungsten-rich (Parnell *et al.* 2022). Tungsten in sinters and other rocks becomes incorporated in titanium oxides including rutile. The content of tungsten in rutile is a widely measured indicator used in gold exploration (Agangi *et al.* 2019; Sciuba and Beaudoin 2021).

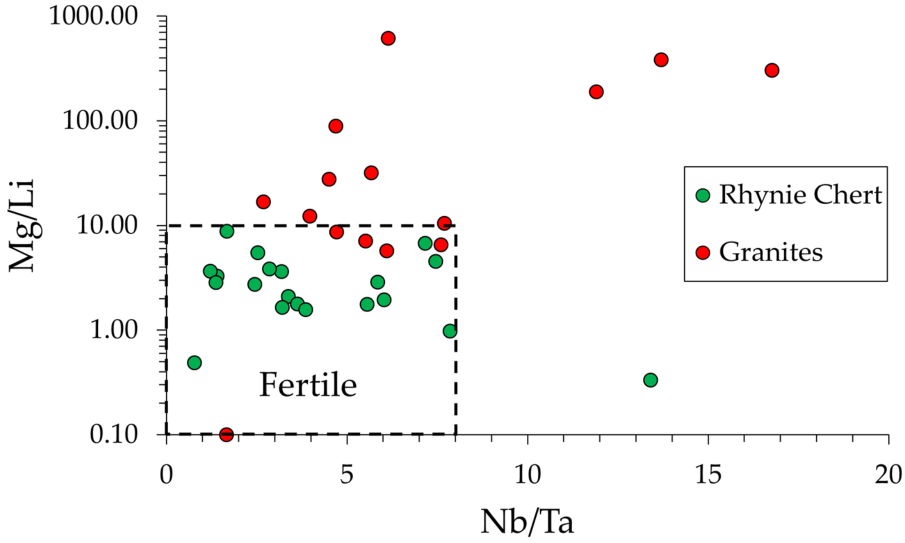

Fig. 8. Cross-plot of Mg/Li and Nb/Ta ratios for Rhynie Chert samples and selected Late Caledonian granites. Rhynie Chert samples plot in field of Mg/Li <10 and Nb/Ta <8 commonly used to indicate granite ‘fertility’ for rare elements, including lithium.

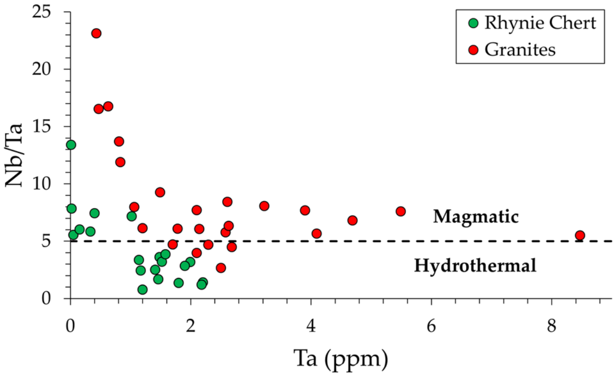

Fig. 9. Cross-plot of Nb/Ta ratio and Ta content for Rhynie Chert samples and selected Late Caledonian granites. Compositions define a fractionation curve as magmatic processes transition to hydrothermal processes. Rhynie Chert samples mostly have Nb/Ta <5, typical of the hydrothermal stage. Granite samples typically have higher Ta contents.

Measurement of over 100 titanium oxide grains in the Rhynie sinters shows that many contain tungsten contents typical of gold-bearing systems (Fig. 11). This is consistent with the occurrence of anomalously high lithium contents in gold-mineralized geothermal systems (e.g. Uysal *et al.* 2011; Hamilton *et al.* 2019). Tungsten mineralization is also recognized in the Late Caledonian lithium-bearing granites of the region around Rhynie (Colman *et al.* 1989; Webb *et al.* 1992). Together, the data from the Rhynie Chert and the granites give a picture of tungsten–lithium–gold-rich fluid that compares well with modern geothermal systems.

Late Caledonian lithium anomaly

Although the lithium contents of the granites in NE Scotland are lower than the chert values, the granites are still relatively lithium-rich, and include an outcrop characterized by the lithium mica zinnwaldite (Plant *et al.* 1980; Gould 2001). Together with the formation of pegmatites containing the lithium mica lepidolite, related to the granite complexes (Jackson 1982; Starkey and McMullen 2017) and lithium enrichment in iron–manganese ores including the lithium-bearing oxide lithiophorite (Nicholson 1986), the data represent a regional flux in lithium at about 410 Ma (Fig. 12). These components were directly related. The mineralized lineaments, including the iron–manganese ore veins, are rooted in hydrothermally altered zones of the plutons (Hall and Gillespie 2017). The iron–manganese veins exhibit open fabrics which suggest (near-) surface formation along with the Rhynie hot springs (Nicholson 1987).

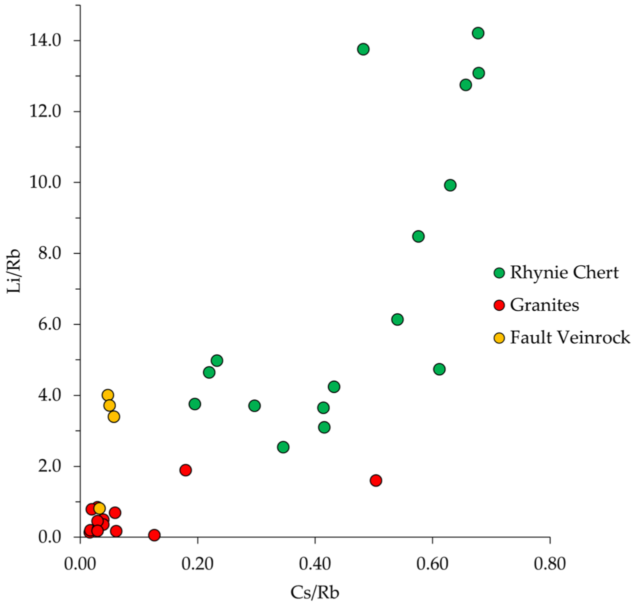

Fig. 10. Cross-plot of Li/Rb and Cs/Rb ratios for Rhynie Chert samples, fault rock samples and selected Caledonian granites. Fault rock samples are relatively enriched in lithium, and Rhynie Chert samples are relatively enriched in both lithium and caesium, relative to the granites. Three chert samples with Li/Rb >15 or Cs/Rb >1 omitted for clarity.

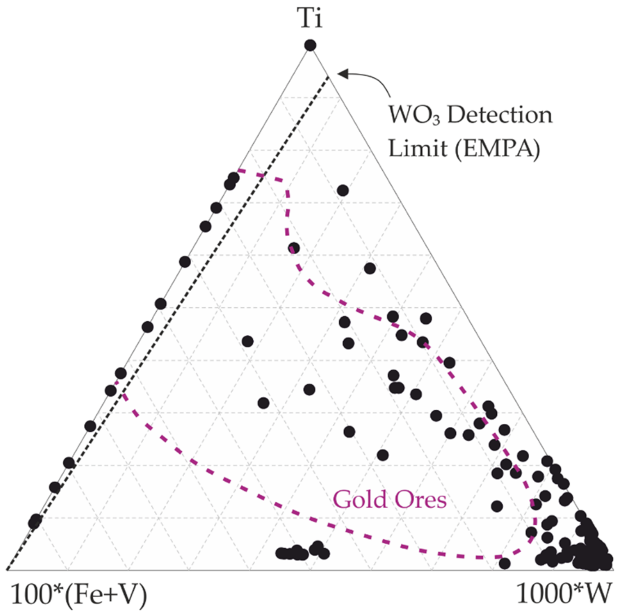

Fig. 11. Ternary plot showing trace element (W, Fe, V ppm) composition of titanium oxide grains in Rhynie Chert. Many compositions fall in field of rutile from orogenic gold deposits from Clark and Williams-Jones (2004) and Agangi *et al.* (2019). EMPA, electron microprobe analysis.

The Late Caledonian granites in the Grampian region were coeval with other granites in the Trans-Suture region of Britain and Ireland where the Iapetus Ocean had closed to stitch Laurentia with Avalonia (Miles *et al.* 2016; Barros *et al.* 2017; Woodcock *et al.* 2019). All the granites in this region are considered to belong to a single phase of plutonism (Miles *et al.* 2016), although it may have lasted 20 myr and involved evolving magma chemistry. This commonality brings a new perspective to the Grampian lithium

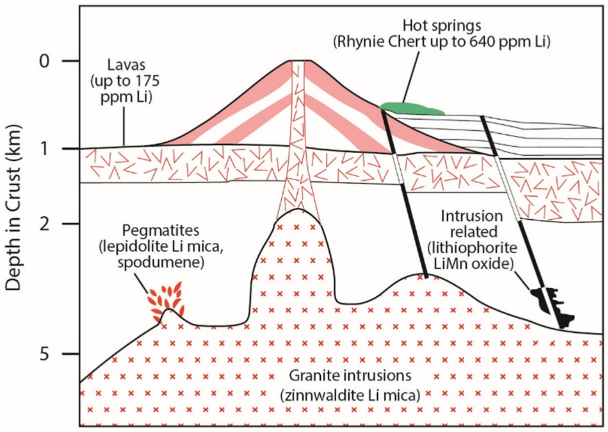

Fig. 12. Schematic summary of Late Caledonian magmatic-related rock types in NE Scotland, including Rhynie Chert, showing occurrences of lithium minerals and enrichments in each type. Rock associations after Kesler (1994).

anomaly. The Trans-Suture region includes the Leinster Granite, Ireland and the Lake District batholith, England. The Leinster Granite hosts lithium mineralization which is commercially prospective (Barros *et al.* 2022; Wall Street Journal 2022) and in the Lake District the Shap and Skiddaw granites also have high (>100 ppm) lithium values (Supplementary Table 1). Immediately to the east of the Lake District batholith, the North Pennine batholith (Weardale Granite), dated at about 400 Ma (Kimbell *et al.* 2010), is a target for lithium extraction (Whitfield 2021).

Lithium enrichment is documented in numerous collisional zones (Zagorsky *et al.* 2014; Bradley *et al.* 2016, 2017; Li *et al.* 2019), which could reflect magmatism due to ordinary arc processes, slab breakoff during or after collision, slab delamination related to collision, or late collisional decompression melting (Bradley *et al.* 2017). The enrichment in magmas is reflected in high values in both granites and lavas, especially rhyolites (Benson *et al.* 2017; Chen *et al.* 2020). The Late Caledonian magmatic suite includes lithium-rich granites/pegmatites, lithium-rich andesites and the associated Rhynie Chert (Fig. 12). There is evidence, therefore, for the introduction of lithium through a broad region of crust, the surface expression of which is preserved at Rhynie.

Although anomalously lithium-rich, the Rhynie Chert would not represent a commercial prospect, even if it was not a fossiliferous deposit of international importance. Sources of lithium in brines and pegmatites are richer and much easier to process. However, the Rhynie Chert is valuable in emphasizing the importance of Late Caledonian magmatism in lithium concentration, and thus the potential of exploring in the Caledonides. The contribution of degassing magma to lithium mobility (Lowenstern *et al.* 2012; Berlo *et al.* 2013; Ellis *et al.* 2018) and the concentration of lithium in sediments related to magmatic environments (Hofstra *et al.* 2013; Benson *et al.* 2017) indicate that exploration strategies could be innovative in their choice of target rocks.

Lithium at the surface

The identification of anomalous lithium contents in the Rhynie Chert shows that the Late Caledonian lithium anomaly in Britain and Ireland extends from several kilometres depth where plutons were emplaced, up to the surface. The anomaly is not limited to granites and associated pegmatites. This implies that the search for lithium deposits could include exploration in ancient sedimentary basins, as has been shown commercially (Borojević Šoštarić and Brenko 2023). Models for lithium concentration in modern sediments, and consequent exploration plays, can be extended into comparable settings in the geological record. Lithium is introduced to the surface in solution, but requires a mineral residence to become concentrated at the surface. Understanding this is central to exploration strategies. The mapping of lithium distribution in rocks by laser-induced breakdown spectroscopy and laser ablation ICP-MS are suitable methods for identifying the mineral residence of lithium in the range of 10s to 1000 s ppm (Sweetapple and Tassios 2015; Breiter *et al.* 2017; Jiu *et al.* 2023), and will find a role in future exploration.

The enrichment of lithium in Lower Devonian magmatic rocks has a legacy in the near-surface 400 million years later. The interaction of basin brines with the most Li-rich Caledonian pluton in Britain, the Weardale Granite, yields modern groundwaters with lithium levels high enough to warrant commercial exploration and exploitation (Whitfield 2021). The Weardale Granite also has potential as a source of geothermal energy (Manning and Strutt 1990), which would enhance the water–rock interaction of trace elements in the granite. This scenario is comparable to the uptake of lithium from relatively hot Hercynian granite in Cornwall into commercially viable deep brines (Edmunds *et al.* 1985; Simons *et al.* 2017).

Conclusions

Data for lithium in the Rhynie Chert show that the fossil sinters that constitute the chert are richer in lithium than other measured current and ancient sinters. This implies that the Rhynie hot spring waters were exceptionally lithium-rich. The cherts have higher lithium contents than most other British rocks, including Late Caledonian granites. Contemporary lithium-rich granites and pegmatites within 30 km of Rhynie show that the hot spring was a surface expression of regional-scale Late Caledonian lithium-rich magmatism. This emphasizes the value of exploring for lithium in sedimentary basins, for resources and/or vectors to underlying Li-rich basement. In addition to the high flux of lithium in hot springs during Rhynie Chert deposition, water flow through the Lower Devonian magmatic rocks remains lithium-rich over 400 million years later.

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Data availability All data generated or analysed during this study are included in this published article (and, if present, its supplementary information files).

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