Sulphur isotopes of alkaline magmas unlock long-term records of crustal recycling on Earth

William Hutchison1, Rainer J. Babiel2, Adrian A. Finch1, Michael A.W. Marks2, Gregor Markl2, Adrian J. Boyce3, Eva E. Stüeken1, Henrik Friis4, Anouk M. Borst1 & Nicola J. Horsburgh1

Earth’s surface and mantle sulphur reservoirs are connected via subduction, crustal recycling and volcanism. Although oceanic hotspot lavas currently provide the best constraints on the deep sulphur cycle, their restricted age range (<200 Ma) means they cannot reveal temporal variations in crustal recycling over Earth history. Sulphur-rich alkaline magmas offer the solution because they are associated with recycled sources (i.e. metasomatized lithospheric mantle and plumes) and, crucially, are found throughout the geological record. Here, we present a detailed study of sulphur isotope fractionation in a Mesoproterozoic alkaline province in Greenland and demonstrate that an enriched subduction-influenced source (δ34S of +1 to +5‰) can be reconstructed. A global δ34S compilation reveals secular variation in alkaline magma sources which support changes in the composition of the lithospheric mantle and/or Ga timescales for deep crustal recycling. Thus, alkaline magmas represent a powerful yet underutilized repository for interrogating crustal recycling through geological time.
Magmas are an integral component of Earth’s S cycle and are linked to the surface via subduction, mantle storage, crustal cycling and volcanism. The most significant insights into the connections between the surface and mantle S reservoirs have been gained from studies of oceanic hotspots, particularly ocean island basalt (OIBs). A key observation is that several OIBs show mass independent S isotope fractionation, a feature characteristic of Archaean age sedimentary rocks, which is usually expressed as $\Delta^{33}S$. These OIBs (Mangaiā and Pitcairn) are characterised by negative $\Delta^{33}S$ and $\Delta^{34}S$, which fingerprint Archaean crust in their mantle source. Importantly, other OIBs (Discovery, Samoa and Canary Islands) indicate post-Archaean S ($\Delta^{33}S \approx 0$) with positive $\Delta^{34}S$ (~3‰) and are suggested to represent subducted Proterozoic sediments and/or serpentinitized oceanic peridotites. Isotopic variations between different OIBs suggest that there are chemically distinct reservoirs of subducted crust within the mantle and that plumes sample this ancient crust and return it to the surface.

Despite these advances we do not fully understand how changing subducted S input (from sedimentary records) ties to mantle S output (from igneous records). Although marine sedimentary rocks reveal large S isotopic variations through geological time, there are no comparable igneous time-series; this greatly limits our ability to quantify rates and timescales of surface S recycling. A key issue is that the oceanic record only extends to ~200 Ma; thus, OIBs cannot reveal temporal variations in crustal recycling over Earth history.

Alkaline magmas (silicate rocks and carbonatites) represent low-degree melts of volatile-rich mantle sources. Their trace element signatures and radiogenic isotopes are similar to OIBs and they are often linked to recycled crustal materials. While predominantly found on the continents, there are a number of oceanic alkaline localities related to OIBs (including the Canary Islands). In all cases, alkaline magma sources are associated with mantle plumes and/or subcontinental lithospheric mantle (SCLM) that has been metasomatised by fluids and melts derived from previously subducted slabs.

The advantage of alkaline rocks, compared to more common basaltic or granitic suites, is that their low viscosities, densities and temperatures promote rapid rise to the surface and they generally show limited evidence of crustal contamination. Evolved alkaline rocks are also rich in S-bearing minerals, which reflect the high solubility of S in carbonatitic melts. Carbonatites, for example, have average S concentrations of ~6000 ppm, much greater than other terrestrial magmas erupted through continental crust (granites and degassed basaltic lavas typically have concentrations <100 ppm). In short, because alkaline magmas are S-rich, found throughout the geological record, and genetically linked to previously subducted crust, they are potentially well suited for understanding S cycling between the surface and mantle.

Before we can use S isotopes to investigate the origins of an igneous rock suite, we must account for all processes that may fractionate S from mantle source to surface. While there have been a large number of S isotope investigations of alkaline complexes, few have thoroughly investigated how crustal contamination, degassing and fluid evolution (i.e., changes in temperature-pH-pO₂) altered the primary mantle signature. Understanding these processes is critical to unlocking the alkaline record of magma sources and placing these observations within the context of the global S cycle.

Here, we present a detailed S isotope study of an alkaline igneous province known as the Gardar (Fig. 1). We target primitive dykes and diatremes as well as three well-studied chemically evolved alkaline bodies (Ilímaussaq, Motzfeldt and Ivigtút, Fig. 1). By carefully screening for crustal contamination and interrogating degassing and magmatic fluid evolution processes we demonstrate that the $\Delta^{34}S$ of alkaline rocks can be used to evaluate mantle S sources. We undertake a global compilation and establish a $\Delta^{34}S$ time-series of alkaline magma sources. We show that most complexes require a component of recycled surface S, and find new evidence for a secular variation in their $\Delta^{34}S$. We consider the causes of this temporal variation and demonstrate that alkaline rocks are a powerful data set for understanding connections between surface and mantle S reservoirs over geological timescales.

## Results

**Geological setting and sample selection.** The Gardar province in SW-Greenland (Fig. 1) is a failed Mesoproterozoic continental rift that was volcanically and tectonically active in two cycles from 1320–1260 Ma and 1180–1140 Ma. Magmas were emplaced across and along the boundary between the North Atlantic Craton (2800 Ma Archaean orthogneiss) and the Paleoproterozoic

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**Fig. 1** Locations of the alkaline rocks compiled for this study. The Kola Alkaline Province and the Alto Paranaiba Igneous Province (APIP), discussed in the text, are among the largest alkaline provinces known. Alkaline rocks are mostly found in continental settings although there are a few oceanic occurrences, including the Canary Islands hotspot.

![Locations of the alkaline rocks compiled for this study](https://example.com/alkaline_rocks_map.png)
mobile belt (~1800 Ma Ketilidian granites, Supplementary Fig. 1). While the vast majority of Gardar magmas comprise intrusive suites (i.e., dyke swarms and km-scale plutonic bodies), extrusive lavas and tuffs are preserved as a package of rift-suite intrusions known as the Eriksfjord Formation.

Geochemical investigations of Gardar rocks emphasise that their parental magmas were derived from a metasomatic SCLM. Metasomatism has been linked to an episode of Andean-style subduction that took place during the Ketilidian orogeny and is supported by Gardar Nd-model ages, which mostly range between 1850 and 1720 Ma, overlapping the ages of Ketilidian rocks. Thus, there is consensus that the Ketilidian orogeny led to pervasive mantle metasomatism; hence, Gardar magmas carry a geochemical signature of previously subducted crust and fluid. In this study, we analyse ENE-WSW oriented mafic dykes (commonly referred to as Giant Dykes), as well as lamprophyre and carbonatite diatremes. Previous investigations of these rocks confirm that they have been modified little by crustal interactions and therefore provide the best information on the Gardar mantle source. We also investigate three intrusions: Ilímaussaq, Motzfeldt and Iviqtút (Fig. 1), which comprise alkaline and peralkaline rocks with complex Na-Ca-HFSE minerals and are likely parental to the mineral separates analysed. All δ34S results are provided in Supplementary Data 1–2.

**Fig. 2 Histograms summarising sulphur isotope results for the Gardar.** The bar colour corresponds to the sulphide or sulphate mineral analysed. Note that when sulphide minerals were finely disseminated we undertook a whole-rock sulphide extraction (converting to an Ag₂S precipitate, see Methods). δ34S results from primitive mafic dykes are shown in panel a alongside δ34S analyses of pyrite extracted from carbonatite and lamprophyre diatremes. δ34S analyses of three alkaline complexes (Ilímaussaq, Motzfeldt and Iviqtút) are shown in b–g, with the upper panels b, d and f corresponding to early-formed magmatic rocks and veins, and the lower panels c, e and g corresponding to latest veins and fenites. Note that fenites are country rock around the intrusion that has been metasomatised by alkaline magmatic fluids. Note that in b, d and f the grey bar indicates the δ34S range of magmatic rocks and cumulate that are likely parental to the mineral separates analysed. All δ34S results are provided in Supplementary Data 1–2.

**Sulphur isotope variations in Gardar rocks.** δ34S analyses of Gardar rocks were carried out on mineral separates and whole-rock powders. For the latter, we undertook S concentration measurements and converted sulphides to Ag₂S before isotopic analysis (Methods). Primitive dykes have whole-rock δ34S of 1–5‰ while pyrites from lamprophyre and carbonatite diatremes have δ34S of 2–3‰ (Fig. 2a). Gardar intrusions (Fig. 2b–g) show a greater δ34S span and are divided into early-formed magmatic rocks and veins, and late-stage veins and fenite (i.e., metasomatically altered country rock at the margins of the complex). At Ilímaussaq, early-formed agpaitic rocks and hydrothermal veins (Fig. 2b) are dominated by sphalerite (1.3–3.1‰), with co-existing galena (−1.1 to 0.5‰) in a few samples. Syenitic rocks, cumulate and alkaline dykes that are parental to the agpaitic rocks and veins also show a narrow δ34S range (0.8–2.0‰), indicated by the grey bar in Fig. 2b. In contrast, late-stage fenite in the roof and margins of the intrusion contain sulphides (pyrite and...
chalcoprite) with low and highly variable $\delta^{34}S$ and sulphate (barite) with $\delta^{34}S$ of 5.3% (Fig. 2c).

At Motzfeldt, we found molybdenite and pyrite in early-formed roof-zone pegmatites and veins with $\delta^{34}S$ of 2.6–3.9% (Fig. 2d). Like Ilímaussaq, syenitic cumulate and veins from deeper in the intrusion show a similar $\delta^{34}S$ range (1.3–3.4%) that overlaps with the early-formed units (Fig. 2d). Late-stage fluorite veins injected into the surrounding rock (Fig. 2e) show variable $\delta^{34}S$ with chalcopryrite down to ~15% and barite up to ~9%.

At Ivigtút, sulphides from the early-formed quartz-cryolite-siderite magmatic body show a tight clustering of $\delta^{34}S$ values (~1 to 3‰, Fig. 2f). Although these magmatic fluids were injected into an alkali granite stock, it is uncertain whether the granite is genetically related to the overlying cryolite body. Nevertheless, granophyre dykes radiating from the deep granite reveal comparable $\delta^{34}S$ values of 1‰ (Fig. 2f). Low-sulphide $\delta^{34}S$, down to ~4.5‰, was observed in a few late-stage interstitial veins in cryolite, while high-sulphide $\delta^{34}S$, up to 9.4‰, was observed in the final alteration products that are rich in fluorite and hydrous phases (Fig. 2g). Late-stage barites also show two distinct values of ~10 and ~21‰.

Magmatic processes that impart sulphur isotope variations.

Whole-rock $\delta^{34}S$ represent the total isotope value ($\delta^{34}S_{TS}$) of the melt or magmatic cumulate (depending on the sample) and will mainly be affected by crustal assimilation, magmatic degassing and melt-sulphide segregation. Mineral $\delta^{34}S$ record the isotopic fractionation between the S mineral phase and the melt or fluid. For an individual S-bearing mineral, the measured $\delta^{34}S$ reflects the $\delta^{34}S_{TS}$ but also the temperature and S speciation of the melt/fluid (the latter being controlled by pH and fO2 conditions). Thus, S minerals record $\delta^{34}S$ variations due to changes in temperature-pH-fO2 features that are masked by a whole-rock approach. We first evaluate processes that impact $\delta^{34}S_{TS}$, and then assess changes in temperature-pH-fO2 encoded in mineral $\delta^{34}S$.

Table 1 compares S concentration and $\delta^{34}S$ in local crust with Gardar magmas. Local crust is mostly magmatic in origin (i.e., orthogneiss, granites and rift-related lavas) with low S concentrations (<100 ppm) and a restricted $\delta^{34}S$ range (1–4%). Eriksfjord sediments have high-$\delta^{34}S$ (25‰), consistent with a marine origin, but minimal S concentrations (~10 ppm) and we stress that there is no evidence for evaporitic units or shales with high S contents. Scenarios of crustal assimilation (melting and incorporating 10, 25 and 50% of local crust, Table 1) show that changes in melt $\delta^{34}S$ for the magmatic suites are very low, generally <0.5‰. Calculations for Motzfeldt suggest that extreme crustal assimilation may have increased melt $\delta^{34}S$ by ~1‰. However, it is important to note that the coarsely crystalline roof-zone pegmatites sampled for early-stage sulphide minerals (Fig. 2d) were not analysed for S concentrations (due to the difficulty of obtaining a representative whole-rock sample). As these samples are rich in visible sulphide minerals we expect S concentrations to be comparable to the agpaitic rocks of Ilímaussaq (~1000 ppm), i.e., much greater than the values used for modelling in Table 1. Hence, Motzfeldt magmas are unlikely to have been significantly shifted by crustal assimilation. Gardar magmatic suites show scap geochemical and petrographic evidence for crustal assimilation, but the magnitude of the shift may be comparable to the agpaitic rocks of Ilímaussaq (~1000 ppm), i.e., much greater than the values used for modelling in Table 1. Hence, Motzfeldt magmas are unlikely to have been significantly shifted by crustal assimilation. Gardar magmatic suites show scap geochemical and petrographic evidence for crustal assimilation, but the magnitude of the shift may be comparable to the agpaitic rocks of Ilímaussaq (~1000 ppm), i.e., much greater than the values used for modelling in Table 1.

Table 1 The impact of crustal contamination on sulphur isotopes

| Magmatic suite       | Average S (range), ppm | Average $\delta^{34}S$, ‰ | Local crust | Average S (range), ppm | Average $\delta^{34}S$, ‰ | $\delta^{34}S$ Change due to bulk crustal assimilation, ‰ |
|----------------------|------------------------|-----------------------------|-------------|------------------------|-----------------------------|----------------------------------------------------------|
| Ilímaussaq           | 1430 (246–4413)        | 1.4                         | Eriksfjord sandstones 6 | 25.1†                      | 0.01 0.03 0.05             |
|                      |                        |                             | Eriksfjord mafic lavas 63 (38–79) | 0.6                      | 0.00 0.00 0.00             |
|                      |                        |                             | Ketilidian granites 52 (12–76) | 2.7                      | 0.01 0.02 0.05             |
| Motzfeldt            | 150 (100–200)          | 2.4                         | Eriksfjord sandstones 11 | 25.1                      | 0.18 0.46 0.92             |
|                      |                        |                             | Eriksfjord mafic lavas 37 (31–42) | 1.0                      | 0.03 0.06 0.13             |
|                      |                        |                             | Ketilidian granites 25 (19–34) | 4.4                      | 0.07 0.18 0.36             |
| Ivigtút              | 1000 (670–8100)        | 0.9†                        | Archaean gneiss 51 (31–99) | 1.0                      | 0.03 0.08 0.17             |
| Regional dykes and   | 500 (357–772)          | 2.3                         | Eriksfjord sandstones 6 | 25.1†                      | 0.03 0.08 0.15             |
| diatremes            |                        |                             | Eriksfjord mafic lavas 63 (38–79) | 0.6                      | 0.00 0.00 0.00             |
|                      |                        |                             | Ketilidian granites 52 (12–76) | 2.7                      | 0.03 0.07 0.14             |

S concentration measurements and $\delta^{34}S$ analyses of Gardar magmas and local crust are shown for whole-rock samples only (Supplementary Data 2). At Ivigtút whole-rock $\delta^{34}S$ analyses (*) were only carried out on granophyre dykes radiating from the granite stock that underlies the main cryolite body. Note also that Eriksfjord sandstones labelled with † yielded insufficient Ag,S for isotopic analysis and a $\delta^{34}S$ value of similar sandstones from Motzfeldt was used in calculations. The alkaline magmatic suites are significantly richer in S than the local crust (by 1–3 orders of magnitude). Thus, models of bulk crustal assimilation generate little variation in melt $\delta^{34}S$ (generally, <0.5‰).
residual melt (0–5%) and cannot explain the positive values observed in primitive magmatic rocks and early stages of the alkaline intrusions (Fig. 2a, b, d, f). Moreover, when comparing δ34S of magmatic cumulate with late-stage melts for Ilímaussaq and Motzfeldt samples, we find their values are indistinguishable (mostly within 1‰, Supplementary Data 2). Thus, our observations and models indicate that sulphide segregation played a negligible role modifying δ34S of Gardar melts.

Having established that crustal assimilation, degassing and sulphide segregation had minimal effects on melt δ34S, we now consider how changes in temperature–pH–fO2 impact mineral δ34S. Given the isotopic and mineralogical distinctions between the early- and late-stage samples (Fig. 2), we consider these groups separately when modelling these processes.

Early magmatic rocks and veins contain only sulphide (Fig. 2b, d, f) and in a few samples from Ilímaussaq and Ivigtüt we identified multiple sulphide phases. This allows us to quantify temperature variations using iso- tope geothermometry53. At Ilímaussaq, sphalerite–galena pairs yield temperatures of 500–200 °C (Fig. 4a), in agreement with temperature estimates from fluid inclusions54,55 and phase equilibria56 (600–200 °C). At Ivigtüt, sulphides from the early-formed magmatic rocks support temperatures of 400–200 °C, also consistent with independent temperature constraints14,42,57 (Fig. 4c). To evaluate whether temperature variations explain the observed δ34S range in all early-stage samples, we modelled δ34S fractionation for different sulphide minerals at each intrusion (shown as the coloured arrows in left hand plots in Fig. 4a–c). At Ilímaussaq and Ivigtüt, an elevated δ34S of 1.8‰ and 2.5‰, respectively, provides a good fit, encompassing almost all samples with mineral pairs and individual sulphides where temperatures are unconstrained. Although sulphide mineral pairs were absent in early-stage Motzfeldt samples (Fig. 2b) the high-δ34S of molybdenite and pyrite (2.6–3.9‰) again suggests a high-δ34S source (δ34Sres ≈ 2‰) since falling temperatures increase sulphide δ34S by only ~1.5‰ (Fig. 4b). Thus, early magmatic sulphides at Ilímaussaq, Motzfeldt and Ivigtüt require an elevated δ34S (1.8–2.5‰) to yield credible estimates on formation temperatures (Fig. 4a–c).

Although variable temperatures account for the δ34S range in early-stage sulphides, it is important also to consider pH, which controls S speciation (i.e., the abundance of H2S, HS−, and S2−) and might impart isotopic fractionation in a reduced magmatic fluid36 (Supplementary Fig. 2). Ours and previous modelling36 (Supplementary Fig. 3) show that when pH is <7, H2S is the dominant S fluid phase and there is minimal fractionation between the fluid and the precipitated sulphide. At Ivigtüt and Motzfeldt pH was likely <7 (see Supplementary Discussion) and their values are indistinguishable (mostly within 1‰, Supplementary Data 2). Thus, our observations and models indicate that sulphide segregation played a negligible role modifying δ34S of Gardar melts.

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δ34S\textsubscript{S} of 0‰, a feature not seen in our samples and contrary to Ilímaussaq whole-rock δ34S, which are mostly between 1 and 2‰ (Table 1). We conclude that the close correspondence between ZnS δ34S from Ilímaussaq and the temperature modelling results in Fig. 4a (also shown as the red bar in Fig. 3c) support temperature as the main control on δ34S. Varying temperature provides the best explanation of all early-stage δ34S (Fig. 4) and also requires an elevated source δ34S, consistent with all whole-rock δ34S observations from the Gardar (1–5‰).

Unlike the early-stage samples, late-stage veins and fenites (Fig. 2c, e, g) contain sulphates and sulphides. The difference between sulphate and sulphide δ34S is up to 15–25‰ in these late-stage samples (Fig. 4a–d) and suggests low temperatures of formation 200–300 °C (for reference isotope fractionation at magmatic temperatures, ~600 °C, is ~8‰). Sulphates require increased concentrations of oxidised S species (SO\textsubscript{4}²⁻), suggesting that late magmatic fluids underwent an IO\textsubscript{2} increase. Models calculating δ34S variations from oxidation of a magmatic fluid are

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**Fig. 4** Sulphur isotope results for the Gardar alkaline intrusions. a) Ilímaussaq, b) Motzfeldt and c) Ivigtût. Data symbols and colours correspond to the sulphide or sulphate mineral analysed. Isotopic fractionation caused by changing temperature and IO\textsubscript{2} are shown as the bold lines and are specific to each mineral phase. Temperature variations were modelled using compiled fractionation factors\textsuperscript{53}, while IO\textsubscript{2} variations applied the methods of ref. 36. Fixed model parameters are shown in white boxes and detailed in the Supplementary Discussion. Note that d) has a different scale from the other plots and so an orange bar is used to orient the reader to the range of the Ivigtût magmatic phases of Ivigtût cannot be explained by oxidation of a magmatic sulphide or sulphate mineral analysed. Isotopic fractionation caused by changing temperature and fO\textsubscript{2} are shown as the bold lines and are specific to each mineral phase. Temperature variations were modelled using compiled fractionation factors\textsuperscript{53}, while fO\textsubscript{2} variations applied the methods of ref. 36.
shown in Fig. 4a–c (right hand panels). Oxidation causes sulphate to become the dominant S phase and approach the δ34S value. At equilibrium, differences in bond stiffness between oxidised and reduced S species favour heavy δ34S isotope substitutions in sulphate and lead to a sharp δ34S decrease in co-existing sulphides. Increasing IO2 adequately explains both the appearance of barite and the negative isotopic shifts in late-stage sulphides (Fig. 4a–c and Supplementary Fig. 4). Late-stage oxidation was most likely driven by an influx of externally derived fluids and at both Ilímaussaq and Motzfeldt, there is δ18O and fluid inclusion evidence14,46 for external brines and meteoric fluid infiltrating along the margins of the intrusions (where our late-stage minerals were sampled).

At Ivigtüt late-stage sulphides reveal both low- and high-δ34S. Barites also show groupings of ~10 and ~21‰ (Fig. 2g). While oxidation of a reduced alkaline fluid, by infiltration and mixing with an external brine14, explains the low-δ34S sulphides in late-stage veins (Fig. 4c and Supplementary Fig. 5) it cannot explain the array of high-δ34S sulphides associated with fluorite and hydroxyl fluorite (Fig. 4d, note different scale from other panels). To account for these high-δ34S samples we envisage a reverse process, whereby an infiltrating brine with Mesoproterozoic seawater-like δ34S (δ34S 3S = 20‰) is reduced on mixing with the magmatic fluids (Supplementary Fig. 6). As noted above, differences in bond stiffness between oxidised and reduced S species favour heavy isotopic substitutions in the sulphate and our model rationalises the presence of barite with δ34S up to 22.5‰ as well as the pyrite and galena with elevated and wide-ranging δ34S (since small variations in redox lead to large isotopic shifts, 3–10‰, Fig. 4d). Although these final-stage sulphates and sulphides are rarely found in direct contact (and do not provide unequivocal evidence for equilibrium), our model complies with previous evidence for late-stage brine influx (e.g., fluid inclusions14), and strengthens the case that Ivigtüt represents a heterogeneous mixing zone between a reduced CO32− and F− rich magmatic fluid (δ34S 2S = 2.5‰) and oxidised brine (δ34S 3S = 20‰). Finally, although we invoke external fluids as a cause for late-stage oxidation at Ilímaussaq and Motzfeldt, at Ivigtüt a greater ratio of external to internally derived fluids is required, reflecting the much smaller size of Ivigtüt (~300 m in diameter), compared to Ilímaussaq and Motzfeldt (km-scale).

Sulphur isotope signature of the Gardar magma source. Primitive dykes and diatremes provide the best constraints on the Gardar mantle source41 and all possess high-δ34S (1–5‰). Magmatic cumulate and dykes from the alkaline intrusions (Fig. 2b, d, f) also show positive δ34S and, like the primitive dyke and diatremite samples, appear unaffected by crustal contamination, magmatic degassing and sulphide segregation (Table 1 and Fig. 3a, b). This has two important implications. First, because the δ34S source values calculated for early-stage sulphide-dominated rocks from the alkaline intrusions (Fig. 4a–c) are within ~1‰ of their parental magmatic units (Fig. 2), and also overlap the δ34S of primitive samples; this provides strong evidence that evolved alkaline rocks constrain magma source δ34S. This conclusion resonates with earlier studies30 and suggests that, because alkaline rocks are exceptionally S-rich, their mineral δ34S can be used to evaluate source δ34S (i.e., δ34S 3S). The main caveat is that S minerals must be dominated by either reduced or oxidised phases. Only with our complete data set from multi-phase alkaline intrusions and their associated primitive magmas has it been possible to verify fully this hypothesis.

The second implication is that Gardar magma sources are enriched in δ34S. Gardar δ34S is well above the accepted range for the asthenospheric upper mantle (~1 ± 0.5‰59) and shows closer correspondence to subduction zone settings1, implying there is recycled surface S in their source. This is coherent with virtually all prior geochemical investigations of the Gardar, which have advocated a significant involvement of a metasomatised SCLM component in magmatogenesis13,38 (originating from subduction process ~500 Ma before rift onset22,39,40). While it is clear that Gardar mantle metasomatism resulted from subduction processes59, our δ34S analyses cannot determine the precise source (i.e., slab-derived melts or pore fluids). Trace elements of primitive Gardar melts (e.g., Th/Ce ratios) have been used to argue for fluid-dominated metasomatism13,38, while recent δ34S analyses of arc cumulates30 suggest that sulphate-rich pore fluids are preferentially driven off at the arc front and imply that slab-derived melts are the key metasomatic agent. Although future δ34S investigations of Gardar mantle xenoliths may address this issue, the salient point is that alkaline magmas encode information about the fate of surface S subducted into the mantle.

The origin and evolution of alkaline magmas. Our detailed study of the Gardar intrusions shows that, despite major differences in the origin of the magmatic fluids, S isotopes are fractionated by common evolutionary processes. To explore whether similar redox changes and magma source δ34S typify other alkaline systems we compiled a global data set (Fig. 5).

Our compilation reveals that alkaline rocks span an exceptionally wide δ34S range (~25 to +25‰, Fig. 5). Almost invariably, there is a decrease in δ34S between early and later formed sulphides within a given system. Only at Ivigtüt and Bayan Obo were late-stage sulphides with high-δ34S (~9‰) and sulphates with seawater-like δ34S (~20‰) observed. These data require significant external brine influx and reduction in a magmatic-hydrothermal environment. At Ivigtüt we suggest this took place concurrently with the magmatic phase, while at Bayan Obo a more complex multi-stage evolution is envisaged61 involving Mesoproterozoic and Palaeozoic hydrothermal events.

Sulphur isotope shifts between early and late-stage alkaline rocks have been reported at individual systems30–33 and our global compilation demonstrates the ubiquity of this process. Early stages are almost always reduced and sulphide-dominated (Fig. 5). With cooling, the reduced magmatic systems collapse, oxidised S (sulphate) becomes dominant and this leads to a major δ34S decrease in latest sulphide minerals. It is important to note that while external oxidising fluids were implicated in our study, previous authors30,62 have suggested that alkaline melts might also show a relative IO2 increase (i.e., oxidation) with falling temperatures through natural variations in the crystallising assemblage. Although the precise cause of late-stage oxidation at each complex is beyond the scope of this study, our compilation (Fig. 5) shows that δ34S is exceptionally sensitive to low-temperature oxidation and is an excellent tool for fingerprinting these fundamental changes in fluid chemistry at all alkaline systems.

Our δ34S observations alongside previous studies30 emphasise that S-rich alkaline rocks can be used to evaluate magma source δ34S when they are dominated (>90%) by either sulphide or sulphate. While measurements of primitive alkaline magmas are undoubtedly the best method for determining magma source δ34S, our detailed case study demonstrates that a wide variety of alkaline rocks, including magmatic cumulate, late-stage silicate melts, carbonatites and aluminofluoride melts (Ivigtüt), closely approximate source δ34S (within ~1‰). Given that virtually all alkaline systems mirror the δ34S trends observed in the Gardar (Fig. 5) it is reasonable to assume that the isotope systematics that govern Gardar melts are applicable elsewhere. Thus, for each
In Fig. 5 we averaged $\delta^{34}S$ in the most primitive, high temperature ($>300^\circ$C) phases (mostly magmatic cumulate) to estimate magma source $\delta^{34}S$. We exclude sulphide minerals that show large isotopic fractionation at high temperatures (i.e., galena$^{23}$), and where multiple sulphide minerals were reported we include only the most reduced phase (e.g., taking pyrrhotite over pyrite) and apply temperature corrections similar to our Gardar study (Fig. 4a–c). Well-constrained source values (Fig. 5) were
from trace elements, radiogenic (Sr–Nd–Pb) and stable isotopes (B), which often require a recycled crustal component in alkaline magma sources. Although alkaline rocks originate through a variety of mantle processes, including mantle plumes and subduction-related mantle metasomatism, they undoubtedly play a key role in returning previously subducted S to the surface, and are therefore an integral component of the global S cycle.

Our compilation also shows strong evidence for regional variations in source \( \delta^{34}S \). Gardar intrusions have source \( \delta^{34}S \) of 1–3‰, similar to Proterozoic carbonatites from Canada (Fig. 3), but starkly contrasting with the negative \( \delta^{34}S \) suggested from Russia and Finland (Kola Alkaline Province and Brazil (Alto Paraíba Igneous Province, APIP). We infer that these data represent genuine low-\( \delta^{34}S \) sources because: (1) \( \delta^{34}S \) is consistent between multiple complexes at a regional scale; (2) different regional studies provide consistent isotope values (e.g., all studies of Kola sulphides show isotopically light values); and (3) individual mineral \( \delta^{34}S \) are exceptionally low (e.g., sulphates are always enriched in \( 34S \) and should have \( \delta^{34}S \geq 0 \)), however, barites from Salitre and Tapira in APIP possess negative-\( \delta^{34}S \), requiring a \( \delta^{34}S \sim 0 \)). Additionally, at Kola and APIP, isotopic studies have ruled out assimilation of local Precambrian crust. The regional variations in source \( \delta^{34}S \) (Fig. 5) imply that the processes that enrich the mantle prior to alkaline magmatism, whether SCLM metasomatism or plume-related, are isotopically diverse and take place at a regional scale.

**Links to the global sulphur cycle.** The alkaline rocks compiled here span an age range of \( \sim 2060 \) to \( \sim 0 \) Ma and provide a \( \delta^{34}S \) time-series of magma sources (Fig. 6). While OIBs are limited by the age of oceanic crust (\( \sim 200 \) Ma), alkaline magmas that intruded continental crust are well-preserved over much of Earth history and provide a valuable inventory of mantle evolution. Our igneous \( \delta^{34}S \) time-series shows a temporal trend with Proterozoic alkaline magmas largely restricted to positive \( \delta^{34}S \) values (0–5‰) and Phanerozoic suites showing greater \( \delta^{34}S \) diversity (–5 to 4‰, overlapping the range of OIB sources).

Our igneous \( \delta^{34}S \) compilation also shows a first-order correspondence with the global sedimentary sulphide \( \delta^{34}S \) record from continental shelves and inland seas (Fig. 6). Pyrite from sedimentary rocks shows a long-term \( \delta^{34}S \) evolution from zero to slightly positive values in the Archaean and Proterozoic to
significantly lower $\delta^{34}S$ in the Phanerozoic. This record of oceanic $\delta^{34}S$ represents a shift from an anoxic deep ocean with a small sulphate reservoir to more oxygenated deep waters with a large sulphate reservoir after ~600 Ma, coinciding with the onset of bioturbation. Although Proterozoic sedimentary $\delta^{34}S$ is on average positive, pyrite with negative $\delta^{34}S$ is mainly observed in deeper parts of sedimentary basins. These observations have led several workers to invoke a missing Proterozoic $\delta^{34}S$-depleted S pool, deposited in deep water setting and lost from the surface via subduction.

Our observations raise two key questions: why do igneous and sedimentary $\delta^{34}S$ show similar time-evolving trends, and why are anomalous low-$\delta^{34}S$ alkaline provinces only observed in the Phanerozoic? In Fig. 7 various scenarios are summarised. In the first case, the igneous $\delta^{34}S$ pattern could simply reflect crustal assimilation of sedimentary rocks, i.e., because Phanerozoic sedimentary crust has low-$\delta^{34}S$ (Fig. 6), assimilation would lead to low-$\delta^{34}S$ values in some Phanerozoic magmas. The second hypothesis assumes alkaline magmas are derived from metasomatised SCLM, and that secular variation in $\delta^{34}S$ reflects changing composition of the SCLM. Since subduction exerts an important control on SCLM composition, this would suggest that low-$\delta^{34}S$ sedimentary rocks were subducted in the Phanerozoic, imprinted a low-$\delta^{34}S$ signature on the SCLM, and were tapped by Phanerozoic magmas within ~10–100 Ma. A final hypothesis is that during the Precambrian (both Proterozoic and Archaean) low-$\delta^{34}S$ crust was subducted and stored in the deep mantle, hence the secular evolution represents a Ga time-lag in returning this material to the surface.

Focusing on the anomalous low-$\delta^{34}S$ alkaline provinces, i.e., Kola and APIP, it is easy to eliminate crustal assimilation because the local crust is Precambrian and isotopic studies reject crustal interaction. Discriminating between the other scenarios is more challenging, particularly because $\delta^{34}S$ alone does not allow unambiguous discrimination between deep mantle (OIB) and SCLM sources (Fig. 5). Nevertheless, if both Kola and APIP sources were modified by low-$\delta^{34}S$ sediments subducted in the Phanerozoic, then sutures (former subduction zones) of Phanerozoic age should be present. In Kola and APIP the nearest sutures are Palaeo- and Neoproterozoic, respectively, ruling out Phanerozoic subduction-related source modification.

We suggest that low-$\delta^{34}S$ Phanerozoic alkaline magmas at Kola and APIP are derived from a mantle plume with a low-$\delta^{34}S$ signature. Importantly, noble gas isotope signatures support a deep plume source at both Kola and APIP, and radiogenic isotopes also support ancient (potentially Archaean) sources at Kola. Thus, our favoured hypothesis is that their low-$\delta^{34}S$ signatures reflect deep recycling of previously subducted low-$\delta^{34}S$ crust of either Archaean or Proterozoic age. This implies that the co-variation of igneous and sedimentary $\delta^{34}S$ (Fig. 6) is fortuitous since low-$\delta^{34}S$ provinces reflect recycling ancient (Ga) rather than contemporary (Ma) S. Our suggestion that low-$\delta^{34}S$ alkaline provinces are a Phanerozoic phenomenon is also consistent with timescales of Earth’s geodynamic cycle, i.e., plate tectonics and subduction into the deep mantle initiated around 3.2–2.5 Ga, residence timescales in the lower mantle are calculated to be on the order of 1.5 Ga, thus we would expect to see deep crustal recycling after ~1 Ga (Fig. 6).

Although our final hypothesis complements several OIB studies, which have confirmed recycled Archaean S with characteristic negative-$\delta^{34}S$, other OIB studies have reported positive-$\delta^{34}S$ (Fig. 6) and linked these to recycled Proterozoic $\delta^{34}S$. While we do not suggest that all recycled Proterozoic and Archaean crust has negative-$\delta^{34}S$, our observations require a deep mantle source and, as has been advocated at other OIB sources, this is most plausibly linked to low-$\delta^{34}S$ recycled crust. Likewise, we do not rule out plume origins for the Proterozoic alkaline provinces, but emphasise that they do not carry a low-$\delta^{34}S$ signature.

Ultimately, our global compilation represents an important new $\delta^{34}S$ time-series of mantle source evolution. Key to unravelling the igneous record is determining whether specific $\delta^{34}S$ signatures reflect a deep mantle plume or metasomatised SCLM origin. Further studies should look to combine multiple S isotopes, stable isotopes, radiogenic isotopes and noble gases for the same sample suite. This approach will clarify mantle sources and the temporal patterns in Fig. 6, and provide robust geochemical constraints on the connectivity of Earth’s surface and mantle S reservoirs.

**Methods**

**Sulphur isotopes.** We extracted visible S-bearing minerals using a microdrill. For samples without visible S-bearing minerals we generated a whole-rock powder and measured sulphide phases as Ag$_2$S using a Cz reducer procedure. S isotope analysis ($\delta^{34}S$) was undertaken at three institutes: Scottish Universities Environmental Research Centre (SUERC, East Kilbride, UK); School of Earth and Environmental Sciences (University of St Andrews, UK) and Fachbereich Geowissenschaften (Universität Tübingen, Germany). An Isoprine VIS/NIR isotope ratio mass spectrometer (IRMS) with a linked Vario PYRO cube elemental analyser (EA) was used at SUERC, a Thermo Quest Delta + XL IRMS connected to a NC 2500 was used at Tübingen, and at St Andrews we used an EA IsoLink, coupled to a MAT 253 IRMS via a Conflo IV. Standards were closely spaced throughout the runs and used to calibrate sample isotope compositions. Replicates between the different institutes were consistent to the error within natural $\delta^{34}S$ heterogeneity (generally, ±0.3%) at 2 s.d. for the early-formed high temperature, >300 °C, sulphides.

**Sulphur concentrations.** Sulphur concentrations in whole-rock powders were determined via Combustion-Ion Chromatography (CIC) at the Universität Tübingen (Germany) using a 930 Compact IC Flex chromatograph (Metrohm) combined with a combustion oven (Analytik Jena). Mixtures of equal amounts (10 mg) of powdered sample and Li$_2$O were heated in the combustion oven at 1050 °C in an Ar–O$_2$ atmosphere. The loaded steam was condensed and injected into the ion chromatograph equipped with a Metrosep A Supp 5–250/4.0 column (kept at 55 °C) using an NaOH-Na$_2$CO$_3$–acetone eluent. For the whole analytical procedure, Millipore water (18.2 MΩ.cm) was used and quantification was done using MagLeC Net software (Metrohm). The effective detection limit for powdered samples was about 1–2 μg/g and based on the repeated analyses of samples and reference material GSN, relative uncertainties were generally <15% (1 s.d., depending on the concentrations).

**Isotope modelling.** Models of S isotope fractionation due to magmatic degassing and sulphide (FeS) segregation were calculated using the equations of ref. 35. In both cases melt $\delta^{34}S$ is dictated by: total S isotope value ($\delta^{34}S$$_{total}$); fO$_2$ conditions; the fraction of S remaining in the melt; the choice of open vs. closed-system behaviour and the empirical fractionation factors used. We model all scenarios at QFM since Gardar magmatic suites are accepted to have formed at fO$_2$ conditions at or below the QFM buffer 14,40,49. To evaluate S speciation in the melt and gas we used the models of ref. 37 and ref. 38, respectively. At QFM reduced S species dominate the melt ($S^{2-}$) and gas (H$_2$S). Empirical fractionation factors from ref. 50 (blue, Fig. 3a) are from experiments on molten salts while those from ref. 39 (red, Fig. 3a, b) are from more recent experiments on silicate melts. We expect that the fractionation factors of ref. 51 (red, Fig. 3a, b) to be most appropriate for the silicate melts in the Gardar, but have included those of ref. 38 because they have traditional use and may be suitable for ionic liquids (i.e., carbonatites).

Sulphur isotope fractionation in an evolving magmatic fluid is primarily controlled by temperature, fO$_2$, pH and total S isotope value (or source $\delta^{34}S$$_{OIB}$, $\delta^{34}S$$_{Gardar}$). These methods are described in detail in by ref. 36 and were used here to evaluate how changes in temperature/fO$_2$/pH may have generated the isotope discrimination in our samples (Figs. 3c and 4). It is important to note that although we used identical equations of ref. 36, we updated the fractionation factors using a more recent compilation 35, as well as activity coefficients and equilibrium constants from the SUPCRT92 and LLNL data sets (note that the latter is included in The Geochemists Workbench software 7).

To understand the geological feasibility of the predicted isotope fractionation it is essential to also evaluate mineral stability fields 36,40. We used The Geochemists Workbench to calculate pH–fO$_2$ phase diagrams for simplified element systems, e.g., Fe–Cu–S–O, Pb–S–O and Zn–S–O, and overlay these on the modelled isotope variations (Supplementary Discussion). Previous fluid inclusion, mineralogical and studies of illuminated images in our samples (Figs. 3c and 4). It is important to note that although we used identical equations of ref. 36, we updated the fractionation factors using a more recent compilation 35, as well as activity coefficients and equilibrium constants from the SUPCRT92 and LLNL data sets (note that the latter is included in The Geochemists Workbench software 7).
Discussion we outline these constraints for each system and justify our preferred trajectories that explain both the isotopic and mineralogical changes observed in Fig. 4.

Data availability
The data that support the findings of this study are available within the article and its Supplementary Information files.

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